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# Microscopic and electrochemical characterization of lead film electrode applied in adsorptive stripping analysis

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#### ABSTRACT

Lead film electrodes (PbFEs) deposited in situ on glassy carbon or carbon paste supports have recently found application in adsorptive stripping voltammetric determination of inorganic ions and organic substances. In this work, the PbFE, prepared in ammonia buffer solutions, was investigated using scanning electron microscopy, atomic force microscopy and various voltammetric techniques. The microscopic images of the lead films deposited on the glassy carbon substrate showed a considerable variability in microstructure and compactness of the deposited layer depending on the selected experimental conditions, such as the concentration of Pb(II) species, the nucleation and deposition potential, and the time applied. The catalytic adsorptive systems of cobalt and nickel in a solution containing 0.1 ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime and 0.25 M NaNO<sub>2</sub> were employed to investigate the electrochemical characteristics and utility of the in situ prepared lead films.

The optimal parameters, i.e. the lead concentration in the solution, the procedure of film removal, and the time and potential of lead nucleation and film deposition for the adsorptive determination of metal traces, were selected, resulting in the very good reproducibility (RSD=4.2% for 35 scans) of recorded signals. The voltammetric utility of the lead film electrode was compared to that of glassy carbon, mercury film and bismuth film electrodes, and was subsequently evaluated as superior.

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#### 1. Introduction

Metal film electrodes are widely applied in electroanalysis. The most commonly used examples are mercury film electrodes (MFEs) [1–4], gold film electrodes (AuFEs) [5–8], and, recently, also film electrodes from non-noble metals, such as bismuth (BiFE) [9–21], antimony (SbFE) [22–26], gallium (GaFE) [27] or tin [28].

Compared to metal bulk electrodes, films exhibit many advantages:

- the consumption of metal, actually of its precursor, is rather small; this aspect seems to be of some importance if the metal is toxic in its nature (e.g. mercury) or if noble metals, which are expensive, are involved;
- films may be prepared from metals in cases when bulk electrodes are not commercially available;
- as films are deposited immediately before or during analyses, they are not subject to corrosion (mainly oxide formation) as is the case with bulk electrodes;

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• films may exhibit improved analytical performance due to their micro- and nano-structure (droplets or crystallites) leading to a better accumulation of the analyte or to catalytic effects.

Films are deposited on substrate electrodes usually made of glassy carbon (GC). Carbon paste electrodes (CPEs) or screen printed electrodes (SPEs) may also serve for this purpose [6,8,10]. The preparation of films usually imposes no restrictions to the analysis and may proceed in one of the following ways:

- ex situ—the film is plated on the substrate prior to the analysis, therefore the properties of films may be controlled very deliberately before the interaction with the analyte starts;
- in situ—the film is generated during the analysis itself, so interaction between film and analyte starts before a complete film is formed already; in this case some influence of the support electrode on the analyte may also occur;
- with heterogeneous electrodes (carbon paste electrodes or screen printed electrodes) it is possible to add the precursor of the film directly to the electrode material, so that the film could be formed from the electrode material itself.

Recently, the lead film electrode (PbFE) was described in Refs. [29–36] as one of the substitutes for liquid mercury electrodes. It

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was shown that the in situ plating of lead films is possible in fairly alkaline media, as Pb(II) ions do not hydrolyze but form soluble  $[Pb(OH)_4]^2$ . This type of metal deposited as a film on a support seems to import some interesting properties, which could be valuable for electroanalytical applications.

So far, the lead film electrode has only been applied for analytical purposes, i.e. for the adsorptive stripping determination of selected metal ions and some organic substances [29-32,35,36]. In the vast majority of the above quoted works, the ammonia buffer was used as a main component of a supporting electrolyte. The use of metal film electrodes in stripping voltammetry, however, carries with it some risk of artifacts caused by differences in the kinetics of film deposition, scratches and crystal faces on the GC support from mechanical polishing, and incomplete removal of the deposited film from the surface of the substrate after the stripping step [37]. To avoid the above problems at least partially and to obtain reproducible and accurate analytical results, Compton's team suggested the application of microscopic techniques (SEM and AFM) for initial examination of the surface of solid electrodes before the proceeding to the stripping experiments, in order to better recognize the physical properties of the electrode surface [37].

