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ELECTROCHEMICAL BEHAVIOR OF TETRA(4-METHOXYPHENYL) PORPHYRIN THIN FILMS OBTAINED BY LASER DEPOSITION ON GRAPHITE ELECTRODE

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Thin films of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin (TMeOPP) were deposited by pulsed laser technique (PLD) on graphite electrodes (G) resulting in G_L/TMeOPP modified electrodes. Their electrochemical behavior was investigated by cyclic voltammetry, in various electrolyte solutions. Besides, for better understanding of the behavior of TMeOPP modified graphite electrodes, several electrodes obtained by drop-casting method (G_D/TMeOPP) were also comparatively studied. Potentiometric detection experiments were performed on the G_L/TMeOPP electrode in order to identify a potential application as sensor for metals detection. A linear dependence of the electrochemical potential versus Ag^+ concentration was obtained in the range of $1\times10^{-6} \div 1\times10^{-1}$ M, with a near-Nernstian slope of 55,16 mV/decade of activity.

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1. Introduction

One of the most prominent applications of porphyrin derivatives deposited as thin films is in the sensors field. Different types of sensors with signal transduction based on absorption [1], fluorescence [2] and electrical resistance and/or capacitance [3] have been reported.

The most common techniques used for deposition of such films are spin coating [4], Langmuir–Blodget [5], laser induced forward transfer (LIFT) [6], matrix assisted pulsed laser evaporation (MAPLE) [7, 8] and electropolymerization [9].

The electrochemical behavior and electrocatalytic activity of CoTMeOPP modified anisotropic pyrographite plates towards oxygen electroreduction in 0.5 M H_2SO_4 medium, was previously reported [10]. The electrodes were modified using the drop-casting method, by applying the porphyrin from a chloroform solution. The surface behavior of adsorbed CoTMeOPP on a graphite electrode and its catalytic activity for O_2 and H_2O_2 reduction [11] was studied by cyclic voltammetry using a rotating disk electrode. In this case, the electrode surface was modified by immersion into a mixture of deionized water and ethanol containing the porphyrin.

Tesakova [12] studied the kinetic parameters of the electroreduction of oxygen on a graphitized carbon electrode activated by tetrakis(4-methoxyphenyl)porphyrin and its cobalt

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complexes. The thin layer catalyst was obtained from a suspension of fluorocarbon polymer and the analyzed porphyrin.

Different glassy carbon electrodes modified with adsorbed cobalt porphyrins substituted with one, two, three or four bis(methoxyphenyl) groups were comparatively analyzed to establish the influence of the number of the methoxyphenyl donating groups on the electrocatalyst behavior for the reduction or oxidation of sulfite [13].

New selenite-selective electrodes using CoTMeOPP as electroactive materials, that are highly selective and sensitive to selenite, were reported [14]. Three types of electrodes were modified by incorporating the porphyrin in PVC matrix, in carbon paste and as active membrane deposited on coated wire (different electrodes were coated with active membranes by repeated dip-dry technique until a plastic film was formed). Using the same cobalt porphyrin as ionophore in a PVC matrix, Gupta et al. [15] developed a MoO_4^{2-} membrane based sensor.

Conventional techniques of immobilization (i.e. Langmuir–Blodgett, drop-casting) faced a weak interaction between the sensitive element and the support, significantly effecting the response and stability of the electrodes. PLD allows the obtaining of stable uniformly sized thin films with nanoparticles having diameters decreasing with increasing distance from the target LASER deposition [6]. In order to surpass contamination limits, matrix assisted pulsed laser evaporation (MAPLE) technique was implemented [8]. In 2010, Cristescu et al. [8] reported the deposition of functionalized and nanostructured Co(II)-5,10,15,20-tetrakis(4-methoxyphenyl)-porphyrin (CoTMeOPP) thin films by matrix assisted pulsed laser evaporation (MAPLE) at different laser fluencies values onto screen-printed carbon nanotube electrodes, which proved to be selective to dopamine.

In the present study we focused on the development and investigation of the electrochemical behavior of graphite electrodes (G) modified with thin films of TMeOPP obtained by laser ablation (G_L/TMeOPP) and drop-casting (G_D/TMeOPP). Both types of modified electrodes were comparatively characterized by cyclic voltammetry in various media, such as: 0.1M Na_2SO_4, 0.1M KOH, 0.5M H_2SO_4 and 0.1M tetrabutylammonium perchlorate in acetonitrile. Besides, an approach for evaluation of potentiometric response of the G_L/TMeOPP electrode in the presence of various metal ions for sensing applications has been done.

