Bulgarian Chemical Communications, Volume 49 Special Issue C (pp. 227 – 232) 2017

Synthesis and characterization of poly(azulene-thiophene vinyl pyrylium) salt

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Received November 14, 2016 Revised December 20, 2016

This work presents the electrochemical characterization of 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**) by voltammetric techniques such as cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode voltammetry. Poly**L** modified electrodes obtained by controlled potential electrolysis were used to detect the presence of heavy metal ions. Good results have been obtained for Cd(II), Pb(II), Cu(II), Hg(II) ions, but the best limit of detection (10^{-7}M) has been obtained in the case of Pb(II).

Key words:. 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate, electrochemical characterization, modified electrodes, detection of heavy metals.

INTRODUCTION

Azulenes are organic compounds that have a seven carbon atoms ring (electron-poor) connected to a five carbon atoms ring (electron-rich) [1] structure that confers electroactive properties and leads to interesting applications in optoelectronics [2], assessment of antiretroviral activity [3], electrochemical sensors [4]. This paper is related to the last mentioned application and proposes a new azulene based modified electrode which can be used as sensor for heavy metals detection.

The most used methods for the determination of heavy metals are the spectral methods, mainly atomic absorption spectroscopy (AAS) [5], emission spectrometry by inductive coupled plasma (ICP) [6], and lately neutron activation analysis [7, 8]. However, these methods are dedicated especially to very well equipped laboratories. A sensitive and versatile analytical method to detect heavy metals that can be used *on site* is that using electrochemical sensors [9, 10].

This work proposes a new modified electrode based on azulene-thiophene vinyl pyrilium salt, namely 2,6-bis((E)-2-(2-thienyl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**) (Fig. 1) which has been tested for the following heavy metal ions detection: Cu(II), Pb(II), Hg(II) and Cd(II).

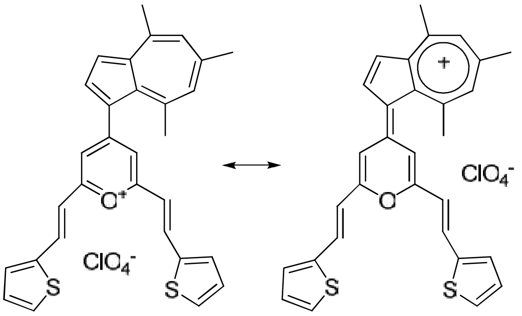

Fig. 1. Chemical structure of 2,6-bis((E)-2-(2-thienyl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**).

EXPERIMENTAL

All the reagents used in the electrochemical experiments were of analytical grade. As supporting electrolyte tetra-*n*-butylammonium perchlorate (TBAP, Fluka puriss, electrochemical grade>99%) solved in acetonitrile (CH3CN, Sigma Aldrich, electronic grade 99.999% tracemetals) was used. Metal cation salts were purchased as follows: mercury(II) acetate, cadmium nitrate tetrahydrate, lead(II) nitrate of analytical purity from Sigma Aldrich, and copper(II) acetate monohydrate from Fluka (≥ 99.0%). The aqueous solutions were prepared with Millipore Simplicity UV. 0.1M buffer acetate pH = 5.5 was prepared from 0.2M acetic acid and 0.2M sodium acetate.

The electrochemical experiments were carried out in a three-electrode cell connected to a PGSTAT 12 AUTOLAB. The working electrode consisted in a glassy carbon disk from Metrohm (3 mm in diameter), which was polished before each

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experiment with diamond paste (0.25μm) and cleaned with acetonitrile. A platinum wire was used as auxiliary electrode. As reference electrode, Ag/10mM $AgNO_3$ in 0,1M TBAP/CH_3CN was used in acetonitrile solvent, and Ag/AgCl, 3M KCl in water solvent.

Cyclic voltammetry (CV) curves were recorded at 0.1 V/s scan rate, the rotating disk electrode voltammetry (RDE) curves were recorded at 0.01 V/s. Differential pulse voltammetry (DPV) curves were recorded at 0.01 V/s with a pulse height of 0.025 V and a step time of 0.2s.

For the curves recorded in acetonitrile, the applied potentials were referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+), which in the experimental conditions was +0.07 V.