The aim of this work is to present some fundamental investigations of the surface properties of this new sensor by means of microscopic and electrochemical techniques. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to obtain information about the morphology and topography of the lead film in situ deposited in alkaline media. The deposition of the lead film for the microscopic studies was performed under conditions more similar to those in typical AdSV experiments carried out to quantify Co and Ni. To show the analytical potentiality of this new sensor, catalytic adsorptive systems of cobalt and nickel were investigated in a solution containing 0.1 M ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime and 0.25 M NaNO<sub>2</sub> [38–40] by means of LS-, DP- and SW-AdSV, as well as stripping chronopotentiometry. Moreover, to characterize the electrochemical behaviour of the examined PbFE better, its accessible potential windows in other supporting electrolytes potentially useful in adsorptive stripping voltammetry were also evaluated.

#### 2. Experimental

#### 2.1. Apparatus

All voltammetric experiments were performed with a potentiostat Autolab (ECO Chemie BV, The Netherlands) controlled by a PC equipped with the corresponding software (GPES 4.9). All measurements were carried out in a three-electrode cell with an Ag/AgCl/3 M KCl reference electrode and a platinum wire auxiliary electrode. The working electrode consisted of glassy carbon (3 mm diameter, BAS, USA) covered with a lead film. Microscopic examinations were carried out with a scanning electron microscope (SEM; Jeol LSM-5400), and an atomic force microscope (AFM; NanoScope E, Digital Instruments, USA) in the contact mode.

#### 2.2. Methods of surface characterization

The microstructure of the samples was studied with a scanning electron microscope (JSM 5400, JEOL, Japan; accelerating voltage 15 kV). Elemental composition of the samples was studied by energy dispersive X-ray (EDX) spectroscopy (Link AN 10,000, UK).

Topography measurements were performed under ambient laboratory conditions with an explorer atomic force microscope (ThermoMicroscopes, Vecco, USA). Contact mode topographic images were recorded using  $Si_3N_4$  probes with a spring constant of 0.05 N/m and a nominal radius of curvature of 20 nm (Vecco NanoProbe<sup>TM</sup> Tips, model MLCT-EXMT-A). The images were recorded at scan areas of  $20 \,\mu\text{m} \times 20 \,\mu\text{m}$  for three randomly chosen places ( $300 \times 300 \,\text{data points}$ ) and with scan rate of 3 lines/s. All images were flattened using a third order polynominal algorithm provided with the instrument. The average surface roughness ( $R_a$ ) was calculated from the following formula:

$$R_{\rm a} = \frac{1}{N} \sum_{i=1}^{N} |Z_i - \bar{Z}|$$

where *N*, number of measured points (in this case:  $300 \times 300 = 90,000$ ).  $Z_i$ , the height of the topographic element in point '*i*'. *Z*, the arithmetic mean of the heights of all topographic elements.

#### 2.3. Reagents

All solutions were prepared from deionized water (conductivity below 0.08  $\mu$ S cm<sup>-1</sup>) produced by an ion-exchanging system (Cobrabid-Aqua, Warszawa, Poland). Stock solution of lead of 1 g L<sup>-1</sup> was a standard solution from Merck. A 2 M stock solution of ammonia buffer was prepared by mixing the corresponding amounts of NH<sub>4</sub>Cl and ammonia solution (both suprapur<sup>®</sup>, Merck). A 1 M stock solution of acetic buffer was prepared by mixing an appropriate amount of CH<sub>3</sub>COONa (per analysis grade, POCH, Poland) with 99.5% acetic acid (per analysis, POCH, Poland). Solutions of nioxime (0.1 M) and sodium nitrite (0.25 M) were prepared by dissolving appropriate amounts of analytical grade reagents in ethanol (96%, analytical grade) and water, respectively. Cobalt and nickel standard solutions (1 g L<sup>-1</sup>) were obtained from Merck and diluted as required.

