ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY INVESTIGATIONS ON GLASSY CARBON ELECTRODES MODIFIED WITH POLY(4-AZULEN-1-YL-2,6-BIS(2-THIENYL)PYRIDINE)

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*Se prezintă o caracterizare a electrozilor de carbon vitros (GC) modificați prin electroliză la potențial controlat a 4-azulen-1-il-2,6-bis(2-tienil)piridinei (**L**) în soluții de acetonitril care conțin perclorat de tetra-n-butilamoniu. Proprietățile electrochimice ale electrozilor GC nemodificat şi modificat au fost studiate prin spectroscopie de impedanță electrochimică (EIS) în soluții de tampon acetat. Datele EIS au fost fitate utilizând programul de prelucrare Zview şi un circuit electric echivalent adecvat. S-au observat variații mici ale proprietăților de impedanță ale interfeței în timpul etapelor de preparare ale electrozilor modificati cu filme de poli**L**. Parametrii EIS ai filmului poli**L** nu prezinta o variație regulată cu creşterea grosimii filmului, ceea ce se poate datora variatiei porozității filmului de poli**L**.*

*A characterization of glassy carbon (GC) electrodes modified by controlled potential electrolysis of 4-azulen-1-yl-2,6-bis(2-thienyl)pyridine (**L**) in acetonitrile solutions containing tetra-n-butylammonium perchlorate is presented. The electrochemical properties of bare and modified GC electrodes were investigated by electrochemical impedance spectroscopy (EIS) in acetate buffer solutions. EIS data were fitted using the Zview fitting program and the appropriate equivalent electrical circuit. Small variations in the electrochemical properties of the interface during the steps of preparation of the modified electrodes with poly**L** films were observed. The EIS parameters of the poly**L** film have no regular variation with the increase in film thickness, most probably due to significant effect of poly**L** films porosity.*

Keywords: electrochemical impedance spectroscopy, modified electrodes, polyazulenes films, poly(4-azulen-1-yl-2,6-bis(2-thienyl)pyridine)

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1. Introduction

Modification of the glassy carbon surface is highly promoted for material science, electrochemistry and sensing, because of the good conductivity and inertness of the carbon material towards the environmental and chemical attack [1]. The extensive use of the carbon surface as substrate support for catalytic, analytical, and biotechnological applications justifies the wide efforts for the development of different modification pathways. The method of controlled potential electrolysis (CPE) was used previously for modifying the glassy carbon surfaces through poly(4-azulen-1-yl-2,6-bis(2-thienyl)pyridine) film formation [2]. The appropriate choice of the polymer leads to opportunities for designing new tools for metal ion detection through complexation within the complexing sites of the polymer film. The importance of the detection of heavy metal ions levels originates from the fact that high concentration levels of metal ions (e.g., Cd^{2+}, Pb^{2+}, Hg^{2+}, $As^{3+/5+}$) can be connected to different diseases due to their toxicity, as well as to their tendency to accumulate in the body with a low rate of clearance [2, 3].

The electrochemical impedance spectroscopy (EIS) is an effective method to investigate the interfacial properties of the modified electrodes especially for multilayer films [4]. It was also shown to be an efficient tool for recognition of appropriate interface properties of the modified electrode surfaces that could be successfully applied in biosensing [5].

In this work, EIS method was used to investigate the glassy carbon electrode surface modification with poly(4-azulen-1-yl-2,6-bis(2-thienyl)pyridine) in acetate buffer.

2. Materials and methods

2.1. Materials

The following materials were used as received: acetonitrile (Rathburn, HPLC grade S) and tetra-n-butylammonium perchlorate (TBAP, Fluka puriss). Suprapur grade sodium acetate and acetic acid (Merck) were used for the acetate buffer solution preparation. The pH of 0.2 $molL^{-1}$ sodium acetate solution was adjusted using 0.2 $molL^{-1}$ acetic acid in order to reach the final buffer strength of 0.1 $molL^{-1}$. 4-azulen-1-yl-2,6-bis(2-thienyl)pyridine (**L**) was synthesized according to the procedure previously reported by Razus *et al*. [6].

