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ELECTROSYNTHESIS AND OPTICAL PROPERTIES OF POLYAMINOTHIAZOLE

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Conductive polymers are an interesting subject of research due to their electronic and redox properties and potential applications in many fields. Poly(2-aminothiazole) (PAT) is an electrically conductive conjugated polymer that has valuable properties: anticorrosive, antitumor activities, heavy metal sensing.

The conditions of 2-aminothiazole (AT) electrodeposition on the optical transparent electrode, covered with conductive SnO₂ layer and on the Pt sheet, were studied. Thin films of PAT were synthesized from aqueous solution of AT in cyclic voltammetry mode at the presence of (NH₄)₂C₂O₄ or H₂SO₄ as electrolytes. The optical absorption spectra of PAT films were studied. Doping of PAT with K₃[Fe(CN)₆] significantly affects the optical characteristics of films due to the redox processes.

Key words: poly(2-aminothiazole), cyclic voltammetry, electrochemical polymerization, doping, optical spectroscopy.

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1. Introduction

Conductive polymers have been a subject of intense research, since their discovery in 1970s, due to their electronic properties and potential applications in various fields, such as biosensors, corrosion inhibitors, ion sensors, electrochromic devices and electrochemical batteries [1–5]. In particular, poly(2-aminothiazole) (PAT) is an electrically conductive conjugated polymer that exhibits anticorrosion properties [1]. Materials based on poly(2-aminothiazole) adsorb heavy metals ions, such as Ni(II), Cu(II), Cd(II), Zn(II), and Pb(II) from aqueous and organic medium. Selective concentration or even determination of one of the ions in the presence of others is possible using poly(2-aminothiazole) [2]. In addition, 2-aminothiazole is biologically active compound with antimicrobial, antitumor properties and thiazole ring is a part of the active substances of many drugs [5]. However, despite the prospects of applications of PAT the number of publications on its synthesis and usage of the polymer itself is limited.

Synthesis of poly(2-aminothiazole) can be carried out by two methods: chemical synthesis and electrochemical. Chemical synthesis is mostly carried out in organic solvents with various oxidants as initiators of reaction [6–7]. It allows to obtain a great amount of polymer, even for industrial purposes. Electrochemical polymerization enables studying of thin polymer films properties on different surfaces, allows to control film thickness [8]. Particularly interesting (for creating optical sensors) is applying active films to optically transparent electrodes, for example, SnO₂ electrode. Moreover, electrochemical synthesis technique allows obtaining a simultaneously doped conductive polymer, the deposition of insoluble polymers.

Electrochemical synthesis can be conducted in three different regimes: galvanostatic, when current is constant, potentiostatic, when potential is constant, voltammetry, when potential is function of time. Voltammetry allows to study processes that take place on electrode surface during the polymerization. Therefore, the aim of our research is to find optimal ways of electrochemical synthesis of poly(2-aminothiazole) by cyclic potential scanning or voltammetry (CVA) on different electrodes and to study properties of produced films.

2. Materials and experimental procedures

2-aminothiazole (CAS-number: 96-50-4; $M=100.14$ g/mol; UOSlab,) – light yellow crystals; soluble in water (100 g / l at 20°C), alcohols, diethyl ether.

Electrolytes – sulfuric acid (fixanal), ammonium oxalate monohydrate ($(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, >98%). Complex salt $\text{K}_3[\text{Fe}(\text{CN})_6]$ was “chemical pure” grade Reagents were purchased from “Сфера Сім”.

All solutions were prepared with distilled water.

Electrochemical measurements were carried out with the help of potentiostat MTechPGP-550M. Electrochemical cell consisted of a three-electrode system: as a working electrode platinum sheet ($S = 2$ cm²) was used. As optical transparent electrode we used glass covered with conductive SnO_2 layer ($S = 2$ cm², $T > 80$ %, SHOTT Korea); as a reference electrode – saturated Ag/AgCl; as a counter electrode – platinum mesh. Synthesis was carried out at a sweep rate 20 mV/s in potential range from –0.2 V to 1.5 V. Thin films of PAT were deposited from 0.1 M monomer solution at the presence of 0.3 M ammonium oxalate or 0.5 M sulfuric acid as electrolytes after 20 cycles of potential sweep.

