STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, Sp.Iss. 1, 2009

ELECTROCHEMICAL IMPEDANCE CHARACTERIZATION OF POLY{N,N′-ETHYLENEBIS[N-[(3-(PYRROLE-1-YL)PROPYL) CARBAMOYL)METHYL]-GLYCINE]} MODIFIED ELECTRODES

GEORGE-OCTAVIAN BUICĂ[a], IOANA MAIOR[a], ELEONORA-MIHAELA UNGUREANU[a], DĂNUȚ-IONEL VĂIREANU[a], CHRISTOPHE BUCHER[b], ERIC SAINT-AMAN[b]

ABSTRACT. Glassy carbon disk electrodes modified with film of poly N,N′-ethylenebis[N-[(3-(pyrrole-1-yl)propyl)carbamoyl)methyl]-glycine] (polyL) have been studied by electrochemical impedance spectroscopy (EIS) in order to get a better understanding of their complexing properties towards metal ions. Investigation of the EIS equivalent circuit clearly demonstrated that the morphological structure of the polyL depends on the film thickness and of the complexing species (ions of Hg^{2+}, Cu^{2+} or Pb^{2+}) and their oxidation state as well.

Keywords: Poly(N,N′-ethylenebis[N-[(3-(pyrrole-1-yl)propyl) carbamoyl)methyl]-glycine]) films; Modified electrodes; Electrochemical Impedance Spectroscopy.

INTRODUCTION

There are numerous health problems associated with exposure to high levels of metal ions such as Cd^{2+}, Pb^{2+}, Hg^{2+}, $As^{3+/5+}$ because of their tendency to accumulate in the body, their toxicity and their low rate of clearance. For instance, the biological half-life of cadmium is 10–30 years, while that of lead in bones is more than 20 years [1]. The Environmental Protection Agency (US EPA) estimates that nearly 20 % of human exposure to lead occurs through contaminated drinking water [2]. It is therefore critical for humans to experience minimal exposure to these contaminants and to develop reliable tools allowing fast and accurate quality monitoring. Also, the great concern in recent years regarding the toxicity of mercury has contributed to the motivation for developing new electrode materials without mercury for electroanalytical applications. Such materials include various forms of carbon, widely applied as electrodes and as electrode substrates [1]. Glassy carbon has particularly played an important role in voltammetric studies due to

[a] *Faculty of Applied Chemistry and Material Sciences, University "Politehnica" of Bucharest, Gheorghe Polizu 1-7, 011031 Bucharest, Romania, em_ungureanu2000@yahoo.com*

[b] *Université Joseph Fourier Grenoble 1, Département de Chimie Moléculaire, UMR CNRS-5250, Institut de Chimie Moléculaire de Grenoble, FR CNRS-2607, BP 53, 38041, Grenoble Cedex 9, France*

its low permeability to gases, low porosity, hardness, good electrical conductivity and large accessible potential range. Carbon film electrodes, obtained by coating a substrate with a thin pyrolytic carbon layer, have recently emerged as a promising alternative form of carbon electrode. Carbon film electrodes usually exhibit large potential windows after electrochemical surface pre-treatment [3] and have been successfully applied to the development of sensors [4–10] and biosensors [11–14].

Electrochemical impedance spectroscopy (EIS) is a reliable and accurate technique perfectly suited to investigate the properties of polymeric materials [4, 5, 15, 16]. Such analyses used in connection to model circuit simulations lead to essential information concerning the ohmic resistance of the electrolyte solution, the charge transfer resistance at the solid polymer matrix / solution interface, the double layer capacitance and redox capacitance of the film and also on diffusion characteristics (diffusion coefficients of electronic and ionic charge carriers) [16].

There are two principal approaches to model the impedance of electronically conducting polymers; one describes the system as a uniform homogenous solid, while the other refers to a porous polymer membrane. In both approaches, electronic and ionic fluxes are regarded as separable participants in the whole conduction phenomena of this material. For the compact model, with a diffuse transport polarons and counter ions in the polymer layer, the charge transfer process take place at the polymer / solution interface only. This process leads to a finite diffusion low-frequency limit of the impedance, where the thickness and density of the membrane limit the diffusion rate of ions. However, the charge transfer and the interfacial charge are related to the coupled fluxes of electrons and ions [17-19]. Bard *et al.* have applied this technique to polypyrrole materials for the first time [5]. Although polypyrrole films exhibit porous structures, the authors have shown that electron transfer reactions may also occur at the polymer surface.

