U.P.B. Sci. Bull., Series B, Vol. 79, Iss. 2, 2017 ISSN 1454-2331

NEW AZULENE BASED MODIFIED ELECTRODES FOR HEAVY METALS SENSING

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The electrochemical characterization of (Z)-2-thioxo-5-((4,6,8-trimethylazulen-1-yl)methylen)imidazolidin-4-one has been performed by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode. Modified electrodes were obtained by cycling the potential in anodic scans or by controlled potential electrolysis (CPE) at different anodic potentials and charges. The modified electrodes have been tested for mercury, cadmium, copper, and lead ions detection.

Keywords: (Z)-2-thioxo-5-((4,6,8-trimethylazulen-1-il)methylen)imidazolidin-4-one, voltammetric techniques, modified electrodes, heavy metals sensing

1. Introduction

Azulenes have a five-member (electron-rich) cyclic moiety connected with a seven-member (electron-poor) cyclic moiety. Azulene derivatives present an irreversible electrooxidation, and an irreversible [1] or quasi-reversible reduction [2]. By electrooxidation polymeric films can be obtained in order to build electrochemical sensors, as shown also in our recent works [2]. The research performed lately in our group aims to obtained modified electrodes for heavy metal ions detection.

There are different methods for determination of heavy metals from water samples based on iron oxide/graphene composite [3], bismuth nanoparticle-porous carbon paste [4], and zinc oxide-graphene composite [5]. The approach in our group is based on complexing modified electrodes by using azulene derivatives [6]. In order to develop new sensors for heavy metals (Z)-2-thioxo-5-((4,6,8-trimethylazulen-1-yl)methylene)imidazolidin-4-one (**L**) has been synthesized and used to prepare modified electrodes with poly**L** (Fig. 1).

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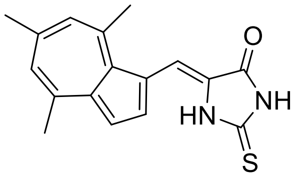

Fig. 1. Structure of **L**

The investigated compound has been characterized by electrochemical techniques, and the preparation of the modified electrodes has been studied. The heavy metals recognition based on poly**L** modified electrodes has been tested.

2. Experimental

Acetonitrile (CH_3CN) and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolyte. The azulene derivative (**L**) was synthesized according to the previous described methods [7]. Metal salts used for recognition were commercial products: mercury (II) acetate, cadmium nitrate tetrahydrate, and lead (II) nitrate from Sigma Aldrich, copper (II) acetate monohydrate from Fluka.

The electrochemical experiments were carried out using a potentiostat PGSTAT 12 AUTOLAB connected to a three-electrode cell. The working electrode was a glassy carbon electrode from Metrohm (diameter of 3 mm). Its active surface was polished before each determination with diamond paste (1 μm) and cleaned with the solvent. A platinum wire was used as auxiliary electrode, and the reference electrode was dependent on the solvent (Ag/Ag^+ in acetonitrile or Ag/AgCl in water).

The electrochemical characterization of **L** was performed in 0.1M TBAP, CH_3CN. Ag/ 10mM $AgNO_3$, 0.1M TBAP, CH_3CN was used as reference electrode. The applied potential was finally referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+) which in our experimental conditions was +0.07 V. Cyclic voltammetry (CV) curves were recorded at different scan rates (between 0.1 V/s and 1.0 V/s). Differential pulse voltammetry (DPV) curves were recorded at 0.01V/s with a pulse height of 0.025 V and a step time of 0.2 s. Rotating disk electrode (RDE) curves were recorded at 0.01 V/s. The anodic and cathodic CV, DPV and RDE scans have been recorded starting from the stationary potential. The heavy metals ions detection was carried out in 0.1 M acetate buffer at pH = 5.5 which has been used as supporting electrolyte. The acetate buffer was prepared from 0.2 M acetic acid and 0.2 M sodium acetate solutions. The detection was studied using as working electrode a glassy carbon disk (3 mm diameter) modified with poly**L**, and the reference electrode was Ag/AgCl, 3 M KCl from Metrohm. The heavy metals detection has been performed from heavy metals solutions with concentrations between 10^{-4} and 10^{-6} mol/ L, prepared by successive dilutions from a stock solution containing all cations at the same concentration (10^{-2} M). All electrochemical experiments have been performed at 25ºC under argon atmosphere.

