Electrochimica Acta 56 (2011) 3975–3980

Contents lists available at ScienceDirect

Electrochimica Acta

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

The fabrication and characterization of an ex situ plated lead film electrode prepared with the use of a reversibly deposited mediator metal

Katarzyna Tyszczuk*

Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie Sklodowska Sq. 3, 20-031 Lublin, Poland

ARTICLE INFO

Article history:
Received 6 December 2010
Received in revised form 4 February 2011
Accepted 4 February 2011
Available online 1 March 2011

Keywords:
Lead film electrode
Mediator metal
Stripping analysis
Microscopic study

ABSTRACT

In this paper an ex situ plated lead film electrode prepared with use of the mediator metal (Zn) was elaborated. The electrochemical method for lead film formation is based on a co-deposition of a metal of interest (Pb) with a reversibly deposited mediator metal (Zn) and then on an oxidation of zinc and further deposition of lead by the appropriate potential. This serves to increase the density of islands of lead atoms, promoting lead film growth. The lead-based sensors were characterized by optical method (atomic force microscopy (AFM)) and as well as cyclic, linear sweep and square wave voltammetry. The adsorptive system of folic acid was employed to investigate the electrochemical characteristics a novel type of lead film electrode. Well-formed stripping peaks and a linear dependence of the stripping current on the folic acid concentration were observed on the lead film electrode prepared with use of the mediator metal while comparative measurements attempted with the lead film electrode prepared without use of the mediator metal were unsuccessful.

1. Introduction

Metal film electrodes have become widespread in electrochemical stripping analysis due to their relatively simple fabrication and surface regeneration [1]. The most commonly used examples are mercury film electrodes [2–4], and recently, also film electrodes from non-noble metals, such as bismuth [5–10] or antimony [11–15]. In 2005, a new type of electrode, a lead film electrode, was proposed as an alternative to mercury electrodes [16–23]. The lead film electrode exhibited interesting characteristics, such as lower toxicity compared to the mercury electrodes, a wide potential window and the ability to operate in a wide range of pH media, simple preparation, good reproducibility and a simple way of electrochemical surface renewal.

The method of coating the substrate with film is critical for a satisfactory performance of the resulting metal film electrodes. There are three general methods of electrochemical coating the substrate surface with a metal deposit. In the first method, in situ plating, metal ions are added directly into the sample solution and the film is deposited on the electrode surface during the analysis. The second method, ex situ plating, involves electroplating film before transferring the electrode to the sample solution for analysis. The third plating method is based on modifying the heterogeneous electrodes (carbon paste electrodes or screen printed electrodes) with a metal precursor, such as Bi_2O_3 [24].

In this paper the lead film electrode was prepared using an electrochemical, defect-mediated, thin-film growth method [25,26]. In this approach, the metal of interest (Pb) is co-deposited with a reversibly deposited mediator metal. A necessary characteristic of the mediator is that it must be less noble than the metal of interest, so for further study zinc was used as mediator. Such an electrode was tested using solutions containing acetate buffer and folic acid by adsorptive stripping voltammetry. The results were compared to those already reported for in situ lead film electrode [18] and to those obtained at ex situ plated lead film electrode prepared without use of the mediator metal. The main aims of this paper were to obtain a mechanically stable sensor useful in electroanalytical applications and present some fundamental facts concerning the surface properties of this sensor.

2. Experimental

2.1. Reagents

An acetate buffer, used as a supporting electrolyte, was prepared from CH_3COOH and NaOH obtained from Merck. 0.01 mol L^{-1} solutions of $Pb(NO_3)_2$ and $ZnCl_2$ were prepared from reagent obtained from POCh, Poland. Folic acid was obtained from Fluka. A stock standard solution of folic acid (10^{-2} mol L^{-1}) was prepared in

---

* Corresponding author. Tel.: +48 81 5375592; fax: +48 81 5333348.
E-mail address: ktyszczuk@poczta.umcs.lublin.pl

0013-4686/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2011.02.015

0.02 mol L^{-1} NaOH and stored in a refrigerator until used. Working solutions were prepared daily by dilution of the stock solution. All solutions were prepared in deionized water of resistivity not less than 18.2 MΩ cm^{-1} at 298 K (Millipore, UK).

2.2. Apparatus

All voltammetric measurements were performed using a μAutolab analyser made by Eco Chemie, The Netherlands. A classical three-electrode quartz cell of volume 10 mL was used throughout, consisting of a glassy carbon working electrode, with an Ag/AgCl reference electrode and a platinum wire as an auxiliary electrode. The homemade working electrode included an easy-to-take-out disk (diameter 10 mm, thickness 5 mm) with a glassy carbon surface (diameter 1 mm). The PEEK housing was equipped with a stainless steel piston to make electrical contact with the disk.