2. Experimental

5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin (TMeOPP) (Fig. 1) powder was synthesized by an improved variant based on Adler method [16], implying the reaction between *p*-methoxy-benzaldehyde and pyrrole in propionic acid medium, purified and characterized in accordance with previously published procedures [17-19].

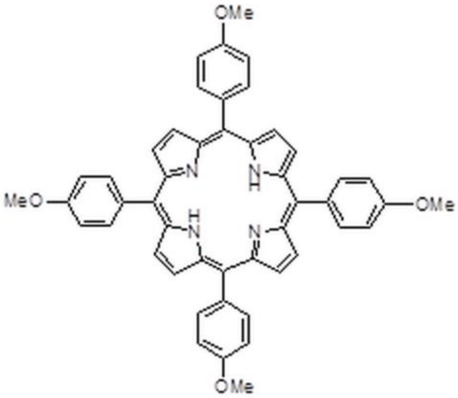

Fig. 1. Chemical structure of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyin (TMeOPP).

Acetonitrile (ACN) containing 0.1M tetrabutylammonium perchlorate (TBAP), purchased from Merck and Sigma-Aldrich respectively, were used in cyclic voltammetry experiments and tetrahydrofuran (THF) purchased from Fluka was used for the drop-casting procedure. The behavior of the G_L/TMeOPP electrodes was also investigated in aqueous solutions (0.1M Na_2SO_4, 0.1M KOH and 0.5M H_2SO_4). All used salts, acids and bases were of analytical reagent grade (Sigma-Aldrich).

The ion detection performance of the G_L/TMeOPP electrodes was investigated by measuring its potential in various solutions containing different metal cations in the concentration range 10^{-5}-10^{-1} M ($10^{-6} \div 10^{-1}$ M in case of Ag^+). Stock solutions (0.1 M) were prepared by dissolving metal nitrates (cations: Co^{2+}, Cu^{2+}, Al^{3+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Ag^+) in double distilled water. All working solutions were prepared by gradual dilution of the stock solutions. The pH was adjusted by adding NaOH or HNO_3 to the tested solutions.

Preparation of the thin film on graphite substrate: Graphite modified electrodes with TMeOPP obtained by laser ablation (G_L/TMeOPP), were manufactured using a PLD vacuum chamber in combination with an HL 124P LCU (Trumpf) – Nd:YAG with pulse shaping capabilities. The experimental parameters were: pulse energy (Ep) = 0.3J; N pulses from 12-20 x 15 to 25 series; chamber pressure: $1.6 – 1.2 \cdot 10^{-6}$ mbar. The thickness of the TMeOPP film is in the range 50-80 nm.

The graphite electrode was also modified by drop-casting method (G_D/TMeOPP) applying 5 μL from a 10^{-6} M porphyrin solution in THF.

Atomic force microscopy studies (AFM) were performed by using Nanosurf® EasyScan 2 Advanced Research AFM (Switzerland), equipped with a stiff (450μm × 50 μm × 2 μm) piezoelectric ceramic cantilever (spring constant of $0.2\ N\cdot m^{-1}$) with an integral tip oscillated near its resonance frequency of about 13 kHz. The surface imaging investigations were done in ambient conditions. AFM images were obtained in contact mode and are quantitative on all three dimensions.

Cyclic voltammetry tests were carried out with a PGZ 301 Dynamic-EIS Voltammetry potentiostat with VoltaMaster 4 software. An electrolysis water jacketed glass cell employing a three-electrode system was used. The working electrode was either G or the G_L/TMeOPP and G_D/TMeOPP modified electrodes (S = 0.06; 0.28 or 0.23 cm^2), a platinum wire was used as counter electrode (0.3 cm^2) and the Ag/AgCl/KCl sat. electrode was used as reference.

All experiments were carried out at ambient temperature. The potential scan rates are specified for each case throughout the study. All potentials are expressed with respect to the SHE.

The changes in the electrochemical behavior of G due to the porphyrin film were investigated by comparing the voltammetric responses of the bare G with those of the G_L/TMeOPP and G_D/TMeOPP electrodes.

Potentiometric measurements were carried out at room temperature using a Hanna Instruments HI2216 pH/mV-meter by setting up the following electrochemical cell:

$Ag|AgCl|KNO_3$ (1 M)|sample|TMeOPP|G_L|Cu.