In order to get information about electrochemical activity of PAT films, cyclic voltammograms at different sweep rates at the presence of 0.3 M ammonium oxalate or 0.5 M sulfuric acid as electrolytes were obtained. Film thickness was determined by microinterferometer MII-4 for the films on the SnO_2 surface, while for Pt sheet we use gravimetric method.

Optical properties of PAT were studied on the surface of SnO_2 -electrode in comparison with clean SnO_2 -electrode. Spectral measurements were carried out on photocolimeter KFK-3 in the range of wavelength 310–990 nm.

Doping was carried out as follows: electrode with PAT film on it was soaked for 20 min at 0.005 M solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ as a dopant, further it was pulled out, washed with distilled water and used for studies.

3. Results and discussion

During the studies was found out that in the medium of ammonium oxalate on working electrode surface thin film of PAT forms (Fig. 1), while in the presence of sulfuric acid polymerization does not happen. In the result of the electrosynthesis, a light yellow-brown polymer film was formed on the working electrode surface. The multiple cyclic voltammogram showed that electrooxidation of AT on the optical transparent electrode take place during first potential sweep at the peak potential $E = 1.0$ V (versus Ag/AgCl reference), while on the platinum sheet peak potential was $E = 0.8$ V. This peak disappeared after the first cycle due to the film formation that blocks access to the electrode surface and in the second cycle – a new peak at $E = 0.7$ V (at both electrodes) appeared that corresponds to the formed electroactive film. The potential value did not change in subsequent cycles on both electrodes, while peak current slightly changed to the bigger values with every cycle, that means that film was slowly growing.

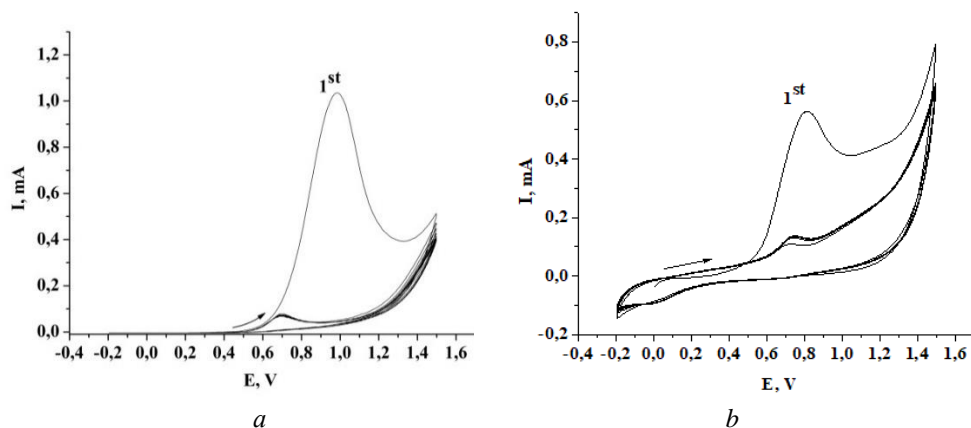


Fig. 1. Cyclic voltammograms obtained in the electrochemical polymerization process from 0.1 M aqueous solution of monomer at the presence of 0.3 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ on SnO_2 electrode (a) and on platinum sheet (b)

Possible mechanism of electrooxidation of 2-aminothiazole (Fig. 2) was suggested in the literature [9], in the first stage the oxidation of the monomer occurs with the formation of cation-radical on amino group. In the following stages the recombination of radicals with simultaneous deprotonations takes place. Then there is rearrangement with one more deprotonation.

