

# Electrochemical formation of polyaniline on Ti and electrochemically oxidized Ti electrodes

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Aniline electropolymerization at a titanium electrode, covered with a TiO<sub>2</sub> layer of a controlled thickness, has been studied in a sulphuric acid solution. An unexpected phenomenon has been observed for polyaniline at the TiO<sub>2</sub> covered titanium electrode, i. e. decrease of anodic and cathodic peak currents with increasing potential scan rate. Some possible causes of this behaviour are presented and discussed.

**Key words:** polyaniline, electropolymerization, titanium electrode

## INTRODUCTION

Titanium with its good ductility, light weight and corrosion resistance has been applied to various engineering fields such as capacitor, aircraft, vessel component and paint, despite of its low thermal and electric conductivity [1]. Titanium anodizing technology is not as much consolidated as for aluminium, which has been largely studied for the last 20 years. The parameters that most affect the oxide characteristics are the electrolyte solution, the electrical potential difference imposed between cathode and anode and the current density imposed to reach the value of the potential difference. As concerns the electrolyte, an important requirement is that it should not be aggressive towards the growing oxide to avoid its dissolution during the process, or at least it should be ensured that the oxide growth rate is higher than the dissolution one.

Titanium can be selected as a substrate for electrodeposition of polyaniline (PANI) because of its good corrosion resistance and human body biocompatibility [2]. When the working electrode of titanium is anodized, a non-conducting dielectric film of TiO<sub>2</sub> is forming on the electrode surface [3].

Formation of porous films of TiO<sub>2</sub> in aqueous solutions of HF was first observed by C. A. Grimes et al. [4]. Grimes's group has thoroughly investigated various aqueous electrolytes and has concluded that the diameter of TiO<sub>2</sub> nanotubes, thickness of their borders and deployment density depend on the composition of the electrolyte, anodizing mode, even on the nature of the cathode [5–7]. It was noticed [8–10] that the coatings of TiO<sub>2</sub> nanotubes can be obtained by anodizing titanium in aqueous acid solutions with chloride or perchlorate additives.

It is known that electrochemical deposition of conductive polymers onto substrate surfaces is usually accompanied by the passivation of substrate electrode (particularly for active metals). The passive film generated causes a stronger connection of the electroactive film to the electrode surface, as it contains more suitable sites for the deposition of the electroactive material [11].

A lot of information was published on the most attractive conducting polymer – polyaniline because its conductivity can reach values of semiconductors or even metals. PANI has been considered as one of the most potential conducting polymers due to its low cost, high environmental stability, and potential applications in the molecular electronics [12], chemical sensors [13], electrochromic display and light emit-

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ing diode [14]. Vertically aligned polyaniline nanotubes have a great potential application in supercapacitor electrode material [15].

Electrodeposition of PANI on some non-platinum metals by cyclic voltammetry (CV) in the acidic electrolytes has been investigated in ref. [16]. A very strong dependence of the shape of CV curves on the metal of the electrode was shown. It was mentioned that there were differences not only in the relative height of peaks, but also in their position. Shapes of CV curves are very different on different electrodes, although conditions of electrochemical polymerization of aniline (concentration of polyaniline and potential sweep rate) are the same [16]. Peaks obtained on non-platinum metals are significantly smaller than those obtained on the Pt electrode. Investigating the redox reactions on the PANI deposited non-platinum electrode by means of impedance spectroscopy and cyclic voltammetry, it was determined [16] that exchange current density ( $i_0$ ) (calculated from  $R_{ct}$ ) depends on the concentration of a reactant and significantly more on the metal of the electrode.

Recently Mujawar et al. [15] have reported that growth of PANI nanotubes on a titanium nanotube template (TNT) using electrochemical polymerization is strongly influenced by the potential scan rate. Influences of electrochemical polymerization parameters on the morphology and electroactivity of polymer films have been reported in many literatures [17–22]. This means that the PANI films prepared at different conditions have different electrochemical activity.