Atomic force microscopy (AFM) measurements were performed using a Digital Instruments NanoScope III (USA, 2001). Contact mode topographic images were recorded using Si_3N_4 probes with a spring constant of 0.05 N m^{-1} and a nominal radius of curvature 20 nm (NANOPROBE^{TM} SPM Tips, type NP-1). The images were recorded at a scan area of 5 μm × 5 μm for three randomly chosen places (512 × 512) and with the scan rate of 1 Hz. The software used in data acquisition and analysis was the NanoScope version 5.12 (Digital Instruments, Veeco Metrology Group, CA) and the Scanning Probe Microscopy Software (WSxM 4.0 Develop 8.0 June 2005, Nanotec Electronica S.L.). The square root of average surface roughness (R_{RMS}) was calculated from the following formula:

$$R_{RMS} = \sqrt{\frac{1}{N}\sum_{i=1}^{N} \left|Z_i - Z\right|}$$

where N is tfhe number of measured points (in this case: 512 × 512 = 262,144); Z_i is the height of the topographic element in point 'i'; and Z is the arithmetic mean of the heights of all topographic elements.

2.3. Preparation of the lead film with the use of a reversibly deposited mediator metal

The lead film electrode was prepared by an electrochemical method with the use of a reversibly deposited mediator metal. As a substrate for plating, a glassy carbon electrode was chosen based on the published experiments with the use of such an electrode support for the preparation of the lead film electrode [16–23]. The glassy carbon surface was polished daily using 0.3 μm alumina slurry on a Buehler polishing pad and then was washed and sonicated for 2 min. After mechanical cleaning the electrode was transferred into the plating solution containing 0.1 mol L^{-1} acetate buffer (pH 3.5), 5×10^{-5} mol L^{-1} Pb(II) and 7.5×10^{-5} mol L^{-1} Zn(II). Before each deposition experiment the electrode was cleaned electrochemically at 0.5 V for 30 s. In the course of electrodeposition the potential of the electrode was changed in the following sequence: −1.4 V for 45 s and −0.7 V for 45 s. In the first step Pb (metal of interest) and Zn (reversibly mediator metal) were deposited simultaneously on a glassy carbon surface. During the second step Zn atoms were stripped from surface as Pb continued to deposit resulting in islands of lead atoms growth. During both steps the solution was stirred using a magnetic stirring bar. After preparation the electrode was carefully rinsed with water and immersed in the tested solutions. In the case of microscopic measurements the disk with a lead-coated surface was taken out from the housing and the sample was carefully placed in the detection chamber of the microscope.

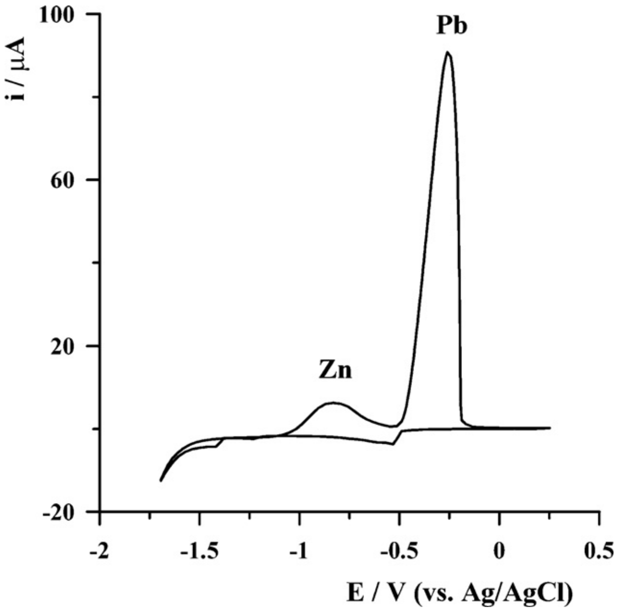

Fig. 1. Cyclic voltammograms obtained from the solution containing 0.1 mol L^{-1} acetate buffer (pH 4.6), 1×10^{-4} mol L^{-1} of Zn(II) and 5×10^{-5} mol L^{-1} of Pb(II). The lead and zinc were deposited at −1.4 V for 60 s. Instrumental parameters: start potential of −1.4 V; first vertex potential of −1.7 V; second vertex potential of 0.25 V; and scan rate of 50 mV s^{-1}.

2.4. Electroanalysis

The prepared lead film electrode was tested by adsorptive stripping voltammetry of folic acid according to the procedure earlier described in literature [18]. All voltammetric measurements of folic acid were carried out in 0.1 mol L^{-1} acetate buffer (pH 5.6) containing variable concentration determined organic compound. A preconcentration potential of −0.88 V (vs. Ag/AgCl) was applied for 120 s to the working electrode under stirring, to effect adsorption of folic acid on the lead film surface. Then the stirring was stopped and after 5 s equilibration time, the square wave voltammograms were recorded between −0.88 and −1.2 V with a frequency of 200 Hz and amplitude of 50 mV. The potential step was 4 mV. All voltammetric measurements were carried out in undeaerated solutions.