Poly**L** modified electrodes were prepared by controlled potential electrolysis (CPE) at different potentials and charges. After preparation, the modified electrodes were cleaned with acetonitrile, then transferred in a three electrode transfer cell containing 0.1M buffer acetate pH = 5.5 as supporting electrolyte. 15 cycles (between – 0.9 V and + 0.6 V) and 15 cycles (between -0.2 V and +2.5 V) were applied. Then the electrode was cleaned with water and then introduced in water solutions of heavy metals for 15 minutes, under mechanical stirring. A multielement stock standard solution (10^{-2} M) of Cd, Pb, Cu, Hg was prepared and working heavy metals solutions (10^{-5} – 10^{-8} mol/ L) were prepared daily by successive dilutions.

All electrochemical experiments were performed in standard conditions at 25ºC under argon atmosphere.

RESULTS AND DISCUSSION

The electrochemical behaviour of **L** has been investigated by CV, DPV, and RDE on glassy carbon electrode. The curves were recorded starting from open circuit voltage potential of around 0 V. The anodic and cathodic CV and DPV curves were recorded at different concentrations (0 – 2 mM) in 0.1M TBAP/CH_3CN (Fig. 2). CV and DPV curves show 2 oxidation peaks (a1 and a2) and 5 reduction peaks (c1 – c5). The current peaks are increasing with **L** concentration. The dependences of the significant peak currents (μA) on concentration (mM) for CV and DPV curves are presented in Figure 3. Table 1 presents the equations of the peak current dependencies on **L** concentration for the main peaks and their correlation coefficients for CV and DPV curves.

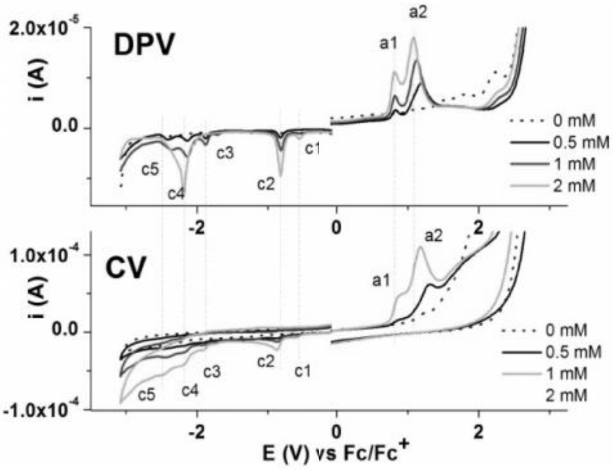


Fig. 2. DPV (0.01 V/s) and CV (0.1 V/s) curves for **L** at different concentrations on glassy carbon (3mm in diameter) in 0.1M TBAP, CH_3CN.

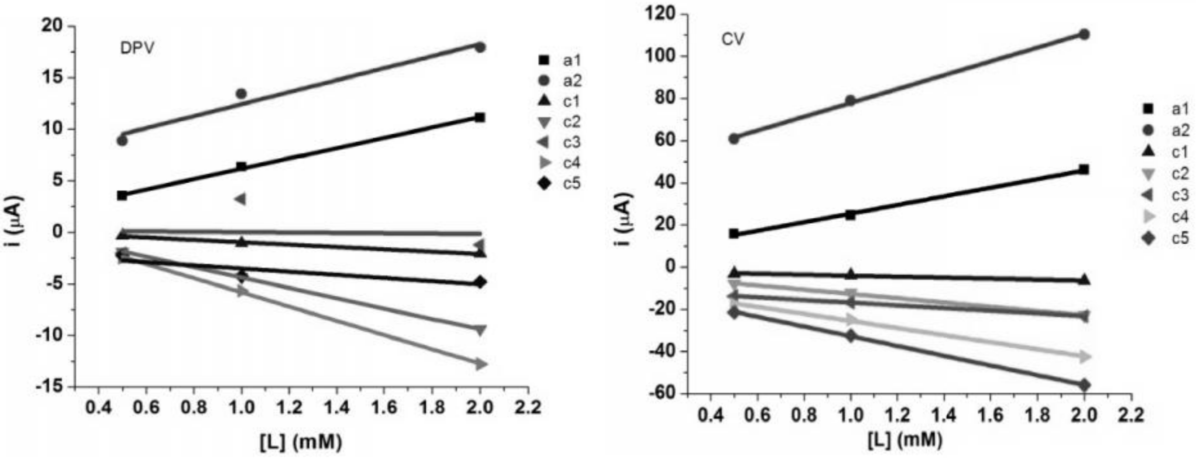


Fig. 3. Dependences of the DPV and CV peak currents on concentration of **L**.

