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IMPEDANCE STUDIES ON CHEMICALLY MODIFIED ELECTRODES BASED ON 5-[(AZULEN-1-YL) METHYLENE]-2-THIOXOTHIAZOLIDIN-4-ONE

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Electrochemical Impedance Spectroscopy (EIS) technique has been used to characterize chemically modified electrodes based on 5-[(azulen-1-yl) methylene]-2-thioxothiazolidin-4-one (L). EIS curves have been recorded using GC or GC/poly L modified electrodes at open circuit potential in 0.1M tetrabutylammonium perchlorate in acetonitrile solutions. EIS spectra were processed for modified electrodes obtained in different conditions (at different anodic potentials for the same charge, and at constant potential and different charges), as well as in different stages of their preparation.

Keywords: 5-[(azulen-1-yl) methylene]-2-thioxothiazolidin-4-one, modified electrodes, Electrochemical Impedance Spectroscopy

1. Introduction

Azulenes have a five-member cyclic moiety (electron-rich) connected with a seven-member cyclic moiety (electron-poor). According to reference [1], the azulene derivatives present an irreversible character in the anodic domain, a quasi-reversible character for the cathodic domain. They can lead to polymeric films either by oxidation or reduction; these films can be used to create electrochemical sensors. Particularly, it has been shown [2] that polymer films can be obtained on the basis of (5-[(azulen-1-yl) methylene]-2-thioxothiazolidin-4-one (**L**), which has complexing groups specific for the recognition of heavy metal ions.

This paper concerns the characterization of poly**L** modified electrodes by electrochemical impedance spectroscopy (EIS). The study aimed to put in

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evidence the influence of preparation method on their EIS spectra. The modified electrodes based on poly**L** films were prepared either by potential scanning, or by controlled potential electrolysis (CPE). Taking into account that these modified electrodes based on poly**L** films have to be used for heavy metals recognition, the electrodes have been tested after each step of preparation, in order to find the specific changes in electrochemical impedance properties of the surface in view of further recognition.

2. Experimental

Acetonitrile (CH_3CN) and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received for the solvent and supporting electrolyte, respectively. The azulene derivative 5-[(azulen-1-yl) methylene]-2-thioxothiazolidin-4-one **(L)** was synthesized according to the previous described methods [3]. The electrochemical syntheses and characterizations were carried out using a PGSTAT 12 AUTOLAB potentiostat connected to a three-electrode cell, shown in Fig. 1. The working electrode was a glassy carbon disk (3 mm diameter). The active surface was polished before each determination with diamond paste (1 μm) and cleaned with acetonitrile. Ag/10mM $AgNO_3$ in 0.1M TBAP, CH_3CN was used as reference electrode and a platinum wire was used as auxiliary electrode. However, for all curves the potential was referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+), which in our experimental conditions was +0.07 V.

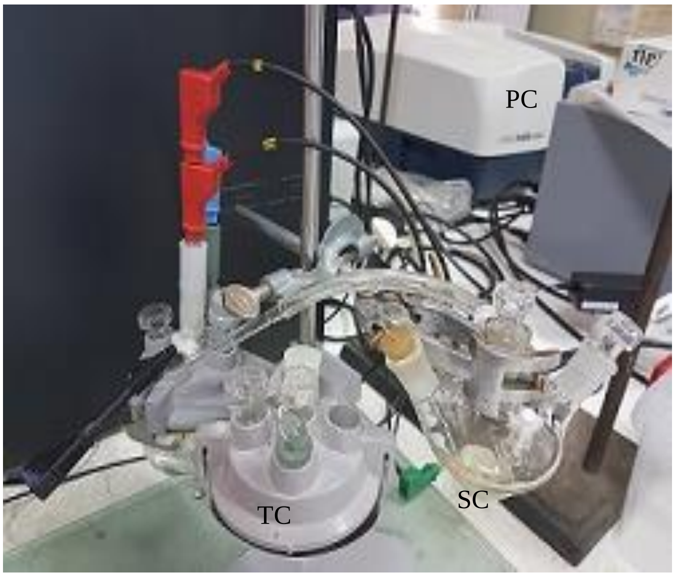


Fig. 1. Experimental set up for preparation and characterization of modified electrodes: synthesis cell (SC); transfer cell (TC); potentiostat (PC)