3. Results and Discussion

3.1. Electrochemical characterization of L

The electrochemical experiments were performed by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and rotating disk electrode (RDE) in 0.1M TBAP, CH_3CN using millimolar solutions of **L**. CV and DPV curves at different concentrations (0 – 2 mM) of **L** are presented in Fig. 2.

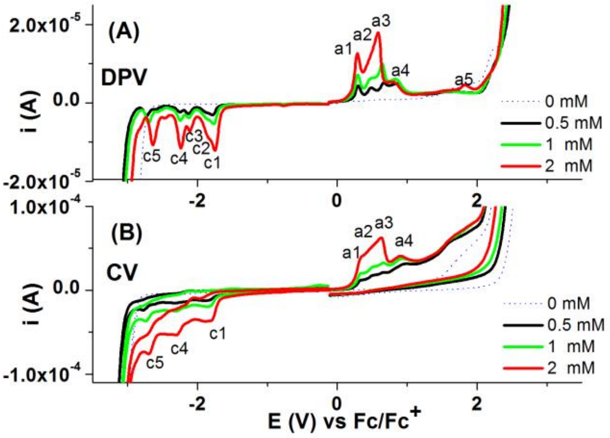

Fig. 2. DPV (**A**) and CV (**B**) curves on glassy carbon electrode (3 mm in diameter) for **L** at different concentrations in 0.1M TBAP, CH_3CN

4 anodic and 5 cathodic main peaks are distinguished in DPV. They were denoted in the order of their apparition in anodic (a1 – a4) or cathodic (c1 – c5) scans. DPV peaks potentials are given in Table 1.

Table 1

Peak potentials (V) vs Fc/Fc$^+$ from DPV and CV curves for L (0.5mM)

Peak	Method	
	DPV	CV
a1	0.287	0.330 (i)*
a2	0.491	0.4832 (i)*
a3	0.669	0.672 (i)*
a4	0.862	0.947 (q)*
c1	-1.75	-1.83 (i)*[a]
c2	-1.878	-
c3	-2.129	-2.170 (q)*
c4	-2.255	-2.290 (q)*
c5	-2.723	-2.739 (q)*

*r - reversible process; q - quasi-reversible process; i - irreversible process

[a] the peak current correspond to both c1 and c2, which are situated at very closed potentials

The anodic and cathodic processes put in evidence in DPV are less visible in CV. The observed CV anodic (a1, a3, a4) and cathodic (c1, c4, c5) processes (peaks or shoulders) were denoted in connection with the notation given from DPV curves. Their potentials are given in Table 1.

The peak currents increase with concentration, both in CV and DPV curves. Fig. 3 shows the linear dependences of the peak currents on **L** concentration.

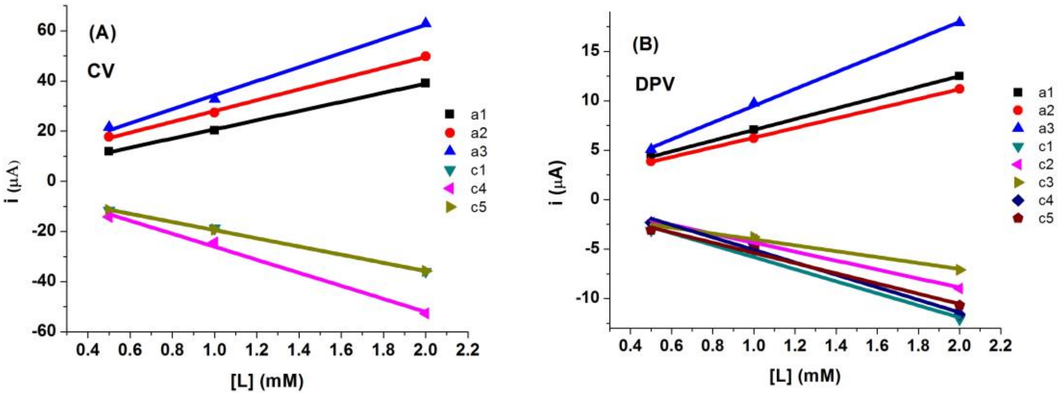

Fig. 3. Dependences of the peak currents on **L** concentration in CV (**A**) and DPV (**B**)

Table 2 presents the equations and correlation coefficients for these CV and DPV dependences. Good correlation coefficients have been obtained for a1, a3, c1, c3, c5 in CV, and a1, a2, a3, c1, c4, c5 in DPV.

