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Electrochemical Oxidation of Catechol at Poly(indole-5-carboxylic Acid) Electrode^{1, 2}

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Abstract—In this work we examined the electrochemical properties of poly(indole-5-carboxylic acid), PIn_5COOH . The polymer was produced by electrochemical polymerisation using cyclic voltammetry (CV). It was shown that PIn_5COOH is electroactive in aqueous solutions showing two redox processes in acidic solution and one redox process in solutions with $\text{pH} > 4$. The oxidation of catechol (CT) on Pt/ In_5COOH modified electrodes was investigated by cyclic voltammetry (CV) and rotating disc electrode (RDE) voltammetry. It was established that CT was oxidised only after the oxidation of polymer film was initiated and that polymer significantly enhanced the oxidation and reduction peak currents in comparison with bare Pt electrode. The variation of peak currents (i_{pa} , i_{pc}) as a function of CT concentration was found to be linear up to 6 mM. Experiments with a rotating disk electrode show that the oxidation reaction of catechol occurs not only at the polymer/electrolyte interface but also in the polymer film.

Keywords: poly(indole-5-carboxylic acid), catechol, electrooxidation

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1. INTRODUCTION

In the last years, the investigations of phenols, diphenols and their derivatives received considerable attention. Phenolic compounds are known as important contaminants of food, medical and environmental, so their quantification in such media is of great interest. As many of phenolic compounds like phenol, catechol, aminophenols, chlorophenols and so on, are easily oxidized the substantial effort has been made to develop simple amperometric or voltammetric methods for their detection. Unfortunately, the direct redox reactions of these species on unmodified electrodes are quasi-reversible or irreversible [1–5]. Moreover, the electrochemical oxidation of phenolic compounds often causes electrode inactivation because of polymer film formation [6–8]. Additionally, the oxidation products are very susceptible to the nucleophilic attack which results in the changes of electrode response [9, 10].

The most promising approach to overcome experimental difficulties in phenolic compound detection is to use chemically modified electrodes [11–15] or chemically modified electrodes with adequate bonded enzymes [16–20]. It is well known that conducting

polymers deposited on electrode surface can significantly improve the reversibility of redox reaction and enhanced their efficiency, as can work as mediator and demonstrate catalytic properties [19]. Also they can act as excellent template for enzyme immobilization as their molecular structure can be easily tailored by the proper choice of monomers containing functional groups which facilitate covalent coupling of the enzymes [21].

In the previous report [22] we described the application of modified electrode Pt/ PIn_5COOH /PPO (PPO—polyphenol oxidase, tyrosinase) for determination of catechol (CT) concentration. It was shown that reduction current of *o*-quinones produced in enzymatic reaction depends linearly on CT concentration up to 15 M. The aim of this investigations was to study the oxidation of catechol on Pt/ PIn_5COOH bare electrode by means of electrochemical methods and to find the relation between CT concentration in higher concentration range.

In_5COOH was for the first time electropolymerized by Waltman et al. [23]. Subsequently, Bartlett et al. [24] investigated the influence of pH and the mechanism of electron transfer between the PIn_5COOH and redox couples like ferro/ferricyanide and $[\text{Fe}(\text{bipy})_2]^{2+/3+}$. The molecular structure of PIn_5COOH in acetonitrile and acidic aqueous solution was determined by Talbi et al. [25, 26].

¹ The article is published in the original.

² The paper was prepared for a special issue dedicated to the birth centenary of Ya.M. Kolotykin.

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2. EXPERIMENTAL

2.1. Poly(indole-5-carboxylic acid) Deposition

Poly(indole-5-carboxylic acid) (PI₅COOH) was deposited from acetonitrile solution containing 10⁻² M of monomer and 0.1 M LiClO₄, according to the procedure previously described [22, 25]. For polymer film formation cyclic voltammetry (CV) was used with the potential scanned from -0.2 to 1.1 V and back to -0.2 V at 10 mV/s. After polymerisation the electrode was repeatedly washed with a mixture of acetonitrile and water and finally rinsed with pure water. Then, the polymer was examined in monomer free solution (0.1 M LiClO₄ + CH₃CN) and in aqueous acid solution (2.5 M HClO₄) by cyclic voltammetry. The results were in good agreement with those published by Talbi et al. [25, 26]. However, our experiments showed that the thickness of polymeric film was crucial for PI₅COOH application in aqueous solutions. If the film was too thick the polymer layer stripped off Pt electrode surface. Consequently, in our experiments we typically used the films formed during four deposition cycles. To control polymer's thickness we monitored the charge passed during polymerization reaction. The charge consumed by film doping was subtracted from the polymerization charge value. For that purpose after each polymerization cycle a CV curve was recorded in a monomer free acetonitrile solution. The average charge passed during four electropolymerization cycles was found to be 0.56 C/cm². In some experiments we used the films obtained in two or in six polymerization cycles. The average charge passed in those cases was 0.22 and 1.15 C/cm² respectively. Based on the data (density, number of electron) for polypyrrole [27] the roughly estimated thickness values were in the range from 1.2 to 6.5 μm. The polymer films of different thickness were applied in RDE experiments.

