Electrochemical Impedance Characterization of Poly (Pyrrole-EDTA Like) Modified Electrodes

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*Carbon disk electrodes with film of poly ethylenediamine tetra-N-(3-pyrrole-1-yl)propylacetamide (poly**L**) coatings have been studied by electrochemical impedance spectroscopy (EIS) in order to estimate their advantages and limitations in the electroanalysis of metal ions by anodic stripping voltammetry. Investigation of the EIS equivalent circuit clearly demonstrated that the morphological structure of the poly**L** depends on the film thickness. EIS curves of poly**L** modified electrodes have also been recorded in the presence of copper and mercury ions in solution, and after their reduction to metal at the electrode surface.*

Keywords: electrochemical impedance spectroscopy, poly(pyrrole-EDTA) films, modified electrodes

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 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 pyrrolytic 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 [2] and have been successfully applied to the development of sensors [4–9] and biosensors [10–13].

Electrochemical impedance spectroscopy (EIS) is a reliable and accurate technique perfectly suited to investigate the properties of polymeric materials [3, 4, 14, 15]. Such analyses lead to essential information concerning the solution resistance R_S, the charge transfer resistance Rct and the double layer capacity Cdl [15].

There are two principal approaches to modelize the impedance of electronically conducting polymers (ECP); 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. However, the charge transfer and the interfacial charge are related to the coupled fluxes of electrons and ions [16-18]. This technique has been applied to polypyrrole materials for the first time [4] and although polypyrrole films exhibit porous structures, the authors have shown that electron transfer reactions may also occur at the polymer surface

We have recently reported 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 [19]. The purpose of the present work was to characterize poly**L** carbon film resistor disk electrodes by EIS.

Experimental part

Reagents and Materials

Synthesis of ethylenediamine tetra-N-(3-pyrrole-1-yl)propylacetamide was performed according to the procedure described in [19]. 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 and mercury(II) acetate - $Hg(CH_3CO_2)_2$ were used as source of metal ions. Copper(II) acetate was from Prolabo and Mercury(II) acetate was from Strem. All reagents were used without further purification. Distilled water was obtained from an Elgastat water purification system (5 MΩ cm).

Electrochemical Equipment

The electrochemical impedance spectroscopy (EIS) measurements were carried out using a VoltaLab 40 – PGZ 301 Potentiostat in conjunction with VoltaMaster v 4.0 software. The working electrode was a modified carbon disk (3 mm diameter, purchased from CH Instruments). The counter electrode was a platinum gauze (2.5 cm^2). The reference was an Ag/AgCl CH-instrument electrode. A Denver Instrument Model 220 *p*H-conductivity meter was used to measure the *p*H of the buffer solutions.

Preparation of the Modified Electrodes

The preparation of the poly**L** glassy carbon modified electrodes (C/poly**L**) was performed according to a previously reported procedure [19]. These modified electrodes exhibit typically high background currents leading to a major limitation of the electrochemical window and thereby making difficult the metal detection [20]. One solution to this problem is to overoxidize the polypyrrole matrix [21-23]. The polypyrrole-based electroactivity was thus destroyed before each impedance experiments upon cycling the electrode potential (5 cycles) between -0.2 V and +1.2 V in a buffer acetate (*p*H = 4.5).

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This procedure leads to C/poly**L** electrode covered with non-conducting polymer which was used for all impedance investigations.

Electrochemical Impedance Measurements

The EIS measurements of the poly**L**–modified electrode were carried out in a three electrode cell configuration. The working electrode was a modified 3 mm diameter glassy carbon disk electrode, the counter electrode was a platinum wire and the reference was an Ag/AgCl CH-instrument electrode. EIS measurements were performed on C/poly**L** electrodes covered with non-conducting polymer in the frequency range from 100 kHz to 500 mHz with an amplitude perturbation of 30 mV at the open circuit potential (OCP) [24].

Results and discussion

EIS measurements

Influence of the poly**L** film thickness

Electrochemical impedance spectra were obtained in acetate buffer solutions (*p*H = 4.5) with bare glassy carbon electrodes (C) and with poly**L** modified glassy carbon electrodes (C/poly**L**) with films of increasing thickness after pretreatment in 0.1 M acetate buffer solution.