2.2. Equipment

The electrochemical measurements were carried out using a PG STAT 12 Autolab Potentiostat (Metrohm Autolab). The formation of the modified electrodes by CPE and the EIS measurements were performed in a conventional

three-electrode cell inside a Faraday cage. A Denver Instrument Model 220 pH-conductivity meter was used to measure the pH of the buffer solutions.

2.3. Procedure for preparation of the modified electrodes

The modification of glassy carbon (GC) electrodes was performed by controlled potential electrolysis using the procedure described in [2]. Complete GC electrode modification consisted of three steps:

Step 1 *Formation of the poly***L** *film on the bare GC electrode*. It was performed by CPE in a three-electrode cell containing CH_3CN as solvent and 3×10^{-3} molL^{-1} 4-azulen-1-yl-2,6-bis(2-thienyl)pyridine (**L**) as monomer and 0.1 molL^{-1} TBAP as the electrolyte component. A 1.6V value of the applied potential was selected during CPE electrolysis, which is in the range of the monomer oxidation region shown by cyclic voltammetry [2]. In the preparation cell the working electrode was a glassy carbon disk with a 3 mm diameter (polished with 0.2 mm diamond paste), the counter electrode was a platinum wire and the reference electrode was Ag/10^{-2} molL^{-1} $AgNO_3$ in CH_3CN + 0.1 molL^{-1} TBAP solution.

Step 2 *Equilibration of the poly***L** *film by cyclic voltammetry*. It was carried out in the transfer cell in 0.1 molL^{-1} acetate buffer aqueous solution. The potential scan consisted in 15 cycles (with a scan rate of 0.1 V s^{-1}) from –0.9 V to +0.6 V. The working electrode in the transfer cell was the previously modified glassy carbon disk, the counter electrode was a platinum gauze (2.5 cm^2) and the reference was Ag/AgCl/KCl (3 M) electrode with double junction.

Step 3 *Overoxidation of the poly***L** *film*. It was performed by cyclic voltammetry (0.1 Vs^{-1} scan rate) in the same 0.1 molL^{-1} acetate buffer solution in order to obtain more active sites for the complexation (with heavy metal ions, aiming to detect them); 5 voltammetric cycles were recorded by potential scanning from –0.2 V to +1.2 V. The resulted modified electrodes were further called GC|poly**L**.

2.4. Electrochemical impedance spectroscopy studies

Electrochemical impedance spectroscopy (EIS) measurements were performed in acetate buffer solutions. The frequency range of EIS measurements was 1 MHz – 10 mHz, at 100 measuring points and 10 steps per decade, with the *ac* voltage perturbation of 5 mV. Two polarization potentials were applied on the GC electrodes: either 0.1 V, which is the open-circuit potential (E_{ocp}) of the bare GC electrode in acetate buffer, or 0 V (E_{ocp} of the modified glassy carbon electrodes in acetate buffer). All experiments were done at least in duplicate. Data obtained by EIS were fitted using Zview (Scribner Assoc.) fitting program.

3. Results and discussion

EIS measurements were performed in 0.1 molL^{-1} acetate buffer solutions using a bare GC electrode and a GC electrode modified with poly**L**. As it can be seen from Figs. 1-5, the plots in the complex plane (Nyquist plots) specifically exhibit two parts: a semicircular one and a linear one. The high frequency range semicircle is related to the charge-transfer controlled process, while the linear part in the low frequency range is due to the diffusion processes. The diameter of the semicircle represents the magnitude of charge-transfer resistance, R_{ct}, at the electrode surface.

3.1. Impedance properties of GC electrode

Fig. 1 presents Nyquist plots for the bare GC electrode obtained at two values of the polarization potential: 0.1 V (E_{ocp} of the bare GC electrode in acetate buffer) and 0 V (E_{ocp} of the modified GC electrodes in acetate buffer). It can be observed that the variation of the polarization potential caused a slight change in the electrochemical properties of the response. The smaller semicircle at high frequencies observed for bare GC at 0.1V suggests a small value of charge-transfer resistance, while the slope angle of the linear part, closer to 45^0, observed for bare GC at 0 V suggests more pronounced diffusion from the bulk electrolyte to the GC electrode surface at this polarization potential.