2.2. Electrode, Apparatus, Chemicals

Electropolymerization of indole-5-carboxylic acid (In₅COOH) was carried out on a Pt disc (geometric surface area 0.03 cm²) or on ITO (indium tin oxide coated glass electrodes. Before electropolymerization, the disc electrode was polished to a mirror finish with alumina powder. ITO electrodes were cleaned in sonic bath.

All electrochemical measurements were carried out by AUTOLAB equipped with the potentiostat PGSTAT (Ecochemie, Netherlands). Voltammetry at RDE (rotating disc electrode) was performed with Tacussel set-up. The CV measurements were made in a three electrode cell with a platinum gauze counter electrode and aqueous 1 M silver chloride electrode as the reference electrode, in the case of RDE measure-

ments SCE was used as a reference one. Optical spectra were recorded using a double beam UV-Vis spectrophotometer (Lambda 12, Perkin-Elmer).

Before the measurements the solutions were deoxygenated with pure argon. Indole-5-carboxylic acid, CH₃CN, LiClO₄, HClO₄ were purchased from Aldrich and used as received. 0.1 M phosphate buffer was prepared with KH₂PO₄ and NaOH (POCH). Catechol was of analytical grade (from POCh and Fluka respectively). All solutions were prepared with milliQ water (Millipore).

3. RESULTS AND DISCUSSION

3.1. Characterisation of Pt/PI₅COOH Electrode in Aqueous Solutions

The influence of pH on PI₅COOH electroactivity was investigated in a broad pH range. Figure 1 presents the CV curves of polymer modified electrode recorded in supporting electrolytes: HClO₄ and LiClO₄ + xHClO₄.

It can be seen, that at pH < 2 two, different in character, redox processes exist. The first process, taking place at low potential values is pH independent in acidic solution (2 M, 1 M) This redox pair shifts to more positive potentials as the pH increases and finally disappears at pH > 4. The peaks of the second redox pair observed at higher potentials are narrower and the positions of the matching anodic and cathodic peaks are strongly pH dependent. Considering the relation between anodic E_{pa} and cathodic E_{pc} peak potentials and pH (the slopes of E_p vs. pH curves were about -115 and -111 mV/pH respectively), one may conclude that in the solutions with pH < 2 two protons per one electron are involved in the oxidation and reduction of the polymer segment. At higher pH values the relation is more complicated and cannot be described by a simple Nernst equation.

The CV curves were also recorded in solutions at pH: 4.1, 5, 6.5. It can clearly be seen (from the inset in Fig. 1) that in the crucial, from the application point of view in biosensors, pH range (5–6.5) PI₅COOH is still electroactive and conducting. Moreover, the CV curves recorded at higher pH show, that only a single redox process take place. The formal potential E_F of the polymer in buffered solution (at pH 6.5) calculated according to: $(E_{pa} + E_{pc})/2$ is equal to 0.25 V at 40 mV/s. The plot of the anodic (j_{pa}) and cathodic (j_{pc}) peak currents densities as a function of the square root of sweep rate $v^{1/2}$ was linear. This suggests that the rate of redox process of PI₅COOH film is probably limited by the diffusion of counter ions. On the other hand, in acidic solutions with lower pH (2 and 1 M HClO₄) the peak currents of the second redox pair vary linearly with the sweep rate suggesting surface polymer redox reaction. Our pH results only partially agreed