3. Results and discussion

The most notable advantages of an ideal working electrode used in stripping analysis are a high hydrogen overpotential, a well-defined electrochemical behaviour in a wide potential range, with a low background and noise, and the possibility of obtaining low detection limits. Although reports on metal ions and organic compounds determinations at an in situ plated lead film electrode can be found in literature [16–23], it is obvious that the elaboration of an electrode with properties similar to those possessed by an ideal working electrode is the crucial point for successful research work in applied electroanalysis. Due to this fact, the aim of this paper was the application of an electrochemical method with use of the mediator metal, in order to improve some properties of the lead film electrode already described in literature.

Preliminary electrochemical measurements were carried out in the plating solutions after electrodeposition of lead and zinc on a glassy carbon surface, in order to identify the oxidation potentials of those metals. Fig. 1 displays the cyclic voltammogram obtained from the solution containing 0.1 mol L^{-1} acetate buffer (pH 4.6), 1×10^{-4} mol L^{-1} $ZnCl_2$ and 5×10^{-5} $Pb(NO_3)_2$. The lead and zinc were deposited at −1.4 V for 60 s. It was found that the oxidation lead and zinc start at the potentials around −0.6 and −1.1 V,

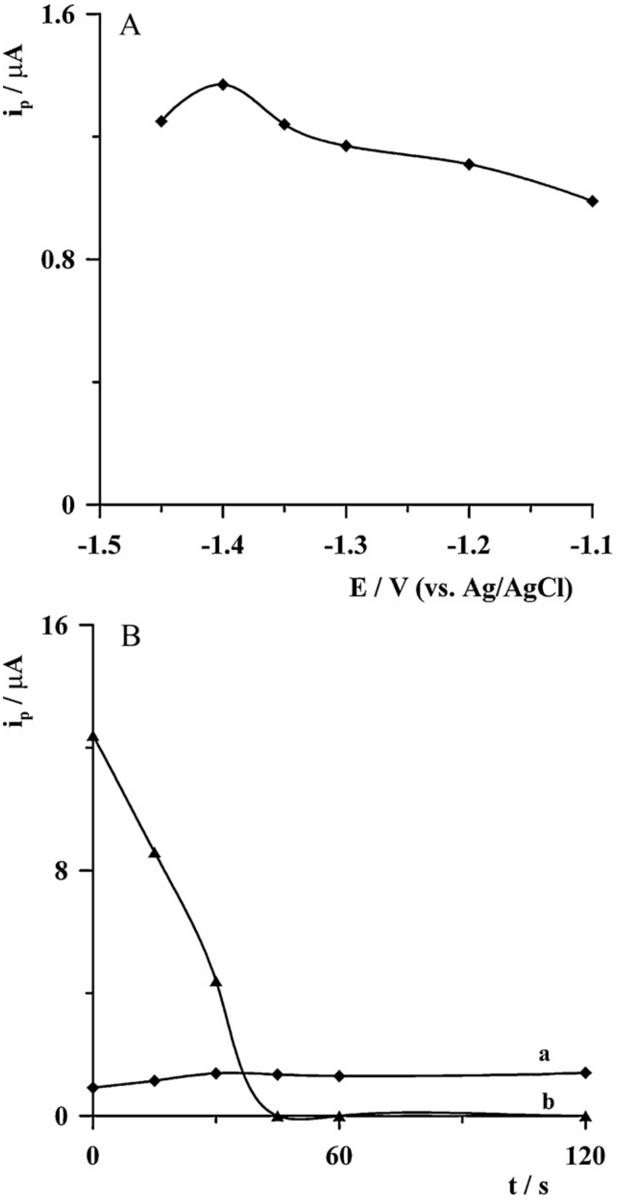

Fig. 2. (A) The dependence of folic acid peak current on the deposition potential of lead and zinc. (B) The influence of the time of the oxidation zinc and further deposition of lead on: (a) the folic acid peak current and (b) the oxidation peak current of zinc. The plating solution contained 0.1 mol L^{-1} acetate buffer (pH 3.5), 7.5×10^{-5} mol L^{-1} Zn(II) and 5×10^{-5} mol L^{-1} Pb(II). The folic acid at concentration of 1×10^{-7} mol L^{-1} was accumulated at −0.88 V for 120 s. The deposition potential of lead and zinc in (B) was −1.4 V. The deposition time of lead and zinc in (A) and (B) was 45 s. The potential of the zinc oxidation and further deposition of lead in (A) was −0.7 V. The time of the zinc oxidation and further deposition of lead in (A) was 60 s.