3. Results and discussion

2D and 3D AFM images of surfaces (1 μm × 1 μm) for laser porphyrin deposited on graphite (Fig. 2) and (1 μm x 1 μm) for bare graphite (Fig. 3), measured in contact mode, combined with particle analysis, demonstrated unequivocally that the surface topography was significantly changed. Analyzing Fig. 2, we presume that H type aggregation based on π–π interaction between hydrophobic porphyrin groups occurred with priority and produces conk architectures of similar packing, with dimensions varying from 89 to 147 nm in diameter. Hydrogen bonding can be responsible for oriented organization of head to tail arrangements blocks, due to the fact that both hydrogen bond acceptor and donor functionalities are present [20].

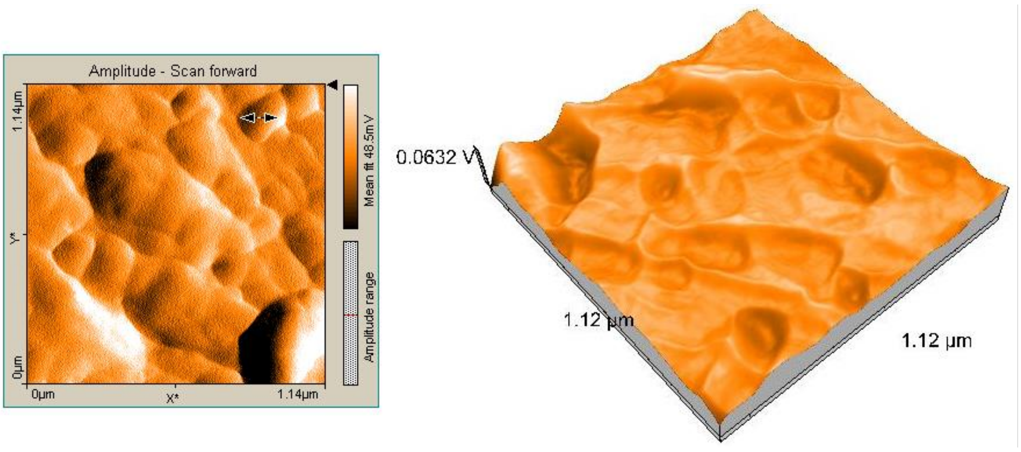

Fig. 2. 2D and 3D AFM images for the G_I/TMeOPP electrode.

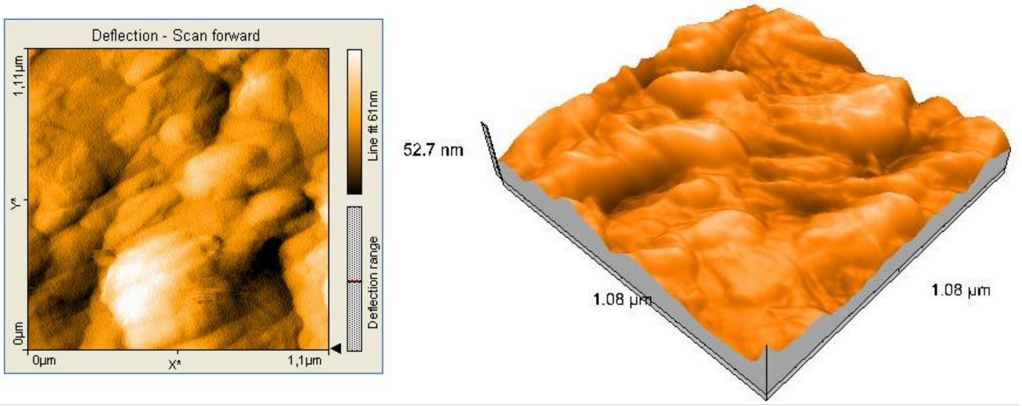

Fig. 3. 2D and 3D AFM images for the bare graphite electrode.

AFM measurements of the laser deposited porphyrin on graphite (Fig. 2), comparatively with the bare graphite (Fig. 3), reveal that the rugosity is diminished by porphyrin deposition. The surface roughness (Sa) is smaller (19 nm) for laser porphyrin deposited on graphite in comparison with the bare graphite (24 nm).

All the other parameters in connection with rugosity, the valley depth (Sv) and the peak height (Sp) are varying in the same way as Sa proving the formation of a smooth and more uniform surface by laser deposition. For example the valley depth (Sv) is decreasing from -62 nm measured for bare graphite to -54 nm in case of deposited porphyrin surface.