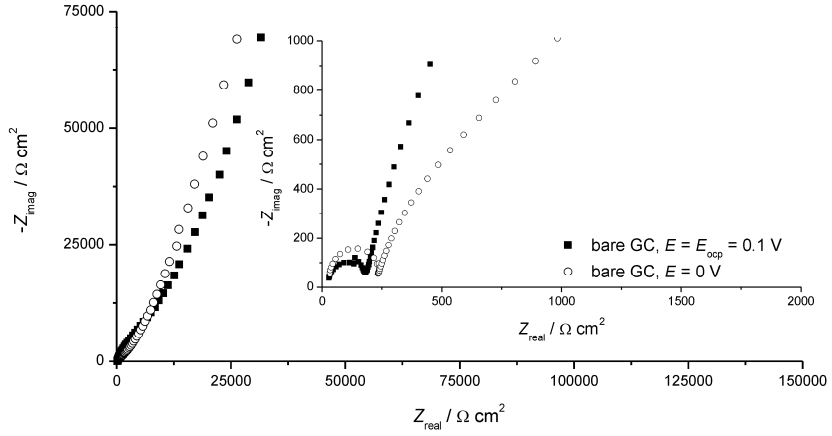

Fig. 1. Nyquist plots for the bare GC electrode at two values of the polarization potential: 0 V and 0.1 V. Inset: Corresponding high frequency region.

3.2. Impedance properties of the modified GC electrodes during the preparation procedure

In order to find the change of the interface properties during the preparation of the GC|poly**L** modified electrodes EIS spectra of the electrodes

were recorded after each preparation step. Step 1 was performed at +1.6V by controlled potential electrolysis (CPE); step 2 consisted in the equilibration of the poly**L** film by cyclic voltammetry in 0.1 molL^{-1} acetate buffer aqueous solution. Ans step 3 in the overoxidation of the poly**L** film in the same 0.1 molL^{-1} acetate buffer solution during 5 voltammetric cycles from –0.2 V to +1.2 V.

Fig. 2 presents Nyquist plots obtained at constant polarization potential (0.1 V) for the bare GC and for the GC|poly**L** modified electrodes after each of these steps. There are small differences between the impedance properties of the bare and modified GC electrodes. It is obvious from Fig. 2 that the largest semicircle corresponds to the electrode after step 1 of synthesis. Therefore, it suggests that the highest value of charge-transfer resistance can be seen in this step. In the next steps, R_{ct} diminished but always remained higher in comparison to bare GC. Regardless the nature of preparation step, the slope of the linear parts did not change significantly, indicating the same type of diffusion process. However, compared to the bare GC, the slope angle of the linear parts, which is closer to 90^o in the cases of charge consumption, suggests a more pronounced diffusion from the bulk electrolyte for the bare GC electrode. This is clearly due to the presence of a film on the electrodes.

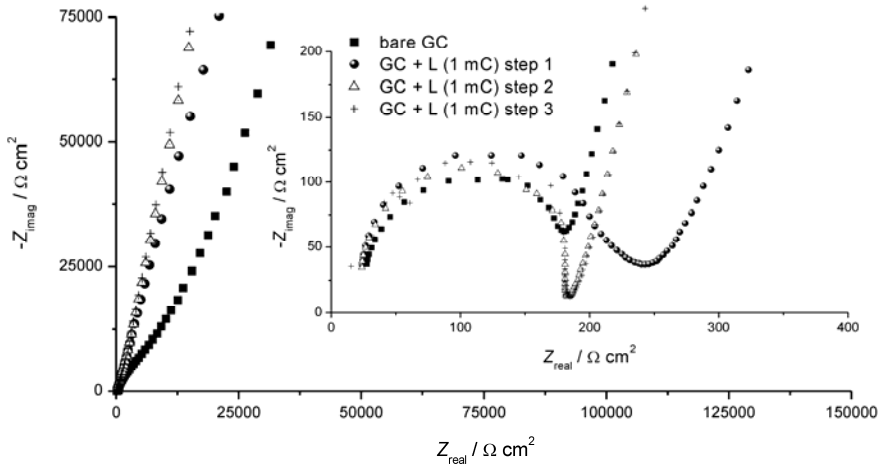

Fig. 2. Nyquist plots for bare GC and for GC | poly**L** (obtained by using a charge of 1 mC) after each step of coating modification (see 2.3); the polarization potential was 0.1 V. Inset: corresponding high frequency region.

