Electrochemical Synthesis and Characterization of Ti Modified Electrodes with Polypyrrole – Polyethylene Glycol Hybrid Coating

SIMONA POPESCU, CRISTIAN PIRVU*, MIHAELA MINDROIU, CLAUDIU MANOLE, IOANA DEMETRESCU
University Politehnica Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061,
Bucharest, Romania

The preparations and characterization of polypyrrole – polyethylene glycol (PPy-PEG) films are reported in this paper. The composite films were synthesized by electrochemical method in 0.2 mol·L^{-1} Py and 5% PEG in 0.2 mol·L^{-1} oxalic acid. The electrochemical behaviour of PPy and PPy-PEG coatings has been investigated in phosphate buffer solution (PBS) by cyclic voltammetry, Tafel plots and electrochemical impedance spectroscopy. The surface topography and the roughness were checked by atomic force microscopy.

Keywords: titanium, polypyrrole, polyethylene glycol, electropolymerization

Due to their multiple applications in the field of biomedical engineering [1,2], solar cells [3] electronic and optical devices [4,5], as well as in anticorrosion protection [6,7] the conducting polymers based on heterocyclic compounds are very often used. One of the most studied polymer among these is polypyrrole (PPy) that is easily electrosynthesized on gold or platinum [8,9] but is more difficult to generate PPy films with good adherence on other metals like Al or Ti and its alloys, that form a highly stable protective oxide layer [10,11] that blocks electron transfer [12,13]. In order to change the structure, electrochemical conductivity or chemical permeability of deposited films, a polypyrrole / polyethylene glycol (PEG) composite coatings were proposed [14-16].

In the present paper, we report the electrochemical preparation and characterization in buffer solution of both PPy films and PPy composite films with PEG added as insulating polymer. Several techniques, such as cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM) have been used to study the behaviour of the composite films deposited on Ti. The attention has been focused on the role played by the PEG presence in the film on the adherence and electrochemical stability of polymeric films.

Experimental part

Materials

The metallic substrates were represented by commercially pure Ti discs of 1 mm thickness and 10 mm diameter (99.6% purity, Goodfellow Cambridge Ltd., UK). The deposition surfaces of test specimens were polished with SiC paper to grade 4000. Before deposition, the discs were cleaned in acetone and rinsed well with distilled water.

The electrochemical deposition of PPy was performed in aqueous solution of 0.2 mol·L^{-1} Py and 0.2 mol·L^{-1} oxalic acid. For composite PPy-PEG films electropolymerization of pyrrole was performed in the presence of 5% PEG (400 molecular weight) in the same aqueous solution.

Pyrrole monomer was purchased from Aldrich, and stored in the dark at 4°C before use. All solutions were prepared using ultra pure deionised Milli-Q water. The composition of buffer solution used for characterization was: NaCl 8.74 g/L; $NaHCO_3$ 0.35 g/L; $Na_2HPO_4 \cdot 12H_2O$ 0.06 g/L; NaH_2PO_4 0.06 g/L;

Methods

The electrochemical data were recorded at room temperature using a conventional cell with three electrodes: a Ti working electrode, a platinum counter-electrode and an Ag/AgCl, KCl reference electrode, all connected to Autolab PGSTAT 302 N potentiostat with general-purpose electrochemical system software GPES 4.9. Potentiodynamic polymerisation was used for the synthesis of the polypyrrolle film on the electrode surface. Cyclic voltammetry, electrochemical impedance spectroscopy were used as electrochemical characterisation techniques. The electrochemical impedance spectroscopy data were obtained with the Autolab frequency response analyzer FRA 4.9 and fitted with NOVA 1.4 software. The surface topography of polypyrrole films was studied with Atomic Force Microscopy (AFM) in non contact mode, at room temperature with a scan rate of 7 μm/s.

Results and discussion

Electrochemical deposition of polypyrrole - polyethylene glycol coatings on Ti electrode

Figure 1a presents the electrochemical behaviour of titanium electrode in oxalic acid aqueous solution. The first cyclic voltammogram is characterised by a first large anodic plateau starting from 0.2 V which is followed by a passivation of the surface in the following cycles.

PPy and PPy-PEG films were deposited electrochemically by potentiodynamic polymerization in 0.2 M oxalic acid aqueous solution in the presence of 0.2 M pyrrole (fig. 1b) and by adding 5% PEG (fig.1,c). If the pyrrole monomer is added to the electrolyte, the behaviour of the Ti electrode changes totally; a rapid increase of current is observed starting with potentials of 0.6V, corresponding to Py oxidation and formation of visible black film of polypyrrole on Ti electrode surface. In the presence of polyethylene glycol, (fig. 1.c), the current corresponding to electro-oxidation of pyrrole has a three times decrease comparing to electro-oxidation in the absence of PEG.