Table 2

Equations and correlation coefficients for CV and DPV peak currents

Method	Equation*	Correlation coefficient
CV	$i_{\text{peak a1}}\ (\mu A) = 2.5 + 18.22 \cdot [\mathbf{L}]$	0.999
	$i_{\text{peak a2}}\ (\mu A) = 6.5 + 21.54 \cdot [\mathbf{L}]$	0.998
	$i_{\text{peak a3}}\ (\mu A) = 6.4 + 27.97 \cdot [\mathbf{L}]$	0.991
	$i_{\text{peak c1}}\ (\mu A) = -3.1 - 16.34 \cdot [\mathbf{L}]$	0.996
	$i_{\text{peak c3}}\ (\mu A) = -0.1 - 25.97 \cdot [\mathbf{L}]$	0.989
	$i_{\text{peak c5}}\ (\mu A) = -3.2 - 16.25 \cdot [\mathbf{L}]$	0.999
DPV	$i_{\text{peak a1}}\ (\mu A) = 1.62 + 5.44 \cdot [\mathbf{L}]$	0.999
	$i_{\text{peak a2}}\ (\mu A) = 1.38 + 4.90 \cdot [\mathbf{L}]$	0.999
	$i_{\text{peak a3}}\ (\mu A) = 1.01 + 8.49 \cdot [\mathbf{L}]$	0.997
	$i_{\text{peak c1}}\ (\mu A) = 0.29 - 6.10 \cdot [\mathbf{L}]$	0.980
	$i_{\text{peak c2}}\ (\mu A) = 0.18 - 5.43 \cdot [\mathbf{L}]$	0.987
	$i_{\text{peak c3}}\ (\mu A) = -1.03 - 2.99 \cdot [\mathbf{L}]$	0.982
	$i_{\text{peak c4}}\ (\mu A) = 1.25 - 6.32 \cdot [\mathbf{L}]$	0.976
	$i_{\text{peak c5}}\ (\mu A) = -0.26 - 5.16 \cdot [\mathbf{L}]$	0.979

*[**L**] is expresed in mM

The absolute slopes for a1 and c1 are similar in CV and also in DPV; these peaks can be attributed to the formation of radical anion and radical cation, respectively. The other peaks from CV and DPV curves have lower correlation coefficients, showing complex processes which occur at these potentials. The current drops which occur suddenly after the peak a3 indicate the surface covering with insulating films, as shown in experiments performed for similar ligands [1].

RDE curves have been recorded for different concentrations of **L** and different rotation rates. In Fig. 4 are shown the curves obtained at **L** concentration of 0.5 mM at rotation rates between 500 and 1500 rpm. In the anodic scans the curves present two anodic processes a2' and a5, denoted according to the corresponding peaks in DPV (curves presented ones above the other for comparison). The currents for a2' RDE process increase with increasing the rotation rate, but this increase is stopped at potentials higher than a2, (after which the current drops suddenly to values closer to zero). Then the current is kept constant over a large scan range of potential (till 1.5 V). This drop is characteristic for the electrode coverage with insulating films. Consequently, the aspect of RDE curves has confirmed the coverage of the electrode with an insulating layer, fact that has been noticed also in DPV and CV curves. The process a5 appears rather high in RDE curves, but shows no variation with the rotation rate. Two isosbestic points can be put in evidence at 1.76 V and 1.88 V in this anodic domain. Consequently, the process a5 has been attributed to the oxidation processes occurring in the film.

In the RDE cathodic scans regular waves could be seen, all increasing with the rotation rate, in agreement with homogeneous diffusion controlled processes. However, the waves are difficult to be separated as the processes are situated at close potentials (only c1, c4 and c5 can be identified).