The experiments were performed by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and rotating disk electrode (RDE). CV curves were recorded from 0.1 V/s to 1.0 V/s scan rate. DPV curves were recorded at 0.01 V/s with a pulse height of 0.025 V and a step time of 0.2 s. RDE curves were recorded at 0.01 V/s.

Electrochemical Impedance Spectroscopy (EIS) curves have been recorded using GC or GC/poly L modified electrodes at open circuit potential in 0.1M TBAP in acetonitrile solutions. EIS spectra were processed using ZView 2.4 software from Scribner Association Inc., Derek Johnson.

All determinations were performed at 25^{o}C, under argon atmosphere.

3. Results and Discussion

The electrochemical behaviour of **L** was studied on glassy carbon electrode by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and rotating disk electrode (RDE).

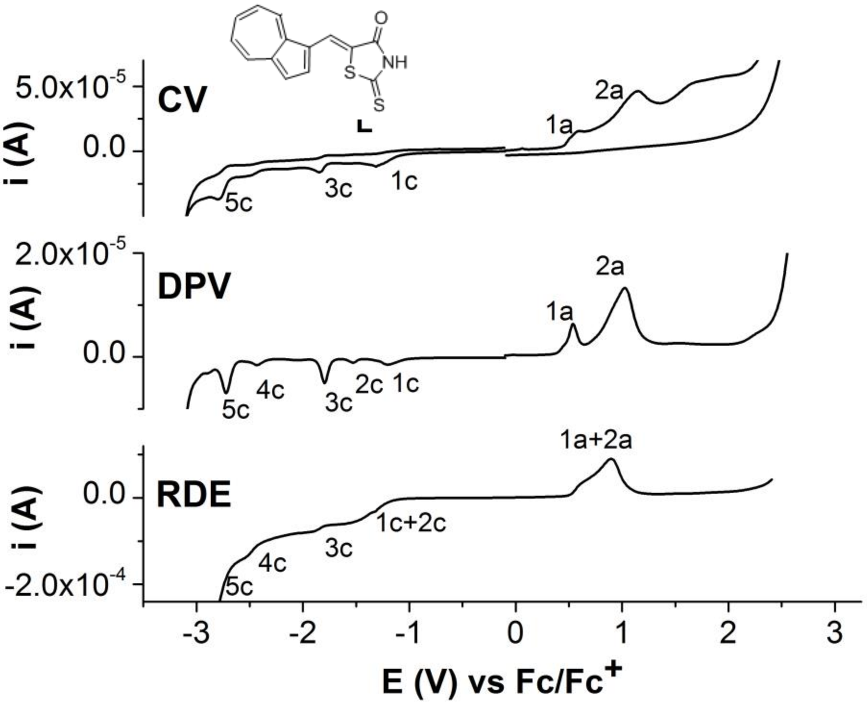


Fig. 2. CV, DPV and RDE curves on glassy carbon disk for L in 0.1M TBAP, CH_3CN

Anodic and cathodic CV, DPV, and RDE curves have been recorded starting from the stationary potential. These curves, recorded on glassy carbon electrode in millimolar solutions of **L** in 0.1M TBAP in CH_3CN, are shown together in Fig. 2. A detailed study has been reported previously [2]. The fingerprint of the compound is given by its DPV peaks, which are the most precisely defined, and were used to discuss the other curves.