The synthesis of an original EDTA-like pyrrole-containing dendronic ligand, the ethylenediamine tetra-N-(3-pyrrole-1-yl)propylacetamide **L**, and the sensing properties of poly**L** coated carbon electrodes towards Hg(II) and Cu(II) cations, using the open circuit preconcentration-anodic stripping technique have been previously reported [20]. The purpose of the present work was to characterize the poly**L** glassy carbon modified electrodes by EIS.

RESULTS AND DISCUSSION

The poly**L** films have been deposited as previously shown [20], using a specific electropolymerization charge Q, and they have been investigated using EIS technique. The complex plane impedance (Nyquist diagram) and Bode plots have been recorded for the poly**L** modified glassy carbon electrodes (C/Poly**L**) of various film thicknesses, after pre-treatment in 0.1M acetate buffer solution, *p*H = 4.5. The electrochemical parameters have been

evaluated from the circular regression of electrochemical impedance (EI) spectra. An equivalent circuit that fits the experimental data has been proposed and the elements of the circuits have been evaluated and discussed.

a) Influence of the PolyL film thickness

The complex plane impedance (Nyquist diagram) and Bode plots for poly**L** modified glassy carbon electrodes of various film thicknesses are presented in Figures 1 and 2. From these dependencies the electrochemical parameters were evaluated by circular regression and then they were used as entry values for the fitting step.

Analyzing the Nyquist diagrams for the various film thicknesses, it can be observed that, at high frequencies, capacitive loops are obtained. The depressed semicircles are followed by diffusives regions at medium and low frequencies. This aspect shows a typical slope for Warburg impedance due to the mass transfer effects that can be interpreted as a result of the diffusion process adjacent to the electrode interface [16].

The real impedance axes intercept at high frequency agrees with the uncompensated resistance of the bulk solution (R_S) for all the data presented.

From Figure 1 it can be observed that with the increase of the electropolymerization charge Q the capacitive loop becomes wider and higher; therefore the charge transfer resistance has higher values, meaning that the composite film is thicker and more adherent.

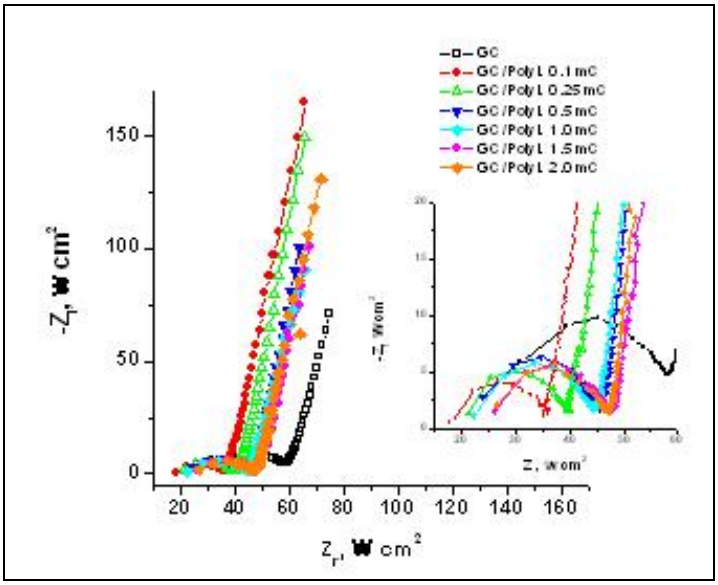

Figure 1. Complex plane impedance plots for glassy carbon and poly**L** modified glassy carbon electrodes of various film thicknesses, in 0.1 M acetate buffer solution, pH = 4.5. Inset: detail of the high frequency region.

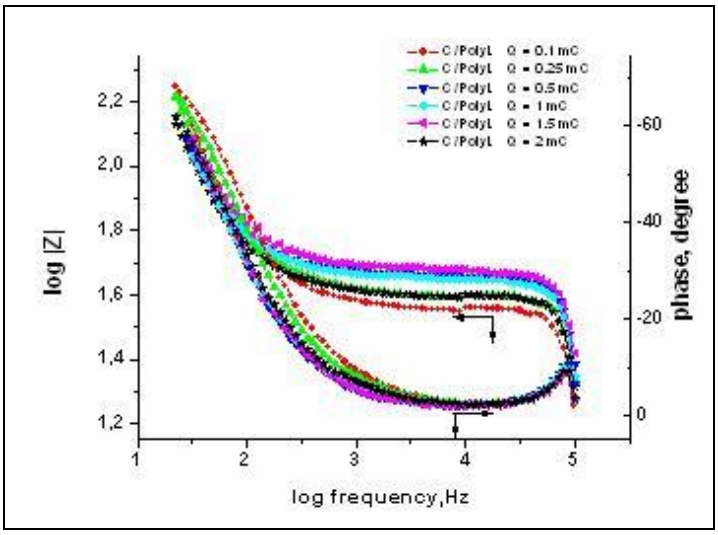

Figure 2. Bode plots for glassy carbon and poly**L** modified glassy carbon electrodes of various film thicknesses, in 0.1 M acetate buffer solution, pH = 4.5.