3.3. Influence of the coating thickness upon the impedance properties of the GC modified electrode

In order to verify the data described in chapter 3.2, the influence of polymer film thickness on the electrochemical properties of the glassy carbon

modified electrode was investigated by loading different amounts of electrical charge (0.5 mC – 1.8 mC) during electrolysis at constant potential (CPE).

Figs. 3 and 4 present the comparative Nyquist plots of bare and modified GC with poly**L** films grown after consumption of different charge amounts.

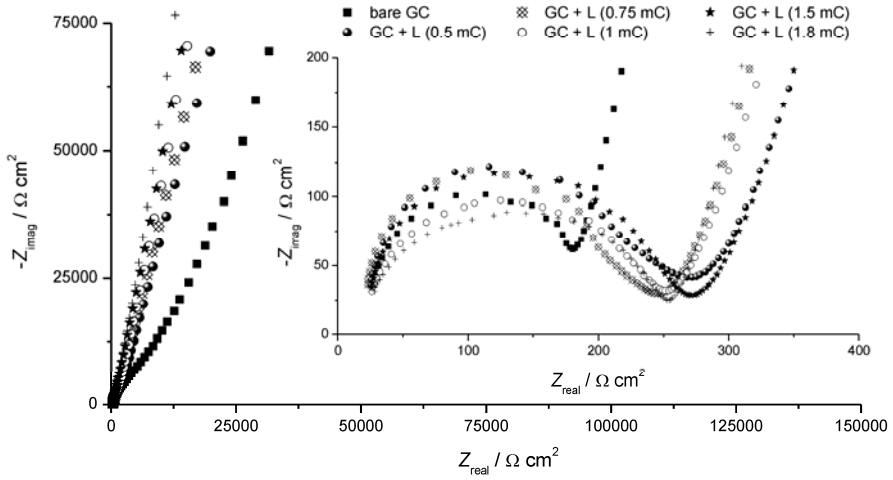

Fig. 3. Comparison of Nyquist plots in transfer solution obtained at 0 V potential for GC and for GC|poly**L** modified electrodes prepared using different amounts of polymerization charge: 0.5; 0.75; 1 ; 1.5 and 1.8 mC. Inset: corresponding high frequency region.

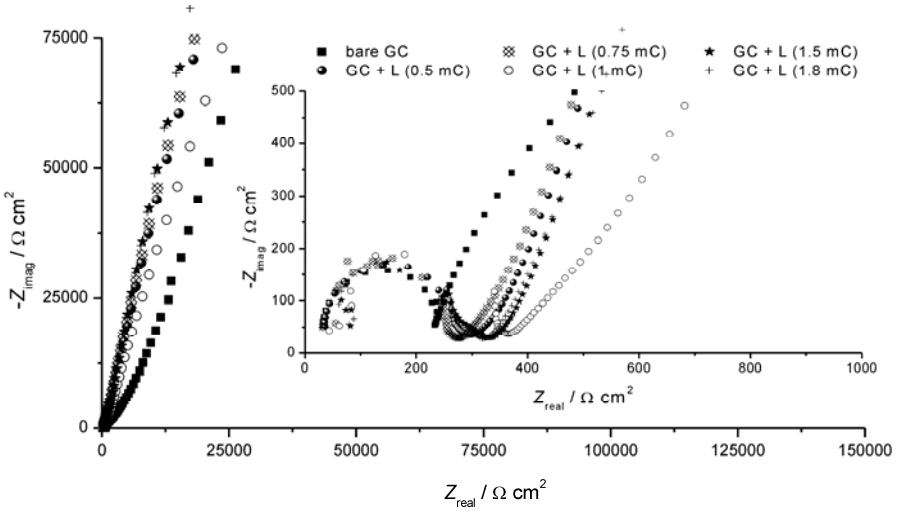

Fig. 4. Comparison of Nyquist plots in transfer solution obtained at 0.1 V potential for bare GC and for GC modified with poly**L** film formed using different amounts of polymerization charge: 0.5; 0.75; 1; 1.5 and 1.8 mC. Inset: corresponding high frequency region

