Talanta 128 (2014) 132–140

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Lead detection using micro/nanocrystalline boron-doped diamond by square-wave anodic stripping voltammetry

Tatiane M. Arantes [a],*, André Sardinha [b], Mauricio R. Baldan [a], Fernando H. Cristovan [b], Neidenei G. Ferreira [a]

[a] LAS/INPE-Instituto Nacional de Pesquisas Espaciais, Av. dos Astronautas 1758, São José dos Campos-SP, Brazil
[b] Universidade Federal de São Paulo, Instituto de Ciência e Tecnologia, R. Talin 330, José dos Campos-SP, Brazil

ARTICLE INFO

Article history:
Received 13 January 2014
Received in revised form
24 April 2014
Accepted 25 April 2014
Available online 6 May 2014

Keywords:
Boron-doped diamond
Nanocrystalline diamond
Lead
Heavy metals
Square-wave voltammetry

ABSTRACT

Monitoring heavy metal ion levels in water is essential for human health and safety. Electroanalytical techniques have presented important features to detect toxic trace heavy metals in the environment due to their high sensitivity associated with their easy operational procedures. Square-wave voltammetry is a powerful electrochemical technique that may be applied to both electrokinetic and analytical measurements, and the analysis of the characteristic parameters of this technique also enables the mechanism and kinetic evaluation of the electrochemical process under study. In this work, we present a complete optimized study on the heavy metal detection using diamond electrodes. It was analyzed the influence of the morphology characteristics as well as the doping level on micro/nanocrystalline boron-doped diamond films by means of square-wave anodic stripping voltammetry (SWASV) technique. The SWASV parameters were optimized for all films, considering that their kinetic response is dependent on the morphology and/or doping level. The films presented reversible results for the Lead [Pb (II)] system studied. The Pb (II) analysis was performed in ammonium acetate buffer at pH 4.5, varying the lead concentration in the range from 1 to 10 $\mu g\,L^{-1}$. The analytical responses were obtained for the four electrodes. However, the best low limit detection and reproducibility was found for boron doped nanocrystalline diamond electrodes (BDND) doped with 2000 $mg\,L^{-1}$ in B/C ratio.

1. Introduction

The trace detection of toxic or heavy metal ions in water is essential for the human health and environmental safety. There are numerous health problems caused by the exposure of humans with high levels of heavy metal ions (Cd^{2+}, Pb^{2+}, Hg^{2+}, $As^{3+/5+}$). Moreover, these toxic ions tend to accumulate in the body with a slow removal rate. For example, the biological half-life of cadmium is from 10 to 30 years, while the presence of lead in the bone is more than 20 years [1]. The Environmental Protection Agency (EPA) estimates that about 20% of human exposure to lead occurs through contaminated drinking water [1]. The monitoring of these contaminants with adequate selectivity, sensitivity and reproducibility is essential for the government rules impose the maximum permissible exposure levels of these heavy metals in the water to protect public health. The monitoring process is available using various techniques, such as: atomic absorption, atomic emission, and electrochemical techniques [1]. Alternatively, electroanalytical techniques have attractive features, including sensitivity, easy operational procedures, and portability. However, the conventional electroanalytical determination of metals typically involves the use of mercury-based electrodes, for example, hanging mercury drop electrode (HMDE) [2,3] or electrodes coated with mercury, and glassy carbon [1,4] or iridium [5,6] substrates. The mercury electrode is considered standard for analysis of dissolved metals. However, mercury toxicity has been a great concern of environmentalists and it has motivated several researches for the development of mercury-free electrodes [1,5].