The present work reports an electrochemical oxidation of titanium electrode in sulphuric acid forming  $TiO_2$  layer of a controlled thickness. The aniline electropolymerization on both “naked” titanium and titanium, covered with  $TiO_2$  layer, electrodes was also investigated. An unexpected voltammetric behaviour for polyaniline at investigated electrodes has been observed, and some possible reasons for this phenomenon are presented and discussed.

## EXPERIMENTAL

Vacuum-distilled aniline and 96%  $H_2SO_4$  of p. a. quality were used for experiments. All measurements were carried out at room temperature ( $\sim 22^\circ C$ ). 99% pure titanium tin of the total square  $2\text{ cm}^2$  was used as a working electrode. The reference electrode was a saturated Ag/AgCl, KCl electrode ( $E_H = 0.2\text{ V}$ ). Pt cylinder of  $20\text{ cm}^2$  was used as a counter electrode.

Before polymer synthesis and anodizing of the titanium electrode, the surface of titanium tin was treated mechanically, i. e. polished with diamond paste with consequent washing in ultrasonic baths of acetone and distilled water. The anodization of Ti electrode was performed with the use of a two-electrode cell with sheet titanium as a working electrode and copper foil as a counter electrode in  $0.5\text{ M } H_2SO_4$  solution under the potential control (30 V). The resulting current density was  $1\text{ mA cm}^{-2}$ . The time of anodization process was calculated according to Faraday's law, and for the thickness

of 50, 100, 500 and 1000 nm it was equal to 18, 36, 180 and 360 s, respectively. A polyaniline layer was formed by cycling the potential of the electrode between  $-1\text{ V}$  and  $2\text{ V}$  in solution containing  $0.5\text{ M } H_2SO_4$  and  $0.05\text{ M}$  aniline (potential sweep rates  $0.02$  to  $0.1\text{ V s}^{-1}$ ).

Voltammetric measurements were performed by use of the  $\mu AUTOLAB$  (Type III) measurement system. Evaluation of the surface roughness of the investigated electrodes was performed by the Nanoscope III (USA). Relief of the electrode surface was scanned at a constant tunnel current.

## RESULTS AND DISCUSSION

Two kinds of titanium electrodes have been used for electropolymerization of aniline. One of them relates to “naked” titanium. This kind was prepared by a simple polishing of the electrode, without any subsequent electrochemical treatment. Because titanium metal shows a high chemical activity towards ambient oxygen and water, the “naked” electrode obviously contains a thin layer of titanium dioxide on its surface. However, this surface layer is of rather uncontrolled thickness. Therefore, a different type of electrodes was prepared by the controlled potentiostatic anodization of titanium in  $0.5\text{ M}$  solution of sulphuric acid for definite time periods. Following this way, four different electrodes have been prepared, containing a surface-bound titanium dioxide layer with the thickness of 50, 100, 500, and 1000 nm, respectively. Fig. 1 compares cyclic voltammograms for these four  $TiO_2$  coated electrodes. No specific redox processes are observed within the entire potential range used, from  $-1.00$  to  $2.00\text{ V}$ , except for negligible increase of background current at the anodic and cathodic tips of the potential scan.

The morphology of anodized titanium electrodes was characterized by atomic force microscopy. The images obtained (Fig. 2) show no clear relationship between the thickness