The Bode diagrams from Figure 2 confirm these results. As one can notice from this figure, on the dependence of phase angle versus frequency logarithm, one maximum tends to be reached. It corresponds to a single relaxation time constant. Thus, for obtained composite films, the relaxation time constant corresponds to a phase angle between 60 and 70°, which means a capacitive behavior with slight diffusive tendency.

Capacitance values decrease when the film thickness increases (from 99 nF cm^{-2} at 0.1mC to 77.7 nF cm^{-2} at 0.5mC) reaching a minimum value for Q = 0.5mC. Beyond this minimum value, the capacitance remains constant regardless the film thickness (applied electrical charge of polymerization).

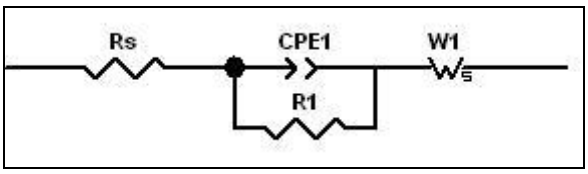

Figure 3. Equivalent circuit used to fit the impedance results: R_S – uncompensated ohmic solution resistance between working electrode and reference electrode; R_1 – charge transfer resistance of the polymer | electrolyte interface; CPE_1 - constant phase element of the polymer | electrolyte interface; W_1 – Warburg element as the diffusional control element for the polymer | electrode interface.

The equivalent circuit that fits the experimental data is shown in Figure 3. This circuit was used to fit the impedance spectra and extract the values of electrical parameters. It contains an uncompensated ohmic resistance of the electrolyte solution R_S, a sub-circuit related to the poly**L** | electrolyte interface and a Warburg element related to the GC | poly**L** interface, respectively. This circuit is inspired by the one proposed by Waller and Compton [18], but in this case we added a Warburg element that is responsible for the diffusional part of the impedance spectra of the thicker films (diffusion of ions from the bulk of the electrolyte to the interface). The constant phase CPE1 element is associated to the double layer capacitance at the polymer | electrolyte interface. CPE1 is a constant phase element with a roughness factor α_1 (where the value of 1 represents a perfectly smooth surface); this element is related to the charge capacitance or to the counter-ion accumulation at the polymer | electrolyte interface. R_1 is related to an electronic charge transfer resistance during the electrochemical process or to an ionic charge transfer resistance associated to the redox process of the polymer.

The use of CPE instead of capacitor in case of micro-heterogeneous surfaces (rough or porous) is necessary to compensate the geometrical in-homogeneity of the electrode surface. The fractional exponent α takes values between 0 and1; for α = 0, CPE describes an ideal resistor and for α = 1 it describes an ideal capacitor; for α = 0.5 it represents homogenous semi-infinite diffusion. CPE also describes the distribution of relaxation times of the process occurring in the in-homogeneous polymer film.

The results obtained by fitting the data supplied by the EI spectra into Zview modelling software containing the above proposed equivalent circuit (Figure 3) for poly**L** modified glassy carbon electrodes of various film thicknesses are shown in Table 1.

Table 1. Calculated data obtained by fitting the supplied EI spectra into a ZView modeling software analysis for C/poly**L** modified glassy carbon electrodes with various film thicknesses obtained by using different polymerization charges Q (mC).

Circuit elements \ Q, mC	0*	0.1	0.25	0.5	1	1.5	2
R_S, Ω·cm^2	52.7	33.25	36.82	42.6	42.95	44.25	44.45
CPE_1, μF·cm^{-2}	14.51	54.8	56.54	66.72	57.65	52.20	62.18
α_1	0.93	0.95	0.96	0.97	0.97	0.99	0.97
R_1, Ω·cm^2	5483	1975	1761	1257	1250	808	1165
W_1-R, F	14.58	7.21	8.38	8.00	8.59	9.26	7.41
W_1-T·10^3, s·rad^{-1}	0.258	0.517	0.655	0.793	0.708	0.732	0.672
W_1-P, Ω s$^{-1/2}$	0.435	0.444	0.447	0.446	0.438	0.443	0.446

*bare glassy carbon electrode

The charge transfer resistance R1 for C/poly**L** modified electrodes is lower than for bare glassy carbon. This implies that the charge transfer process is relatively fast compared to the bare glassy carbon.