#### 2.4. Procedure

The surface of the glassy carbon electrode (GCE) was polished to a mirror-like appearance with alumina slurry (0.3 and 0.05  $\mu$ m, Buchler, USA) on a polishing cloth (Micropolish II, Buchler, USA). In voltammetric experiments the GCE was exposed to the test solution containing 0.1 ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime and  $0.25\,M\,NaNO_2$  as the supporting electrolyte,  $5\times10^{-5}\,M$  of lead and  $5 \times 10^{-9}$  M of cobalt and  $5 \times 10^{-8}$  M of nickel as analytes. The electrode was cleaned electrochemically either at 0.5 V for 10 s, or by triple cycling of the potential from -0.53 to 0.5 V with a scan rate of 0.1 V s<sup>-1</sup>. The electrochemical activation was followed by the nucleation of the lead layer at -1.45 V for 20 s, and by co-deposition of lead with Co and Ni at -0.75 V for 120 s. During all three steps the solution was mixed using a magnetic stirring bar. After a resting period of 15 s the voltammogram was recorded in differential pulse mode with scanning in negative direction. The other experimental parameters were as follows: step potential 2 mV, pulse potential 20 mV, scan rate 8 mV s $^{-1}$ .

In situ plating solutions containing ammonia buffer, lead ions and nioxime were used in all analytical measurements in Co and Ni determination. As was earlier mentioned in Korolczuk's team's works [29–33] the stabilisation of Pb(II) at a mild, alkaline pH used for the determination of those elements was achieved through the presence of ammonia buffer and dioximes (dimethylglyoxime or nioxime) in the solutions. In the microscopic experiments performed in our work, the authors' intention was to show how the amount and size of the deposited Pb grains was dependent on the concentration of Pb in the plating solution. Any differences in amount, size and morphology of the deposited Pb grains could be observed easier when the plating solutions contain a relatively high Pb(II) concentration up to the  $10^{-4}$  M level. Thanks to the complexation of Pb(II) by OH<sup>-</sup> ions, we did not find any visible effect of



**Fig. 1.** The SEM images of lead film deposited from solution 0.1 ammonia buffer and  $5 \times 10^{-5}$  M of Pb under the following conditions: (a) -1.45 V for 20 s; (b) -1.45 V for 20 s and then -0.75 V for 120 s; (c) as in (b) but at higher magnification; (d) XRF along the line shown in (c).

precipitation of Pb(II) in the solution containing  $1\times 10^{-4}$  M Pb(II) in 0.1 M ammonia buffer.

For the preparation of BiFEs, the bismuth film, obtained by applying a constant charge, was deposited from a separate solution consisting of 0.02 M Bi(NO<sub>3</sub>)<sub>3</sub>, 0.5 M LiBr and 1 M HCl, by plating at -0.25 V for 10 mC [13].

For the deposition of the mercury film, a solution of 0.001 M  $Hg(NO_3)_2$ , 0.01 M  $HNO_3$  and 0.1 M  $KNO_3$  was used. It was plated by electrolysis at a potential of -1.1 V vs. Ag/AgCl for 5 min while stirring the solution. After the plating procedure, the BiFE or the MFE was rinsed with deionized water and immersed into the test solution.

#### 3. Results and discussion

#### 3.1. Deposition of lead film on glassy carbon substrate

Glassy carbon is a popular choice as a substrate material due to its useful analytical properties—chemical and electrochemical stability, low porosity, relatively high hydrogen overpotential and, from a more practical view, wide availability and simplicity of surface renewal [2]. GC is also the typical substrate of choice in the case of film electrodes, e.g. mercury and bismuth film electrodes. Consequently, glassy carbon was selected as the substrate for the deposition of lead films. The surface of the polished glassy carbon, obtained with alumina particles of around 0.1  $\mu$ m size, is smooth and has mirror-like appearance, but microscopic investigations show that its surface is covered with a network of scratches drawn by the alumina grains during polishing. The AFM investigation revealed that they were up to 25 nm wide and up to 20 nm deep [41].