The differences in EIS behaviour of both bare and modified with poly**L** GC electrodes seen in Figs. 3 and 4 are not significant at 0V polarization potential, compared to those evidenced at a polarization potential of 0.1V. The differences in the semicircle diameters at different amounts of charge are not significant, as well. However, regardless the amount of charge, the semicircle for any GC electrode modified with poly**L** is larger than that of the bare GC electrode, indicating a greater value of charge-transfer resistance. Also, the slope angle of the linear part which is closer to 90^o for all the GC electrodes modified with poly**L**, at different amounts of charge. It suggests a hampered diffusion from the bulk electrolyte to the bare GC electrode, due to the presence of a film.

3.5. Fitting the data obtained by EIS

The EIS data were fitted with a simple Randles equivalent electrical circuit (EEC) shown in Fig. 5.

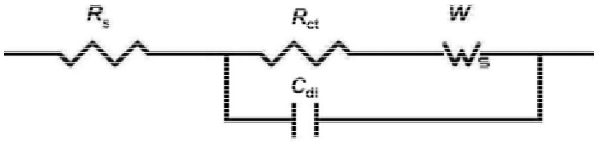

Fig. 5. Equivalent electrical circuit used for fitting of EIS data obtained for bare GC and GC|poly**L** modified electrode with poly(4-azulen-1-yl-2,6-bis(2-thienyl)pyridine) film: R_s = electrolyte solution resistance; C_{dl} = double-layer capacitance; R_{ct} = charge-transfer resistance; W – Warburg impedance

This equivalent electrical circuit used for fitting the EIS data obtained for both bare and modified GC electrodes is in agreement with the literature data [1,4,5,7-10]. It consists in the electrolyte ohmic resistance, R_s, the double-layer capacitance, C_{dl}, the charge-transfer resistance, R_{ct}, and the Warburg impedance, W. W component represents the process of the diffusion of ions from the bulk of the electrolyte to the interface and has three parts: W_R –ohmic resistance, W_T – capacitive part, and W_P – its exponent. The electrochemical parameters obtained for bare and modified GC electrodes by EIS data fitting are presented in Tables 1 and 2.

Table 1 shows the influence of each step of coating modification on the impedance properties of the GC modified electrode. As expected, the value of the charge-transfer resistance, R_{ct}, increases significantly after first step of synthesis comparing to the value for bare GC. However, it decreases after the equilibration step 2 and it shows a further decrease after the overoxidation step 3. This gradual decrease in charge-transfer resistance denotes an increase in the interface surface area of GC electrode in contact with the electrolyte [11], suggesting the increase in porosity of poly**L** films. This observation is in agreement with the proposed mechanism of poly**L** film formation [2]. Namely, in addition to usual procedure of equilibration of the poly**L** film in transfer solution by cyclic voltammetry, an

overoxidation step is recommended for the activation of the poly**L** film, as it leads to the formation of more C=O bonds. By decomposition of the azulene moiety, these bonds will become active sites for complexation of metal ions within the poly**L** film, similarly to those observed at other conducting polymers [12-15]. Therefore, the third step provides for some good sensing properties to the modified GC electrode.

Table 1

Electrochemical parameters obtained by fitting EIS data in the successive steps of preparation*

EEC parameter	GC	GC + 1 mC (step 1)	GC + 1 mC (step 2)	GC + 1 mC (step 3)
R_s / Ω cm^2	13.63 ± 3.58	13.52 ± 0.28	9.38 ± 0.66	6.53 ± 2.98
R_{ct} / Ω cm^2	**170.93 ± 10.27**	**226.33 ± 6.55**	**180.97 ± 5.68**	**188.40 ± 3.11**
C_{dl} / nF cm^{-2}	5.10 ± 0.79	5.05 ± 0.28	4.78 ± 0.23	4.57 ± 0.08
W_R / Ω cm^2	37102 ± 11455	4843 ± 259	5403 ± 558	5890 ± 1064
W_T / µF cm^{-2}	0.0312 ± 0.0004	0.0542 ± 0.0050	0.0781 ± 0.0016	0.0849 ± 0.0172
W_P	0.78 ± 0.006	0.75 ± 0.02	0.86 ± 0.003	0.86 ± 0.02
Slope	4.00	2.36	3.80	3.80