The film morphology affects the impedance responses due to the interactions between specific interfaces (polymer | electrolyte interface and electrode | polymer interface) when the polymer is in its oxidized or reduced form. In the case of low porosity (high values for α_1), the charge transfer resistance (R1) is higher and can control the impedance response. If the film is very porous (roughness factor α_1 is near 0), the surface of the electrode | electrolyte interface is larger relatively to the electrode | polymer interface, and the charge transfer between the metal and the electrolyte is favoured in appropriate conditions. From Table 1 it can be seen that the values of α_1 characteristics of the polymer | electrolyte interface are essentially unchanged by the film thickness. Meanwhile, in the full range of measured frequencies, the impedance phase and module values are dependent on the films morphology, being controlled by the electrical charge of synthesis. Thus, the diffusional phenomena are visible in all the recorded spectra due to the Warburg impedance that remains constant whatever the film thickness.

b) Influence of the metal ion nature

The influence of the complexing ions nature absorption during the accumulation stage was investigated for poly**L**–coated film glassy carbon electrodes which were complexed with Hg^{2+}, Cu^{2+} or Pb^{2+} ions to see if they exhibit any alterations of the electrochemical impedance parameters. Before the electrochemical impedance measurements, the modified electrode (obtained using 0.5mC polymerization charge) was soaked for 20 minutes under stirring in 10^{-5}M Hg^{2+}, Cu^{2+} or Pb^{2+} ions acetate buffer solution, then the EI spectra were recorded at open circuit potential (OCP).

The impedance spectra (Nyquist and Bode plots) are shown in Figures 4 and 5 and the analysis of the experimental results is given in Table 2 using the equivalent circuit shown in Figure 3.

After recording these EI spectra, the poly**L** modified electrodes containing Hg^{2+}, Cu^{2+} or Pb^{2+} ions were submitted to controlled potential electrolysis (CPE) for 3 minutes in order to reduce the metallic ions. The reductions of metal ions were performed at -1.8; -1.4 and -0.9V for Hg, Pb and Cu, respectively. After reduction the EI spectra (Figures 6 and 7) were recorded at OCP. The analysis of the results is given in Table 2 using the same equivalent circuit as for the modified electrodes in absence of metal ions (Figure 3).

Comparison of the EI spectra from Figure 4 shows that, although the impedance is greater in the presence of Hg^{2+}, Cu^{2+} or Pb^{2+} ions than in their absence, the shape of the spectra is not altered by the presence of

metal ions in the polymer film. The larger impedance values in the presence of metal ions than in their absence reflects a higher charge transfer resistance (due to the partial blocking of the polymer film near the electrode surface by the metal) and a lower value of the capacitance C ($C_{polyL–M}^{z+} < C_{polyL}$). This feature could be attributed to the formation of a more stable passive layer, which is the complexed film.

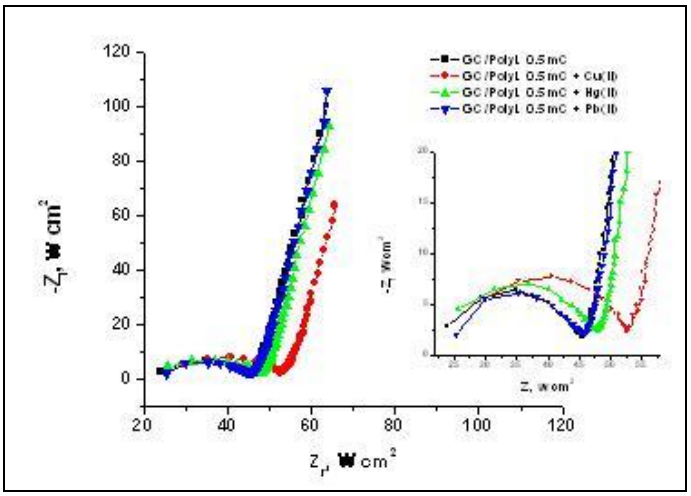

Figure 4. Complex plane impedance plots for C/poly**L** modified electrodes after complexation with 10^{-5} M Hg^{2+}, Cu^{2+} and Pb^{2+}in 0.1 M acetate buffer solution (*p*H = 4.5). Inset: detail of the high frequency region.