Table 1. CV and DPV equations of significant peak currents (i_{peak})* on **L** concentration [**L**]

Method	Equation	Correlation coefficient
DPV	$i_{peak\ a1} = 1.17 + 5.01\ [\mathbf{L}]$	0.9964
	$i_{peak\ a2} = 6.63 + 5.82\ [\mathbf{L}]$	0.9247
	$i_{peak\ c1} = 0.22 - 1.16\ [\mathbf{L}]$	0.9764
	$i_{peak\ c2} = 0.65 - 5.02\ [\mathbf{L}]$	0.9999
	$i_{peak\ c4} = 1.09 - 6.90\ [\mathbf{L}]$	0.9986
CV	$i_{peak\ a1} = 5.03 + 20.42\ [\mathbf{L}]$	0.9949
	$i_{peak\ a2} = 45.16 + 32.78\ [\mathbf{L}]$	0.9975
	$i_{peak\ c1} = -1.75 - 2.28\ [\mathbf{L}]$	0.9789
	$i_{peak\ c2} = -2.51 - 10.15\ [\mathbf{L}]$	0.9964
	$i_{peak\ c3} = -10.48 - 6.33\ [\mathbf{L}]$	0.9995
	$i_{peak\ c4} = -8.72 - 16.77\ [\mathbf{L}]$	0.9963
	$i_{peak\ c5} = -9.65 - 23.09\ [\mathbf{L}]$	0.9996

* ipeak is given in μA and [**L**] in mmol/L (mM)

From Table 1, it can be seen that the DPV peaks denoted a1 and c2 have the same slope (of 5) in respect to concentration. The other peaks have higher slopes in absolute value. It can be assumed that these peaks correspond, respectively, to the oxidation of azulene derivative to its radical cation and to its reduction to the corresponding radical anion. They are both one-electron processes. The process c1 has very weak DPV and CV slopes with **L** concentration and could be assed to an impurity. Figure 4 presents the CV curves on different scan rates (0.1 – 1 V/s) for a1 and c1 peaks in 1mM solution of **L**, and the linear dependences of the peak currents (i) on square root of the scan rate. The peak currents increase with the scan rate in agreement with the Randles-Sevcik equation.

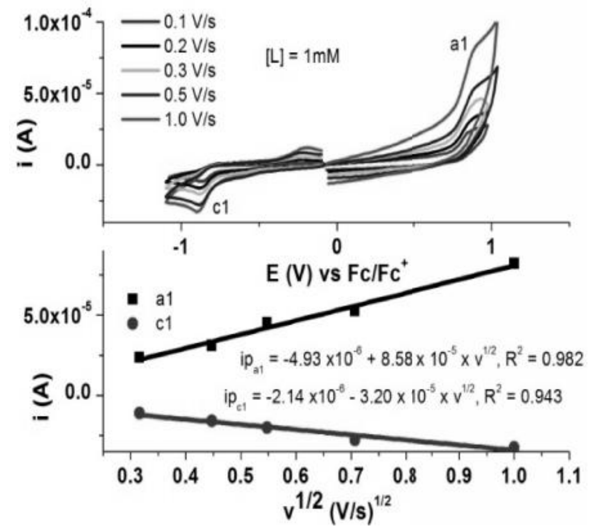


Fig. 4. CV curves at different scan rate and dependences of the peak currents (A) on the square root of the scan rate for **L** (1mM) in 0.1M TBAP, CH_3CN.