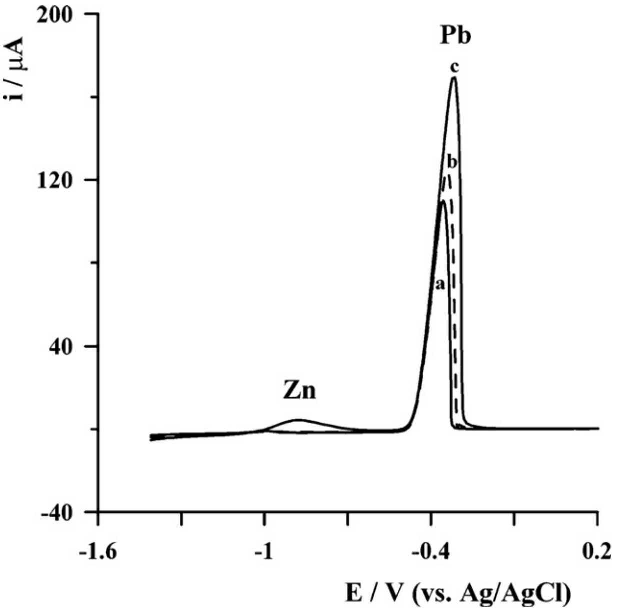

Fig. 3. Linear sweep voltammograms obtained at electrode after: (a) deposition of lead and zinc at a potential of −1.4 V for 45 s (solid line); (b) deposition of lead and zinc at a potential of −1.4 V for 45 s and then at a potential of −0.7 V for 45 s oxidation of zinc and further deposition of lead (dash line); and (c) deposition of lead at a potential of −1.4 V for 45 s and then at a potential of −0.7 V for 45 s (solid line). The solution contained 0.1 mol L^{-1} acetate buffer (pH 3.5), 5×10^{-5} mol L^{-1} Pb(II) and 7.5×10^{-5} mol L^{-1} Zn(II). In the case of a lead film electrode prepared without use the mediator metal the solution contained 0.1 mol L^{-1} acetate buffer (pH 3.5) and 5×10^{-5} mol L^{-1} Pb(II) (c). Scan rate of 50 mV s^{-1}.

respectively. On the basis of the above experimental result it can be stated that at a potential in the range from −0.6 to −0.75 V zinc will be stripped from the surface as lead will continued the deposition. Additionally, lead and zinc can be deposited simultaneously at potential more negative than −1.1. In further measurements a potential of −1.4 V and time of 60 s were used for plating zinc and lead, and a potential of −0.7 V and time of 60 s were used for stripping zinc and further plating of lead.

3.1. Conditions of lead film formation and electrode regeneration

The influence of the conditions of lead film formation was optimised. The time and the potential of lead and zinc deposition were fixed at 60 s and −1.4 V, respectively. In these experiments zinc was stripped and lead was further deposited at −0.7 V for 60 s. The folic acid at concentration of 1×10^{-7} mol L^{-1} was accumulated at −0.88 V for 120 s. The influence of the pH of 0.1 mol L^{-1} acetate buffer added to the plating solution on the peak current of folic acid was studied. The concentrations of Zn(II) and Pb(II) were 1×10^{-4} mol L^{-1} and 5×10^{-5} mol L^{-1}, respectively. It was observed that the change of the pH of the solution from 3.5 to 6.1 did not influence significantly the peak current of folic acid. However, the lowest background current at a pH of 3.5 was obtained, so for further study this value of the pH of the solution was chosen. Then the concentration of Pb(II) added to the plating solution was changed in the range from 0 to 2×10^{-4} mol L^{-1} and its influence on the folic acid peak was studied. The measurements were done at a constant concentration of Zn(II) equal to 1×10^{-4} mol L^{-1}. It was found that the folic acid peak current increases as the concentration of Pb(II) increases to 4×10^{-5} mol L^{-1} and then is stable. In the absence of Pb(II) the peak of folic acid was not observed on the voltammogram because it was not adsorbed on the glassy carbon electrode. The increase of the folic acid peak current with the increase of Pb(II) concentration added to the plating solution probably is connected with the increase of the lead film area accessible for adsorption of folic acid. It must be noted that the lead was further deposited in the course of the second step of film plating. For further measurements a concentration of Pb(II) 5×10^{-5} mol L^{-1} was chosen. The results show also that prolongation of the deposition time of lead and zinc from 45 to 240 s did not influence the peak current of folic acid, so in further measurements the deposition time of 45 s was used. Then the influence of concentration of Zn(II) added to the plating solution on the folic acid signal was studied. The measurements for this optimisation were done at a constant concentration of Pb(II) equal to 5×10^{-5} mol L^{-1}, while the concentration of Zn(II) was changed from 0 to 2×10^{-4} mol L^{-1}. It was found that the folic acid peak current increases as the con-