Cyclic voltammetry studies were performed in order to put into evidence and to determine the electrochemical parameters of the porphyrin thin films in various media. The results are presented in Fig. 4, 5, and 6 for aqueous solutions of KOH 0.1M, H_2SO_4 0.5M and Na_2SO_4 0.1M, respectively and scan rate: 0.1 V/s.

The potentials and currents corresponding to the anodic (a) and cathodic (c) peaks are given in Table 1 for all the tested electrodes.

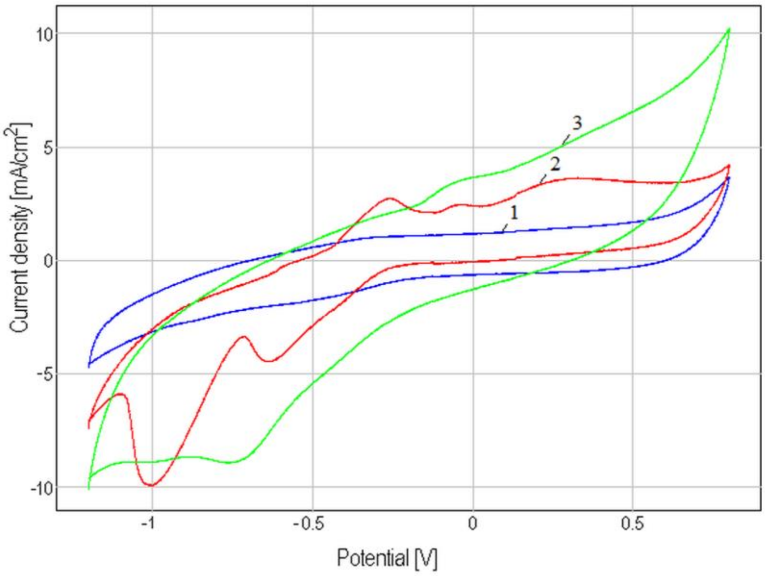

Fig. 4. Cyclic voltammograms in 0.1M KOH for bare graphite (1), G_L/TMeOPP (2) and G_D/TMeOPP (3) electrodes.

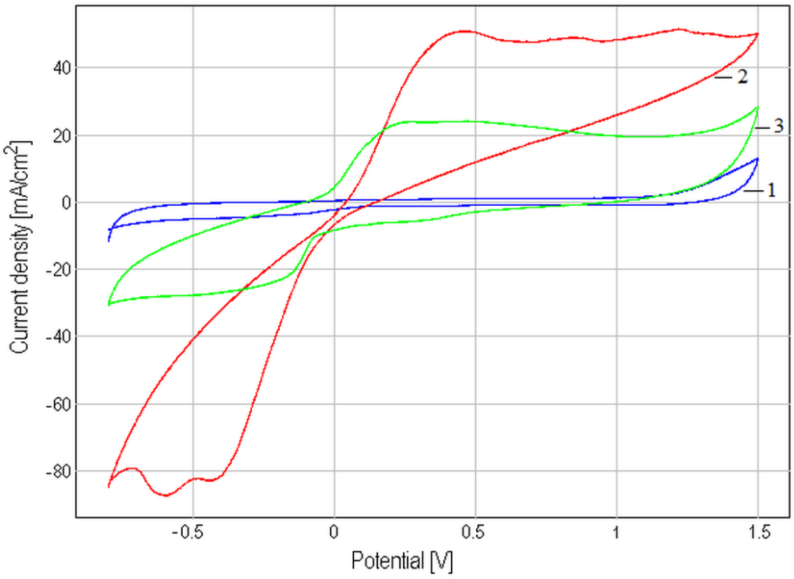

Fig. 5. Cyclic voltammograms in 0.5M H_2SO_4 for bare graphite (1), G_L/TMeOPP (2) and G_D/TMeOPP (3) electrodes.