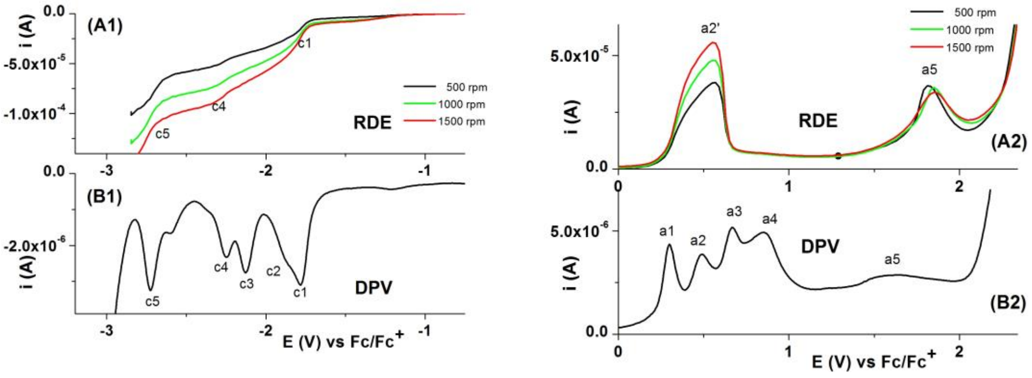

Fig. 4. RDE (**A1**, **A2**) and the corresponding DPV (**B1**, **B2**) curves on glassy carbon electrode (3mm in diameter) at different rotation rate (rpm) for **L** (0.5 mM) in 0.1M TBAP,CH_3CN;

Fig. 5 shows the CV curves for different scan rates and domains. The influence of the scan rates (0.1 V/s – 1.0 V/s) shown in Fig. 5A1 is quantified for a1 and c1 processes by plotting the currents vs square root of the scan rate (Fig. 5A2). Linear dependences have been obtained for a1 and c1 peaks with slopes of 56.4 μA $(V/s)^{-1/2}$, and -42.5 μA $(V/s)^{-1/2}$, respectively.