For lead film electrodes, scanning electron microscopy imaging was used to study the morphology of the electrode surface, its composition and the distribution of the metal film. The microscopic image (Fig. 1) reveals that the deposited metal film is not plated as a homogeneous layer. The surface of glassy carbon is covered with a number of individual but otherwise rather uniform crystallites of a few microns diameter (bright areas). As it was mentioned in Section 2.4, the process of deposition of the lead film occurs in two steps. The formation of a thin layer of lead starts at the potential of -1.45 V by the generation of nuclei on the most active sites (e.g. scratches) of the supporting surface, where as a consequence only a small amount of crystallites is visible (Fig. 1a). At less negative plating potentials the reduction of lead ions becomes slower and the growth of the earlier formed nuclei takes place. Gradually, the microstructure of the lead film changes to crystallites as shown in Fig. 1b and c. An XRF line analysis over the surface (Fig. 1d) confirmed that these crystallites consist of lead.

In order to estimate the influence of the deposition potential directly on the analytical result, i.e. the adsorptive stripping response of Co(II) and Ni(II) as an outcome of the progressing nucleation process of lead, the film formation was studied in a solution containing 0.1 M ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime, 0.25 M NaNO<sub>2</sub>, and  $5 \times 10^{-9}$  M Co, the latter as an analyte. Upon the application of a nucleation potential in the range of -1.10 to -1.45 V, an immense increase in the cobalt signal was obtained. The peak current of the cobalt reduction increased also with the prolongation of the nucleation time for all applied nucleation potential up to a period of 20 s, but did not cause any significant changes beyond.

Surface morphology was also characterized by atomic force microscopy (Fig. 2). AFM imagines were taken of the bare GCE (Fig. 2a) and of GCE plated in a solution containing 0.1 M ammonia buffer and either  $5\times10^{-5}$  M Pb (Fig. 2b) or  $1\times10^{-4}$  M Pb (Fig. 2c). A lead film deposited from a solution containing  $5 \times 10^{-5}$  M Pb is not homogenous. A strong tendency to form nuclei along the scratches was observed, as reported earlier at the glassy carbon support for mercury [42], silver, lead [37] and bismuth [41]. The crystallites of around 1.3  $\mu$ m high and up to 5  $\mu$ m in diameter are separated by a large number of smaller particles. The complete coverage of the surface of the glassy carbon substrate by Pb crystallites causes nevertheless that the baseline of the current recorded in voltammetric experiments for the investigated systems of Co and Ni is much more flat at PbFEs and does not rise at negative potentials, in contrast to the background current recorded at BiFEs. In the case of deposition of lead from solutions containing a higher concentration of Pb ( $1 \times 10^{-4}$  M Pb), the obtained film is much more homogenous and compact, built from small crystallites a few microns in diameter. Apparently, at higher concentrations of Pb in the solution, the formation of new nuclei is prevalent over crystal growth, and, in consequence, the formed film is more uniform and consists of smaller grains. This can indicate that the higher concentration of lead in the plating solution increases the surface coverage of lead nuclei and can enhance the nucleation of lead on the GCE, thus facilitating the formation of small crystallites with a less defined structure. A similar behavior was observed in the electrodeposition of bismuth and cobalt on GCEs [43,44]. Obviously, the smaller crystallites are significantly less effective in adsorbing the ligand and the complex than the larger ones formed at lower concentrations of lead, either due to different structure, composition or surface activity. However, the different chemical composition of the investigated layers may be another, more likely explanation of the significant difference in the microstructure of the two investigated lead films.