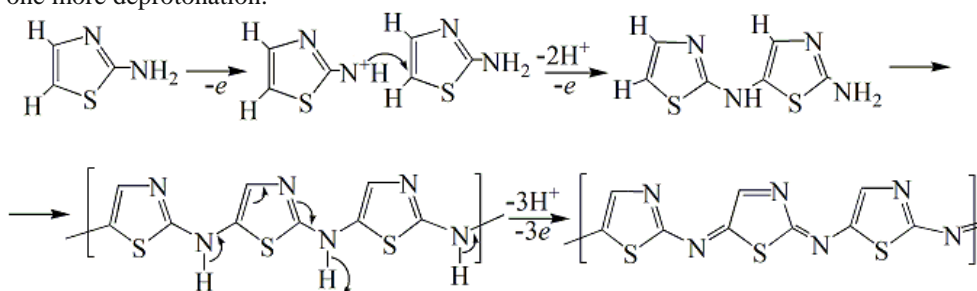


Fig. 2. Mechanism of electrooxidation and oxidative coupling of 2-aminothiazole

Synthesized films of PAT show electrochemical activity. Dependence between the peak current and the scan rate was studied at the presence of 0.5 M sulfuric acid and 0,3 ammonium oxalate as electrolytes on platinum electrode. The peak current increased with increasing of scan rate in both cases (Fig. 3). As can be seen from cyclic voltammograms the electrolyte nature significantly affects electrochemical activity. In particular, at the presence of sulfuric acid one more zone of electrochemical activity at $E = 0.25$ V appears (Fig. 3, a), that is not present in ammonium oxalate medium (Fig. 3, b). Sulfuric acid is a strong acid that acts as a dopant for PAT film, it intensifies film conductivity and electrochemical activity.

Linear dependence between the peak current and the scan rate at 0.5 degree was obtained, which can be explained by diffusion limitation of electrochemical processes in PAT film (Fig. 4). The different slop of the peak current dependencies is evidence of the distinguish of the charge transport rate because cathode process proceeds with reorganization of polymer in thin layer.

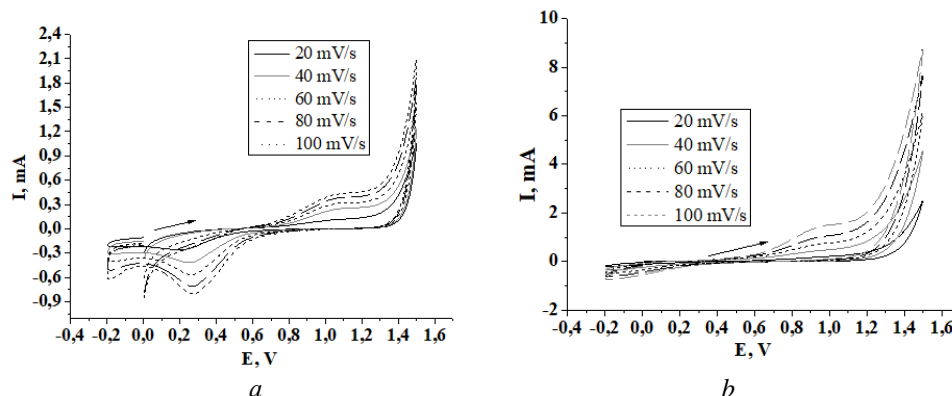


Fig. 3. CVA of PAT films on Pt at different scan rates in aqueous solutions: *a* – 0.5 M H₂SO₄; *b* – 0.3 M (NH₄)₂C₂O₄. Films deposited on Pt from 0.1 M aqueous solution of monomer in the presence of 0.3 M (NH₄)₂C₂O₄ during 20 cycles of potential scanning

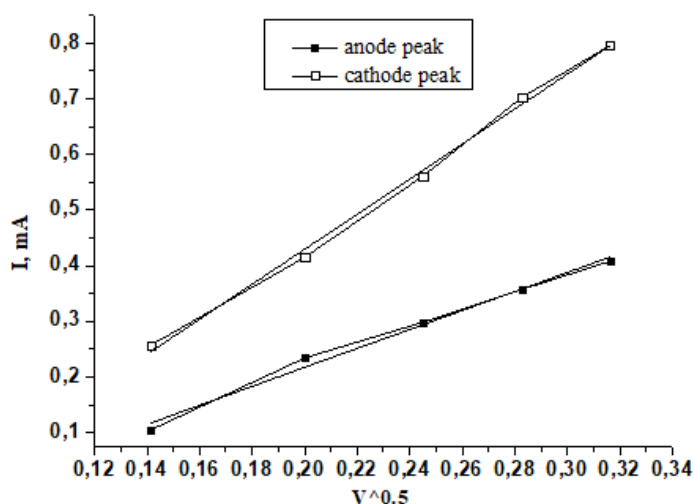


Fig. 4. Dependence between the anodic and cathode peak current and the scan rate at 0.5 degree in 0,5 M H₂SO₄ for PAT film deposited on Pt from 0,1 M aqueous solution of monomer in the presence of 0,3 M (NH₄)₂C₂O₄