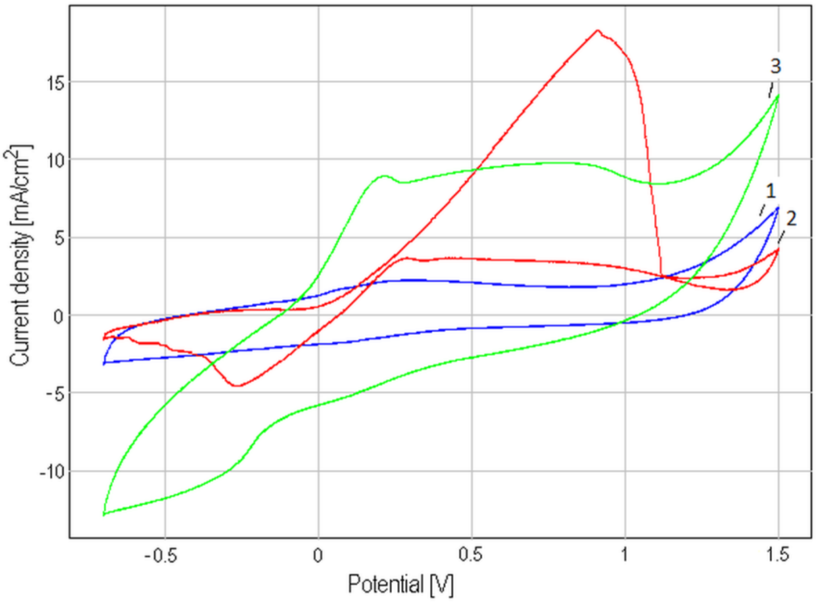

Fig. 6. Cyclic voltammograms obtained in 0.1M Na_2SO_4 for bare graphite (1), G_L/TMeOPP (2) and G_D/TMeOPP (3) electrodes.

Table 1. The electrochemical parameters E (mV) and i (mA/cm^2) corresponding to the maximum peak value of the investigated electrodes.

Electrode	**a 1**		**a 2**		**a 3**		**c 1**		**c 2**	
	E	i	E	i	E	i	E	i	E	i
0.1M KOH										
G	-300	1.04					-420	-1.56		
G$_L$/TMeOPP	-258	2.74	-42	2.46	324	3.63	-637	-4.46	-1000	-9.9
G$_D$/TMeOPP	-295	1.95	-52	3.47	330	5.44	-760	-8.91	-1000	-8.86
0.5M H_2SO_4										
G	102	0.78	520	1.25			-331	-4.61	-350	-1.2
G$_L$/TMeOPP	461	50.9	850	48.9	1220	51.51	-440	-82.76	-597	-87.23
G$_D$/TMeOPP	261	23.88	456	24.06			-180	-22.20	270	-5.76
0.1M Na_2SO_4										
G	280	2.3					130	-1.63		
G$_L$/TMeOPP	910	18.34	950	17.85			-250	-4.55	-500	-1.8
G$_D$/TMeOPP	220	8.95	400	9	800	9.78	-300	-10		

In KOH 0.1 M (Fig.4), the absence of the porphyrin layer causes the typical behavior of the graphite electrode, involving surface oxidations and the corresponding reductions of the former generated oxygenated groups (curve 1). Oxygen evolution starts at about 0.7 V. The voltammogram recorded with the G_L/TMeOPP electrode (curve 2) put into evidence the presence of reversible oxidation and reduction processes. The peaks are associated to the generation of a cation-radical (324 mV), an anion-radical (-637 mV), and a dianion (-1000 mV) [12]. The peak from -42 mV is associated to the reactions involving the generation of oxygenated functional groups on the graphite surface. The G_D/TMeOPP electrode has a similar behavior (Fig. 4, curve 3); the maxima being not so well separated as in case of the G_L/TMeOPP electrode because of the different association of the porphyrin molecules onto the electrode surface.

In H_2SO_4 0.5M (Fig. 5), the peaks obtained for the modified electrodes are significantly higher than in alkaline medium, the protonation of the porphyrin having an activation effect on the deposited layer. The voltammogram obtained on the G_L/TMeOPP electrode has three anodic and two cathodic peaks. Those from 461 mV and -440 mV are associated to a reversible process, the other to irreversible processes involving the porphyrin. The curve obtained on the G_D/TMeOPP electrode has a similar allure, but the peaks are not so clearly separated, only two anodic and two cathodic peaks can be observed. Oxygen evolution starts at about 1.4 V in all cases.

In Na_2SO_4 0.1M (Fig. 6) the reaction peaks are not so well defined as in alkaline and acid solutions. On curve 2 (G_L/TMeOPP electrode), there is an intense oxidation wave in the potential range 910-950 mV, that seems to be composed of two very close anodic peaks, and a well-defined cathodic peak (at -250 mV). Oxidations are related to the reaction of porphyrin with formation of the radical-cation and further oxidation to the corresponding dication (anodic shoulder joined to the high peak). The cathodic reactions generate the corresponding anionic derivatives of porphyrin. Two anodic peaks of medium intensity can be observed on curve 3 (G_D/TMeOPP electrode) at 220 mV (well defined - probably related to the formation of oxidized groups on the surface of graphite) and 400-800 mV (very large, possibly consisting of several overlapping peaks – related to the porphyrin oxidation). The anodic limit, given by oxygen evolution is at about 1.5V.