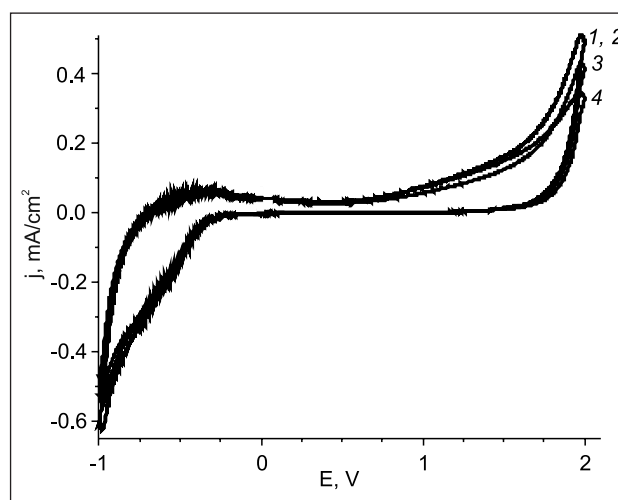


Fig. 1. Cyclic voltammograms recorded on electrochemically oxidized titanium electrodes in  $0.5\text{ M } H_2SO_4$  without aniline at a scan rate of  $50\text{ mV s}^{-1}$ . Thickness of  $TiO_2$  layer (nm): 1, 2 – 50 and 100; 3 – 500; 4 – 1,000

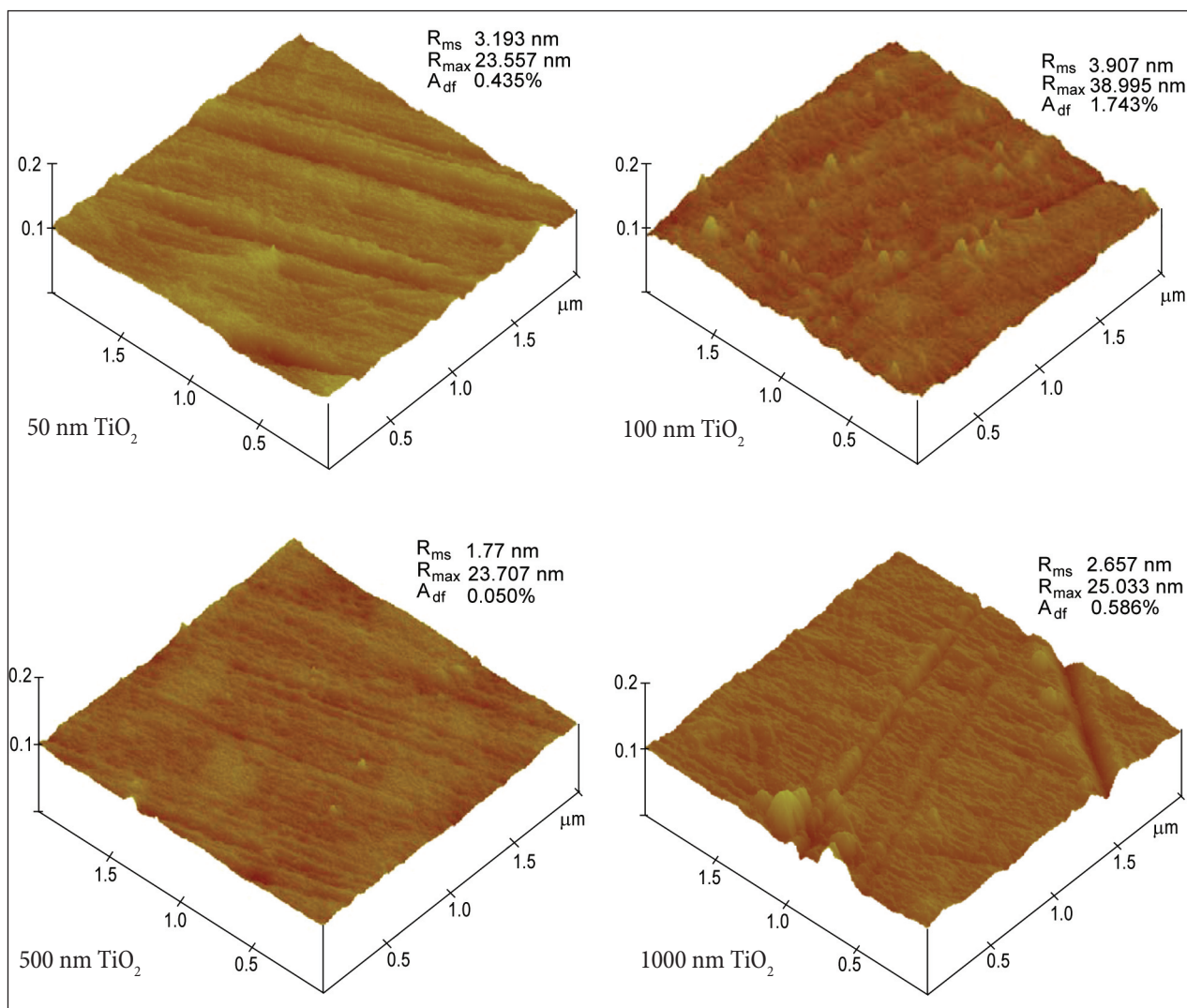
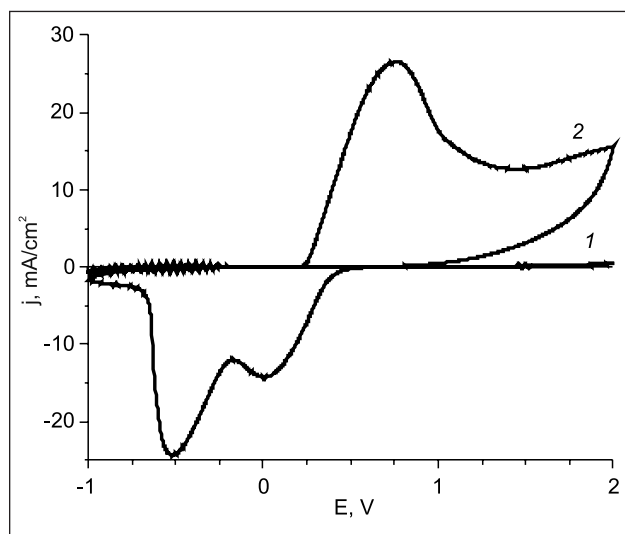