Fig. 2 shows that DPV curves presented two anodic peaks: 1a (at 0.541 V), 2a (at 1.022 V) and five cathodic peaks: 1c (at -1.202 V), 2c (at -1.529 V), 3c (at -1.802 V), 4c (-2.431 V), and 5c (at -2.721 V). RDE curves presented a single anodic process (at potentials between peaks 1a, 2a) and two cathodic processes (at potentials corresponding to the peaks 1c and 3c from DPV).

The shape of DPV and RDE curves for this azulene derivative in anodic domain is characteristic for the formation of films [2]. By polarizing more positive than about 0.8 V the current drops to background level current values, and the electrode is covered by blue colored films.

3.1. Formation of polyL films

Poly**L** films were obtained either by successive scanning of potential or by controlled potential electrolysis (CPE) in millimolar solutions of **L** in 0.1M TBAP, CH_3CN in the domain of the anodic processes identified by CV, as it has been shown previously [2]. An evidence for the films formation on the electrode surface was obtained by transferring the modified electrodes in ferrocene solutions in 0.1M TBAP, CH_3CN. The signal for ferrocene on the modified electrodes is very different from that recorded in the same solution on bare electrode. As Fig. 4 shows, both anodic and cathodic peaks are diminished in intensity and shifted to more positive potentials, indicating that a thick insulating layer film was formed on the electrode.

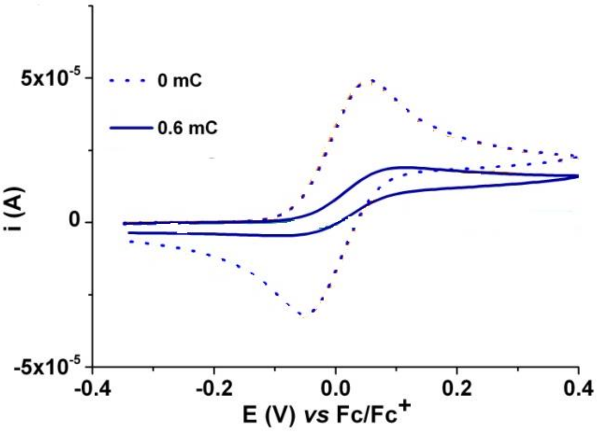


Fig. 4. CV curves (0.1 V/s) in 0.5 mM ferrocene solutions in 0.1M TBAP, CH_3CN on bare GC (dashed line) and on the modified electrode (full line) prepared by CPE at 1.45 V for an electropolymerization charge of 0.6 Mc

In order to have the control over the number of complexing sites in the films, the modified electrodes were prepared by controlled potential electrolysis (CPE) either at different electropolymerization charges, or at different electropolymerization potentials, in millimolar solutions of **L** in 0.1M TBAP, CH_3CN.

3.2. EIS characterization of polyL films

For the first tests the polyL modified electrodes were prepared by controlled potential electrolysis in 0.25 mM solutions of L in 0.1M TBAP, CH_3CN using a constant electropolymerization charge (0.8 mC), at different polarization potentials (Table 1). After the preparation, the modified electrodes were cleaned with acetonitrile, transferred in the supporting electrolyte (0.1M TBAP in acetonitrile), and then their EIS curves were recorded at open circuit potential. The obtained curves were compared to those for bare GC electrode (Fig. 5). The curves were fitted to the equivalent circuits shown in Fig. 6, and the obtained circuit parameters for films were compared to those for bare GC electrode (Table 1). They have been examined in connection with other impedance studied on modified electrodes [4 - 9]. In Table 1, C is the capacitive part of Q_{dl}, n is the exponent in the expression of Q_{dl}, and R_W is the resistive part of Warburg impedance.