The influence of the scan rate on G_L/TMeOPP electrode was investigated in the basic, acid and neutral solutions, the results obtained for 0.1M Na_2SO_4 being presented in Fig. 7. In all cases an increase in the scanning rate increases the anodic and cathodic peaks and yields a shift of the cathodic maxima towards more negative potentials, while the anodic maxima are shifted towards more positive potentials. The linear relationships between the scan rate and the peak current could be a feature of a reversible redox surface process corresponding to an adsorbed compound [11].

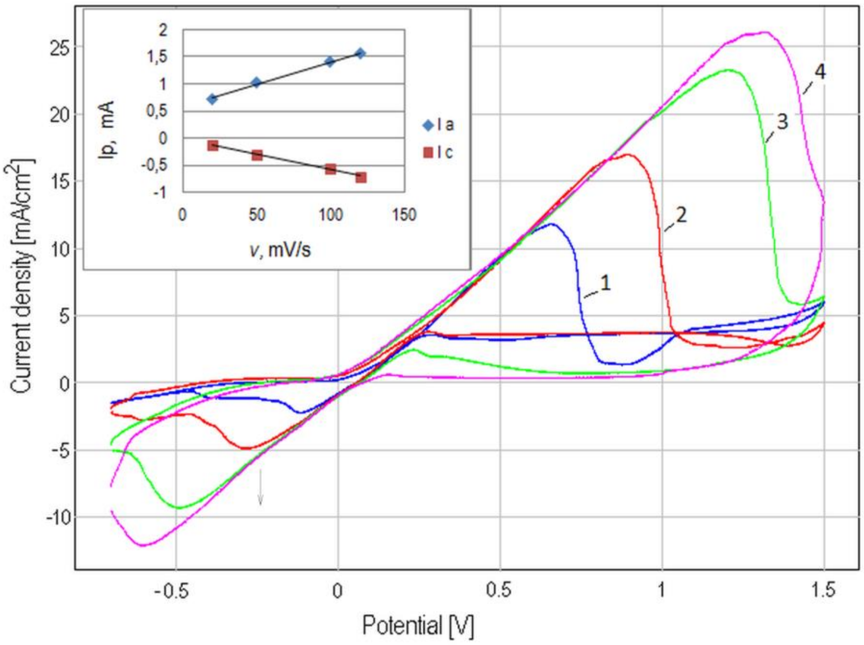

Fig. 7. Cyclic voltammetry in 0.1M Na_2SO_4 for the G_L /TMeOPP electrode at different scan rates (mV/s): 20 (1), 50 (2), 100 (3) and 120 (4); inset: anodic and cathodic peak current (Ip) vs. potential sweep rate.

Voltammetric studies were also carried out in an aprotic medium. The results obtained for the TBAP/ACN system are presented in Fig. 8 for the G_L/TMeOPP electrode and for the graphite electrode in the presence of dissolved TMeOPP. The curves are very much alike; differences being generated by the different forms of the organic substrate presence (fixed on the electrode or dissolved in solution).

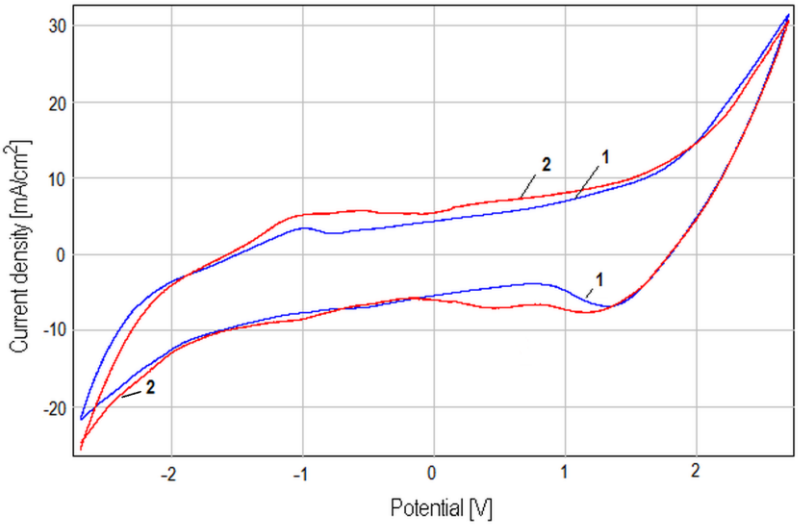

Fig. 8. Cyclic voltammograms in 0.1M TBAP/ACN: (1) G_L/TMeOPP electrode, (2) bare graphite electrode and TMeOPP 0.23mM. Scan rate: 0.1 V/s.