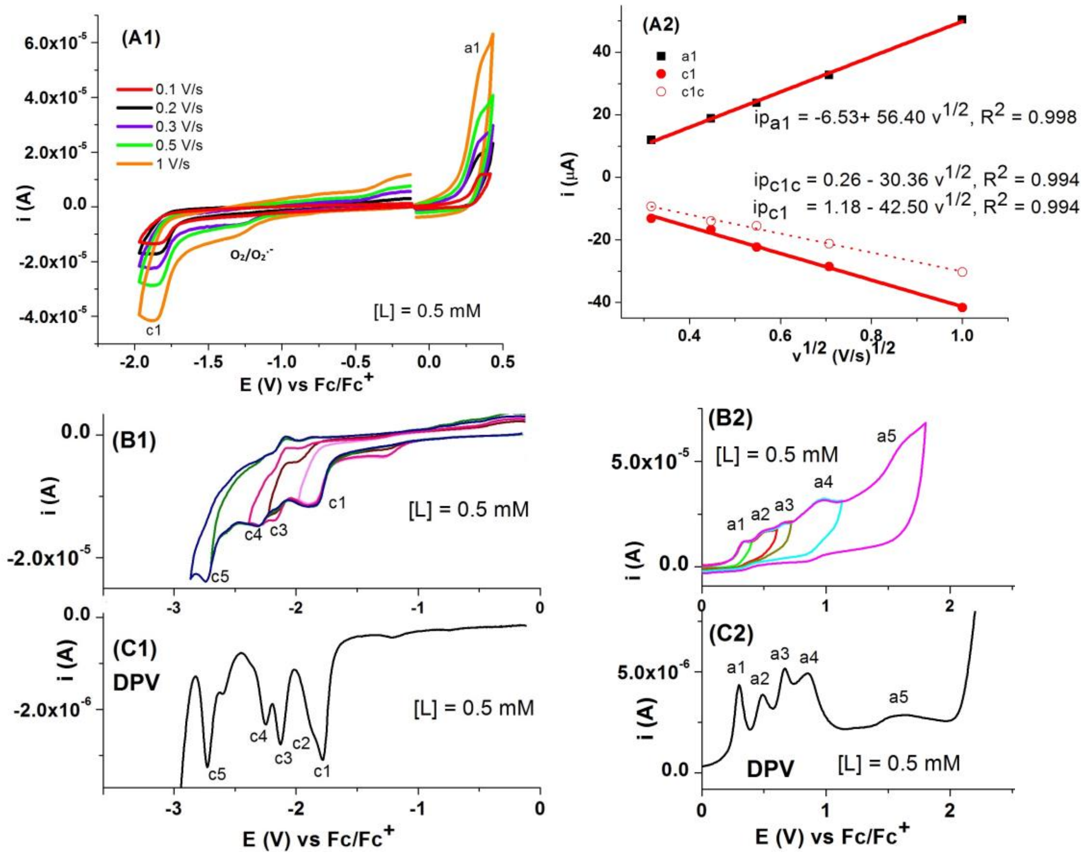

Fig. 5. **A1 -** CV curves at different scan rates; **A2 -** linear dependences of a1 and c1 peak currents vs. square root of the scan rate; **B1, B2** - CV curves in cathodic and anodic scans, respectively; **C1, C2 -** DPV curves in cathodic and anodic scans, respectively; all curves have been recorded on gassy carbon electrode (3 mm diameter) in solutions with [**L**] = 0.5mM, 0.1M TBAP,CH_3CN

The height of c1 peak is slightly affected by undesirable oxygen traces, but when the correction has been done (by subtracting oxygen reduction current from c1 peak current) a slope of -30.4 μA $(V/s)^{-1/2}$ is obtained for the corrected c1 peak current (c1c). This value is about half of the value for the anodic peak (ip_{c1c}/ip_{a1}~ 0.5). However, these values cannot be correlated with the number of the electrons involved in these processes because both c1 and a1 are situated at potentials close to other peaks (c2 and a2, respectively), and the peak current is in fact a contribution of more superposed processes.

Figs. 5B1 and 5B2 show the CVs obtained on different anodic and cathodic scan domains (at 0.1 V/s), in comparison with the corresponding DPV curves for the same concentration of **L**. They enable establishing the irreversible (i) or quasi-reversible (q) character of each process (Table 1).

3.2. Modified electrodes based on polyL

Poly**L** films were obtained by successive scanning or by controlled potential electrolysis (CPE) in millimolar **L** solutions in 0.1 M TBAP, CH_3CN. Evidence on the films formation on the electrode surface was obtained by transferring the modified electrodes in a solution of ferrocene (0.5 mM) in 0.1M TBAP, CH_3CN.

Fig. 6A shows the CV curves during the preparation of the modified electrode by successive scans in the domain of the anodic processes identified to lead to insulating films. The film formation on the electrode surface was confirmed by transferring the modified electrode in a solution of ferrocene. Fig. 6B shows the CV curves recorded after the transfer of the modified electrode obtained by 20 successive scans. It can be seen that the signal for ferrocene couple on the modified electrode is slightly diminished in intensity and broadened in comparison with that recorded on the bare electrode, indicating the formation of a thin layer film.

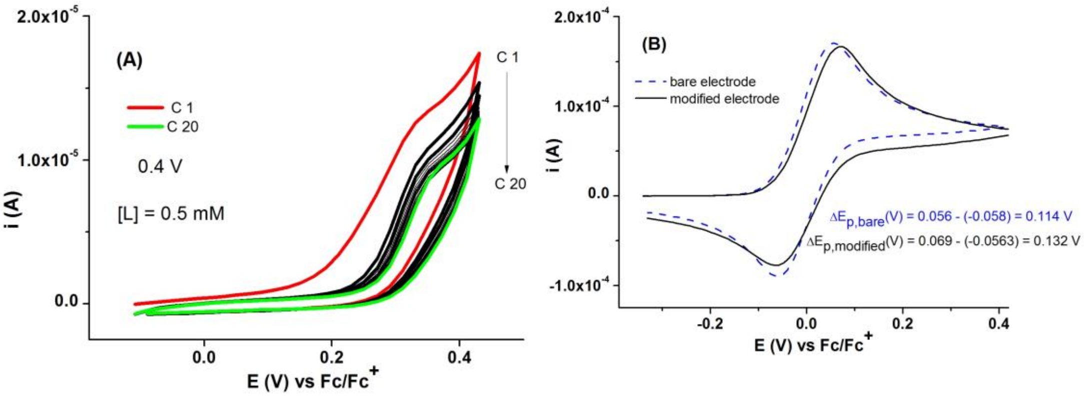

Fig. 6. **A** - CV curves (0.1 V/s) during the preparation of the modified electrode by 20 successive cycles in 0.5 mM solution of **L** in 0.1M TBAP, CH_3CN; **B** - CV curves (0.1V/s) recorded in 1mM ferrocene solution in 0.1M TBAP, CH_3CN on bare and on the modified electrode obtained after the 20th cycle

In Fig. 7, there are given the CV curves connected to the modified electrodes obtained by CPE. In Fig. 7A are given the curves of the modified electrodes obtained by CPE at 0.63V vs Fc/Fc^+ using different electropolymerization charges (0 – 0.8 mC) after the transfer in ferrocene solution. It can be seen that the signal of ferrocene couple on modified electrodes is stepwise diminished in intensity and broadened in comparison with that recorded on bare electrode. This behavior indicates the formation of films with a thickness that increases with the amount of charge used.