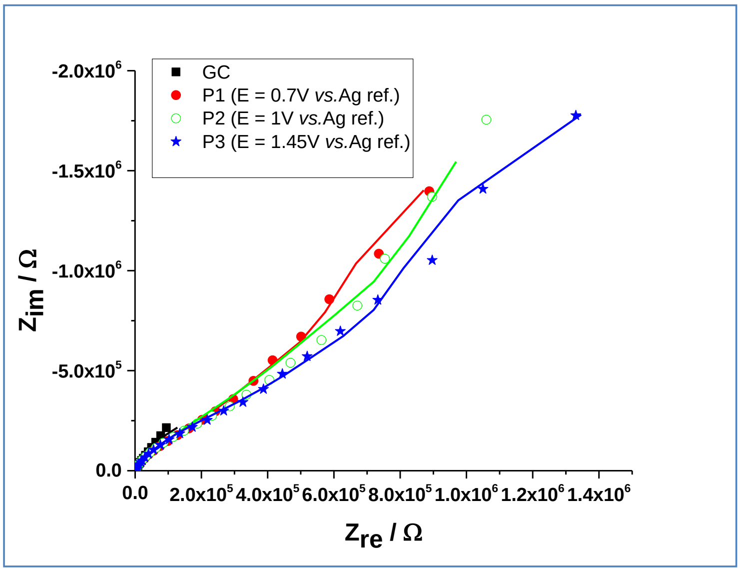
According to Fig. 5, the film acts as an electrical insulator because the charge transfer resistance, Rct (i.e. the diameter of semicircles in Nyquist diagram), is very large and the impedance response is dominated by the resistance of the polymeric phase deposited onto the electrode surface. Changes of maximum phase angle from Bode diagram are related to the Faradaic process of the electron transfer at the polymer/electrode interface. Moreover, a capacitive behavior may be evidenced in Bode diagram, as the phase angle (negative values) is around 70-75 degrees, with a slight decrease, when the formation potential shifts towards more positive values.

Table 1

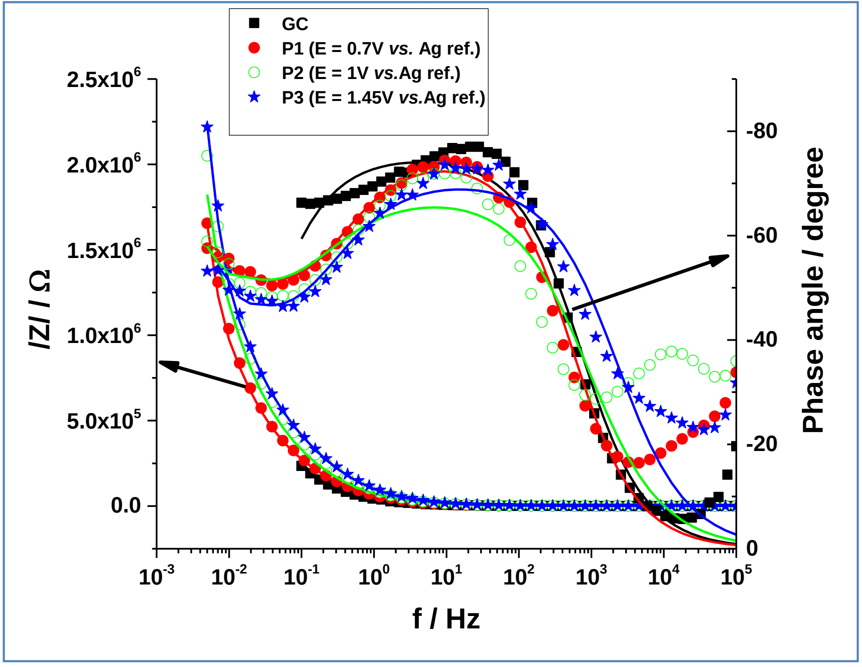
Fitted values of equivalent circuit elements for the polyL film samples prepared by CPE at 0.8 mC from 0.5 mM solutions of L in 0.1M TBAP, CH_3CN

(EC model – the equivalent circuit model chosen for fitting)