Fig. 2. AFM images of the anodized titanium surface containing TiO<sub>2</sub> layer of different thickness

of TiO<sub>2</sub> layer and its roughness. Commonly, the surface of anodized titanium becomes more homogeneous with increasing thickness of TiO<sub>2</sub> layer. By comparing the images of the anodized and naked titanium surface and taking into account the roughness parameters for naked titanium ( $R_{ms} = 4.1$  nm) and anodized titanium ( $R_{ms}$  ranging from 1.7 to 3.9 nm), it could be concluded that the surface area diminishes to some extent upon anodization.

An anodic potential scan, performed at the naked titanium electrode in an acidic solution containing aniline, as expected, results in a relatively high anodic current at electrode potentials exceeding 0.7 V, corresponding to electrooxidation of aniline. After a few repeating potential scans, cyclic voltammogram stabilizes in its shape. At the same time, the electrode surface appears to be covered with a deep-blue layer of polyaniline at positive electrode potentials. Fig. 3 shows stabilized cyclic voltammograms for the naked titanium electrode in a solution containing aniline, obtained after a few repeating potential scans at a scan rate of 50 mV s<sup>-1</sup>. The well expressed anodic peak is seen located

at 0.77 V, whereas no other anodic peaks are observed at lower potentials. As compared to the corresponding CVs, obtained at the platinum electrode, this peak appears to be shifted by about 0.4 V towards the positive direction. Also, no second anodic peak around 0.8 V is observed, characteristic for polyaniline deposited at platinum or related inert electrodes. It is noteworthy that the anodic current does not drop to zero after passing this anodic peak, indicating electrooxidation to proceed even at higher potentials. In the back cathodic potential scan, two cathodic peaks are observed, located at 0.03 and -0.51 V (Fig. 3). Again, as compared to the platinum electrode ( $E_{pa}$  around 0.2 V), these peaks appear shifted to lower potentials. Surprisingly, the number and the position of these peaks depend on the potential scan rate applied. By decreasing the scan rate up to 20 mV s<sup>-1</sup>, little changes are observed for the anodic peak potential, however, the only cathodic peak (instead of two peaks) is observed around 0.55 V. On the contrary, an increase of potential scan rate up to 100 mV s<sup>-1</sup> results in a shift of the anodic peak to lower potentials up to 0.50 V,