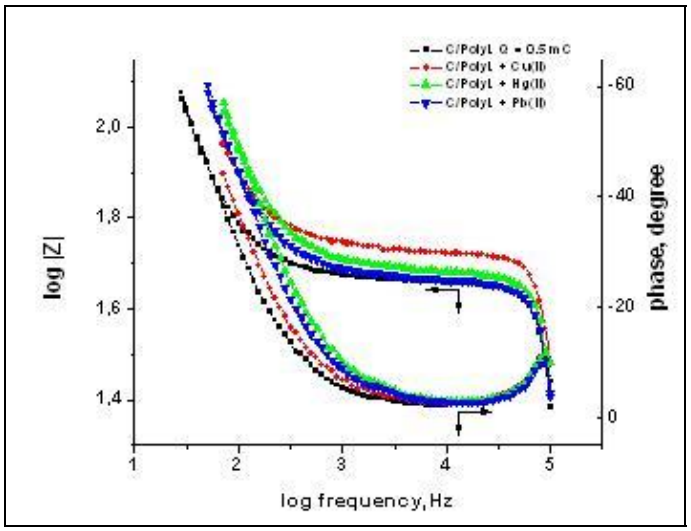

Figure 5. Bode plots for C/poly**L** modified electrodes after complexation with 10^{-5} M Hg^{2+}, Cu^{2+} and Pb^{2+}in 0.1 M acetate buffer solution (*p*H = 4.5).

From Table 2, one can also notice that the capacitance is irreversibly decreased after metal ion insertion. Variations in double layer capacitance CPE1 and α_1 values with addition of metal ions confirms the changing of the morphology of the modified electrode surface due to the polymer / metal ions interactions. The lowest value of double layer capacitance CPE1 in case of C/poly**L** – Hg^{2+} modified electrode confirms the formation of a more stable passive layer by addition of this complexing ion, than in the case of Cu^{2+} and Pb^{2+}. This behavior is in agreement with the better complexation properties of the poly**L** film toward Hg^{2+} which were found by other methods [21].

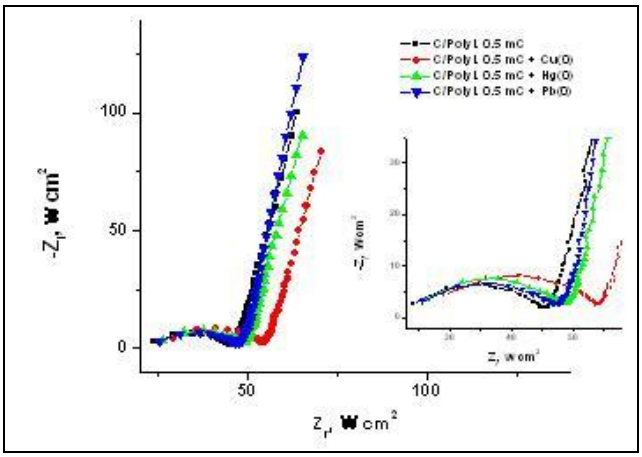

Figure 6. Complex plane impedance plots for C/poly**L** modified electrodes after complexation and reduction of Hg(II), Cu(II) and Pb(II) ions. Inset: detail of the high frequency region

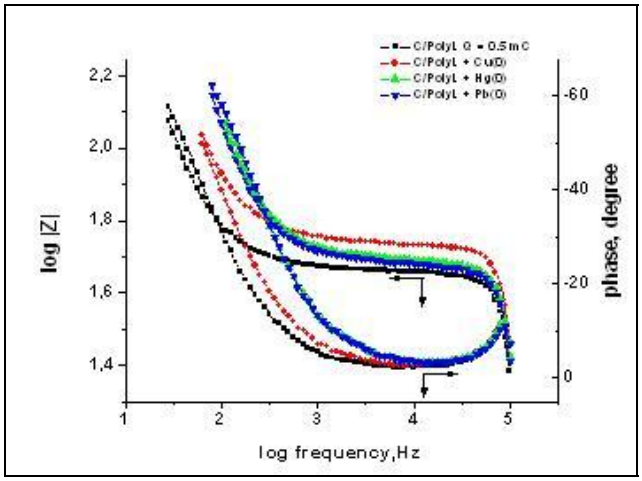

Figure 7. Bode plots for C/poly**L** modified electrodes after complexation with Hg^{2+}, Cu^{2+} and Pb^{2+} and reduction of the ions

Table 2. Calculated data obtained by fitting the supplied EI spectra into a ZView modeling software analysis for 0.5 mC C/poly**L** modified glassy carbon electrodes after complexation with Hg^{2+}, Cu^{2+} and Pb^{2+} and reduction