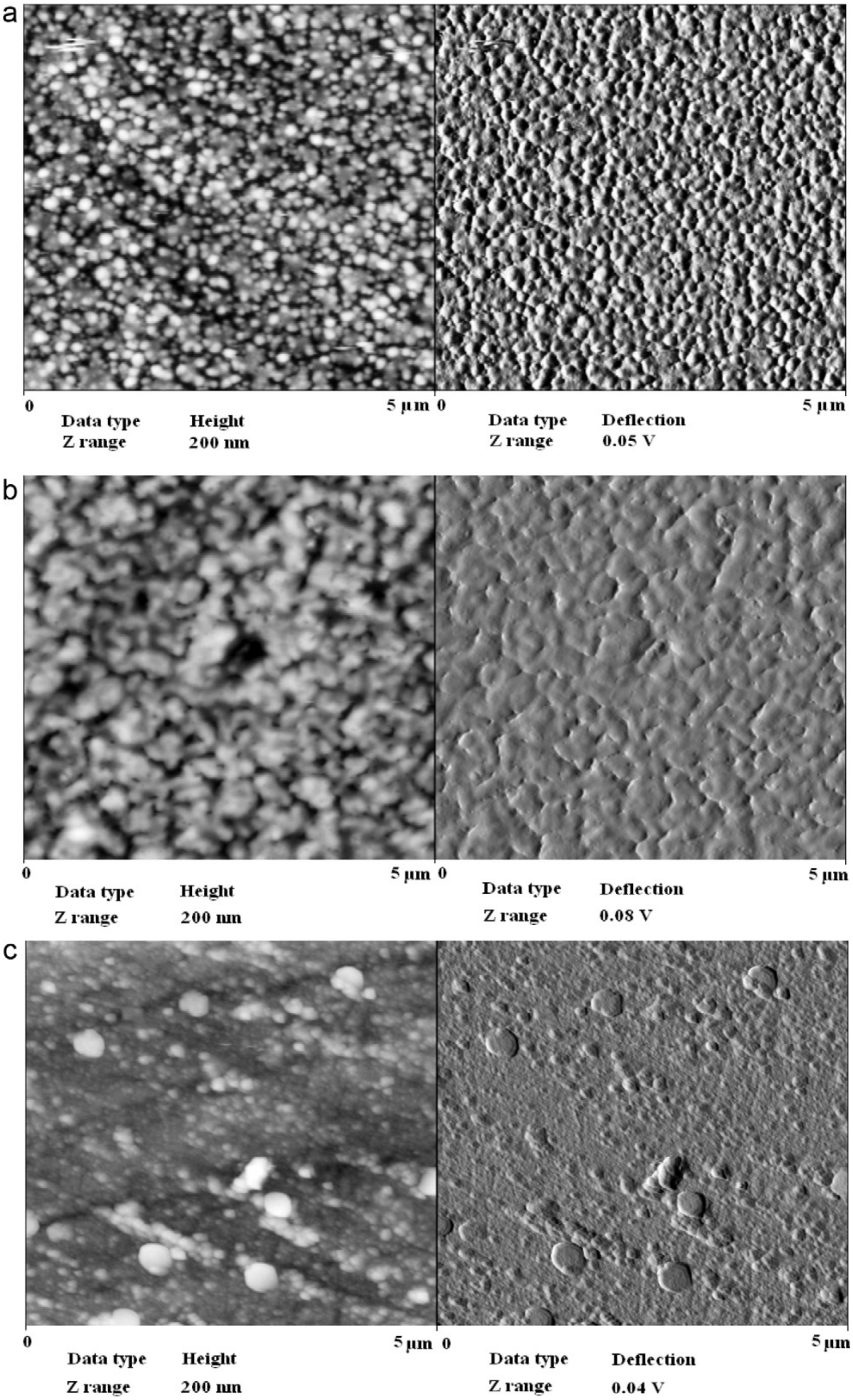

Fig. 4. AFM images of the electrode surface after: (a) the deposition of lead and zinc at a potential of −1.4 V for 45 s; (b) the deposition of lead and zinc at a potential of −1.4 V for 45 s and then at a potential of −0.7 V for 45 s oxidation of zinc and further deposition of lead; and (c) the deposition of a lead at potential of −1.4 V for 45 and then at potential −0.7 V for 45 s. The plating solution contained 0.1 mol L^{-1} acetate buffer (pH 3.5), 0 or 7.5×10^{-5} mol L^{-1} Zn(II) and 5×10^{-5} mol L^{-1} Pb(II).

centration of Zn(II) increases to 5×10^{-5} mol L^{-1}. On the basis of the experimental results for further study the concentration of Zn(II) 7.5×10^{-5} mol L^{-1} was chosen. Next, the potential of the deposition of zinc and lead was changed in the range from −1.1 to −1.45 V and its influence on the peak currents of folic acid was studied. The obtained results are presented in Fig. 2A. The potential of the zinc oxidation and further deposition of lead was equal to −0.7 V. The folic acid peak attained the maximal value as the deposition potential of the lead film was −1.4 V, so for further study this potential was chosen. The results show also that the changes of the potential of the oxidation zinc and further deposition of lead in the range from −0.6 to −0.75 V did not influence the peak current of folic acid, so in further measurements the potential of −0.7 V was used. Next, the time of the oxidation of zinc and further deposition of lead film was studied. The time was changed in the range from 0 to 120 s and its influence on the oxidation peak of zinc and the reduction peak of folic acid was studied (Fig. 2B). It was observed that the folic acid peak current increases with the prolongation of the time to 30 s and then is nearly stable. However, all zinc is stripped from the surface of the electrode, while the time of the oxidation is equal to 45 s. As a compromise between the value of the peak current of folic acid and the complete oxidation of zinc the time of 45 s was chosen for further study.