This allows to apply the model of semi-infinite diffusion and Randles – Shevchik equation (1) to determine effective coefficients of charge diffusion.

$$i_p = 2.69 \cdot 10^5 n^{3/2} S D_{ef}^{1/2} \nu^{1/2} C^* \quad (1)$$

Equation for calculating the concentration of active centers

$$C^* = Q/nFSl, \quad (2)$$

where *n* is the number of electrons involved in the redox process, here *n* = 1; *S* is the area of the film (2 cm²); *C** is the concentration of active centers in the film (mol/cm³); *Q* is the total charge calculated by integrating the anode or cathode part of the CVA curve; *F* is the Faraday constant, *C*; *l* is the film thickness, here *l* = 1.2 · 10⁻⁵ cm, was calculated from the mass of polymer film deposited on the electrode.

To determine the concentration of active centers in the PAT film, graphical integration of CVA curves was performed using the mathematical program Origin6.0. To calculate the concentration of active centers, the anode and cathode branches of the CVA curve, obtained at $\nu = 20$ mV/s, were used, under conditions when the largest number of redox centers of the polymer layer have time to oxidize or reduce.

As can be seen from the values of the diffusion coefficients, the rate of electron transfer is higher for the anode process, as confirmed by the higher diffusion coefficient (Table 1).

Table 1

Electrochemical activity of PAT films

| Medium | Process | E, V | $C^* \cdot 10^4$, mol/cm ³ | D_{ef} , cm ² /sec |
|---|----------|------|--|---------------------------------|
| 0.5 M H ₂ SO ₄ | Cathodic | 0.25 | 2.47 | $5.6 \cdot 10^{-10}$ |
| | Anodic | 1.03 | 2.69 | $1.37 \cdot 10^{-8}$ |
| 0.3 M (NH ₄) ₂ C ₂ O ₄ | Anodic | 0.93 | 7.32 | $2.03 \cdot 10^{-8}$ |

PAT film has a characteristic spectrum of conjugate polymer systems (Fig. 5). In particular, the absorption inherent in such systems within wavelengths of 400 nm (λ_1), which extends into the UV range, and is associated with (π - π^*) electronic transition of aromatic structures in the conjugate system. The second intense band with a maximum at $\lambda_2 = 600$ nm, characteristic of the electronic transition (n - π^* in imino-quinoid structures) of polyamino-aromatic compounds. Absorption in the range of 850–900 nm, extending to the near IR region, may be due to absorption of delocalized charge carriers in the film of PAT [11].

Among doping reagents, potassium ferrocyanide and potassium ferricyanide attract a lot of attention. Potassium ferricyanide $K_3[Fe(CN)_6]$ is used in many amperometric biosensors as an agent for electron transfer. Doping of conjugated polymers with these complexes leads to changes in electro-optical characteristics [10]. Chemical doping of PAT with the complex compound $K_3[Fe(CN)_6]$ significantly affects optical characteristics of thin films due to the course of redox processes. After doping of PAT with the $K_3[Fe(CN)_6]$ complex, the optical density of the central band increases at λ_2 and the hypsochromic shift of this band is observed by almost 50 nm ($\lambda_2 = 550$ nm). In addition, there is another band at approximately 680 nm, which in the literature is associated with the appearance of free charge carriers [11, 12].