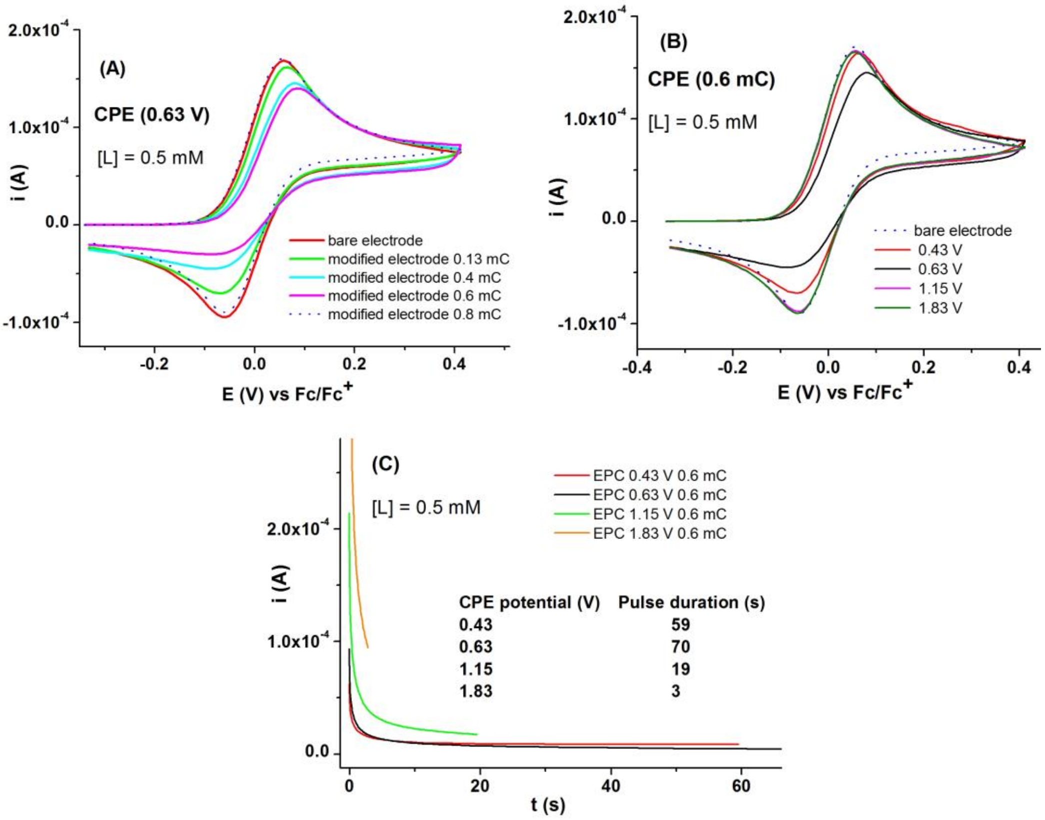

Fig. 7. CV curves (0.1 V/s) of modified electrodes recorded in transfer solution (0.5 mM ferrocene in 0.1M TBAP, CH_3CN); the modified electrodes were prepared by CPE at 0.63 V using different electropolymerization charges (**A**) and at different electropolymerization potentials for 0.6 mC (**B**), corresponding chonoamperograms for the modified electrodes preparations by CPE (0.6 mC) at different electropolymerization potentials (**C**)

The modified electrodes were prepared also by CPE at different electropolymerization potentials (0.43 – 1.83 V vs Fc/Fc^+) using the same charge (0.6 mC). The transfer of the modified electrodes in ferrocene solution (Fig. 7B) also indicates the coverage of the electrode with films, because the ferrocene signal is modified in comparison with that on bare electrode. The influence of the applied potential in CPE has been evaluated (Fig. 7B). It can be seen that ferrocene signal is more disturbed at 0.63 V than at 0.43 V, meaning a better coverage of the electrode with films at more positive potential. Surprisingly, for modified electrodes obtained at higher potentials (1.15 V and 1.83 V) the ferrocene signal was less perturbed than at 0.63 V. These decreases are due to the short duration of CPE pulse (Fig. 7C) that not enables the polymerization processes to occur. The CPE pulse durations are given in the Fig. 7C inset table. However, it is clearly seen that there is an optimal potential around 0.63 V, as a result of these two antagonist factors (charge and pulse duration).