After performing the voltammetry studies on G_L/TMeOPP in ACN, the solutions became coloured suggesting the dissolution of the deposited porphyrin. The final solutions were analyzed by UV-Vis spectroscopy (data not shown). The solubilised laser deposited porphyrin suffered structural changes indicating the presence of a deprotonated form of porphyrin.

The voltammetric studies proved the presence of TMeOPP on the graphite for both tested electrodes: G_L/TMeOPP and G_D/TMeOPP. The laser deposited layer is stable and can be used in aqueous solutions. In organic solutions (ACN) the electrode is not stable because of the dissolution of the deposited porphyrin.

Potentiometric studies

Evaluation of potentiometric response of the G_L/TMeOPP electrode in the presence of various metal ions was made in the concentration range $10^{-1} \div 10^{-5}$ M. Prior to EMF (electromotive force) measurements the sensors were stabilized by immersion in 10^{-5} M cation solutions for 30 minutes. The results are presented in Fig.9.

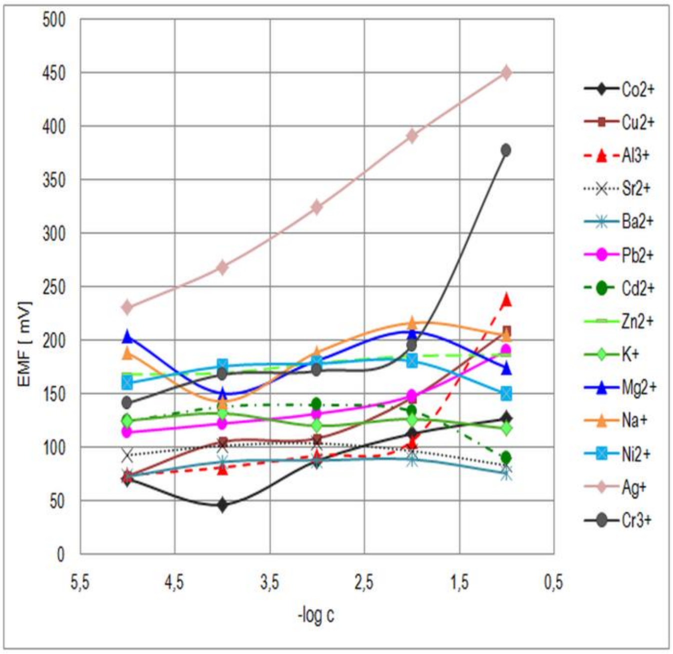

Fig. 9. Potentiometric responses of the G_L/TMeOPP electrode in various separate aqueous test solutions in the $10^{-1} \div 10^{-5}$ M concentration range.

The G_L/TMeOPP electrode was tested in silver solutions in a concentration range, 10^{-6} – 10^{-1} M and the obtained results are presented in Fig. 10.

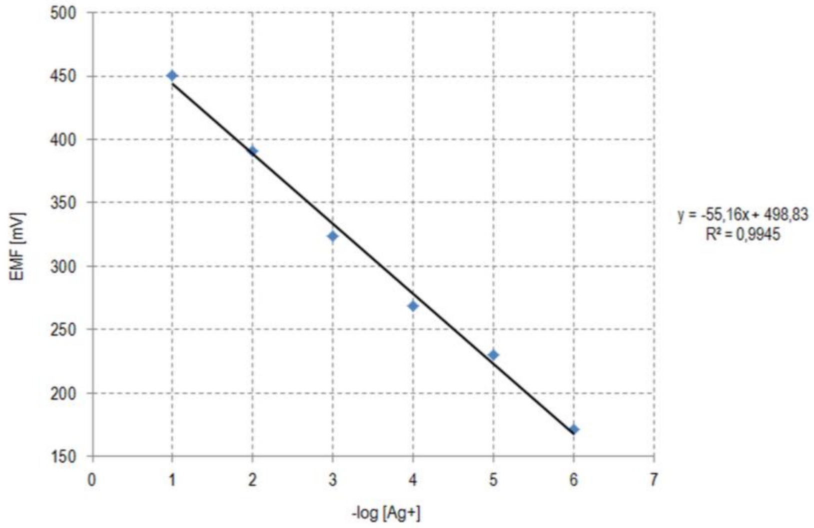

Fig. 10. Potentiometric responses of the G_L/TMeOPP electrode.