From the figures 1.b,c an increase of the current density with cycles number can be observed corresponding to polymeric film growth on the electrode surface.

Electrochemical characterization

Cyclic voltammetry

In order to evaluate the stability of the electrodeposited polymeric films the repeated ten cyclic voltmmograms

---

email: c_pirvu@chim.upb.ro

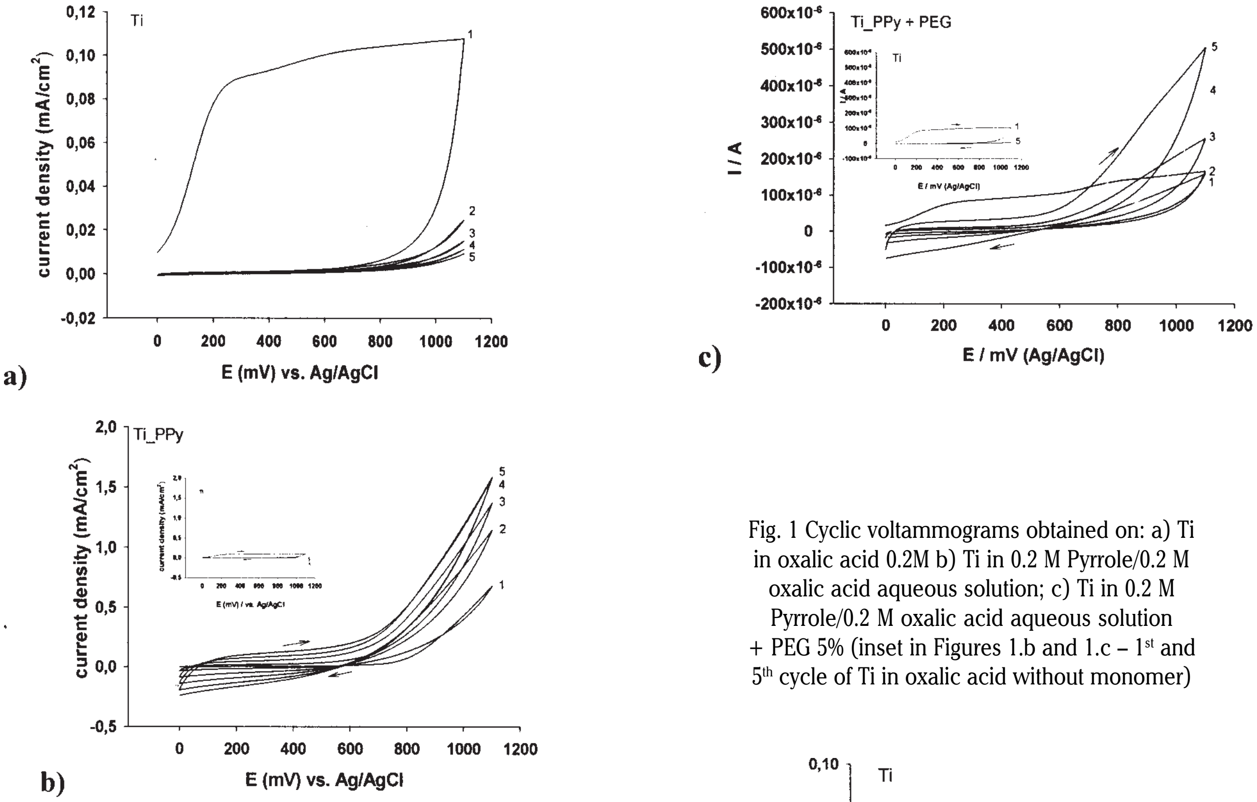


Fig. 1 Cyclic voltammograms obtained on: a) Ti in oxalic acid 0.2M b) Ti in 0.2 M Pyrrole/0.2 M oxalic acid aqueous solution; c) Ti in 0.2 M Pyrrole/0.2 M oxalic acid aqueous solution + PEG 5% (inset in Figures 1.b and 1.c – 1st and 5th cycle of Ti in oxalic acid without monomer)

were performed using either uncoated Ti or coated Ti. From the figure 2.a it was observed that uncoated Ti is rapidly passivated by the formation in the aqueous solution of TiO_2 passive film, beginning with 0.3 V (more positive than that observed in oxalic acid), that increases the stability of the Ti substrate.