Complex impedance plots (Nyquist diagrams) have been recorded for each electrode and the electrochemical parameters have been evaluated by circular regression of the impedance spectra.

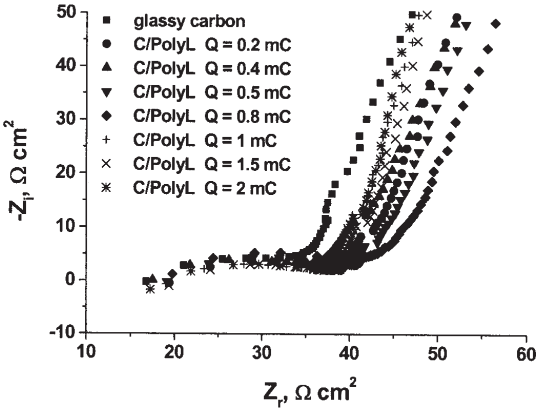

Fig. 1. Nyquist diagrams for poly**L** modified glassy carbon electrodes of various film thickness in 0.1 M acetate buffer solution (*p*H = 4.5).

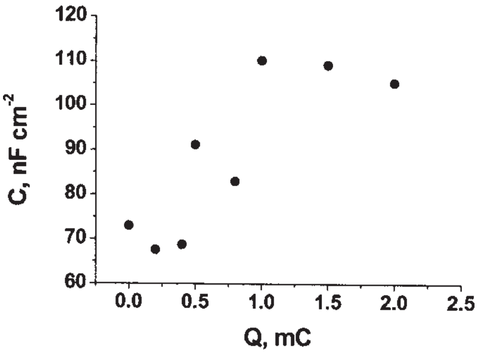

Fig. 2. Dependence of the modified glassy carbon electrode capacitance, C, on the poly**L** film thickness; 0.1 M acetate buffer solution, *p*H = 4.5

Nyquist diagrams plotted for poly**L**–modified glassy carbon electrodes of various film thicknesses are shown on figure 1. The electrochemical parameters evaluated by circular regression of impedance spectra are shown in table 1.

The capacitance values C increase with increasing film thickness up to a maximum value of Q = 1 mC (fig. 2). Beyond this maximum, the capacitance remains constant regardless the film thickness, which is proportional to the electrical charge consumed during the polymerization process [19].

The interception of the real impedance axes with the Nyquist semicircle at high frequency agrees in all cases with the uncompensated resistance of the bulk solution (R_S). The common feature is a depressed semicircle (at high frequency) followed by a straight line at lower frequencies with a slope angle close to 50° for all the Nyquist plots. This feature shows a typical slope for a Warburg impedance. The depressed semicircles can be assigned to the roughness of the polymer surface [15].

The experiment shown on figure 1 can be simulated with the equivalent circuit presented in figure 3 where R_S is the ohmic resistance, CPE1 the constant phase element of the double layer, R_1 the charge transfer resistance and W1 the Warburg element being responsible of the diffusion process.

Numeric values for each parameter were calculated upon fitting our model circuit to the experimental data (table 2, where CPE–T is the time constant component of the constant phase element and CPE–P is the exponential part of the constant phase element).

Table 1

DATA OBTAINED FROM EIS (NYQUIST DIAGRAM) FOR POLY**L** MODIFIED GLASSY CARBON ELECTRODES OF VARIOUS FILM THICKNESSES.

No.	Electrode surface	E$^{(a)}$, mV/(Ag/AgCl)	$R_a$$^{(b)}$, ohm·cm^2	$R_b$$^{(c)}$, ohm·cm^2	C$^{(d)}$, nF·cm^{-2}
1.	C (glassy carbon)	+215	23.25	27.47	72.97
2.	C/poly**L** (Q = 0.2 mC)	+107	23.03	32.97	67.57
3.	C/poly**L** (Q = 0.4 mC)	+198	21.61	29.17	68.74
4.	C/poly**L** (Q = 0.5 mC)	+225	19.25	24.44	91.13
5.	C/poly**L** (Q = 0.8 mC)	+307	18.23	26.86	82.94
6.	C/poly**L** (Q = 1 mC)	+198	19.77	20.22	110.1
7.	C/poly**L** (Q = 1.5 mC)	+214	20.55	20.42	109.1
8.	C/poly**L** (Q = 2 mC)	+242	19.26	21.18	105.1