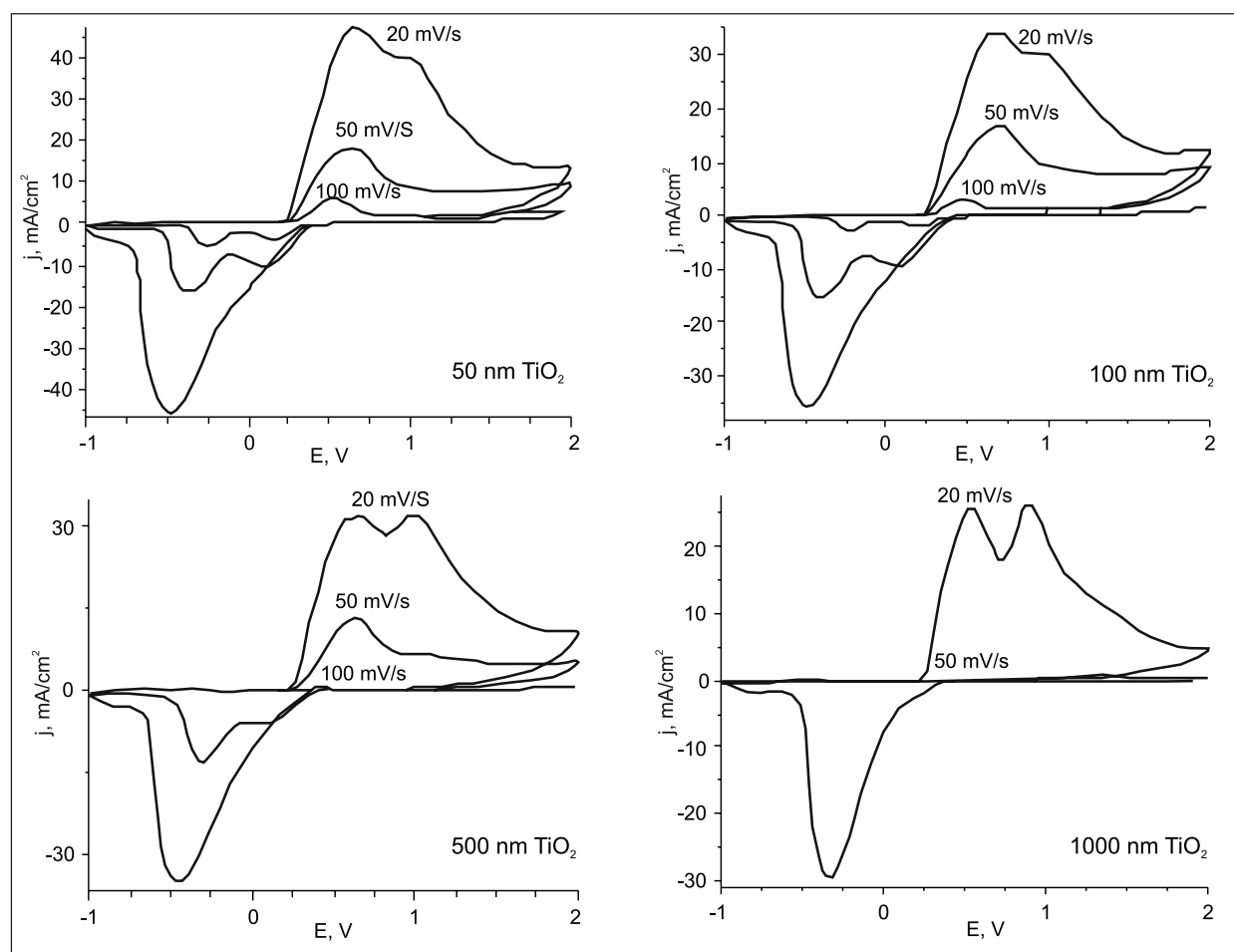


**Fig. 3.** Multicycle voltammogram (as obtained in the 10th cyclic potential scan) of the naked titanium electrode within potential scan limits of  $-1.00$  to  $2.00$  V at a potential scan rate of  $50$  mV/s in a solution of  $0.5$  M of sulfuric acid (1), and in the same solution containing additionally  $0.05$  M of aniline (2)

whereas the two cathodic peaks appear at  $0.19$  and  $-0.26$  V, *viz.* shifted to more positive potentials.