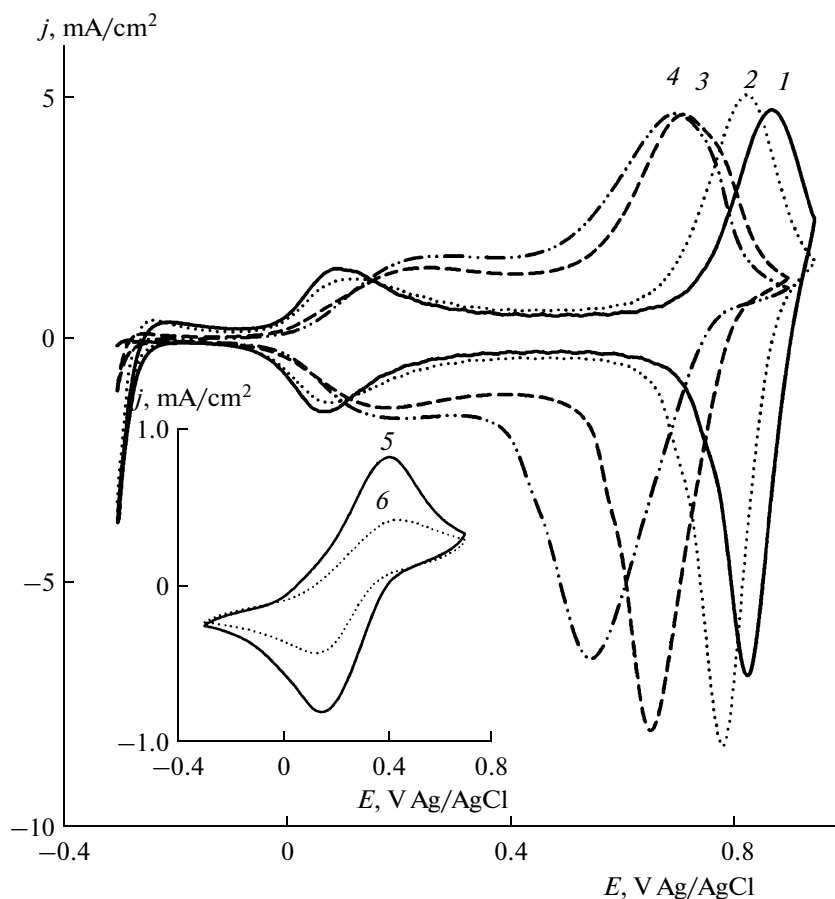


Fig. 1. CV curves recorded on Pt/PIn₅COOH electrode in 2 M (1), 1 M (2), 0.1 M (3) HClO₄ and in HClO₄ + 0.1 M LiClO₄ solutions at pH 1.8 (4). CV recorded at pH 5 (5) and in buffer solution pH 6.5 (6)—inset, sweep rate 40 mV/s, $Q_p = -0.56$ C/cm².

with earlier studies of Bartlett et al. [24] who found linear variation of formal potential with pH for the second oxidation process in pH range changed from 0.5 to nearly 6.

The existence of a single electron transition in polymer film in buffer solution was confirmed by in situ UV-Vis measurements. In Figs. 2a, 2b the UV-Vis spectra of PIn₅COOH, recorded at various potentials in acidic and buffer solutions, are compared. The CV curves obtained on ITO electrodes are presented as insets. In both cases the fully neutral, undoped state of polymer (−0.2 V) is characterized by one electronic transition (π to π^* transition). This transition is manifested by increasing absorption towards the UV part of the spectra. Polarization of electrode in the potential range from −0.2 to 0.6 V, which corresponds to the first oxidation peak (acid solution) and single oxidation peak in buffer solution, results in steady growth of the 770–780 nm transition band. This band grows at the expense of the π to π^* transition peak and as result a clear isobestic point is observed at 560 nm (acid solu-

tion) and at 440 nm (in buffer solution). The appearance of the isobestic point suggested the co-existence of two, optically different phases: the neutral, undoped polymer form and the one consisting of radical-cations (polarons). There are no changes in UV-Vis spectra of the polymer in buffered solution upon further polarisation of electrode in anodic direction. In the acidic medium, however the two additional isobestic points appear at 420 and 680 nm when potential is changed from 0.8 to 1.1 V indicating, that the second redox process is rather complex.

The results pointed out that redox properties of PIn₅COOH are strongly depended upon pH of solutions. The great problem during polymerization of indole molecules and its derivatives is possibility of formation of polymers with different molecular structure [28, 29]. It means that polymer composition is complicated and may be responsible for complex redox behaviour.

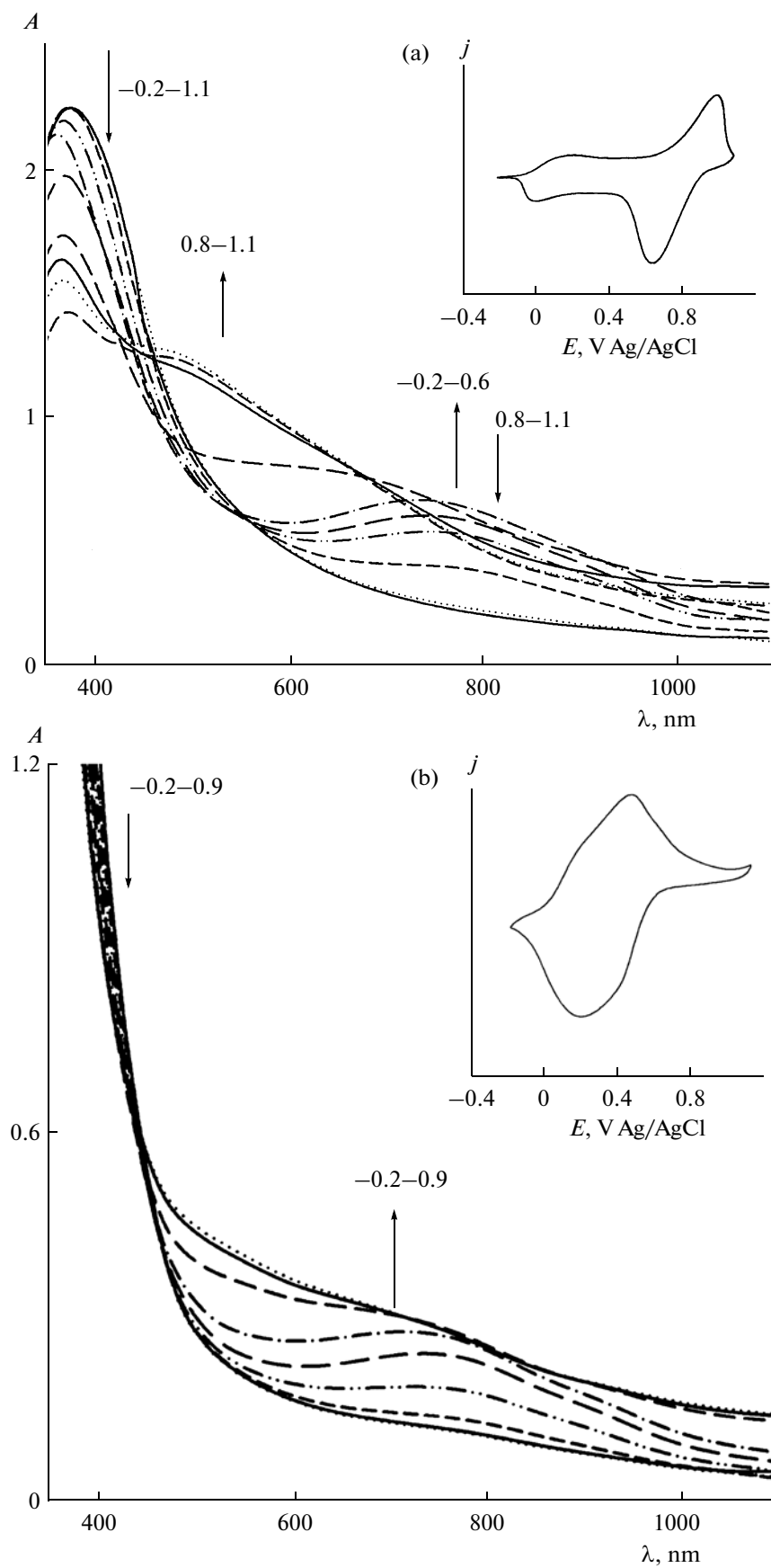
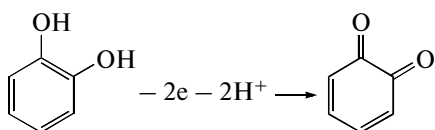