(a) E – open circuit potential; (b) R_a – ohmic resistance multiplied by the area of the electrode surface; (c) R_b – polarization resistance multiplied by the area of the electrode surface; (d) C – double layer capacity

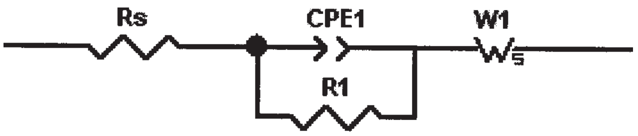

Fig. 3. Equivalent circuit used to fit the impedance results: R_S – solution resistance; R_1 – ohmic resistance of the polymer | electrolyte interface; CPE_1 – constant phase element of the polymer | electrolyte interface; W_1 – Warburg element as the diffusion control element for the polymer | electrode interface

This study led us to propose an equivalent circuit in accordance with the experimental data (fig. 3), containing an uncompensated resistance R_S, and two sub-circuits accounting for the poly**L** | electrolyte interface and for the glassy carbon electrode | poly**L** interface. This circuit derives from the one proposed by Waller and Compton [17], upon adding a Warburg element to take into account the diffusion part of the films impedance spectra. R_1 is related to an electronic charge transfer resistance during the electrochemical process and/or to an ionic charge transfer resistance associated to the redox process. CPE_1 is a non-ideal capacitor, of capacity CPE_1–T and roughness factor CPE_1–P (where the value of 1 represents a perfectly smooth surface), related to the space charge capacitance and/or to the counter-ion accumulation at the polymer | electrolyte interface. W_1 corresponds to a Warburg element, responsible for the diffusion control of the system. According to the modeling software ZView, at very low frequencies, Z_{im} approaches Ws-R (the coefficient of Warburg element) and Z_r goes to zero; Ws-T (the time constant part of Warburg element) depends on the effective diffusion thickness and on the effective diffusion coefficient of the particle; Ws-P (the exponent part of the Warburg element) takes values between 0 < Ws-P < 1.

The results obtained by fitting the data supplied by the impedance spectra into a ZView modeling software containing the above proposed equivalent circuit (fig. 3) for PolyL modified glassy carbon electrodes of various film thicknesses are shown in table 2.

The film morphology affects the impedance responses due to the interactions between specific interfaces (polymer | electrolyte and electrode | polymer) when the polymer is in its oxidized or reduced form.

From the values reported in table 2, it can be seen that up to an electrical charge of 0.8 mC, there is an increase in R_S, followed by a slight decrease leading to a constant value around 36 Ω. There is no direct correlation between CPE_1–T and film thickness; CPE_1–P values are essentially unchanged by the film thickness for the polymer | electrolyte interface. One may also notice a direct influence of the applied electrical charge Q on R_1, this effect getting stronger as electrical charge Q increases.

As long as W_1-R is concerned, there is a direct correlation between its value and the value of the electrical charge, this element behaving in an almost identical manner to R_S, with the same flat value (3.5) when Q > 0.8 mC.

Thus, the diffusion phenomena are visible in all the recorded spectra of the films due to the Warburg impedance which value remains constant.

Influence of the metallic ions

EIS experiments were conducted similarly with poly**L**–coated film glassy carbon electrode in the presence of different metal ions in solution, (10^{-5} M). Before each electrochemical impedance measurements, the modified electrodes (polymerization charge of 1 mC) were soaked for 20 min under stirring in 10^{-5} M Hg^{2+} or 10^{-5} M Cu^{2+} ions acetate buffer solutions and a spectrum was then recorded at OCP. The poly**L**–coated films containing Hg^{2+} or Cu^{2+} ions were then submitted to a controlled potential electrolysis (CPE) for 3 min in order to reduce all the complexed metallic ions. The reduction of the metal ions was performed at –1.8 V for Hg and at –0.9 V for Cu.

The analysis of the experimental results is given in table 3 and 4 using the same equivalent circuit as in absence of the metallic ions.