Related tendencies have been observed at the anodized titanium electrodes. Fig. 4 presents a set of CVs, obtained for the anodized titanium electrodes containing  $\text{TiO}_2$  layer of different thickness. For the thinnest  $\text{TiO}_2$  coating, the anodic peak at  $0.68$  V is observed for the lowest potential scan rate of  $20$  mV s $^{-1}$ , followed by the second not well resolved anodic wave around  $1.00$  V. Thickening of  $\text{TiO}_2$  layer results in development of two well separated anodic peaks at  $0.54$  and  $0.90$  V (for  $\text{TiO}_2$  layer of maximum  $1000$  nm thickness). In a cathodic part of CVs, the only peak is observed, located around  $-0.48$  V, and shifted to  $-0.33$  V for the thickest  $\text{TiO}_2$  coating (Fig. 4). As for the naked titanium electrode, an increase of the potential scan rate results in a shift of the anodic peak to lower potentials and the development of two well separated cathodic peaks, subjected to variations in their position on the potential scale depending on the thickness of  $\text{TiO}_2$  layer.

The most striking observation, as it could be concluded from Fig. 4, is the decrease of peak currents with increasing



**Fig. 4.** Multicycle voltammogram (as obtained in the 10th cyclic potential scan) of the anodized titanium electrode containing  $\text{TiO}_2$  layer of different thickness ranging from  $50$  to  $1000$  nm (as indicated), obtained within potential scan limits of  $-1.00$  to  $2.00$  V at different potential scan rate (as indicated) in a solution of  $0.5$  M of sulfuric acid containing  $0.05$  M of aniline

potential scan rate. This relates both to anodic and cathodic peaks (Fig. 5). For thin layers of  $\text{TiO}_2$  (50 or 100 nm), the peak current drops up to 10–15% of its initial value by changing the potential sweep rate from 20 to 100  $\text{mV s}^{-1}$ , whereas for thick  $\text{TiO}_2$  films (1000 nm) both peaks almost disappear by fastening of a potential sweep from 20 to 50 or even more to 100  $\text{mV s}^{-1}$  (Fig. 5). The reasons for this unexpected effect remain unknown, however, it deserves a more detailed discussion.

At least three reasons should be taken into account. First, somewhat related effect has been described earlier for polyaniline electropolymerized at the aluminum electrode [23]. Within a low range of potential sweep rate ( $\nu$ ), not exceeding 50  $\text{mV s}^{-1}$ , a linear increase of anodic peak current with increasing  $\nu$  has been observed, as it could be expected for surface-bound redox couple, whereas a gradual decrease of peak current proceeded at  $\nu$  exceeding 50  $\text{mV s}^{-1}$ . The authors attributed this behaviour to the presence of a passive (non-conducting)  $\text{Al}_2\text{O}_3$  layer at the aluminium surface that prevents fast electron transfer between the background electrode and the polyaniline layer [23]. This reason also seems to be very likely for titanium electrode covered with a semiconducting or insulating  $\text{TiO}_2$  layer. However, following this model, it is difficult to understand why the peak heights depend on the potential sweep rate, since the electric conductivity of a passive layer does not depend on it.