In the previous articles about the application of an in situ plated lead film electrode to the determination of folic acid the potential of +0.5 V for 10 s was applied to clean the electrode surface [18]. The reproducibility of the ex situ plated lead film electrode was evaluated measuring the peak current of 1×10^{-7} mol L^{-1} folic acid twenty times. Before each measurement the electrode was cleaned electrochemically at the potential +0.5 V for 10 s and the lead film was deposited with use of the mediator metal on a glassy carbon surface. The relative standard deviation was 5.9%. Prolongation of the cleaning time to 30 s caused a better reproducibility of the electrode. The relative standard deviation was 4.3% ($n = 20$), so for further study the cleaning potential of +0.5 V and the cleaning time of 30 s were chosen.

3.2. Characterisation of deposits on a glassy carbon surface

In order to present evidence of the role of the mediator metal in the increase of the lead film mass linear sweep voltammetric measurements from a solution containing 0.1 mol L^{-1} acetate buffer (pH 3.5), 5×10^{-5} mol L^{-1} Pb(II) and 0 or 7.5×10^{-5} mol L^{-1} Zn(II) were performed (Fig. 3). Using the peak areas under Zn and Pb stripping peaks, and Faraday's law, it was calculated that approximately 0.026 μg of Zn and 0.183 μg of Pb (for the time of zinc oxidation and further deposition of lead equal to 0 s) (Fig. 3a), and 0 μg of Zn and 0.361 μg of Pb (for the time of zinc oxidation and further deposition of lead equal to 45 s) (Fig. 3b), and 0.229 μg of Pb (the lead film electrode prepared without use of the mediator metal) were stripped from the glassy carbon surface. The results showed that the application of the mediator metal (Zn) increases the mass of Pb plated on the surface to 60% of its value obtained when no zinc was present in the plating solution.

The surface morphology of the electrode surface was characterized by atomic force microscopy (Fig. 4). AFM images show the electrode surface prepared with and without use of the mediator metal. As was mentioned in Section 2.4, the process of the deposition of the lead film occurs in two steps. In the first step, at a potential of −1.4 V Pb and Zn grow in the active areas of the surface forming a random particle array (Fig. 4a). The whole substrate surface is covered with rather uniform particles of 0.1–0.25 μm diameter and an average height of 50 nm (bright areas in the left picture). In the second step of lead film formation, at a potential of −0.7 V the zinc particles are oxidised and stripped from the surface. During this step, also the growth of the earlier formed nuclei of Pb takes place (Fig. 4b). The microstructure of the lead film changes from the nuclei to crystallites with the size found in the range of 70–180 nm in height. The surface coverage and roughness (R_a) are about 100 ± 5% and 12.5 ± 2.1, respectively. Fig. 4c shows that the lead deposit obtained without use of the mediator metal in the same conditions than those formed with use of the mediator zinc, consists of smaller grains with the size found in the range of 35–50 nm in height, and approximately 0.1–0.4 μm in diameter and separated by a small number of bigger ones. The surface coverage and roughness (R_a) were about 50 ± 8% and 7.2 ± 3.3, respectively. The microscopic images showed considerable variability in the morphology of the deposited layer depending on the way of the preparation of the lead film (Fig. 4b and c). On the basis of the results it can be stated that the application of the mediator metal to the preparation of the lead film causes an increase of the surface coverage and roughness of the deposit.

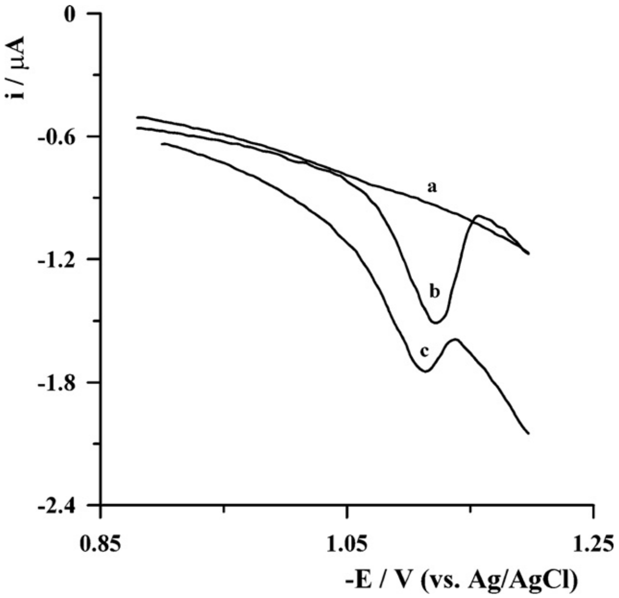

Fig. 5. Square wave voltammograms obtained at a lead film electrode: (a) prepared without use of the mediator metal; (b) prepared with use of the mediator metal; and (c) in situ plated, in a 0.1 mol L^{-1} acetate buffer (pH = 5.6) in the presence of 5×10^{-8} mol L^{-1} folic acid. The plating solution contained 0.1 mol L^{-1} acetate buffer (pH 3.5), 0 or 7.5×10^{-5} mol L^{-1} Zn(II) and 5×10^{-5} mol L^{-1} Pb(II). The lead and zinc were deposited for 45 s at −1.4 V and then. at −0.7 V for 45 s zinc was stripped from the surface and lead was deposited. Stripping parameters: frequency 200 Hz; step height 4 mV; and amplitude 50 mV.