*Data at 0.1 V polarization from Fig. 2 for GC electrode and GC|poly**L** (CPE at 1.6 V, charge of 1 mC) electrodes in buffer acetate transfer solution.

The influence of the coating thickness on the that the charge-transfer process is relatively fast on both bare and modified GC electrodes [8] and suggesting low thickness of poly**L** films. EEC parameters of the modified GC electrode was also shown (Table 2).

Table 2

Electrochemical parameters obtained by fitting EIS data for different film thicknesses*

EEC parameter	Polymerization charge				
	0.5 mC	**0.75 mC**	**1 mC**	**1.5 mC**	**1.8 mC**
R_s / Ω cm^2	16.91 ± 2.40	12.54 ± 3.64	6.53 ± 2.98	19.83 ± 3.96	29.08 ± 3.46
R_{ct} / Ω cm^2	**241.67 ± 27.22**	**225.07 ± 16.52**	**188.40 ± 3.11**	**240.27 ± 10.04**	**215.40 ± 21.76**
C_{dl} / nF cm^{-2}	5.39 ± 0.23	4.91 ± 0.53	4.57 ± 0.08	6.31 ± 0.85	8.32 ± 1.06
W_R / Ω cm^2	4601 ± 377	3241 ± 399	5890 ± 1064	888 ± 66	682 ± 96
W_T / µF cm^{-2}	0.056 ± 0.008	0.053 ± 0.009	0.085 ± 0.017	0.021 ± 0.002	0.0206 ± 0.0004
W_P	0.74 ± 0.03	0.76 ± 0.05	0.86 ± 0.02	0.67 ± 0.03	0.66 ± 0.01
Slope	2.44	3.25	2.83	2.60	3.75

*Data at 0.1 V polarization from Fig. 4 for different GC|poly**L** modified electrodes in transfer solution (CPE at 1.6V)

It can be seen that the values of the charge-transfer resistance in the transfer solution are almost constant regardless the amount of the loaded charge. The absence of a increase trend for the charge-transfer resistance suggests, for example, that the increase in charge amount consumption during controlled potential electrolysis does not lead undoubtfully to the increase in thickness, since it would result in a continuous increase of charge-transfer resistance, R_{ct}, until a saturation value, which is not the case. However, it could be assumed that the porosity of obtained poly**L** films varies with the increase in the charge amount. Namely, if the porosity is high, which is also indicated by the use of the same electrochemical parameters for fitting data corresponding to the bare and modified GC electrodes, it becomes the primary factor to influence the impedance properties of the polymer films independent of the thickness increases [16].

4. Conclusions

The modification of the glassy carbon electrode was performed by controlled potential electrolysis of 4-azulen-1-yl-2,6-bis(2-thienyl)pyridine (**L**) in a solution containing tetra-n-butylammonium perchlorate in acetonitrile (Step 1). Then the poly**L** modified electrode was equilibrated by cyclic voltammetry (Step 2) and overoxidated (Step 3). The electrochemical properties of bare and modified glassy carbon electrodes (GC|poly**L**) were investigated after each step of modification by electrochemical impedance spectroscopy in acetate buffer. The obtained data were fitted using the ZView fitting program. The results indicated a small variation in electrochemical properties during the steps of modification of the glassy carbon electrode with poly**L** films. Moreover, it was shown that the influence of the polarization potential on the electrochemical properties of the electrodes was more pronounced for bare GC electrode than for GC|poly**L.**

Low values of charge-transfer resistance, obtained by fitting the EIS data, suggested the fast charge-transfer at the electrode interface. The influence of the poly**L** film thickness was not evidened, most probably due to a significant effect of poly**L** films porosity.

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