In figure 5 are presented the CV curves (0.1 V/s) on different scan domains for **L** (1mM), while in Table 2 are given the peak potentials obtained from CV and DPV curves for **L** (1mM). It can be observed that all anodic process (a1 and a2) and c1 are irreversible (as they do not have corresponding peaks in the reverse scans), while the cathodic ones (c2 – c5) are quasi-reversible (having small peaks in the reverse scans).

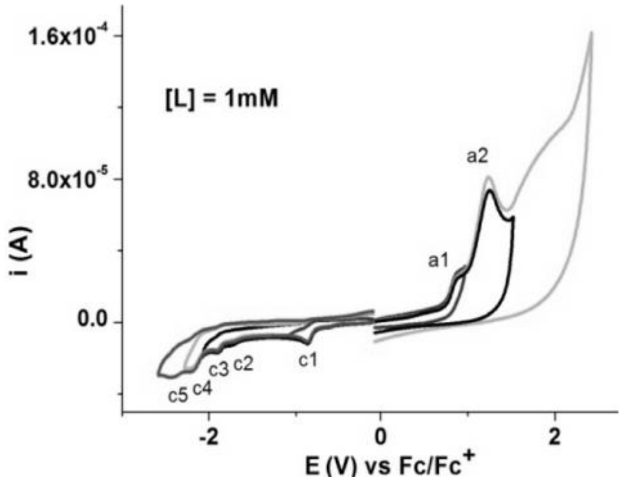


Fig. 5. CV curves at different scan domains for **L** (1 mM) in 0.1M TBAP CH_3CN.

Table 2. Values of peak potentials (V) for [L] = 1mM

Peak	Method		Process type
	DPV	CV	
a1	0.82	**0.86**	(i)*
a2	1.12	1.25	(i)*
c1	-0.54	-0.59	(i)*
c2	-0.81	-0.85	(q)*
c3	-1.87	-1.9	(q)*
c4	-2.12	-2.15	(q)*
c5	-2.35	-2.45	(q)*

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

Figure 6 presents the RDE curves at 500 rpm, 1000 rpm and different concentrations (1mM – 3mM). They show one wave as a peak in the anodic domain, and 3 waves (c2, c3, c5) in the cathodic domain, corresponding to the oxidation and reduction peaks seen in DPV curves. RDE currents increase with **L** concentration and with the rotation rate. The form of the anodic waves as peaks indicates the formation of films in the anodic scans.

However, even in cathodic scans there is a form of a peak of the wave, which indicates either the decomposition of **L**, or its cathodic polymerization.

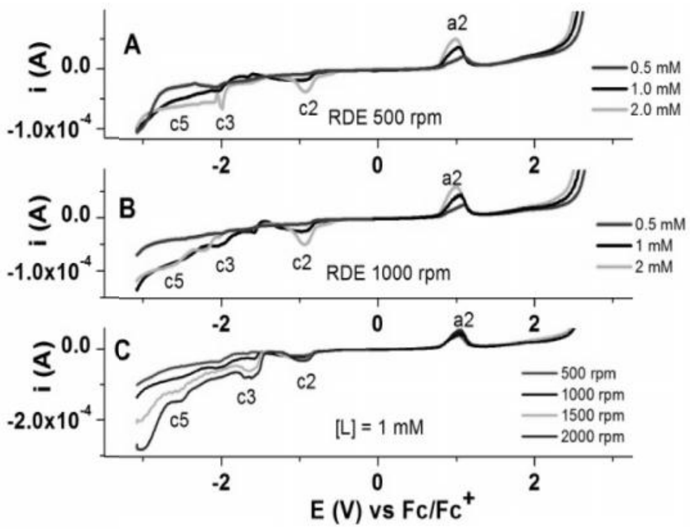


Fig. 6. RDE curves (0.01 V/s) on glassy carbon (3mm in diameter) for **L** in 0.1M TPAB, CH_3CN at different concentrations of **L** at 500 rpm (A) and 1000 rpm (B) and at different rotation rates between 500 and 2000 rpm (C) for [**L**] = 1mM.