It is possible that not only metallic lead, but also insoluble lead compounds are formed at the substrate (co-precipitation or adsorption on the lead nuclei) from the solution containing the higher concentration of Pb ( $1 \times 10^{-4}$  M Pb). These insoluble species can partly inhibit the lead deposition process and hinder the growth of Pb nuclei. The last supposition is supported by the dependence of



**Fig. 2.** AFM images (in 3D format) of: bare GCE (a) and lead film deposited from solution containing 0.1 ammonia buffer and  $5 \times 10^{-5}$  M of Pb (b);  $1 \times 10^{-4}$  M of Pb (c);  $1 \times 10^{-4}$  M of Pb and  $2.5 \times 10^{-5}$  M nioxime (d);  $1 \times 10^{-4}$  M of Pb and  $2.5 \times 10^{-5}$  M nioxime (e).



**Fig. 3.** Influence of Pb concentration on Co(II) and Ni(II) signals in solution containing: (a) 0.1 ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime,  $5 \times 10^{-9}$  M Co,  $5 \times 10^{-8}$  M Ni and 0.25 M NaNO<sub>2</sub>. Concentration of Pb: (1)  $2.5 \times 10^{-6}$  M; (2)  $5 \times 10^{-6}$  M; (3)  $2.5 \times 10^{-5}$  M; (4)  $5 \times 10^{-5}$  M; (5)  $7.5 \times 10^{-5}$  M; (6)  $1 \times 10^{-4}$  M; (b) 0.1 ammonia buffer,  $1 \times 10^{-4}$  M nioxime,  $5 \times 10^{-9}$  M Co and 0.25 M NaNO<sub>2</sub>. Instrumental parameters:  $E_{nuc} = -1.45$  V;  $E_{acc} = -0.60$  V;  $t_{acc} = 120$  s;  $\Delta E = 20$  mV;  $E_{3} = 2$  mV, scan rate = 8 mV/s. Cyclic cleaning.

the voltammetric stripping responses of Co and Ni on the amount of plated lead (Fig. 3).

It was found that the peak currents for Co and Ni increase with increasing lead concentration from  $2.5 \times 10^{-6}$  M up to  $5 \times 10^{-5}$  M Pb. The optimum concentration for the deposition of the lead film was found to be  $5 \times 10^{-5}$  M Pb. This concentration of Pb in the analyzed solution yielded the highest sensitivity and excellent resolution of the Co and Ni catalytic adsorptive stripping voltammetric responses.

For the concentration of  $7.5 \times 10^{-5}$  M of lead the observed peaks are not well-shaped, have lower values and the resolution between the two peaks becomes lower, as well. The signals for Co and Ni obtained at a PbFE deposited from solution of  $1 \times 10^{-4}$  M Pb are poorly shaped. It is obvious that the higher surface roughness (Fig. 2) is advantageous as far as adsorption of Ni and Co complexes is concerned, because it leads to an increase in the active surface area of the electrode.

To elucidate the observed phenomena in more detail, the Pb film deposited from the solution containing not only ammonia buffer and lead ions, but in addition a nioxime, was investigated by means of the AFM technique, and the electrochemical experiments were performed in solutions containing relatively high concentrations of nioxime, which forms complexes with Pb ions. The AFM images of the lead film deposited from the solution of 0.1 M ammonia buffer,  $1 \times 10^{-4}$  M Pb, containing  $2.5 \times 10^{-5}$  M or  $2.5 \times 10^{-4}$  M nioxime are presented in Fig. 2d and e. It can be seen that the morphology of the lead film in the solutions containing the nioxime ligand is similar to that shown in Fig. 2c, even though lead ions are present in the form of nioxime complexes (Fig. 2e). This observation may support the earlier findings that the concentration of Pb is the main chemical factor that determines morphology of the Pb deposit and for higher concentrations of Pb in the plating solution the obtained films are much more compact, and they are built from small crystal-lites, which are less effective in adsorbing the Co and Ni complexes than the larger ones formed at lower concentrations of lead.

This conclusion may be proven further by the dependence of the catalytic adsorptive stripping voltammetric response of Co obtained at the PbFE, on the concentration of Pb ions (Fig. 3b). The Pb films were deposited from the solutions of similar compositions to those used in earlier experiments (Fig. 3a), but contained a four times higher concentration of nioxime. The observed tendency is similar regardless of the nioxime contents, i.e. the Co signal reaches a maximum value for  $5 \times 10^{-5}$  M Pb, and then it rapidly decreases for higher Pb concentrations.

