Polyazulenes Based Materials for Heavy Metal Ions Detection

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Azulene is a special monomer used to functionalize electrodes due to its high polarizability, because it makes possible spontaneous electron drift from the five-membered ring to the seven-membered ring. Our study concerns the electrochemical characterization by cyclic voltammetry, differential pulse-voltammetry and rotating disk electrode voltammetry of a new azulene monomer, 4-(5-isopropyl-3,8-dimethylazulen-1-yl)-2,6-bis((E)-2-(thiophen-2-yl)vinyl) pyridine (L). It has been used to obtain complexing modified electrodes by electrochemical polymerization. PolyL films modified electrodes have been characterized by cyclic voltammetry in ferrocene probe solution. The complexing properties of polyL based functional materials have been investigated towards heavy metals (Pb, Cd Hg, Cu) by preconcentration – anodic stripping technique.

Keywords: 4-(5-isopropyl-3,8-dimethylazulen-1-yl)-2,6-bis((E)-2-(thiophen-2-yl)vinyl) pyridine, electrochemical characterization, chemically modified electrodes, heavy metal ions detection

Functionalized conducting polymer films have received considerable attention due to their great potential as analytical electrode materials [1, 2]. Stable polymer film modified electrodes containing covalently attached dithiocarbamate [3] or EDTA [4] moieties, able to sense copper, cadmium or lead, have been produced by chemical derivatization of films previously coated by electro-polymerization onto electrodes. Incorporation of complexing fragments into polymeric materials can alternatively be done by doping or ion exchange procedures [5]. However, the most efficient approach towards chelating-modified electrodes lies in the direct electropolymerization of complexing monomers, producing in one step stable functionalized polymers films with controlled sizes and sites concentrations. This straightforward approach has, however, seldom been applied to the determination of trace metals and only few examples can be found in literature [6 - 9].

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 [10] or quasi-reversible reduction [11]. By electrooxidation polymeric films can be obtained in order to build electrochemical sensors, as shown in our recent works [12]. The seven-membered ring of the molecule may act as electron acceptor, while the five-membered ring - as electron donor. This leads to very attractive properties for the synthesis of functional advanced materials like: materials with nonlinear optical and photorefractive properties, cathode materials for lithium batteries, or light emitting diodes based on organic materials. Azulene derivatives have been used rarely to the metal ions electroanalysis, Some examples using chemically modified electrodes (CMEs) have been recently published. 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 [12], bismuth nanoparticle-porous carbon paste [13], and zinc oxide graphene composite [10]. The approach in our group is based on complexing modified electrodes by using azulene derivatives [13]. In order to develop new sensors for heavy metals 4-(5-isopropyl-3,8-dimethylazulen-1-yl)-2, 6-bis((E)-2-(thiophen-2-yl)vinyl)pyridine (L) has been synthesized and used to prepare modified electrodes with polyL (fig. 1).



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 polyL modified electrodes has been tested.

Experimental part

Acetonitrile (CH₃CN) 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 μ m) 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).

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The electrochemical characterization of **L** was performed in 0.1M TBAP, CH₃CN. Ag/ 10mM AgNO₃, 0.1M TBAP, CH₃CN 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 -0.1V. 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 polyL, 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^{5} and 10^{8} 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 25°C under argon atmosphere.

Results and discussions

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, CH₂CN using millimolar solutions of **L**.

 $\dot{C}V$ and $\dot{D}PV$ curves at different concentrations (0 – 5 mM) of **L** are presented in figure 2.

3 anodic and 4 cathodic main peaks are distinguished in DPV, and 4 anodic peaks and 3 cathodic peaks in CV. They were denoted in the order of their apparition in anodic (a1 - a4) or cathodic (c1 - c4) scans. DPV peaks potentials are given in table 1.

 Table 1

 PEAK POTENTIALS (V) VS FC/FC+ FROM DPV AND CV CURVES FOR

 L (1.25 mM)

_ ()			
Peak	Method		
	cv	DPV	
a1	0.387 (i)*	0.338	
a2	0.825 (i)*	0.479	
a3	1.439 (i)*	1.349	
a4	2,034	-	
c1	-1.896 (i)*	-1.909	
c2	-2.129	-2.065	
c3	-2.78	-2.436	
c4		-2.724	

* irreversible process

The peak currents increase with concentrations both in CV as well as in DPV curves. Figure 3 shows the linear dependences of the peak currents on **L** concentration. Table 2 presents the equations and correlation coefficients for these CV and DPV dependences.

RDE curves have been were recorded for different concentrations of L. In figure 4 are shown the curves obtained at L concentration of 2.5 mM at different rotation rates (500 - 1500 rpm). In the anodic scans the curves present 3 anodic processes a1, a2 and a3, denoted according to the corresponding peaks in DPV (shown below). RDE a1 peak currents increase with increasing