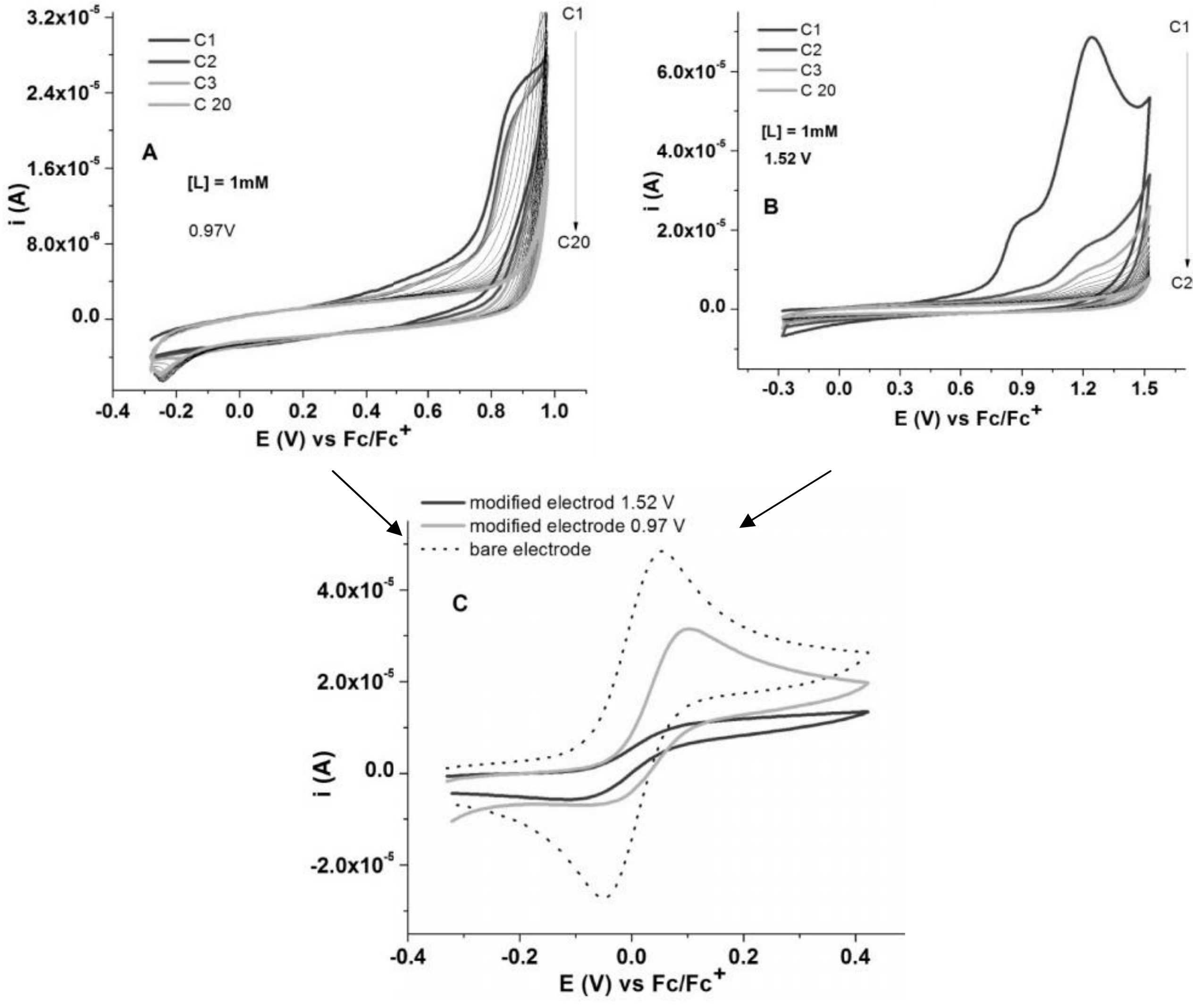


Fig. 7. CV curves (0.1 V/s) during the formation of poly**L** modified electrodes on glassy carbon electrode in 1 mM solution of **L** in 0.1M TBAP, CH_3CN (A, B) by scanning between -0.3 V and different anodic limits: 0.97V (A) and +1.52V (B), and the corresponding CV curves (0.1V/s) obtained after the transfer of the modified electrodes in 1mM ferrocene solution (C).