Table 2

CALCULATED DATA OBTAINED BY FITTING THE DATA SUPPLIED BY THE IMPEDANCE SPECTRA INTO A ZVIEW MODELING SOFTWARE ANALYSIS FOR POLY**L** MODIFIED GLASSY CARBON ELECTRODES FOR VARIOUS FILM THICKNESS

Circuit elements	R_S, Ω	CPE_1–T 10^{-5}, F	CPE_1–P	R_1, Ω	W_1-R, $\Omega \cdot s^{-1/2}$	W_1-T·10^{-5}, $S \cdot s^{1/2}$	W_1-P
C (glassy carbon)	31.23	1.29	0.798	4168	4.59	6.74	0.51
C/poly**L** (Q = 0.2 mC)	29.39	1.72	0.698	10.8	4.79	3.65	0.44
C/poly**L** (Q = 0.4 mC)	34.67	6.86	0.784	$3.65 \cdot 10^{17}$	5.06	15.87	0.42
C/poly**L** (Q = 0.5 mC)	38.31	4.34	0.848	$1.64 \cdot 10^{11}$	7.37	26.39	0.43
C/poly**L** (Q = 0.8 mC)	39.19	8.35	0.767	$3.33 \cdot 10^{15}$	9.15	41.86	0.43
C/poly**L** (Q = 1 mC)	35.62	4.25	0.847	$2.14 \cdot 10^{19}$	3.45	18.99	0.44
C/poly**L** (Q = 1.5 mC)	36.9	5.00	0.848	$1.94 \cdot 10^{14}$	3.23	14.03	0.44
C/poly**L** (Q = 2 mC)	35.74	6.19	0.857	$2.82 \cdot 10^{11}$	3.96	17.91	0.45

R_S – the solution resistance; CPE_1–T – the time constant part of the constant phase element; CPE_1–P – the exponent part of the constant phase element; R_1 – the charge transfer resistance; W_1–R – the coefficient of Warburg element; W_1–T – the time constant part of Warburg element; W_1–P – the exponent part of the Warburg element

Table 3

DATA OBTAINED FROM NYQUIST DIAGRAMS FOR POLY**L** MODIFIED ELECTRODES AFTER COMPLEXATION WITH Hg^{2+} 10^{-5} M OR Cu^{2+} 10^{-5} M AND AFTER IONS REDUCTION

Entry	Electrode surface	E [(a)], mV/(Ag/AgCl)	R_a [(b)], ohm·cm^2	R_b [(c)], ohm·cm^2	C [(d)], nF·cm^{-2}
1.	C (glassy carbon)	+215	23.25	27.47	72.97
2.	C/poly**L** (Q = 1 mC)	+198	19.77	20.22	110.1
3.	C/poly**L** + Hg^{2+}	+173	20.17	21.22	94.49
4.	C/poly**L** + Hg^0	−101	20.22	22.15	100.5
5.	C/poly**L** + Cu^{2+}	+116	20.31	21.68	102.7
6.	C/poly**L** + Cu^0	−251	19.95	21.81	102.1

[(a)] E – open circuit potential; [(b)] R_a – ohmic resistance multiplied by the area of the electrode surface; [(c)] R_b – polarization resistance multiplied by the area of the electrode surface; [(d)] C – double layer capacity

Table 4

CALCULATED DATA OBTAINED BY FITTING THE DATA SUPPLIED BY THE IMPEDANCE SPECTRA INTO A ZVIEW MODELING SOFTWARE ANALYSIS FOR POLY**L** MODIFIED ELECTRODES AFTER COMPLEXATION WITH Hg^{2+} 10^{-5} M OR Cu^{2+} 10^{-5} M AND AFTER IONS REDUCTION