3.3. Comparison of the lead film electrodes prepared with use of different plating methods

The investigated lead film electrode prepared with use of the mediator metal was compared to an ex situ plated lead film electrode prepared without use of the mediator metal and an in situ plated lead film electrode. The adsorptive stripping voltammetric responses were recorded and compared (Fig. 5). As can be seen in Fig. 5, well-defined and sharp peak with relatively low background was obtained using a lead film electrode prepared with use of the mediator metal in contrast to the broader and lower analytical signal recorded at an in situ plated lead film electrode. In the case of use an ex situ plated lead film electrode prepared without use of the mediator metal no signal of 5×10^{-8} mol L^{-1} folic acid was observed.

Calibration curves for determination of folic acid at in situ plated lead film electrodes prepared with and without use of the mediator metal and an in situ plated lead film electrode were carried out under optimal condition. Calibration curves comparing an in situ plated lead film electrode and an ex situ plated lead film electrode prepared with use of mediator zinc for the accumulation time of 120 s are shown in Fig. 6a and b. The stripping currents of the lead film electrode prepared with use of the mediator metal were linear in the concentration range of folic acid from 2×10^{-9} to 1.5×10^{-7} mol L^{-1} (Fig. 6b). The calibration plot is expressed by the first-order equation $y = 12.17x + 4.33$, where y is the peak current (nA) and x is a folic acid concentration (nmol L^{-1}). The linear correlation coefficient (r^2) was equal to 0.999. The relative standard deviation from five determinations of folic acid at a concentration

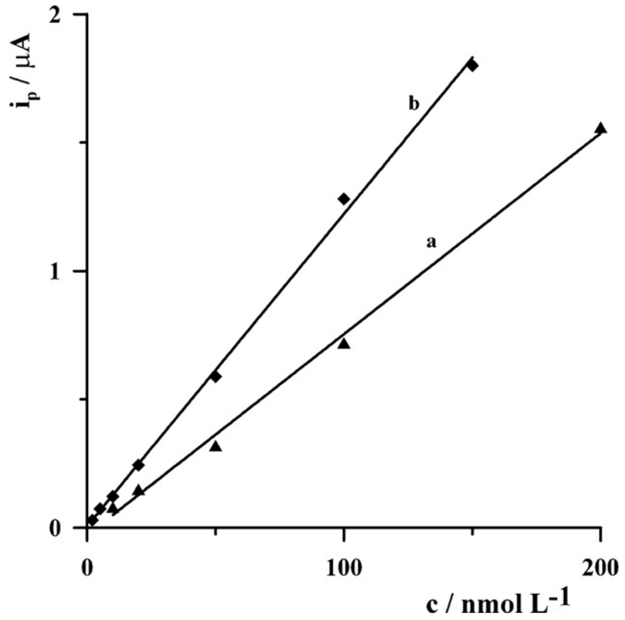

Fig. 6. Calibration curves for folic acid obtained at an in situ plated lead film electrode (a) and an ex situ plated lead film electrode prepared with use of mediator zinc (b). The plating solution contained 0.1 mol L^{-1} acetate buffer (pH 3.5), 7.5×10^{-5} mol L^{-1} Zn(II) and 5×10^{-5} mol L^{-1} Pb(II). The lead and zinc were deposited for 45 s at −1.4 V and then at −0.7 V for 45 s zinc was stripped from the surface and lead was deposited. In the case of an in situ plated lead film electrode the solution contained 0.1 mol L^{-1} acetate buffer (pH 5.6) and 7.5×10^{-5} mol L^{-1} Pb(II). Folic acid was accumulated at −0.88 V for 120 s.

of 5×10^{-8} mol L^{-1} was 3.8%. The detection and quantification limits for an accumulation time of 120 s estimated from 3 and 10 times the standard deviation for the lowest determined concentration of folic acid were about 5×10^{-10} and 1.7×10^{-9} mol L^{-1}, respectively. The favorable performance of the lead film electrode prepared with use of the mediator metal is supported by the calculated detection limit value of 5×10^{-10} mol L^{-1}, eight time lower than that found for an in situ plated lead film electrode (4×10^{-9} mol L^{-1}) [18]. In the case of use an ex situ plated lead film electrode prepared without use of the mediator metal no signal of folic acid in the concentration range from 2×10^{-9} to 2×10^{-7} mol L^{-1} was observed. On the basis of the obtained results it can be speculated that this structure of metal film (Fig. 4c) possesses inferior adsorptive properties than the uniform lead film formed with use of the mediator metal (Fig. 4b).