Modified electrodes

Poly**L** modified electrodes were obtained in L millimolar solutions in 0.1 M TBAP, CH_3CN by successive scanning (20 cycles) between -0.2V and different anodic potential limits (such as 0.97V, or 1.52V), and by controlled potential electrolysis (CPE) at different potentials and charges.

The modified electrodes were then transferred into a solution of ferrocene (1 mM) in 0.1M TBAP, CH_3CN and their CV curves were recorded. It can be seen that, the modified electrode obtained by successive scanning with the anodic limit at the potential of +1.52 V is strongly depressed compared to the bare electrode. As the charge is increased, as the ferrocene signal diminished; the curves for the modified electrodes obtained by CPE at different potentials (for a charge of 1mC) or for different charges (at 0.97V) are shown in Fig. 8. The signal for the modified electrode obtained by EPC at 0.97V 1 mC is different from that on the bare electrode, indicating the electrode coverage by a thin film.

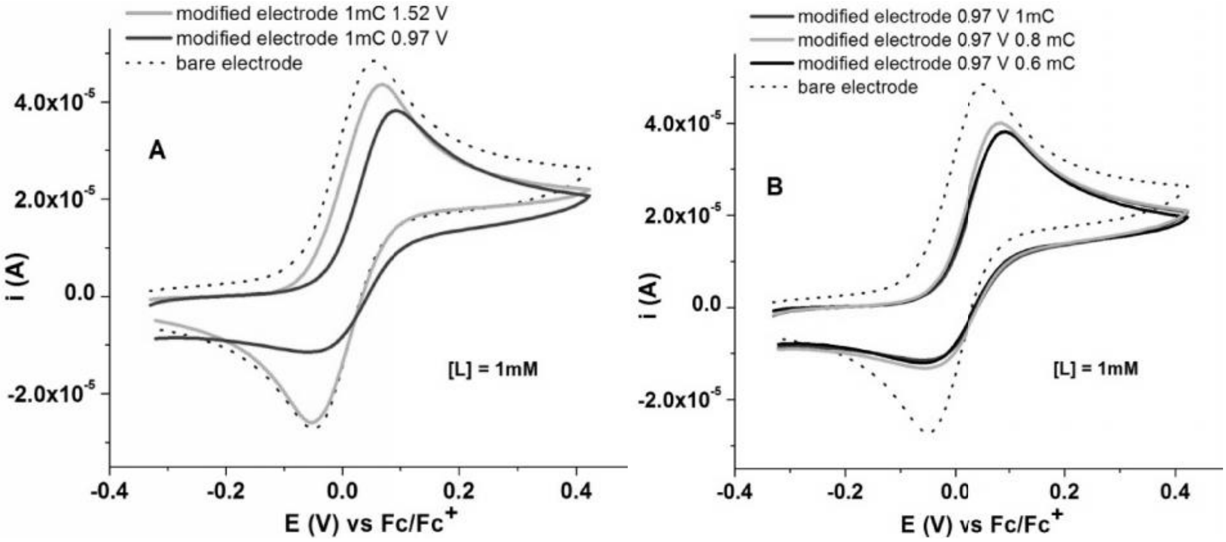


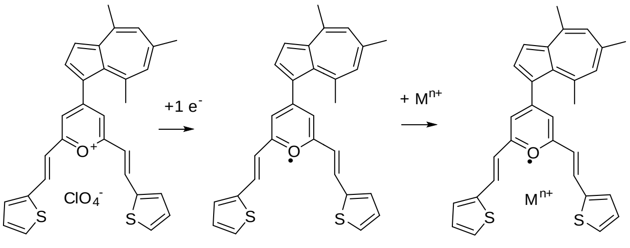
Fig. 8. CV curves recorded in 1 mM ferrocene solutions in 0.1M TBAP, CH_3CN on modified electrodes obtained by CPE in 1 mM solution of **L** in 0.1M TBAP, CH_3CN at different electropolymerization potentials and for 1 mC (A) and at 0.97 V using different electropolymerization charges (B).