Circuit elements	R_S, Ω	CPE_1–T 10^{-5}, F	CPE_1–P	$R_1 \cdot 10^{16}$, Ω	W_1-R	W_1-T·10^{-5}	W_1-P
C (glassy carbon)	31.23	1.29	0.798	4168	4.59	6.74	0.51
C/poly**L** (Q = 1 mC)	35.62	4.25	0.847	$2.14 \cdot 10^3$	3.45	0.00018988	0.44
C/poly**L** + Cu^{2+}	36.85	3.94	0.838	$5.49 \cdot 10^{-2}$	3.83	0.00014	0.44
C/poly**L** + Cu^0	36.61	3.09	0.849	8.77	3.93	0.00014464	0.44
C/poly**L** + Hg^{2+}	37.19	3.27	0.861	$8.36 \cdot 10^{-6}$	3.64	0.00013667	0.45
C/poly**L** + Hg^0	37.34	2.70	0.846	$2.14 \cdot 10^2$	3.38	0.00010998	0.44

R_S – the solution resistance; CPE_1–T – the time constant part of the constant phase element; CPE_1–P – the exponent part of the constant phase element; R_1 – the charge transfer resistance; W_1–R – the coefficient of Warburg element; W_1–T – the time constant part of Warburg element; W_1–P – the exponent part of the Warburg element

The oxidation state has no influence on R_S; the ionic species slightly affects the value of R_S, being higher in the case of mercury. CPE_1–T is affected by the ion's oxidation state and is higher with oxidized species; this effect being more pronounced with copper than with mercury. The value of CPE_1–P estimated around 0.8, suggests a constant roughness of the modified electrode. R_1 decreases with increasing the oxidation state with 2 orders of magnitude for copper and with 7 orders of magnitude for mercury, suggesting an increase in charge transfer resistance for the native state comparing to the oxidized state. As long as W_1-R and W_1-P are concerned, their values are essentially unchanged.

Although the magnitude of the impedance (Z_r) is greater in the presence of Hg^{2+} or Cu^{2+} ions than in their absence, one may notice that the shape of the spectra is not altered by the presence of metal ions in the polymer film (fig. 4). The impedance values are larger in the presence of metallic ions, reflecting a higher charge transfer resistance (due to a partial blocking of the polymer film by metal near to the electrode surface) and a lower value of the capacitance C ($C_{C/polyL\text{–}Mz+} > C_{C/polyL}$).

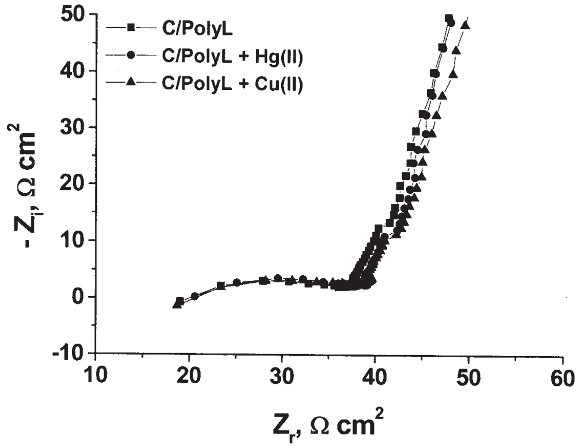

Fig. 4. Nyquist diagrams for poly**L** modified electrodes after complexation with Hg^{2+} (10^{-5} M) or Cu^{2+} (10^{-5} M)

In the case of metal ion reductions, the charge transfer resistance R_b remains higher than its initial value before metal ion insertion and the capacitance also is irreversibly decreased (table 3).

Conclusions

Electrochemical impedance data show that the interfaces that control the charge transfer are: the glassy carbon electrode | electrolyte interface, which determines the ohmic response of the system, the glassy carbon electrode | poly**L** interface that presents a space charge capacitance at very high frequencies and the poly**L** | electrolyte interface, determining the formation of double layer at high frequencies. These interfaces depends on the alterations of the film's morphological structure, namely on its thickness and porosity. The electrolytes characteristics may also contribute to the increase of the total impedance due to the presence of a rate determining diffusion process that controls the mass transfer of ions through the polymer matrix; the rate determining diffusion step is defined by the Warburg element, at lower frequencies, and the charge capacity at very low frequencies, characterized by the limiting film capacitances.

Electrochemical impedance spectroscopy analyses showed that the presence of complexing metallic ions during the accumulation step do not modify the shape of the Nyquist plots but affects directly the values of the electrochemical parameters characterizing the polymeric film, namely: the polarization resistance that presents a significant increase in case of mercury ions, and also the double layer capacitance which shows a pronounced decrease with mercury ions.

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