Complexed species\ Circuit elements	None	Cu^{2+}	Cu^{0}	Hg^{2+}	Hg^{0}	Pb^{2+}	Pb^{0}
R_s, Ω cm^2	42.6	49.42	50.41	44.63	45.17	42.83	44.35
CPE_1, μF cm^{-2}	66.72	55.48	44.36	38.65	23.99	44.51	25.89
α_1	0.97	0.93	0.94	0.93	0.93	0.94	0.94
R_1, Ω cm^2	1257	5855	4817	9009	8736	5153	4223
W_1-R, F	8.00	8.76	9.23	7.47	7.87	7.72	7.23
W_1-T·10^3, s rad^{-1}	0.793	0.654	0.576	0.441	0.320	0.508	0.337
W_1-P, Ω s$^{-1/2}$	0.446	0.442	0.444	0.449	0.451	0.448	0.461

After the metal ion reductions, the charge transfer resistance R_{ct} remains higher than the initial value of the modified electrodes before the metal ion insertion (Table 2). The observed increase of the charge transfer resistance R_{ct} after ions reduction may suggest that the modified electrodes in contact with heavy metals have increased values of the conductivity.

In Figures 8 and 9 are given, as example, the Nyquist and Bode plots for modified electrodes with poly**L** films before and after complexation with Hg^{2+}, and also after reduction of Hg^{2+} to Hg^{0}. They reflect the influence of Hg^{2+}/Hg^{0} on the EI parameters of C/poly**L** modified electrodes.

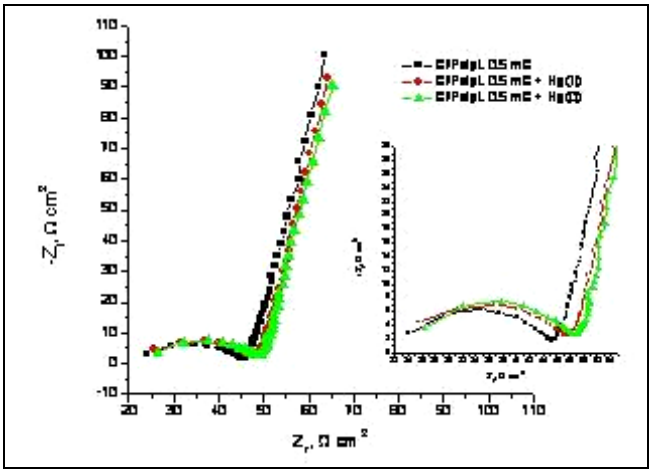

Figure 8. Complex plane impedance plots for C/poly**L** modified electrode (0.5mC) in 0.1 M acetate buffer solution (*p*H = 4.5) (■), after complexation in 10^{-5} M Hg^{2+} (●), and after the reduction of the Hg(II) ions (▲).
Inset: detail of the high frequency region

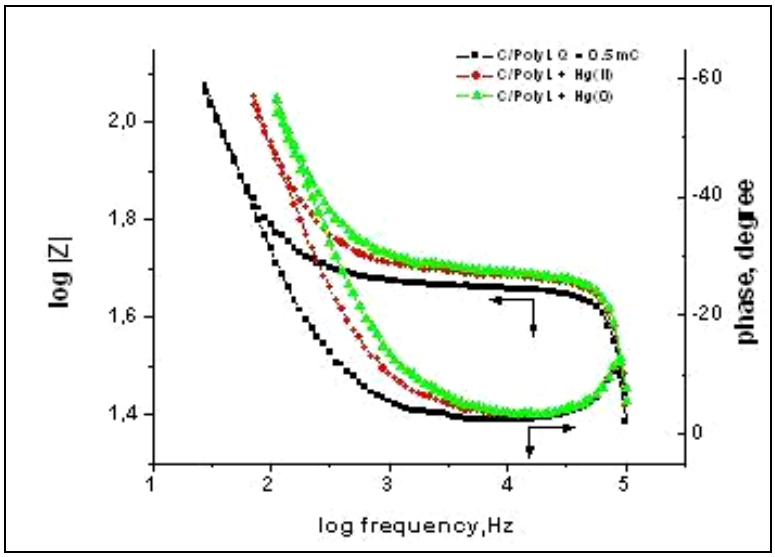

Figure 9. Bode plots for C/poly**L** modified electrode (0.5mC) in 0.1 M acetate buffer solution (*p*H = 4.5) (■), after complexation in 10^{-5} M Hg^{2+} (●), and after the reduction of the Hg(II) ions (▲)

CONCLUSIONS

The poly**L** glassy carbon modified electrodes (C/poly**L**) were characterized by electrochemical impedance spectroscopy (EIS). The modifications of the glassy carbon electrode by various electropolymerization charges lead to the formation of polymer films with different morphologies on the electrode surface depending on their thicknesses. The bulk of the material also contribute to the increase of the total impedance due to the presence of a diffusional control of the ions through the polymer matrix (characterized by the Warburg element at lower frequencies) and to the charge accumulation at very low frequencies (characterized by the limiting capacitance of the film).