3.3. Heavy metals sensing

In order to sense the heavy metals, poly**L** glassy carbon modified electrodes were prepared by controlled potential electrolysis at different potentials and charges. They were obtained from 1 mM solution of **L** in 0.1M TBAP, CH_3CN, and using a charge of 2 mC, taking in to account that an increase of the monomer concentration and synthesis charge ensures the formation of a thicker film expected to give a better complexing capacity.

The modified electrodes obtained by CPE were further introduced into the transfer cell containing 0.1M acetate buffer pH 5.5. The electrode equilibration was done during 15 CV cycles in the domanin -0.9 V to + 0.6 V. Then the overoxidation during 5 CV cycles between -0.2 V to + 1.2 V was performed. After that, the modified electrodes were introduced in the assay solutions containing heavy metals ions, and they were maintained for 10 minutes under magnetic stirring. Finally, the modified electrodes were introduced in a cell containing 0.1M acetate buffer pH 5.5. A potential of -1.2V was applied for 120 s (when the ions in the complexing film were reduced), then the electrode was polarized in anodic sense at a scan rate of 0.01 V/s. The stripping currents for the metals dissolution were recorded. The peaks for Pb, Cu, and Cd appeared at -0.538 V, -0.144 V, and -0.697 V respectively. Fig. 8 shows the stripping curves obtained for modified electrodes prepared at different potentials using a charge of 2 mC (to ensure a high duration of CPE pulse).

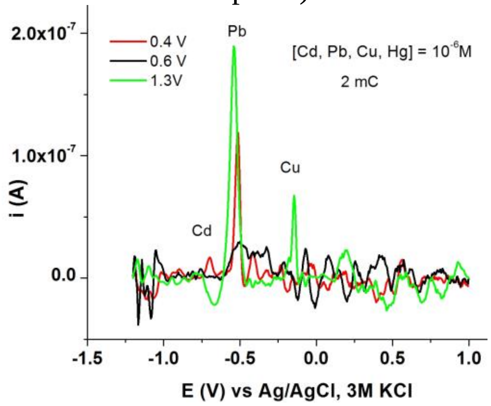

Fig. 8. Anodic stripping curves on poly**L** modified electrodes obtained by CPE at different potentials (vs Fc/Fc^+) in 10^{-6} M solutions of all ions (Cd (II), Pb (II), Cu (II), Hg(II))

From the heavy metals tested (Cd, Pb, Cu, Hg) the recognition was suitable for lead, copper and cadmium, in the order of their analytical signal intensity. The best responses in detection were obtained for the films prepared at 1.3 V for Pb and Cu, and at 0.4 V for Cd. In Fig. 9, there are shown the stripping curves recorded for the modified electrodes introduced in solutions containing the mixtures of heavy metal cations at different concentrations.

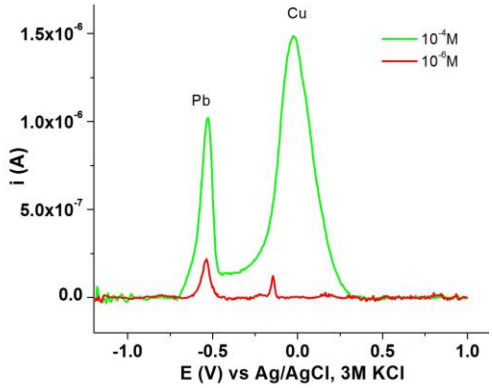

Fig. 9. Anodic stripping curves recorded on poly**L** modified electrodes after immersion in acetate buffer at pH 5.5 (accumulation time 10 min) containing different concentrations of in Cd(II), Pb(II), Cu(II) and Hg(II) ions; the modified electrodes were obtained by CPE (1.3 V vs Fc/Fc$^+$, 2 mC)

Based on the identification of different heavy metal potential values, it can be concluded that the obtained signals can be attributed to Cu (II) and Pb (II).