Boron doped diamond (BDD) electrodes have been extensively studied due to their attractive electrochemical properties, mainly including: high thermal conductivity; high hardness and chemical inertness; a wide electrochemical potential window in aqueous and non-aqueous media; a very low capacitance and a very high electrochemical stability [1,2,7]. These properties have favored the use of diamond to detect a variety of analytes, including traces of heavy metals as well as pesticide determinations, substituting the mercury electrodes in analytical techniques [8–11]. Taking into account the boron-doped diamond films, the production of nanocrystalline diamond films (BDND) may result in the increase of

---

* Corresponding author at: LAS / INPE - National Institute for Space Research, Av. dos Astronautas, 1758, Jd. da Granja, 12227-010 Sao Jose dos Campos – SP, Brazil. Tel.: +55 12 208 6675; fax: +55 12 3308 6717.
E-mail address: tmarantes@yahoo.com.br (T. M. Arantes).

http://dx.doi.org/10.1016/j.talanta.2014.04.074
0039-9140/© 2014 Elsevier B.V. All rights reserved.

electroactive area due to the reduction of diamond grain size, promoting their improving of analytical sensibility and selectivity [1,12,13]. Considering the electrochemical characteristics of sensors based on boron-doped nanocrystalline diamond (BDND), several studies have reported promising results for these electrodes as fast response, low detection limit, high stability, and excellent response accuracy [14–17]. In addition, nanocrystalline films provide a better catalytic activity, decreasing the overpotential of certain oxidation–reduction reactions [18].

Some studies found in the literature have demonstrated the importance of boron-doped nanocrystalline diamond electrodes. May et al. [19] have studied the relationship between the film morphology, conductivity and boron doping level. They suggested that the production of electrodes with controlled roughness and conductivity can be considered excellent candidates for electrochemical applications. Sonthalia et al. [20] made a comparison between the boron-doped nanodiamond electrodes with mercury electrodes for the detection and quantification of Ag (I), Cu (II), Pb (II), Cd (II) and Zn (II) in several water samples. They concluded that the diamond electrode has the same properties from those of mercury, but without toxicity in addition to its chemical inertia and nonvolatility. Recently, Honório et al. [21] used nanocrystalline boron-doped diamond electrode for the determination of Cu(II), Pb(II), Cd (II) and Zn(II) in honey by differential pulse anodic stripping voltammetry (DPASV) and showed detection limits of 0.37, 0.40, 1.28 and 0.16 mg L^{-1} were found for Cu, Pb, Cd and Zn, respectively.

Many electroanalytical methods employ the adsorptive accumulation in the HMDE combined with different stripping voltammetric techniques. One of the most sensitive techniques is the square-wave voltammetry [22,23]. Square-wave voltammetry (SWV) is a powerful electrochemical technique applied in both electrokinetic and analytical measurements. The detection limits can be compared with the chromatographic and spectroscopic techniques [24–27]. Furthermore, the analysis of the characteristic parameters of this technique enables to estimate the mechanism and kinetic of the electrochemical processes in study. Thus, SWV allows analyzing the reversible, irreversible and quasi-reversible electrode reactions, considering the correlations between the following parameters: frequency, period, square-wave potential, and amplitude [21,26,28].

In this work, four types of diamond electrodes of BDD, BDND, and BDUND were produced and characterized in addition to their application to lead detection in ultra pure synthetic electrolytes, using square wave anodic stripping voltammetry (SWASV) technique. For this purpose, a systematic study was conducted using theoretical models of SWV [20–24,29,36,37] to investigate the mechanisms and kinetics for these different diamond electrodes, considering the Pb (II) system as a function of their doping level and grain size. The voltammetric parameters were optimized for all electrodes, taking into account the following results: (1) SWV curves for the net current (I); its forward (I_f) and backward (I_b) components; (2) the dependence of the net peak current of reversible reaction as a function of the frequency square-root; (3) the dependence of the net peak current (I) and net peak current /peak current width at half-height ratio ($I/\Delta E_{p/2}$) as a function of the square wave amplitude (E_{SW}); and (4) the dependence of the net peak current (I) as a function of the step potential (ΔE_s). Afterwards, these parameter optimizations for Pb (II) system and the analytical curves were obtained in pure electrolyte by the standard addition method.