4. Conclusions

In this paper an electrochemical method was used for the preparation of an ex situ plated lead film electrode with use of the mediator metal (Zn). The microscopic images showed considerable variability in structure and compactness of the deposited lead layer depending on the way of the preparation of the film. The application of the mediator metal to the preparation of a lead film caused an increase of the surface coverage and roughness of the deposit. The microscopic observation correlated well with the results of the electrochemical study. The complete coverage of the surface by Pb crystallites causes that the background current recorded for the investigated system of folic acid is more flat and lower, in contrast to the baselines recorded at the in situ plated lead film electrode (Fig. 5). Additionally, as can be seen in Fig. 5, the analytical signal of folic acid is a higher and has a better shape than that recorded at the in situ plated lead film electrode. It is obvious that the higher surface coverage and roughness are advantageous the investigated lead film electrode prepared with use of the mediator metal because they lead to an increase in the active areas of the surface of the electrode and improve its electrochemical properties.

Under the optimized conditions of lead film formation, the proposed procedure of determination of folic acid by adsorptive stripping voltammetry offers a lower detection limit than that obtained at an in situ plated lead film electrode.

In spite of the prolongation of the time of the preparation of an ex situ lead film compared to an in situ lead film, this electrode exhibits notable advantages, so it can be a very promising analytical tool.

Acknowledgements

The author acknowledges the financial support of the Foundation for Polish Science (START Program, 2010).

References

[1] J. Wang, Analytical Electrochemistry, 3rd ed., Wiley-VCH, Hoboken, NJ, 2006.
[2] A. Economou, P.R. Fielden, Analyst 128 (2003) 205.
[3] A. Economou, P.R. Fielden, Trends Anal. Chem. 16 (1997) 286.
[4] Z. Stojek, Z. Kublik, J. Electroanal. Chem. 105 (1979) 247.
[5] J. Wang, J. Lu, S.B. Hocevar, P.A. Farias, B. Ogorevc, Anal. Chem. 72 (2000) 3218.
[6] A. Krolicka, R. Pauliukaite, I. Svancara, R. Metelka, A. Bobrowski, E. Norkus, K. Kalcher, K. Vytras, Electrochem. Commun. 4 (2002) 193.
[7] S.B. Hocevar, J. Wang, R.P. Deo, B. Ogorevc, Electroanalysis 14 (2002) 112.
[8] E.A. Hutton, S.B. Hocevar, B. Ogorevc, M.R. Smyth, Electrochem. Commun. 5 (2003) 765.
[9] A. Krolicka, A. Bobrowski, K. Kalcher, J. Mocak, I. Svancara, K. Vytras, Electroanalysis 15 (2003) 1859.
[10] L. Baldrianova, I. Svancara, A. Economou, S. Sotiropoulos, Anal. Chim. Acta 580 (2006) 24.
[11] S.B. Hocevar, I. Svancara, B. Ogorevc, K. Vytras, Anal. Chem. 79 (2007) 8639.
[12] E. Tesarova, L. Baldrianova, S.B. Hocevar, I. Svancara, K. Vytras, B. Ogorevc, Electrochim. Acta 54 (2009) 1506.
[13] V. Jovanovski, S.B. Hocevar, B. Ogorevc, Electroanalysis 21 (2009) 2321.
[14] K.E. Toghill, L. Xiao, G.G. Wildgoose, R.G. Compton, Electroanalysis 21 (2009) 1113.
[15] V. Urbanova, K. Vytras, A. Kuhn, Electrochem. Commun. 12 (2010) 114.
[16] M. Korolczuk, K. Tyszczuk, M. Grabarczyk, Electrochem. Commun. 7 (2005) 1185.
[17] M. Korolczuk, K. Tyszczuk, Anal. Chim. Acta 580 (2006) 231.
[18] M. Korolczuk, K. Tyszczuk, Electroanalysis 19 (2007) 1959.
[19] K. Tyszczuk, Anal. Bioanal. Chem. 390 (2008) 1951.
[20] A. Bobrowski, K. Kalcher, K. Kurowska, Electrochim. Acta 54 (2009) 7214.
[21] K. Tyszczuk, J. Pharmaceut. Biomed. 49 (2009) 558.
[22] K. Tyszczuk, M. Korolczuk, Bioelectrochemistry 78 (2010) 113.
[23] K. Tyszczuk, M. Korolczuk, Comb. Chem. High T. Scr. 13 (2010) 753.
[24] R. Pauliukaite, R. Metelka, I. Svancara, A. Krolicka, A. Bobrowski, K. Vytras, E. Norkus, K. Kalcher, Anal. Bioanal. Chem. 374 (2002) 1155.
[25] K. Sieradzki, S.R. Brankovic, N. Dimitrov, Science 284 (1999) 138.
[26] S.R. Brankovic, N. Dimitrov, K. Sieradzki, Eletrochem. Solid State Lett. 2 (1999) 443.