Fig. 2. (a) Absorption spectra of ITO/PIn₅COOH in 2 M HClO₄ for various potentials: -0.2, 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 0.9, 1.0, 1.1 V. CV curve of PIn₅COOH in 2 M HClO₄, scan rate 10 mV s⁻¹—inset. (b) Absorption spectra of ITO/PIn₅COOH in buffer solution pH 6.5 for various potentials: -0.2, 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9 V. CV curve of PIn₅COOH in buffer solution pH 6.5, scan rate 10 mV s⁻¹—inset.

3.2. Electrooxidation of Catechol at Pt/PIn₅COOH and Pt Electrodes

Cyclic voltammetry results. During oxidation of catechol (CT) the *o*-quinones, are produced according the following reactions:



Consequently, the CV curves should exhibit a single reversible redox process. Figures 3a, 3b presents a collection of CV curves recorded at Pt and Pt/PIn₅COOH electrodes in buffer solution containing CT. In both cases the values of E_{pa} , E_{pc} and E_f depended on sweep rates. For sweep rates lower than 100 mV/s, the values of E_{pa} of CT oxidation at Pt/PIn₅COOH electrode are less positive than at Pt electrode. E_{pa} values varied from 0.36 to 0.54 V during changes of sweep rate from 5 to 100 mV/s for polymer electrode while for bare Pt they changed from 0.5 to 0.54 V. Formal potential determined at sweep rate 40 mV/s is equal 0.25 and 0.28 V for polymer electrode and Pt electrode, respectively. It suggests that polymer facilitates CT oxidation at lower sweep rates and improves the reversibility of reaction.

In both cases the plot of j_{pa} and j_{pc} vs. $v^{1/2}$ is linear (see inset Figs. 3a, 3b). It indicates that the reaction rate is controlled by CT diffusion. By using Randies-Sevcik equation [30] and assuming a two electron CT oxidation we determined the diffusion coefficient of CT to be $3.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (from data for Pt/PIn₅COOH electrode) and $3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (from data for Pt electrode). These values are two times lower than that determined by others authors [11, 31]. The comparison of CV curves recorded in the presence of CT on bare Pt with that one obtained in supporting electrolyte (buffer solution) (Fig. 4) reveals that CT is oxidized only after the oxidation of polymeric film is initiated. Presence of oxidized polymer on Pt surface enhanced oxidation current of CT values. It suggests that polymer film is permeable for CT. It means that CT penetrates the film and is oxidized not only at polymer surface but also in the bulk of polymer, so that real surface of reaction is much higher than in case of bare Pt electrode.

CV curves were also recorded at Pt and Pt/PIn₅COOH electrodes for different CT concentrations. Fig 5 shows the variation of j_{pa} , j_{pc} as a function of CT concentration on Pt (1) and Pt/PIn₅COOH (2). In both cases the dependence is linear.

In order to look more properly in mechanism of CT oxidation we used the rotating disk electrode (RDE) voltammetry.

RDE voltammetry results. The quasi-steady state j, E curves were recorded at different rotation speed (from 10 to 2100 rpm), sweep rate 2 mV/s and under various experimental conditions (reagent concentrations, thickness of polymeric films) The typical RDE voltammograms recorded on Pt/PIn₅COOH electrode in buffer solutions containing 5 mM of CT are presented in Fig. 6 where as the insets the Levich-Koutecky plots [30] is shown.

The plots of j_L^{-1} versus $\omega^{-1/2}$ gave a straight line. For the conducting polymer electrode we may assume that the redox reaction of solute species can take place at polymer surface/solution interface, within polymer layer and at metal support/solution interface. Since in our case E_{pa} and j_{pa} for CT oxidation depend on the polymer thickness we can suppose that the processes take place not only at the polymer surface but also within polymer film.

Consequently, to analyze the data we followed the Rocklin and Murray [32] approach developed for the reaction of redox couple at polymer modified electrode which was later successfully used by Mandic et al. [33] description of behaviour of polyaniline.