The EIS behavior was also investigated for the complexed C/poly**L** electrodes obtained by immersion of C/poly**L** in Hg^{2+}, Cu^{2+} and Pb^{2+} solutions. Their EIS parameters are different in comparison with the non-complexed C/poly**L** electrodes. Electrochemical impedance spectroscopy has shown that the complexation with heavy metal ions does not affect the shape of the Nyquist plots, but it influences the electrochemical parameters. A selective behavior of the C/poly**L** modified electrodes for Hg^{2+} ions against other heavy metal ions (Cu^{2+}, Pb^{2+}) was found. The Hg^{2+} metal ions determine a high modification of the charge transfer resistance and a decrease of the double layer capacitance.

EXPERIMENTAL SECTION

1. Reagents and Materials

The synthesis of (N,N'-ethylenebis[N-[(3-pyrrole-1-yl) propyl)carbamoyl) methyl]-glycine) (**L**) was performed according to a previously reported procedure [20]. Acetonitrile (Rathburn, HPLC grade S) was used as received. Tetra-n-butylammonium perchlorate (TBAP, Fluka puriss) was dried under vacuum at 80°C for 3 days. Suprapur grade sodium acetate and acetic acid (Merck) were used to prepare 0.1 mol L^{-1} acetate buffers. Copper(II) acetate - $Cu(CH_3CO_2)_2,H_2O$, lead(II) nitrate - $Pb(NO_2)_2$, mercury(II) acetate - $Hg(CH_3CO_2)_2$ were used as source of metal ions. Copper(II) acetate and lead(II) nitrate were from Prolabo. Mercury(II) acetate was purchased from Strem. All reagents were used without further purification. Perchloric acid was obtained from Merck. Distilled water was obtained from an Elgastat water purification system (5 MΩ cm).

2. Electrochemical Equipment

The experiments were performed with a PG STAT 12 Autolab potentiostat, using a conventional three-electrode system. The working electrode was a modified carbon disk (3 mm diameter, from CH Instruments). The counter electrode was a platinum wire. The reference electrode used for electropolymerizations was an Ag/10 mM $AgNO_3$, 0.1 M TBAP, CH_3CN while that used for electroanalytical and EIS experiments was a conventional Ag/AgCl electrode. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a VoltaLab 40 – PGZ 301 Potentiostat controlled with a VoltaMaster v 4.0 software. A Denver-Instrument Model 220 *p*H-conductivity meter was used to measure *p*H.

3. Preparation of the Modified Electrodes

Prior to electropolymerization, glassy carbon disk working electrodes were polished with 0.2 µm diamond paste. Electropolymerization was performed by controlled potential electrolysis (CPE) at a potential of +0.9 V/(Ag/Ag^+) until reaching the desired charge. Poly**L** films were grown on glassy carbon disk electrodes in solution of **L** (10^{-3}M) in 0.1mol L^{-1} TBAP, acetonitrile containing two-molar equivalents of $HClO_4$, using the previously described procedure [20]. Films with Γ_L values between 8×10^{-10} and 2×10^{-9}mol cm^{-2} were typically obtained using polymerization charges of 0.3 to 1mC. Apparent surface coverages in complexing sites Γ_L (mol cm^{-2}) were determined from the charge recorded under the polypyrrole oxidation wave measured by cyclic voltammetry (CV) at the scan rate of 2mV/s, taking into account that one ethylenediaminotetracetamide group is attached to 2 pyrrole rings and assuming that one in three pyrrole units is oxidized [22].

Modified polypyrrole films usually exhibit high background currents leading to major limitations of the electrochemical window and thereby making metal detection difficult [23]. A straightforward solution to this problem was to overoxidize polypyrrole [24-26]. Before each analytical experiment, the pyrrole-based electroactivity was therefore destroyed upon cycling the electrode potential (5 cycles) between -0.2 V and +1.2 V in a buffer acetate (*p*H = 4.5). This treatment leads to C/poly**L** modified electrodes covered with non-conducting polymer which were used for the electrochemical investigation.

4. Accumulation and Voltammetric Procedures

Accumulation of metal ions into poly**L** films was carried out at open circuit upon dipping C/poly**L** modified electrodes for a given time into 5 mL of a stirred buffer solution at *p*H = 4.5 containing a given metal salt. The electrodes were then removed from the accumulation cell and thoroughly washed with purified water to remove uncomplexed ions from the modified electrode surface. After transferring the latter into an electroanalytical cell containing 0.1M acetate buffer solution, the accumulated metal ions were subjected to electrochemical impedance spectra (EIS). The EI spectra were also recorded after 3 minutes reduction of the complexed modified electrodes at specific potential for each complexed cation (-1.8; -1.4 and -0.9V for Hg, Pb and Cu, respectively).