The PPy and PPy/PEG films present a good electrochemical stable behaviour on -0.5 – 0.5 V potential domain, the films remaining stable during the 10 CV scans, as figures 2.b and 2.c show. The PPy films present also a better capacitive character comparing with PPy/PEG composite films. The potentiodynamic measurements were performed with a scan rate of 2 mV/s.

In order to evaluate if the modifications of titanium electrode does changed corrosion stability, Tafel plots were recorded in buffer solution both for uncoated and coated titanium electrodes, as shown in figure 3.

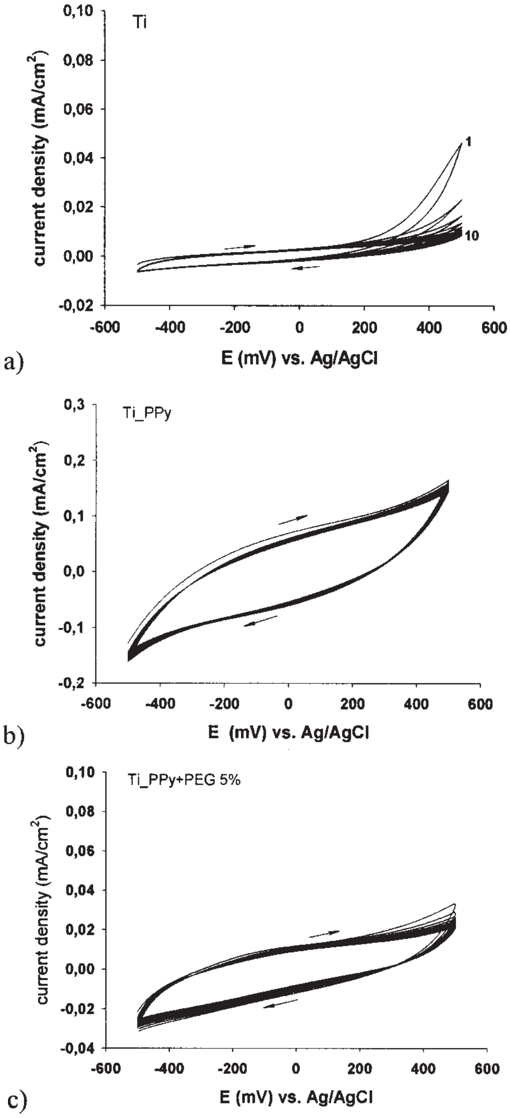
The influence of PEG presence in the polymeric solution on electrochemical parameters calculated from Tafel plots is illustrated in table 1. An increase of the corrosion potential and polarization resistance for Ppy/PEG film were observed. Also, the corrosion current density drastically decreases from 3.35 μA/cm^2 to 0.41 μA/cm^2.

Electrochemical impedance spectroscopy

Nyquist spectra for uncoated titanium electrodes and those electrochemicallly modified by PPy and PPy-PEG films are presented in figure 4.

The proposed circuit comprises the solution resistance (R1), polarization circuit that encloses the constant phase element (Q1) and resistance (R2) and a final constant phase element (Q2) of the deposited film. The N1 and N2 are parts of the constant phase elements Q1 and respectively Q2.

Comparing with the uncoated Ti plot that present only a semicircle in the higher frequency region, the other two samples present also a straight line to lower frequency value. The R2 polarization resistance has values from 2.01 kΩ for PPy coating to 4.67 kW for PPy/PEG films underlining



a)

b)

c)

Fig. 2. Cyclic voltammetric curves on Ti (a), Ti /Ppy (b) and Ti/Ppy-PEG (c) electrode in buffer solution, pH 6.5, after 10 scans. Potential scan rate: 0.05Vs^{-1}

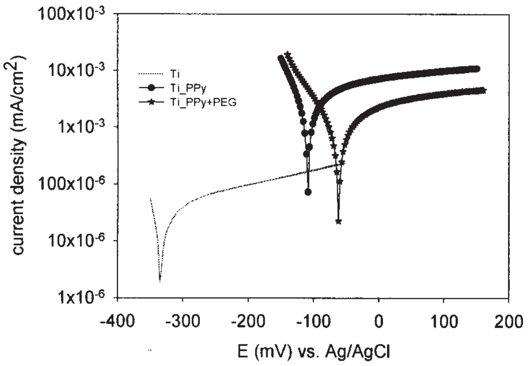


Fig. 3 Tafel plots for uncoated titanium, Ti covered with PPy film and PPy+PEG film