We applied the limiting current density (j_L) dependence on rotating speed to described by equation:

$$j_L = \frac{1}{nFk_{ch}\Gamma c_s} + \frac{1}{nFD_{s,pol}Pc_s/d + nFD_{CT}\Gamma_T/d^2} + \frac{1}{0.62nFD_s^{3/2}v^{-1/6}\omega^{1/2}c_s}, \quad (1)$$

where k_{ch} is the total reaction rate constant, c_s is the concentration of solute species (CT), $D_{s,pol}$ is diffusion coefficient of the solute species in the film, P is the partition coefficient of the solute species between polymer layer and the solution, D_{CT} is the charge transport diffusion coefficient through the polymer, γ is the surface concentration of polymer redox centers available for reaction, γ_T is the total concentration of polymer redox centers, d is the thickness of polymeric film. All other symbols have the usual meaning.

The first term in this equation describes the current induced by electron transfer between reacting species and redox centers in the polymer. The second term is the current resulting from diffusion of reactant through the film and charge transfer through the film. The third term is the Levich diffusion current. In our

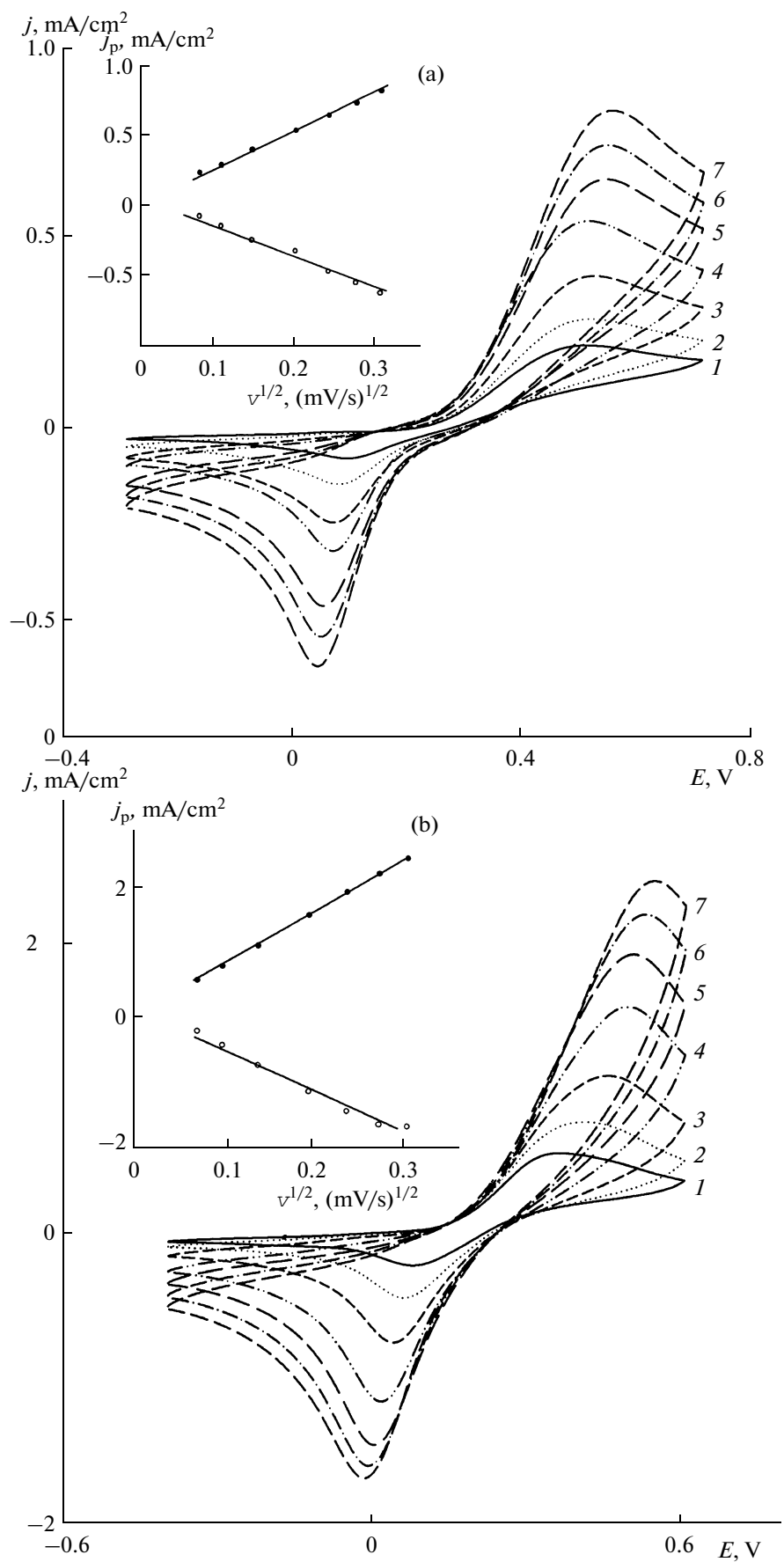


Fig. 3. (a) CV curves recorded on Pt electrode in buffer solution pH 6.5 containing 5 mM catechol at different sweep rate 5 (1), 10 (2), 20 (3), 40 (4), 60 (5), 80 (6), 100 (7) mV/s. Inset— j_{pa}, j_{pc} dependence on $v^{1/2}$. (b) CV curves recorded on Pt/PIn₅COOH electrode ($Q_p = -0.56$ C/cm²) in buffer solution pH 6.5 containing 6 mM catechol at different sweep rate 5 (1), 10 (2), 20 (3), 40 (4), 60 (5), 80 (6), 100 (7) mV/s. Inset— j_{pa}, j_{pc} dependence on $v^{1/2}$.