5. Electrochemical Impedance Measurements

EIS measurements with C/poly**L** modified electrodes were carried out in a three electrode cell configuration. The working electrode was the poly**L** modified glassy carbon disk electrode (3 mm diameter), the counter electrode was a platinum wire and the reference electrode was Ag/AgCl. EIS measurements were performed in the frequency range from 100 kHz to 500 MHz with an amplitude perturbation of 30 mV at OCP.

ACKNOWLEDGMENTS

This work was partially financed by CNMP Romanian REMORESE 71-067/2007 grant.

REFERENCES

1. R. A. Goyer, "Toxicology, The Basic Science of Poisons fifth ed.," McGraw-Hill, New York, **1996**.
2. http://www.epa.gov/safewater/lead/leadfacts.
3. C. M. A. Brett, L. Angnes, H. D. Liess, *Electroanalysis*, **2001**, *13*, 765.

4. O. M. S. Filipe, C. M. A. Brett, *Electroanalysis*, **2004**, *16*, 994.
5. C. Gouveia-Caridade, C. M. A. Brett, *Electroanalysis*, **2005**, *17*, 549.
6. O. M. S. Filipe, C. M. A. Brett, *Talanta*, **2003**, *61*, 643.
7. R. Pauliukaite, C. M. A. Brett, *Electroanalysis*, **2005**, *17*, 1354.
8. R. Pauliukaite, M. Florescu, C.M.A. Brett, *Journal of Solid State Electrochemistry*, **2005**, *9*, 354.
9. R. Pauliukaite, M. E. Ghica, C. M. A. Brett, *Analytical and Bioanalytical Chemistry*, **2005**, *381*, 972.
10. C. Gouveia-Caridade, C. M. A. Brett, *Journal of Electroanalytical Chemistry*, **2006**, *192*, 113.
11. M. E. Ghica, C. M. A. Brett, *Analytical Letters*, **2005**, *38*, 907.
12. M. Florescu, C. M. A. Brett, *Talanta*, **2005**, *65*, 306.
13. R. Pauliukaite, A. M. Chiorcea-Paquim, A. M. Oliveira-Brett, C. M. A. Brett, *Electrochimica Acta*, **2006**, *52*, 1.
14. M. E. Ghica, C. M. A. Brett, *Electroanalysis*, **2006**, *18*, 748.
15. T. Zalewska, A. Lisowska-Oleksiak, S. Biallozor, V. Jasulaitiene, *Electrochimica Acta*, **2000**, *45*, 4031.
16. M. Martinia, T. Matenciob, N. Alonso-Vantec, M. A. De Paoli, *Journal of the Brazilian Chemical Society*, **2000**, *11(1)*, 50.
17. R. A. Bull, F. R. F. Fan, A. J. Bard, *Journal of the Electrochemical Society*, **1982**, *129(5)*, 1009.
18. A. M. Waller, R. G. Compton, *Journal of the Electrochemical Society (Faraday Transactions)*, **1989**, *85(4)*, 977.
19. A. Sezai Sarac, M. Ates, B. Kilic, *International Journal of the Electrochemical Science*, **2008**, *3*, 777.
20. M. Heitzmann, C. Bucher, J.-C. Moutet, E. Pereira, B.-L. Rivas, G. Royal, E. Saint-Aman, *Electrochimica Acta*, **2007**, *52*, 3082.
21. G.-O. Buica, *PhD Thesis,* University Politehnica of Bucharest, **2009**.
22. G. K. Chandler, D. Pletcher, "Electrochemistry, Specialist Periodical Reports", Royal Society of Chemistry, London, 1986, 117 – 150.
23. A. Wanekaya, O. A. Sadik, *Journal of Electroanalytical Chemistry*, **2002**, *537*, 135.
24. D. W. M. Arrigan, D. S. Gray, *Analytica Chimica Acta*, **1999**, *402*, 157.
25. H. Shiigi, H. Yakabe, M. Kishimoto, D. Kijima, Y. Zhang, U. Sree, B. A. Deore, T. Nagaoka, *Microchimica Acta*, **2003**, *143*, 155.
26. H. Shiigi, D. Kijima, Y. Ikenaga, K. Hori, S. Fukazawa, T. Nagaoka, *Journal of the Electrochemical Society*, **2005**, *152*, 129.