2. Experimental

Four different types of diamond films were produced in a hot filament chemical vapor deposition (CVD) reactor with two different boron doping levels in silicon substrates. Boron was obtained from an additional H_2 line passing through a bubbler containing trimethyl borate (Aldrich, 99%) dissolved in methanol with dissolution of 2000 or 20,000 mg L^{-1}. BDD films were grown at 800 °C for 16 h at 40 Torr with a gas mixture of 1.5% CH_4 and 98.5% H_2. BDND_2000 and BDND_20,000 films were obtained at 650 °C for 16 h at constant pressure of 30 Torr and gas mixture of 1.5% CH_4, 80% Ar and 18.5% H_2. The morphologies of the films were observed by scanning electron microscopy (SEM) using a JEOL JSM-5310 model. Diamond film quality were verified by micro-Raman scattering spectroscopy (Renishaw microscope system 2000) using the 514.5 nm line of an argon ion laser, taking the spectra covering in the range from 300 to 3500 cm^{-1}. The crystallinity and the grain size of the films were investigated by XRD using a high resolution Philips diffractometer, X'Pert model, with CuK_α radiation ($\lambda = 1.54$ Å) in grazing incidence mode, incident angle of 2° and resolution limit of 0.02° for all samples.

The electrochemical measurements were made using an Autolab PGSTAT 302 equipment with a three-electrode cell. The BDD or BDND films obtained with two B/C ratios were used as working electrode. The geometric area of the BDD films in contact with the electrolyte was 0.23 cm^2. A platinum coil wire served as counter electrode and Ag/AgCl was used as reference electrode. The Mott–Schottky plots (MSP) measurements were performed for each sample at single sine wave potential of 10 mV peak-to-peak potential perturbations. The MSP curves were taken in 0.5 mol L^{-1} H_2SO_4 solution at three different frequencies (1, 10 and 50 kHz).

The square wave anodic stripping voltammetry (SWASV) experiments were performed in the Pb (II) standard solution using 100 μg L^{-1} $Pb(NO_3)_2$ in 0.2 mol L^{-1} ammonium acetate buffer (pH 4.5) at pH 4.5, purging nitrogen for 5 min in the following different steps: (a) the pre-conditioning step, applying the potential of 0.9 V vs. Ag/AgCl for 45 s before each measurement in order to ensure the dissolution of the remaining deposits on the electrode surface, (b) the pre-concentration step procedure at −1.2 V vs. Ag/AgCl for 180 s, the solution was stirred during the electrodeposition step and (c) the SWASV voltammograms recorded from −0.8 V to 0.0 V. For the optimization of SWASV parameters, the Lead concentration was 100 μg L^{-1}.

After optimization of the voltammetric parameters, analytical curves were obtained in pure electrolyte by the standard addition method in the lead concentration in the range from 1 to 10 μg L^{-1}. In order to estimate the detection and quantification limits (DL and QL), three blank voltammograms were measured in purified electrolyte at oxidation potential of Pb (II). The standard deviation (S_b) was obtained by the average current of these voltammograms. The slope of the straight line (b) was obtained from the analytical curves ($DL = 3S_b/b$ and $QL = 10S_b/b$) [22,23].

3. Results and discussions

3.1. Diamond characterization

The morphology and structure of these films showed different properties. The SEM images allowed observing the morphology of diamond films, as shown in Fig. 1. Significant changes in the diamond grain sizes were observed due to the doping level and addition of argon to the gas mixture. For BDD films (Fig. 1a and b), the decreasing in the diamond grain size is expected when is increased the boron incorporation, causing a reduction in the growth rate [25]. According to Issaoui et al. [30] boron affects the nucleus formation during the first step of growth. Consequently, high doping levels promote a low growth rate compared with the values obtained using low doping levels. However, the change in growth rate cannot be related only to the influence of boron. A small amount of oxygen from the solution can also contribute to