consideration the first term may be neglected, as at the potentials of limiting current the polymer electrode is fully oxidized. This the case, when the concentration of charge carriers is very high, so the electron transfer is not rate determining. For many polymers [34, 35] the limiting current does not depend on polymer thickness, therefore the second term is often omitted. Unfortunately, it is not our case. Figure 7 presents Koutecky–Levich plots for CT oxidation at electrode modified with polymer films of different thickness in comparison with the results obtained on bare Pt electrode. It can clearly be seen that the values of intercepts are thickness dependent. In addition we examined the influence of CT concentration on the values of intercepts of $1/j_L$ vs. $\omega^{-1/2}$ at $\omega = 0$ and plotted the intercept values against $1/c_s$. We found this relation not linear. Concerning Eq. (1), the results point out that probably two processes: diffusion of CT across polymer film and the charge transport through the film are the rate determining steps in CT oxidation on Pt/PIn₅COOH electrode. Comparing the values of limiting current densities obtained for Pt bare electrode and polymer electrode of different thickness we can conclude that the polymer thickness increase causes the increase of permeability of polymer films.

The diffusion coefficient D of CT determined from the slope of Levich–Koutecky plots (Fig. 7) was found to be c.a. 2.4×10^{-6} cm²/s for bare Pt electrode and was in the range from 2 to 3×10^{-6} cm²/s for Pt/PIn₅COOH electrode. The values are in a good agreement with those obtained from Randles–Sevcik equation.

4. CONCLUSIONS

In this paper we described the investigation of diphenol (catechol) electrooxidation on modified electrode with conducting polymer PIn₅COOH. Our results pointed out that, due to its own redox properties, the polymer is able to enhanced oxidation of CT.

We found that, in comparison with Pt electrode, the polymeric film significantly increases the oxidation current of CT and shifts the peak of CT current oxidation to less positive values. The results obtained from cyclic voltammetry measurements pointed out that relation between oxidation peak current of CT and CT concentration is linear in the investigated range (up to 6 mM). To find the rate—determining step of CT electrooxidation, the influence of polymer thickness and CT concentration on RDE results was tested. The results point

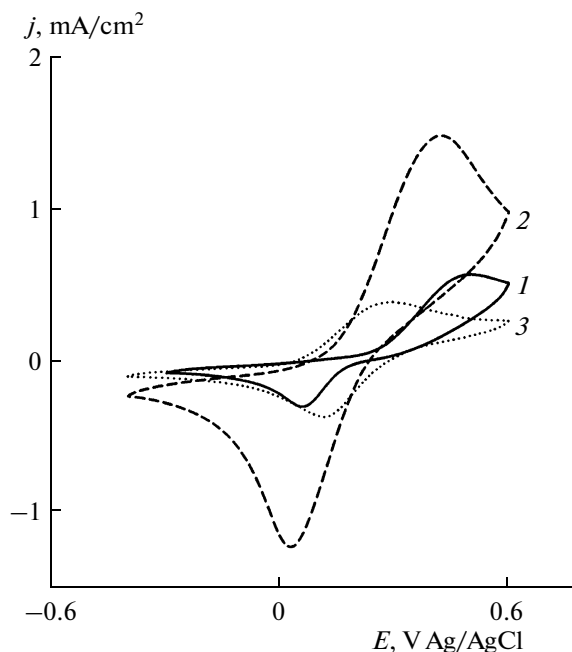


Fig. 4. CV curves recorded on Pt (1) and on Pt/PIn₅COOH (2) electrodes in buffer solution (pH 6.5) containing 5 and 6 mM of catechol respectively. For comparison CV curve recorded on Pt/PIn₅COOH (3) electrode in pure buffer solution is shown. Sweep rate 40 mV/s.

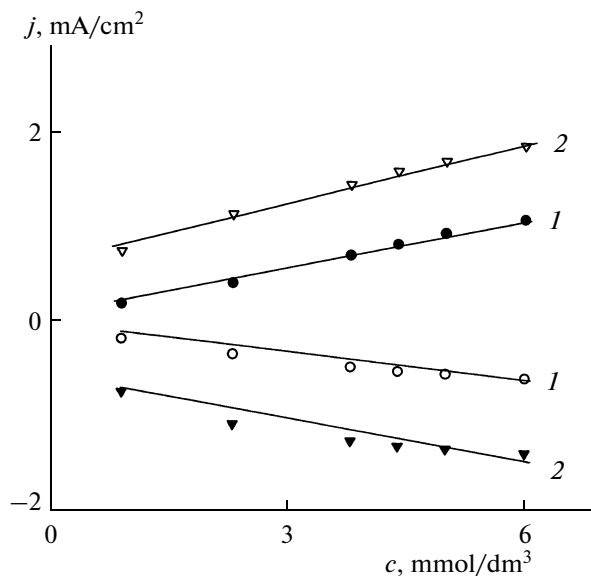


Fig. 5. The dependence of peak current densities on catechol concentration recorded on Pt (1) and Pt/PIn₅COOH (2) electrodes in buffer solution, pH 6.5, scan rate 40 mV/s.