Sample\Specimen (different polarization potentials, constant charge)	Rsol (Ω)	$10^{-5}\cdot$Rct (Ω)	Q_{dl}		10^{-6}. R_W (Ω)	EC model
			$10^6\cdot$C ($\Omega^{-1}\cdot s^n$)	n		
GC (0 V; 0 mC)	162	8.7	5.2	0.84		(A)
P1 (0.7 V; 0.8 mC)	324	3.2	3.2	0.84	3.9	(B)
P2 (1.0 V; 0.8 mC)	444	7.0	3.2	0.75	6.5	(B)
P3 (1.45 V; 0.8 mC)	243	6.1	2.2	0.79	4.0	(B)



(a)



(b)

Fig. 5. Nyquist (a) and Bode (b) plots for polyL films formed onto GC working electrode at different potentials, recorded at open circuit potential in 0.1M TBAP in acetonitrile (solid lines are the fit to the measured points using the equivalent circuits shown in Fig. 6)

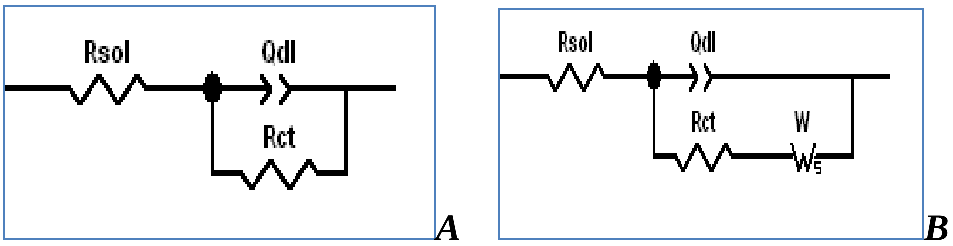


Fig. 6. Proposed equivalent circuits for processed EIS curves using ZView 2.4 software. The circuit elements: Rsol – ohmic resistance of solution; Qdl – constant phase element representing the non-ideal double layer capacitance (C_{dl}); Rct – charge transfer resistance; W – Warburg impedance representing the diffusion of electrochemical species within polymer film

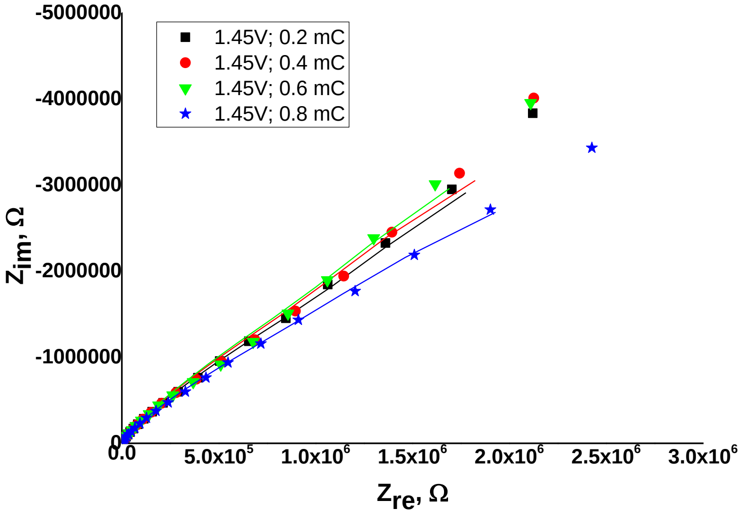
For the second tests, poly**L** modified electrodes were also prepared by controlled potential electrolysis in 0.25 mM solutions of **L** in 0.1M TBAP, CH_3CN, but using different electropolymerization charges (between 0.8 and 3.2 mC), by keeping the same polarization potential (1.45 V), as seen in Table 3. After the preparation, the modified electrodes were cleaned with acetonitrile, transferred in 0.1 M TBAP in acetonitrile, and then characterised by EIS. The obtained fitting results of the recorded EIS spectra were compared to those for bare GC electrode, as shown in Table 3. To fit the experimental results, the same equivalent circuit as mentioned before has been proposed (Model B from Fig. 6).

According to the obtained results, the increase of electropolymerization charge seems to facilitate the formation of a slightly thicker film, with an enhancement of the charge transfer resistance.