The other ions are not seen in the stripping. The response of the modified electrode is controlled by the concentration of these species in accumulation solutions. It can be seen that, from the mixture of Cd(II), Pb(II), Cu(II) and Hg(II) ions at a concentration of 10^{-4}M, the best response is for Cu(II), and Pb(II) in this order; Cd(II) and Hg(II) are not seen. At a concentration of 10^{-6} M, the order is reversed, the best response is for Pb(II), and then for Cu(II). Taking in the account that all steps in the preparation of the modified electrodes and in the recognition event were similar, the results obtained for these two concentrations (of heavy metals in the accumulation solutions) could be attributed to differences in crystallization of both metals after electrochemical reduction. Studies about optimizing the performances of the poly**L** modified electrodes in view of better sensing are underway.

Taking into account our interest for detecting low concentrations of Pb(II) and the fact that Pb(II) detected concentration was lower than 10^{-6} M by using the poly**L** modified electrodes several experiments have been performed, in order to find other parameters that could improve Pb(II) signal. In Fig. 10 there are shown the stripping curves obtained using different overoxidation scan domains and different number of scans. If the overoxidation domain changes from -0.2 V ÷ 2 V to -0.2 V ÷ 2.5 V, the stripping signal for Pb is almost doubled (Fig. 10). If the number of overoxidation cycles changes from 15 to 40, the stripping signal for Pb is more than doubled (Fig. 10). These results are very useful for the optimization studies which are in progress because the search of the parameters for conditioning the modified electrodes has been proven to be also very important.

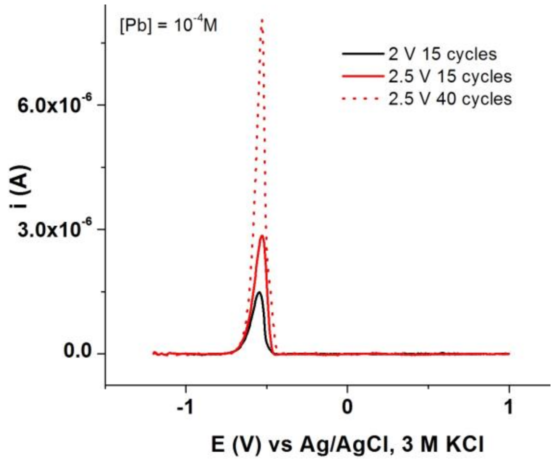

Fig. 10 Anodic stripping curves recorded in buffer acetate, pH 5.5 containing 10^{-4} M Pb (II) for poly**L** modified electrodes after overoxidation at different potential ranges or number of scans; the modified electrodes were obtained by CPE (1.3 V vs Fc/Fc$^+$, 2 mC) in **L** solution (1 mM) in 0.1M TBAP, CH_3CN

Several experiments using poly**L** modified electrodes obtained and conditioned in the same conditions were performed for Pb^{2+} detection. The results obtained indicate a necessity of further research, in order to evaluate the characteristic parameters of the method.

4. Conclusions

The electrochemical characterization of (Z) -2-thioxo-5-((4,6,8-trimethylazulen-1-yl) methylene) imidazolidin-4-one (**L**) was performed by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode methods. The anodic and cathodic processes have been established, and the conditions for obtaining electrodes modified with **L** have been identified. The films formation on the surface of the electrode was confirmed by the transfer of the modified electrode in ferrocene solutions, when the CV signal was found attenuated.

Chemically modified electrodes have been prepared by electropolymerization of **L** at positive potentials. The modified electrodes were tested for the recognition of heavy metal cations. The best results were obtained for lead and for copper, when more concentrated solutions of mixture of heavy metal ions were tested. The detection conditions have to be optimized. Using the present data, the new modified electrodes can be used for analysis of lead and copper in water with a content of these heavy metals higher than 10^{-6} M for Pb and Cu ions.

Acknowledgements

The authors are grateful for the financial support from: Executive Unit for Financing Education Higher, Research Development and Innovation (UEFISCDI) project ID PN-II-RU-TE-2014-4-0594 contract no. 10/2015, PN-II-PT-PCCA-2013-4-2151 contract no. 236/2014, and Romania–China bilateral project 68BM/2016 (CH 41.16.04).

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