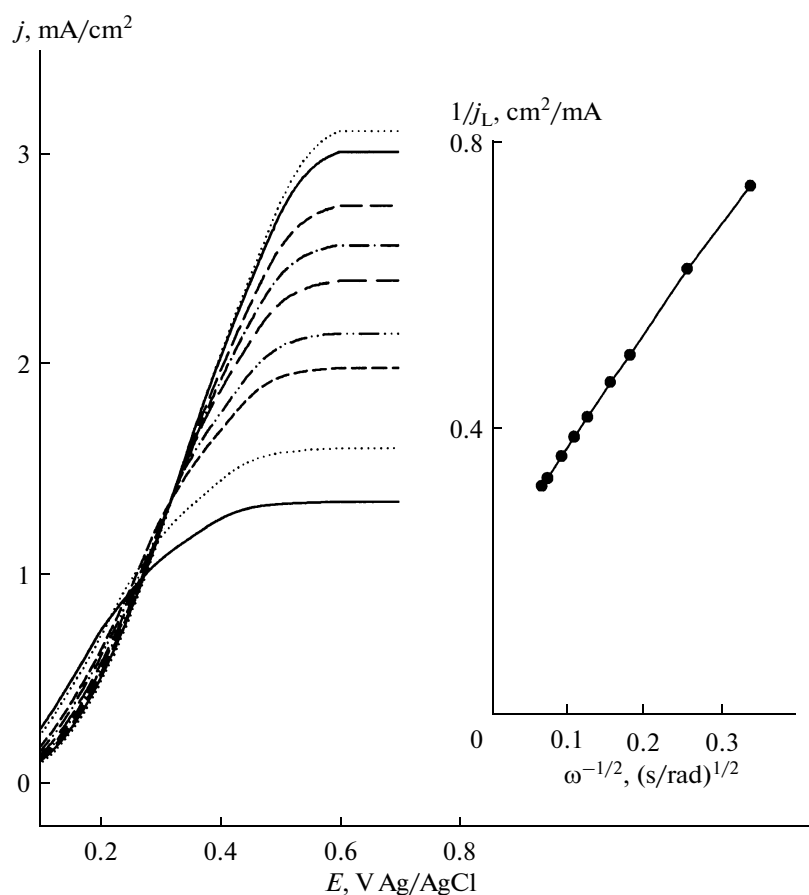


Fig. 6. RDE results obtained for Pt/PIn₅COOH electrode ($Q_p = -0.56 \text{ C/cm}^2$) in buffer solution pH 6.5 containing 5mM of catechol for various rotation speeds: 80, 140, 280, 380, 580, 780, 1080, 1680, 2080 rpm, sweep rate 2 mV/s. The Levich–Koutecky plot is shown as the inset.

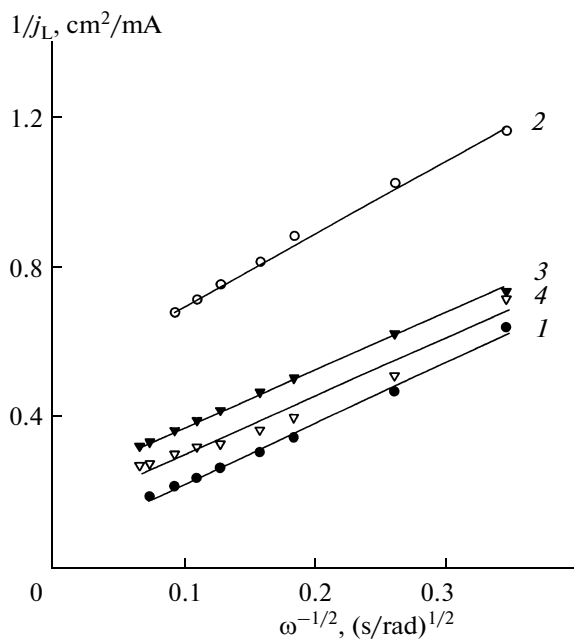


Fig. 7. The Levich–Koutecky plot for catechol oxidation on Pt (1) and Pt/PIn₅COOH electrodes of different thickness. Polymerization charge: 0.22 C/cm² (2), 0.56 C/cm² (3), 1.15 C/cm² (4).

out that the oxidation process take place not only on the polymer surface but also in the vicinity of polymer film. We supposed that the increase in reaction surface is the main reason of enhancement of CT oxidation in the presence of polymer.

Our previous and present studies have proven the suitability of PIn₅COOH electrode to be used as a detector of catechol concentrations. In the lower catechol concentration range the polymer can be used as matrix for enzyme immobilization and simultaneously as an electrode for reduction of *o*-quinones [22]. In the higher concentration range polymer can worked as mediator facilitating oxidation of catechol and increasing reaction surface.

REFERENCES

1. Vermillen, F.J. and Pearl I.A., *Journal of the Electrochemical Society*, 1964, vol. 111, p. 1392.
2. Sistiaga, M., Pierna, A.R., Marzo, F.F., Altube, A., and Lorenzo, A., *Applied Surface Science*, 1998, vol. 133, p. 124.
3. Nematollahi, D. and Rahchamani, R., *Tetrahedron Letters*, 2002, vol. 43, p. 147.