Table 1
ELECTROCHEMICAL PARAMETERS FOR THE COMPOSITE FILMS FROM TAFEL PLOTS

	Ti/PPy	Ti/PPy+PEG
E_{cor}, V	-0.114	-0.072
i_{cor}, μA/cm^2	3.35	0.41
R_p, Ω	$8.84 \cdot 10^3$	$8.32 \cdot 10^4$
V_{cor}, mm/year	$9.38 \cdot 10^{-2}$	$1.15 \cdot 10^{-2}$

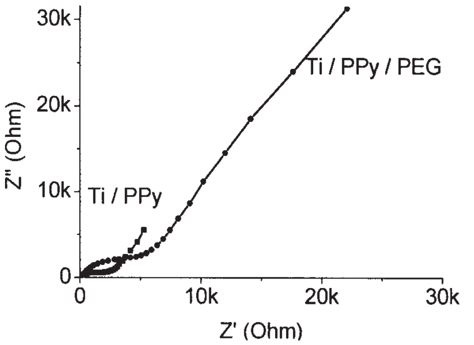


Fig. 4 Nyquist spectra for Ti, Ti/PPy and Ti/PPy-PEG electrodes in buffer solution at open-circuit potential

Table 2
THE PROPOSED EQUIVALENT CIRCUIT FOR BEST FITTING OF EXPERIMENTAL RESULTS

	Ti	Ti/PPy	Ti/PPy-PEG
Equivalent circuit	R1(Q1R2)	[R1(Q1R2)Q2]	[R1(Q1R2)Q2]
R1 (Ω)	150,4	112.7	131.6
Q1		$0.3089 \cdot 10^{-4}$	$0.1826 \cdot 10^{-4}$
N1		0.6651	0.7718
R2 (kΩ)	119.8	2.016	4.67
Q2		$0.9969 \cdot 10^{-3}$	$0.176 \cdot 10^{-3}$
N2		0.6272	0.7167

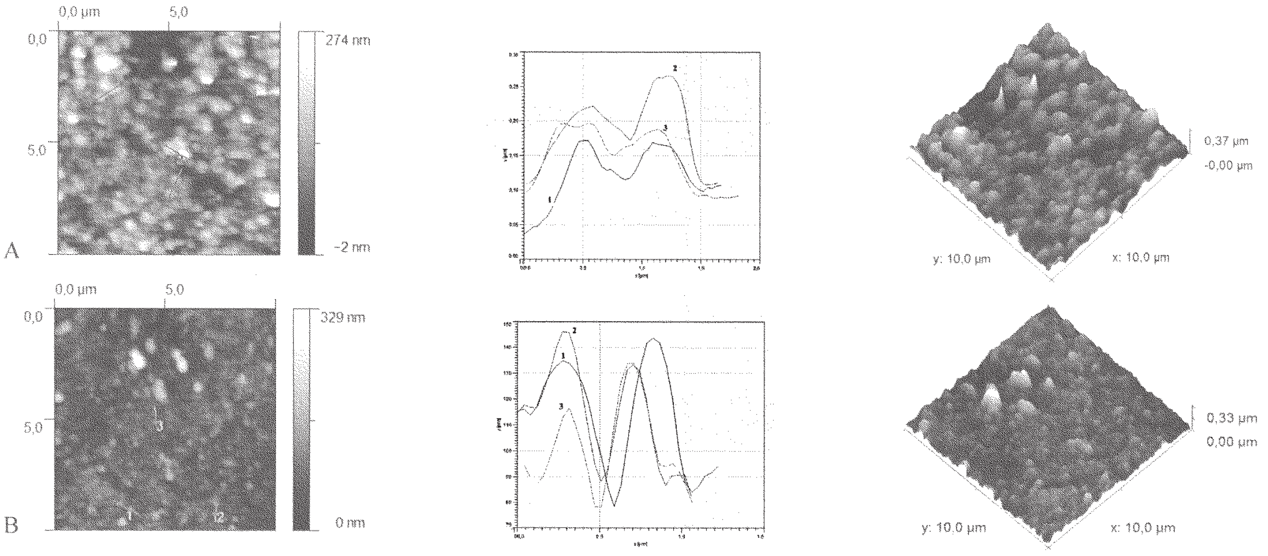


Fig. 5 Two – and three-dimensional images as well as the line profile of 10x10 μm scans for potentiodinamically deposited polypyrrole (A) and polypyrrole – PEG (B) on titanium surface at room temperature with a scan rate of 7 μm/s

the better corrosion protection properties of composite polymer (table 2).