#### 3.2. Electrochemical removal of the lead film

In the case of in situ plated film electrode two issues concerning the cleaning of the electrode surface for re-use must be considered. First, how to clean the surface of the film electrode of any residual analyte or interfering compound, and second, how can the metal deposit is efficiently stripped off before a fresh metal film is plated again.

Oxidation of the lead starts at a potential of around -0.65 V. In the current work as a first step, a constant positive potential of +0.5 V for 10 s was applied as described in Ref. [31]. It was observed that cobalt peak currents for subsequent measurements are not equally high within the experimental error, but show a decreasing trend (around 60% for 20 scans). Prolongation of the cleaning time to 40 s caused still a gradual but slower decrease of the recorded Co signal, whereas application of the cleaning time of 60 s caused a gradual increase of the cobalt peak current. In order to obtain a stable signal of the analyte, the potential was cycled. Scans were started in the positive direction at a potential of -0.53 V; the first anodic half-cycle exhibits a lead oxidation peak, whereas no further signals were observed in the subsequent scans. Thus, triple cycling of the potential from -0.53 to 0.5 V with a scan rate of 0.1 V/s is proposed for the cleaning step. In this way, the value of the cobalt signal recorded during the first five runs gradually decreased by around 14-15% and reached plateau after fifth run. The reproducibility of signal of  $5 \times 10^{-9}$  M Co was found to be 4.2% for the next consecutive 35 scans.

The microscopic investigations also confirmed that cyclic cleaning proved to be more effective than cleaning the electrode at a constant positive potential. As can be seen in Fig. 4, the surface of the glassy carbon support after electrochemical removal is not completely free from the debris of the deposited metal. However, the particles that are visible on the surface of the glassy carbon support cleaned in the cyclic mode are few and far apart (Fig. 4a), whereas there is still a large number of small crystallites on the surface of the glassy carbon cleaned at the constant potential (Fig. 4b).

## 3.3. Catalytic adsorptive stripping voltammetry of cobalt and nickel at the PbFE

#### 3.3.1. Characterization by cyclic voltammetry

In order to characterize the new type of sensor with respect to its analytical performance and electrochemical behavior, cat-



**Fig. 4.** AFM images (in 3D format) of surface of glassy carbon support after electrochemical removal of the lead film: (a) by triple cycling of the potential from -0.53 to +0.5 V with a scan rate of 0.1 V/s; (b) at the constant positive potential of +0.5 V for 10 s.

alytic adsorptive stripping voltammetry of cobalt and nickel was performed with the lead film electrode.

Cyclic voltammetry was used to investigate the behavior of the Co–nioxime and Ni–nioxime complexes at the lead film plated in situ onto a glassy carbon surface. Examples of the voltammograms, recorded after 120 s of adsorptive accumulation, are shown in Fig. 5. The forward scan shows the reduction peak of the absorbed cobalt and nickel complexes, whereas no re-oxidation was observed upon scanning in the positive direction. It was found that the addition of 0.25 M NaNO<sub>2</sub> to the supporting electrolyte containing  $5 \times 10^{-5}$  M Pb, 0.1 M ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime, and  $5 \times 10^{-9}$  M Co and  $5 \times 10^{-8}$  M Ni as analytes resulted in a 9-fold enhancement