Evaluation of recognition properties

Modified electrode obtained in solutions of **L** (1 mM) in 0.1M TBAP, CH_3CN by CPE (1.62V, 2mC) were placed in a cell with three electrodes containing 0.1 M acetate buffer pH 5.5 for equilibration and overoxidation, then each modified electrode was introduced into a solution containing heavy metal ions at different concentration under magneticstirring for 15 minutes. The metal complexation is facilitated by pyranylium salt reduction at around -0.8 V with the formation of a pyranylium radical, which does not contain any more a repulsive positive charge.

The responses of the modified electrodes are shown in Figure 9A, and the dependences of the DPV stripping currents on each heavy metal concentration are given in Fig. 9B. The best response was found for Pb (detection limit lower than 10^{-7} M). The poly**L** modified electrodes can be used for analysis of these heavy metals from water. The work is in progress. It seems that the interaction with Cd^{2+} ion is too weak to form strong complexing bonds leading to a failure of its absorption on the electrode surface.

However, in the case of mercury the interaction is too strong, probably forming covalent bonds at 3-position of azulene moiety. Therefore it will be only partially oxidized at its expected potential.



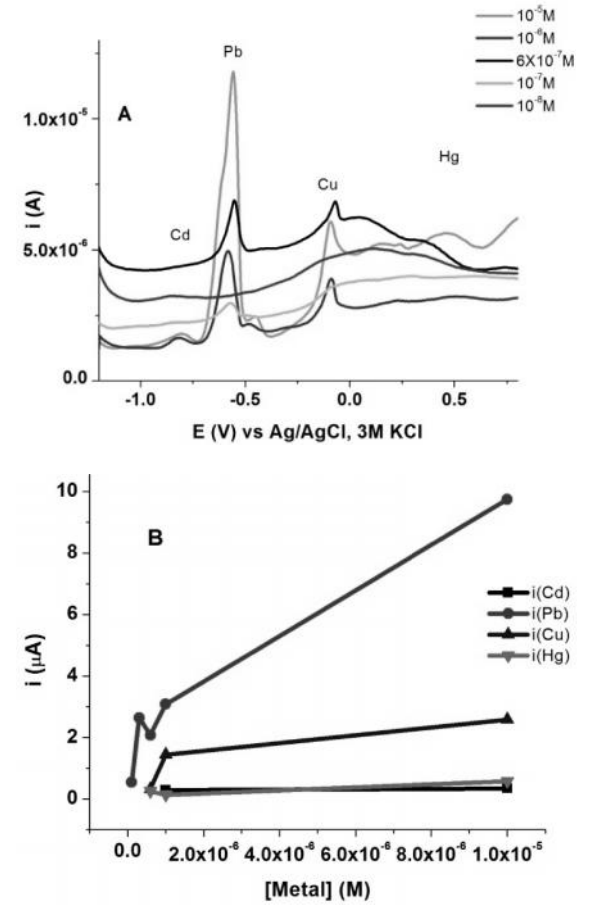


Fig. 9. Stripping DPV curves obtained by CPE (1.62V, 2mC) at different concentrations in acetate buffer at pH 5.5 (A); dependences of the DPV stripping currents on heavy metals concentration (B).

CONCLUSIONS

The electrochemical characterization of 2,6-bis((E)-2-(2-thienyl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**) was performed, and poly**L** modified electrodes were prepared by scanning or controlled potential electrolysis. The response of the modified electrode for heavy metals recognition at different concentrations was examined. The best response was found for Pb (detection limit lower than 10^{-7} M). The work to optimize the modified electrode is in progress.

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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СИНТЕЗ И ОХАРАКТЕРИЗИРАНЕ НА ПОЛ (АЗУЛЕН-ТИОФЕН ВИНИЛ ПИРИЛИЕВА) СОЛ

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Постъпила на 14 ноември 2016 г.; коригирана на 20 декември 2016 г.

(Резюме)

Тази работа представя електрохимично охарактеризиране на 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyrylium perchlorate (**L**) чрез волтамперметрични техники като циклична волтамерия, диференциална импулсна волтамерия и волтамерия на въртящ се дисков електрод. PolyL модифицираните електроди получени чрез електролиза при контролиран потенциал са използвани за откриване присъствието на йони на тежки метали. Получени са добри резултати за Cd (II), Pb (II), Cи (II), Hg (II) йони, като най-добра граница на откриване (10^{-7}M) е постигната за Pb (II).