4. Ureta-Zanartu, M.S., Bustos, P., Diez, M.C., Mora, M.L., and Gutierrez, C., *Electrochim. Acta*, 2001, vol. 46, p. 2545.
5. Salavagione, H.J., Arias, J., Garces, P., Morallon, E., Barbero, C., and Vazquez, J.L., *Journal of Electroanalytical Chemistry*, 2004, vol. 565, p. 375.
6. Wang, J., Jiang, M., and Lu, F., *Journal of Electroanalytical Chemistry*, 1998, vol. 444, p. 127.
7. Lapuente, R., Cases, F., Garces, P., Morallon, E., and Vazquez, J.L., *Journal of Electroanalytical Chemistry*, 1998, vol. 451, p. 163.
8. Sanchez-Cortez, S., Francioso, O., Garcia-Ramos, J.V., Ciavatta, C., and Gessa, C., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2001, vol. 176, p. 177.
9. Nematollahi, D., Tammari, E., Sharifi, S., and Kazemi, M., *Electrochim. Acta*, 2004, vol. 49, p. 591.
10. Nourmohammadi, F., Gloabi, S.M., and Saadnia, A., *Journal of Electroanalytical Chemistry*, 2002, vol. 529, p. 12.
11. Luz, R.C.S., Damos, F.S., Oliveira, A.B., Beck, J., and Kubota, L.T., *Sensors and Actuators B*, 2006, vol. 117, p. 274.
12. Ghanen, M.A., *Electrochemistry Communications*, 2007, vol. 9, p. 2501.
13. Sun, W., Li, Y., Yang, M., Li, J., and Jiao, K., *Sensors and Actuators B*, 2008, vol. 133, p. 387.
14. Mu, S., *Biosensors and Bioelectronics*, 2006, vol. 21, p. 1237.
15. Cabrita, J.F., Abrantes, L.M., and Viana, A.S., *Electrochim. Acta*, 2005, vol. 50, p. 2117.
16. Malhorta, B.D., Chaubey, A., and Gerard, M., *Biosensors and Bioelectronics*, 2002, vol. 17, p. 345.
17. Cosnier, S., Szunerits, S., Marks, R.S., Lellouche, J.P., and Perie, K., *Journal of Biochemical and Biophysical Methods*, 2001, vol. 50, p. 65.
18. Chaki, N.K. and Vijayamohanan, K., *Biosensors and Bioelectronics*, 2002, vol. 17, p. 1.
19. Malinauskas, A., Garjonyte, R., Mazeikiene, R., and Jureviciute, I., *Talanta*, 2004, vol. 64, p. 121.
20. Vedrine, Ch., Fabiano, S., and Tran-Minh, C., *Talanta*, 2003, vol. 59, p. 535.
21. Skotkeim, T.A. and Reynolds, J.R., *Conjugates Polymers, Processing and Applications*, NW: CRC Press, 2007.
22. Bieganski, A.T., Michota, A., Bukowska, J., and Jackowska, K., *Bioelectrochemistry*, 2006, vol. 69, p. 41.
23. Waltman, R.J., Diaz, A.F., and Bargon, J., *Journal of Physical Chemistry*, 1984, vol. 88, p. 4343.
24. Bartlett, P.N., Dawson, D.H., and Farrington, J., *Journal of Chemical Society, Faraday Transactions*, 1992, vol. 88, p. 2685.
25. Talbi, H., Billaud, D., Louarn, G. and Pron, A., *Spectrochimica Acta A*, 2001, vol. 57, p. 423.
26. Billaud, D., Humbert, B., Therenot, L., Thomas, P., and Talbi, H., *Spectrochimica Acta A*, 2003, vol. 59, p. 162.
27. Diaz, A.F., Castillo, J.I., Logan, J.A., and Lee, W.-Y., *Journal of Electroanalytical Chemistry*, 1981, vol. 129, p. 115.
28. Jackowska, K. and Bukowska, J., *Polish Journal of Chemistry*, 1992, vol. 66, p. 1477.
29. Talbi, H., Monard, G., Loos, M., and Billaud, D., *Journal of Molecular Structure*, 1998, vol. 434, p. 129.
30. Bard, A.J. and Faulkner, L.F., *Electrochemical Methods, Fundamentals and Application*, New York, 2001.
31. Anjo, D.M., Corkery, K.K., Gonzalez, E., Marantos, K.A., and Estrada, K.E., *Journal of Chemical and Engineering Data*, 1994, vol. 39, p. 813.
32. Rocklin, R.D. and Murray, R.W., *Journal of Physical Chemistry*, 1981, vol. 85, p. 2104.
33. Mandic, Z. and Duic, L., *Journal of Electroanalytical Chemistry*, 1996, vol. 403, p. 133.
34. Maksymiuk, K. and Doblhofer, K., *Electrochim. Acta*, 1994, vol. 39, p. 217.
35. Kazarinov, V.E., Levi, M.D., Skundin, A.M., and Voro-tyntsev, M.A., *Journal of Electroanalytical Chemistry*, 1989, vol. 271, p. 193.