The second possible reason relates to possible electrocatalytic processes taking place at the  $\text{TiO}_2$  surface. The corresponding reaction scheme includes electrochemical oxidation of the reduced form of polyaniline, leucoemeraldine (LM) to its half-oxidized form emeraldine (EM):



and a catalytic regeneration of LM supported by the catalyst, e. g. by  $\text{TiO}_2$  (Cat):



Following this scheme, the ratio of catalytic to noncatalytic peak current is given by the equation [24]:

$$\frac{i_{\text{cat}}}{i_p} = \frac{k^{1/2} [\text{Cat}]^{1/2}}{0.446a^{1/2}}, \quad (3)$$

where  $k$  denotes the rate constant for catalytic reaction,  $[\text{Cat}]$  is an initial concentration of catalyst, and  $a$  is a function of potential sweep rate ( $\nu$ ):

$$a = \frac{nF\nu}{RT}. \quad (4)$$

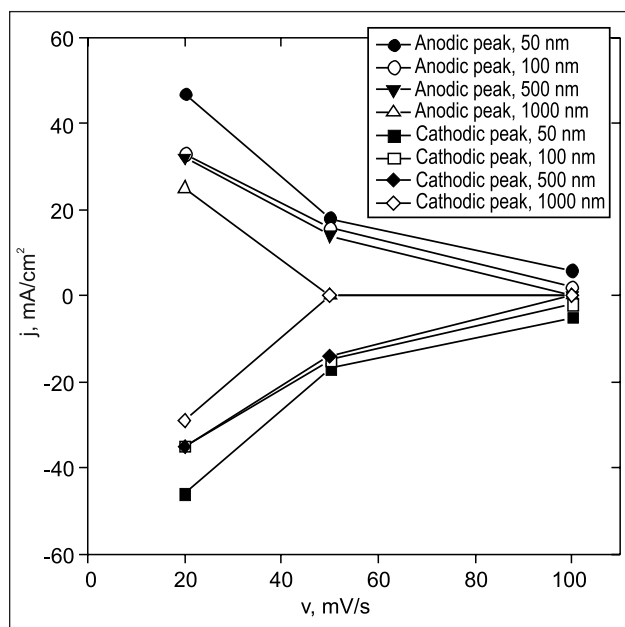
Although this approximation, derived for the case of a homogeneous catalytic reaction, cannot be directly applied for the system studied, it is seen that the ratio of catalytic to noncatalytic peak current, and thus the height of anodic peak should diminish with increasing  $\nu$ .

The third possible reason relates to the specific nature of redox transformation of polyaniline. Electrooxidation of LM form of polyaniline in an acidic solution, as it is commonly accepted, involves the doping of polymer film by solution anions, most likely by sulphate anions. Because of a porous structure of  $\text{TiO}_2$  layer, the diffusion of solution anions to polyaniline, contained within the pores, appears to be restricted. Therefore, the anions cannot penetrate into the polyaniline film during a short time of the anodic potential scan, performed at a high  $\nu$ . On the contrary, a slow potential scan facilitates anion transport, and higher peak currents are observed.

## CONCLUSIONS

$\text{TiO}_2$  layer of a controlled thickness can be formed on the Ti electrode surface anodically treating electrode. Electrodes with 50 nm to 1000 nm thickness of the  $\text{TiO}_2$  layer were prepared and used for investigation of PANI formation. Increase of the  $\text{TiO}_2$  layer thickness causes split of the anodic peak at 0.68 V to two separate peaks at 0.54 V and 0.9 V. Cathodic peaks behave in the opposite way: only one cathodic peak remains at higher thicknesses of the  $\text{TiO}_2$  layer.

Unexpected behaviour of the polyaniline covered  $\text{TiO}_2$  electrode was observed. Peak current densities of polyaniline decrease with the increased potential scan rate. This phenomenon could be explained either by the influence of the passive  $\text{TiO}_2$  layer, presence of catalytic couples or diffusion of anions through the porous surface. The phenomenon requires further investigation.