Method	Equation*	Correlation coefficient	
cv	ipeak a1 (A) = -3.3E-6 + 1.61E-5 · [L]	0.999	
	íреак а2 (A) = -5.05Е-6 + 2.37Е-5 ·[L]	0.999	
	Ipeak a3 (A) = 3.8E-5 + 2.49E-5 · [L]	0,985	
	Ipeak a4 (A) = 9.75E-5 + 2.23E-5 · [L]	0.979	
	Ipeak c1 (A) = 1.53E-5 - 2,8E-5 · [L]	0,999	
	ipeak c2 (A) = 1.09E-5 - 2.5E-5 · [L]	0.999	
	іреак c3 (A) = 1.54Е-5 – 5.04Е-5 · [L]	0.999	0
DPV	ipeak a1 (A) = 6.3E-7 + 4.12E-6 · [L]	0.995	ANI
	Ipeak a2 (A) = 7.34E-7 +3.66E-6 · [L]	0.998	
	іреак аз (A) = 1.98Е-6 + 2. Е-6 · [L]	0.921	
	Ípeak c1 (A) = -4.84E-7 − 3.89E-6 · [L]	0.814	
	Íреак c3 (A) = -8.6Е-7 – 1,82Е-6 · [L]	0.978	
	ipeak c4 (A) = -3.28E-6 - 4.55E-6 · [L]	0.985	

Table 2EQUATIONS ANDCORRELATIONCOEFFICIENTS FOR CVND DPV PEAK CURRENTSDEPENDENCES

*[L] is expresed in mM

the rotation rate, but this increase is stopped at potentials higher than a3, when the current drops suddenly to values closer to zero, and they are kept constant over a large scan range. This drop is characteristic for the electrode coverage with insulating films. Consequently, the aspect of RDE curves have confirmed the coverage of the electrode with an insulating layer, fact that have been noticed in DPV and CV curves.

Figure 5 shows the CV curves for different scan rates (0.1 V/s - 1.0 V/s) in the domains of the first anodic and cathodic peaks, as well as on different scan domains (0.1 V/s), in comparison with the corresponding DPV curve for the same concentration of **L** (0.5 mM). They enable establishing the irreversible (i) or quasi-reversible (q) character of each process. table 1 also shows their peak potentials from CV and DPV curves.







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Modified electrodes based on polyL

PolyL film were obtained by successive scanning or by controlled potential electrolysis (CPE) in L solutions (1.25 mM) in the domain of the anodic processes identified to lead to insulating films. 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, CH₂CN. Figure 6 shows the CV curves obtained after the transfer of the modified electrode obtained by successive potential scanning in the domain of the first anodic peak. It can be seen that the signal for ferrocene couple on the modified electrode is not very different from that recorded on the bare electrode, indicating the formation of a thin layer film.

In figure 7 are given the CV curves of ferrocene recorded on different modified electrodes obtained by CPE. The electrolyses were performed at 1.64 V vs Fc/Fc⁺ using different electropolymerization charges (0 – 4 mC). All



Fig. 5. CV curves at different scan rates and scan domains and DPV curve at the concentration of 2.5mM for L in 0.1M TBAP, CH₂CN

Fig. 6. **A**. CV curves (0.1 V/s) for modified electrode by successive cycles, in 2.5 mM solution of **L** in 0.1M TBAP, CH₃CN; and **B** the corresponding CV curves (0.1V/ s) obtained after the transfer of the modified electrode in 1mM ferrocene solution



Fig. 7. CV curves (0.1 V/s) of a modified electrode in 1.75 mM ferrocene transfer solutions in 0.1M TBAP, CH₃CN; the modified electrodes were prepared by CPE at 1.64 V using different electropolymerization charges

signals indicate coverage of the electrode with films, because the signal is modified in comparison with that on bare electrode. The modified electrode obtained by CPE at the potential of 1.64V when the charges are growing from 2mC to 4mC the signal increases (thicker films are expected to be formed).

Heavy metals sensing

In order to sense the heavy metals polyL glassy carbon modified electrodes were prepared by controlled potential electrolysis at 1.64 V using 2mC from L solutions (1 mM).

Modified electrodes by CPE were 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, and the overoxidation during 15 CV cycles between -0.2 V to + 1.2 V. Then the modified electrodes were introduced in the assay solutions containing heavy metals ions, and they were maintained for 15 min under magnetic stirring. A potential of -1.2V for their reduction was applied for 120 s, 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 -0.56V, -0.068 V, and -0.8 V respectively at 10⁶M.

From the heavy metals tested (Cd, Pb, Cu, Hg) the recognition was suitable for lead, copper and cadmium, in order the intensity of their analytical signal. In figure 8 are shown the results obtained for the modified electrodes introduced in solutions containing different concentrations of heavy metal cations. 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. The detection limits for Pb (II) and Cu (II) were lower than 10^{6} M. Studies about optimizing the performances of the polyL modified electrodes in view of better sensing are underway.

Several experiments using polyL modified electrodes obtained and conditioned in the same conditions were performed for Pb^{2+} detection. The results are promising, and the work to evaluate the characteristic parameters of the method is in progress.

Conclusions

The electrochemical characterization of 4-(5-isopropyl-3,8-dimethylazulen-1-yl)-2,6-bis((E)-2-(thiophen-2-



Fig. 8. Anodic stripping curves recorded on polyL modified electrodes after immersion in acetate buffer at *p*H 5.5 (accumulation time 15 min) containing different concentrations of in Cd(II), Pb(II), Cu(II) and Hg(II) ions; the modified electrodes were obtained by CPE (1.64 V, 2 mC)

yl)vinyl)pyridine (**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.

Complexing 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 these ions have been detected at a concentration less than 10^{-8} M. The detection conditions have to be optimized. Using present data, these 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.

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