The G_L/TMeOPP electrode has a working concentration range from 1×10^{-6} to 1×10^{-1} M with a near-Nernstian slope of 55.16 mV/decade of activity ($y = -55.16x + 498.83$, $R^2 = 0.9945$).

The *potentiometric selectivity coefficients* (log $K^{pot}_{Ag,Y}$) were calculated according to the separate solution method [21] for primary and interfering cations concentration of 1×10^{-2} M and are presented in Table 2.

Table 2. Selectivity coefficients of the G_L/TMeOPP electrode.

Cation	K^+	Na^+	Co^{2+}	Cu^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}
log$K^{pot}_{Ag,Y}$	-4,46	-2,94	-5,69	-5,13	-5,96	-6,09	-4,08
Cation	Pb^{2+}	Cd^{2+}	Zn^{2+}	Ni^{2+}	Al^{3+}	Cr^{3+}	
log$K^{pot}_{Ag,Y}$	-5,09	-5,33	-4,47	-4,55	-6,14	-4,63	

As it could be seen from Table 2, the sensor has very good values of the selectivity coefficients.

The practical *response time* of the sensor represents the time between when the ion-selective electrode assembly is brought into contact with a new solution and when the measured EMF is within 1 mV to the final steady-state value [22].

The obtained response time was about 25s as the concentration of silver(I) varies from 10^{-4} to 10^{-3} M.

The influence of the pH of the test solutions on the potential response of the electrodes was studied by using the 10^{-3} M and 10^{-2} M silver (I) solutions adjusted with HNO_3 and NaOH and the results are given in Fig. 11.

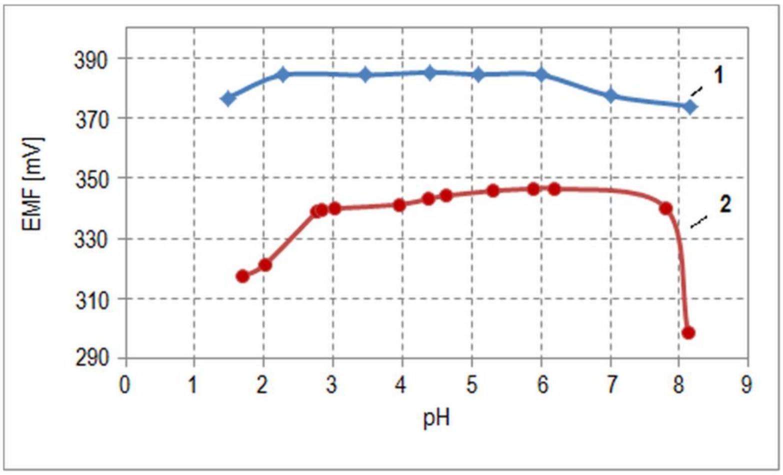

Fig. 11. Effect of the pH on the potential response of the G_L/TMeOPP electrode in 10^{-2}M (1) and 10^{-3}M (2) silver(I) solutions.

As it can be seen, the sensor may be used in a pH range from 2.5 to 6 for 10^{-2} M solution and 2.8 to 7.8 for 10^{-3} M solution. Above these pH values the precipitation of silver(I) hydroxide occurs.

4. Conclusions

Two types of thin films having the thicknesses in the range 50-80 nm, based on 5,10,15,20 tetrakis(4-methoxyphenyl)porphyrin (TMeOPP) were obtained on graphite by PLD and drop casting, and their electrochemical behavior was comparatively studied by cyclic voltammetry using different electrolyte solutions: KOH 0.1M, H_2SO_4 0.5M, Na_2SO_4 0.1M and 0.1M TBAP/ACN.

The electrochemical studies proved the presence of TMeOPP on the graphite for both tested electrodes: G_L/TMeOPP and G_D/TMeOPP. The laser deposited layer is stable and can be used in aqueous solutions. In organic solutions the electrode is not stable because of the dissolution of the deposited porphyrin.

The preliminary studies showed that G_L/TMeOPP electrode performed well in aqueous test solutions as a potentiometric sensor for silver ions in the concentration range $1\times10^{-6} \div 1\times10^{-1}$ M.

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