**Fig. 5.** Dependence of anodic and cathodic peak currents on the potential scan rate, as obtained for polyaniline-modified titanium electrodes containing  $\text{TiO}_2$  layer of different thickness (as indicated)

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## References

1. I. S. Lee, J. Y. Lee, J. H. Sung, H. J. Choi, *Synth. Met.*, **152**, 173 (2005).
2. M. Hosseini, M. M. Momeni, M. Faraji, *J. Mater. Sci.*, **45**, 2365 (2010).
3. V. Branzoi, L. Pilan, *Mol. Cryst. Liq. Cryst.*, **484**, 303 (2008).
4. D. Gong, C. A. Grimes, O. K. Varghese, et al., *J. Mater. Res.*, **16**, 3331 (2001).
5. M. Paulose, K. Shankar, O. K. Varghese, G. K. Mor, B. Hardin, C. A. Grimes, *Nanotechnology*, **17**, 1446 (2006).
6. H. E. Prakasam, O. K. Varghese, M. Paulose, G. K. Mor, C. A. Grimes, *Nanotechnology*, **17**, 4285 (2006).
7. M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes, K. G. Ong, *Nanotechnology*, **17**, 398 (2006).
8. X. Chen, M. Schriver, T. Suen, S. S. Mao, *Thin Solid Films*, **515**, 8511 (2007).
9. N. K. Allam, C. A. Grimes, *J. Phys. Chem.*, **111**, 13028 (2007).
10. N. K. Allam, K. Shankar, C. A. Grimes, *J. Mater. Chem.*, **18**, 2341 (2008).
11. A. Eftekhari, *Synth. Met.*, **145**, 211 (2004).
12. T.-C. Mo, H.-W. Wang, S.-Y. Chen, Y.-C. Yeh, *Ceram. Int.*, **34**, 1767 (2008).
13. S. Srivastava, S. Kumar, V. N. Singh, M. Singh, Y. K. Vijay, *Int. J. Hydrogen Energy*, **36**, 6343 (2011).
14. A. Bessiere, C. Duhamel, J.-C. Badot, V. Lucas, M.-C. Certiat, *Electrochim. Acta*, **49**, 2051 (2004).
15. S. H. Mujawar, S. B. Ambade, T. Battumur, R. B. Ambade, S.-H. Lee, *Electrochim. Acta*, **56**, 4462 (2011).
16. K. R. Prasad, N. Munichandraiah, *Synth. Met.*, **123**, 459 (2001).
17. M. J. Giz, S. L. De Albuquerque Maranhã, R. M. Torresi, *Electrochem. Commun.*, **2**, 377 (2000).
18. S. F. Patil, A. G. Bedekar, R. C. Patil, B. Deore, *Mater. Lett.*, **25**, 43 (1995).
19. Z. Tang, S. Liu, Z. Wang, S. Dong, E. Wang, *Electrochem. Commun.*, **2**, 32 (2000).
20. V. Gupta, N. Miura, *Electrochem. Commun.*, **7**, 995 (2005).
21. H. H. Zhou, S. Q. Jiao, J. H. Chen, W. Z. Wei, Y. F. Kuang, *Thin Solid Films*, **450**, 233 (2004).
22. S. Q. Jiao, H. H. Zhou, J. H. Chen, S. L. Luo, Y. F. Kuang, *J. Appl. Polym. Sci.*, **94**, 1389 (2004).
23. M. H. Pournaghi-Azar, B. Habibi, *Electrochim. Acta*, **52**, 4222 (2007).
24. Z. Galus, *Fundamentals of electrochemical analysis*, Halsted Press, New York (1976).

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## POLIANILINO ELEKTROCHEMINIS FORMAVIMAS ANT TITANO IR ELEKTROCHEMIŠKAI OKSIDUOTO TITANO ELEKTRODŲ

### Santrauka

Tirta anilino elektropolimerizacija sieros rūgšties tirpale ant titano elektrodo, padengto kontroliuojamo storio TiO<sub>2</sub> sluoksniu. Nustatyta, kad polianilino ir TiO<sub>2</sub> sluoksniais modifikuotų elektrodų ciklinių voltamperogramų anodinių ir katodinių smailių srovė mažėja didinant potencialo skleidimo greitį. Aptartos galimos šio reiškinių priežastys.