Surface analysis - Atomic force microscopy

In order to investigate the surface topography of polypyrrole and modified surfaces the contact mode AFM microscopy data were obtained. Figure 5 shows two – and three-dimensional images and the line profile of 10 μm scans for 5 cycles potentiodynamically deposited polypyrrole and polypyrrole/polyethylene glycol composite on titanium surface.

The surface of potentiodynamically deposited polypyrrole on Ti surface is characterised by formation of small grains of about 0.75 μm dimensions for polypyrrole coating and 0.5 μm for polypyrrole/polyethylene glycol which increase on a regulated polypyrrole surface. The presence of polyethylene glycol coating in the polymerization solution acts both in reduction of dimensions of polypyrrole like-cauliflower grains and of roughness (Ra), with values of Ra – 31.1 nm for polypyrrole coating and Ra – 20.1 nm for polypyrrole/polyethylene glycol coating. Ra is an expression of the arithmetic average of the surface texture. This is an indication of higher surface irregularities for the polypyrrole coating than the one for the polypyrrole/polyethylene glycol.

Conclusions

The presence of polyethylene glycol in the polymerization solution improves the corrosion parameters of the coating. From EIS analyse, an increasing in polarization resistance was observed. PEG acts both in reduction of polypyrrole like-cauliflower grains dimensions and of roughness of the surface.

Acknowledgements. The authors gratefully acknowledge the financial support of the Romanian National CNCSIS Grant IDEI No. 624/2009.

References

1. GUIMARD, N.K., GOMEZ, N., SCHMIDT, C.E., Prog. Polym. Sci. **32**, 2007, p. 876
2. GREEN, R.A., LOVELL, N.H., WALLACE, G.G., POOLE-WARREN, L.A., Biomaterials **29**, 2008, p. 3393
3. CARAMORI, S., CAZZANTI, S., MARCHINI, L., ARGAZZI, R., BIGNOZZI, C.A., MARTINEAU, D., GROS, P.C., BELEY M., Inorganica Chimica Acta **361**, 2008, p. 627
4. SONMEZ, G., SCHOTTLAND, P., ZONG, K., REYNOLDS, J.R., J. Mater. Chem., **11**, 2001, p. 289
5. KRAFT, A., ROTTMANN, M., GILSING, H.D., FALTZ, H., Electrochimica Acta **52**, 2007 p. 5856
6. KUNG, E., MERCER, C., ALLAMEH, S. , SOBOYEJO, W.O. , POPOOLA, O., Key Engineering Materials, **197**, 2001, p. 87
7. PIRVU, C., STANCU, R., SOVAR, M., Rev. Chim.(Bucuresti), **58**, no. 9, 2007, p. 861
8. BOHN, C., SADKI, S., BRENNAN, A.B., REYNOLDS, J.R., J. of The Electrochemical Society, **149**, 2002, p. 281
9. PIGANI, L., MUSIANI, M., PIRVU, C., TERZI, F., C. ZANARDI, R. SEEBER, Electrochim. Acta, **52**, 2007, p. 1910
10. MAN, I., PIRVU, C., DEMETRESCU, I., Rev. Chim.(Bucuresti), **59**, no. 6 , 2008, p. 615
11. POPESCU, S., DEMETRESCU, I., GLEIZES, A. N., Rev. Chim.(Bucuresti), **58**, no. 9, 2007, p. 880
12. SHAH, K., IROH, J., Synth Met. **132**, 2002, p.35
13. DE GIGLIO, E., GUASCITO, M.R., SABBATINI, L., ZAMBONIN, P., Biomaterials **22**, 2001, p.2609
14. KASSIM, A., MAHMUD, H.N.M.E., YEE, L.M., HANIPAH, N., The Pacific Journal of Science and Technology, **7**, 2006, p. 103
15. YEE, L.M., KASSIM, A., MAHMUD, H.N.M.E., SHARIF, A.M., HARON, M.J., The Malaysian Journal of Analytical Sciences, **11**, 2007, p. 133
16. YEE, L.M., MAHMUD, H.N.M.E., KASSIM, A., YUNUS, W.M. M., Synthetic Metals, **157**, 2007, p. 386

Manuscript received: 29.05.2009