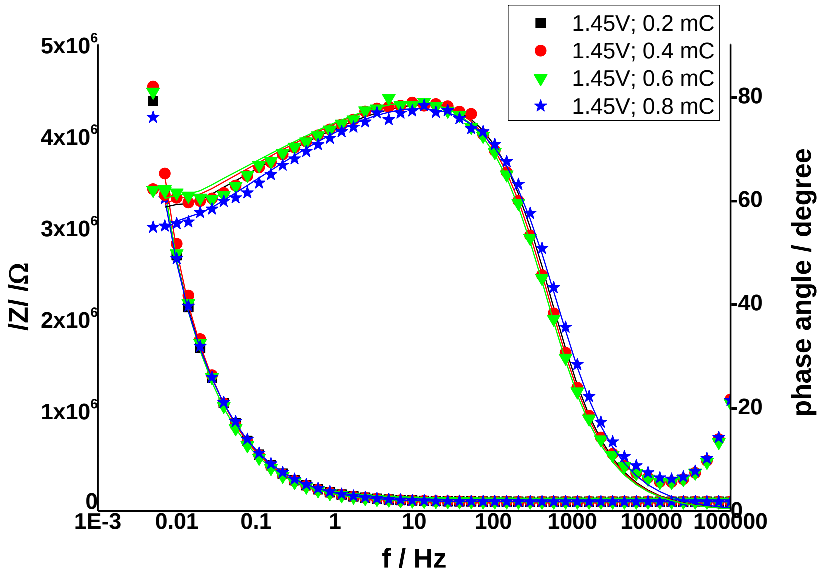
Table 2

Fitted values of equivalent circuit elements for the polyL film samples prepared by CPE at 1.45 V from 0.5 mM solutions of L in 0.1M TBAP, CH_3CN
(EC model – the equivalent circuit model chosen for fitting)

Sample\Specimen (constant polarization potential, different charges)	Rsol (Ω)	Rct (Ω)	Q_{dl}		10^{-6} R_W (Ω)	EC model
			10^6 C ($\Omega^{-1}\cdot s^n$)	n		
GC (0 V; 0 mC)	162	8.7	5.2	0.84		(A)
P3 (1.45 V; 0.8 mC)	327	216110	1.74	0.90	9.48	(B)
P4 (1.45 V; 0.6 mC)	327.7	180000	1.97	0.921	11.5	(B)
P5 (1.45 V; 0.4 mC)	329.5	159780	1.83	0.921	10.8	(B)
P6 (1.45 V; 0.2 mC)	331	86842	1.64	0.928	11.0	(B)



(a)



(b)

Fig. 7. Nyquist (a) and Bode (b) plots for polyL films formed onto GC working electrode at 1.45 V and using different charges, recorded at open circuit potential in 0.1M TBAP in acetonitrile (solid lines are the fit to the measured points using the equivalent circuit B from Fig. 6)

The poly**L** modified electrodes will be used in future research for the determination of heavy metals (Cd, Pb, Cu, Hg). The preparation conditions will be optimized in order to ensure the suitable analytical signal detection. Studies about optimizing sensing properties using modified electrodes with **L** are underway.

4. Conclusions

The electrochemical characterization of the azulene derivative 5-[(azulen-1-yl) methylene]-2-thioxothiazolidin-4-one (**L**) by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode demonstrates that the anodic processes lead to electrode coverage with electrical insulating films, as shown from the ferrocene probe tests. The conditions for obtaining modified electrodes with **L** have been established. The films deposited onto the electrode surface were characterized by EIS technique, indicating that these films act as insulators; their charge transfer resistance is very large and the impedance response is dominated by the resistance of the polymeric deposit. Changes of the maximum phase angle (negative values) are related to the Faradaic process of the electron transfer at the polymer/electrode interface. A capacitive behavior may be evidenced, and it diminishes when the formation potential shifts towards more positive values.

Acknowledgements

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