**Fig. 5.** Cyclic voltammograms obtained at the GCE or PbFE(GC) in the solution: (1) 0.1 ammonia buffer; (2) 0.1 ammonia buffer and  $5 \times 10^{-5}$  M Pb; (3) 0.1 ammonia buffer,  $5 \times 10^{-5}$  M Pb and  $2.5 \times 10^{-5}$  M nioxime; (4) 0.1 ammonia buffer,  $5 \times 10^{-5}$  M Pb and 0.25 M NaNO<sub>2</sub>; (5) 0.1 ammonia buffer,  $5 \times 10^{-5}$  M Pb,  $2.5 \times 10^{-5}$  M nioxime and 0.25 M NaNO<sub>2</sub>; (6) 0.1 ammonia buffer,  $5 \times 10^{-5}$  M Pb,  $2.5 \times 10^{-5}$  M nioxime,  $5 \times 10^{-9}$  M Co and  $5 \times 10^{-8}$  M Ni; (7) 0.1 ammonia buffer,  $5 \times 10^{-5}$  M Pb,  $2.5 \times 10^{-5}$  M nioxime,  $5 \times 10^{-9}$  M Co and  $5 \times 10^{-8}$  M Ni and 0.25 M NaNO<sub>2</sub>. Instrumental parameters:  $E_{nuc} = -1.45$  V;  $E_{acc} = -0.75$ ;  $t_{acc} = 120$  s, scan rate = 100 mV/s.

of the cobalt response whereas no significant increase of the signal was observed for nickel. The addition of nitrite ions not only increased the height of the obtained signal for Co – due to catalytic effect – but also caused a shift of its peak potential to more negative values, i.e. from -1.055 to -1.099 V.

#### 3.3.2. Catalytic adsorptive stripping voltammetry of Co and Ni

To investigate the suitability of PbFE for trace Co and Ni detection, adsorptive stripping voltammetric methods with different modes such as differential pulse, linear sweep, and square wave, as well as stripping chronopotentiometry were examined. Among the voltammetric modes, differential pulse yielded the most symmetric and most well-developed signals. The adsorptive stripping voltammograms obtained with the differential pulse mode were also characterized by very favorable signal-to-noise ratios. Square wave and linear sweep voltammetry gave also well-shaped peaks, but more asymmetric. When the influence of the voltage scan rate (from 0.025 to 2 V) on the Co and Ni signals was investigated using the linear sweep technique, the relationship  $I_p$  versus v ( $I_p$  designating the peak current, v the scan rate) was linear, and the values of  $\Delta \log I_p / \Delta \log v = 1.15$  ( $r^2 = 0.998$ ) for Co and  $\Delta \log I_p / \Delta \log v = 0.67$  ( $r^2 = 0.999$ ) for Ni indicated the adsorptive nature of the reduc-



**Fig. 6.** Accessible potential windows of the PbFE in various supporting electrolytes: (a) 0.1 M ammonia buffer, pH 8.5 ( $E_{int} = -1.8$  V); (b) 0.1 M NaOH ( $E_{int} = -1.6$  V); (c) 0.1 M acetic buffer, pH 4.0 ( $E_{int} = -2.0$  V); (d) 0.1 M KCl ( $E_{int} = -2.0$  V). Positive going differential pulse voltammetric scan from initial potential ( $E_{int}$ ) to 0.1 Instrumental parameters for the lead film formation at nucleation and deposition potentials:  $E_{nuc} = -1.45$  V;  $E_{dep} = -0.75$ ;  $t_{dep} = 120$  s. Other parameters as in Fig. 3.



**Fig. 7.** Comparison of the differential pulse voltammograms obtained at the PbFE (solid line), BiFE (dotted line), MFE (dash dot dot line), GCE (dashed line) in the solution containing 0.1 ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime,  $5 \times 10^{-9}$  M Co,  $5 \times 10^{-8}$  M Ni and 0.25 M NaNO<sub>2</sub>. In the case of the PbFE the solution contained an additional  $5 \times 10^{-5}$  M Pb. Instrumental parameters:  $E_{nuc} = -1.45$  V;  $E_{acc} = -0.75$  V for BiFE, MFE and GCE or  $E_{acc} = -0.65$  V for PbFE,  $t_{acc} = 120$  s,  $\Delta E = 20$  mV.

tion of Co–nioxime and Ni–nioxime complexes. It is also possible to obtain exploitable signals with chronopotentiometric stripping analysis, if a stripping current of 5  $\mu$ A or less is applied. Higher currents yielded smaller, poorly shaped signals and low sensitivity.

The working potential ranges of the PbFE in different supporting electrolytes, both neutral and basic, were also investigated. The accessible potential window is restricted by the decomposition of the supporting electrolytes at the negative potential region, and by the oxidation of lead at the positive potential region, which are strongly dependent on the pH of the solution (Fig. 6).