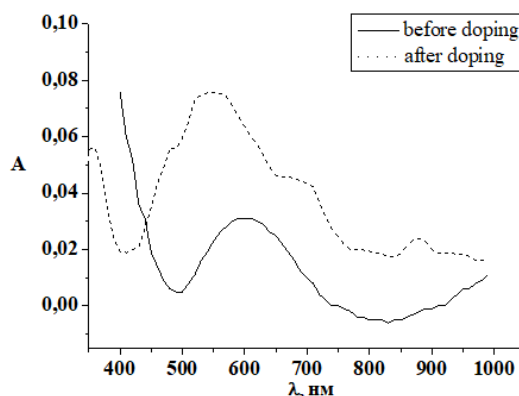
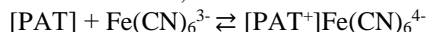


Fig. 5. Absorbtion spectrum of PAT film before and after doping with $K_3Fe(CN)_6$. Film was deposited from 0.1 M monomer solution at the presence of 0.3M ammonium oxalate on SnO₂-electrode

Taking into consideration the hypsochromic shift of the absorption maximum, we can assume that dopant acts as oxidant mainly. As a result, part of neutral fragments of PAT turn into oxidized, while the iron ion changes degree of oxidation from +3 to +2:



Considerable hypsochromic shift and appearance of the absorption maximum at 870 nm probably can be explained by the formation of PAT–Fe(CN)₆ complex.

4. Conclusion

Therefore, conditions of electrooxidation of 2-aminothiazole, that is accompanied by film formation of electroactive polymer (PAT) on the Pt and SnO₂ electrodes were studied. Thin films of PAT were obtained from aqueous solutions by cyclic voltammetry in the presence of ammonium oxalate or sulfuric acid as electrolytes. The electrochemical activity of PAT film in the mentioned electrolytes was investigated. The determined diffusion coefficients indicate a higher electron transfer rate for the anode process. The optical absorption spectra of PAT films are typical for conjugated polymers. Doping of the films with the K₃[Fe(CN)₆] complex significantly affects the optical absorption spectra due to redox processes occurring in the film. Obtained results will be used in further study of properties and fields of application of poly(2-aminothiazole).

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ЕЛЕКТРОСИНТЕЗ ТА ОПТИЧНІ ВЛАСТИВОСТІ ПОЛІАМІНОТІАЗОЛУ

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Електропровідні полімери є об'єктом активних досліджень завдяки своїм електронним властивостям та потенційним застосуванням у багатьох сферах – як біосенсори, іонні сенсори, інгібітори корозії, електрохімічні батареї тощо. Полі(2-амінотіазол) (ПАТ), який є спряженим електропровідним полімером, володіє багатьма цікавими властивостями, зокрема, антикорозійними, протимікробними, протипухлинними, а також сорбційними властивостями важких металів. Електрохімічна полімеризація – це зручний спосіб контрольованого синтезу полімерів на різних поверхнях, який дає змогу досліджувати властивості полімерів у тонких плівках, регулювати їхню товщину, а також допувати полімер одразу під час синтезу. Особливо цікавим є використання оптично прозорих електродів для синтезу, що дає можливість досліджувати оптичні властивості одержаних полімерів.

У цій праці вивчено умови електроосадження 2-амінотіазолу на Pt пластині, а також на оптично прозорому скляному електроді, вкритому провідним шаром SnO₂. Тонкі світло-жовті плівки ПАТ одержано з водних розчинів методом циклічної вольтамперометрії в межах потенціалів від -0,2 В до 1,5 В у присутності амоній оксалату або сульфатної кислоти як електролітів. Досліджено електрохімічну активність ПАТ у присутності згаданих електролітів, середовище сульфатної кислоти спричиняє появу катодну зону електрохімічної активності, якої немає у середовищі амоній оксалату. Вивчено оптичні спектри поглинання тонких плівок ПАТ. Допування плівок ПАТ комплексом K₃[Fe(CN)₆] значно впливає на оптичні спектри поглинання плівок через окисно-відновні процеси, що відбуваються у плівці. Лінійна залежність струму піків від швидкості розгортки потенціалу в ступені 1/2 свідчить про дифузійний контроль електрохімічних процесів у плівці. Визначені коефіцієнти дифузії засвідчують вищу швидкість електронного переносу для анодного процесу.

Ключові слова: полі(2-амінотіазол), циклічна вольтамперометрія, електрохімічна полімеризація, допування, оптична спектроскопія.

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