#### 3.3.3. Comparison with other film electrodes

Four types of electrodes were compared: the investigated lead film electrode (PbFE), the bismuth film electrode (BiFE), the mercury film electrode (MFE) and the bare glassy carbon electrode (GCE). The above electrodes were tested in the solution containing 0.1 M ammonia buffer,  $2.5 \times 10^{-5}$  M nioxime, 0.25 M NaNO<sub>2</sub>,  $5 \times 10^{-9}$  M Co and  $5 \times 10^{-8}$  M Ni and the adsorptive stripping voltammetric responses were recorded and compared (Fig. 7). As can be seen in Fig. 7, the analytical signal of Co recorded at the PbFE has the best shape, as it is the most narrow and symmetrical. Moreover, the separation of the adsorptive stripping peaks of Ni and Co is the best at the PbFE. Another advantage of the PbFE is the largest signal-to-noise ratio of all the four electrodes under consideration. For the determination of Ni or of Ni and Co, accumulation at a potential of -0.65 V is recommended. Application of even more positive accumulation potentials can cause the oxidation of the lead film. Higher but also more asymmetrical signals for nickel are obtained with a BiFE. Fig. 7 also show that the baseline of BiFE is not flat, but raises at negative potentials. This phenomenon is caused by the GC surface being incompletely covered by the metal film. Hence, the observed signals are the superimpositions of the currents for glassy carbon and metal surfaces [1,45,46]. For the tested system the described effect is much smaller for the MFE and PbFE resulting in more symmetrical signals. In case of use GCE as the working electrode no signals could be observed, either for Co or for Ni.

#### 4. Conclusions

The specific surface microstructure and topography of the lead film deposited on GC from mild, alkaline solutions was viewed by SEM and AFM for the first time, revealing the heterogeneous character of the obtained film, strongly dependent on the applied deposition conditions. It was also found that the concentration of Pb in the plating solution strongly affects the microstructure of the formed lead films. For Pb concentrations that do not exceed  $5 \times 10^{-5}$  M Pb, the film was not uniform and crystallites 1.3  $\mu$ m high and up to 5  $\mu$ m in diameter were observed, whereas for the higher Pb concentration ( $1 \times 10^{-4}$  M Pb), a more homogenous and compact film was formed, with smaller crystallites. The microscopic observations correlated well with the results of the electrochemical studies.

It was also confirmed that metal film electrodes, even those produced from a non-noble metal such as lead, might be useful in electroanalytical determination in which sufficiently negative potentials are applied during measurements. One of the reasons why new electrode materials are being developed is the toxicity of mercury. Bismuth, on the other hand, has been one of the most popular environmentally friendly materials for some time now. Lead as an electrode material utilized for film generation on the surface of glassy carbon supports, is also characterized by higher toxicity in comparison to bismuth. However, it is a less toxic substitute for mercury, and has been shown to be more useful than bismuth-based and mercury-based electrodes in adsorptive stripping voltammetry. Furthermore, lead and inorganic lead salts are much less volatile than mercury and its salts. Lead film electrodes may be effectively employed for the determination of cobalt and nickel by catalytic adsorptive stripping voltammetry with nioxime and nitrite in ammonia buffer solutions, yielding better signals and resolutions than other types of film electrodes, such as bismuth film electrodes or mercury film electrodes. High hydrogen overvoltage combined with a favorable signal-to-background ratio, excellent resolution and good reproducibility were obtained using the lead film electrode. These characteristics are comparable to those of hanging mercury drop electrodes. The PbFE can be easily regenerated by stripping the lead film after a preceding measurement and formation of a new film prior to each measurement. Furthermore, the application of the cyclic scan procedure improves the reproducibility of the deposited metal film. Contrary to the BiFE, the PbFE can be easily deposited in situ in ammoniacal solutions, providing good reproducibility. This is undoubtedly a very advantageous analytical feature of the investigated sensor.

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