INFLUENCE OF ELECTRODE STRUCTURE ON THE MORPHOLOGY OF POLYANILINE FILMS

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ABSTRACT

The films of polyaniline (PAn) have been synthesized by oxidation of aniline (An) in potentiodynamic mode in aqueous solution of 0.5 M H_2SO_4 at the both polycrystalline aluminum (Al) and amorphous $Al_{87}Ni_8Y_4Dy_1$ (AlNiYDy) electrodes. The process of electrochemical oxidation of An on AlNiYDy-electrode was analyzed and compared with the process of An's oxidation on the polycrystalline Al-electrode. It was determined that the difference in the form of cyclic voltammograms (CV) is conditioned by the presence of amorphic components in the composition of amorphous metal alloy (AMA) AlNiYDy, which cause of different resistance of surface oxide films on the working electrodes (WE). With the use of X-ray and FTIR-spectral analysis it was showed that the structure of PAn's films that has been deposited on the surface of the Al-electrode and the AlNiYDy-electrode is amorphously-crystalline. At this, the PAn produced on AlNiYD-electrode has a higher degree of crystallinity. An analysis of the images of scanning electron microscopy (SEM) showed that PAn's films have a spongy and porous branched morphology on the surface of the AlNiYDy WEs. An analysis of the energy-dispersive X-ray (EDX) spectra confirmed the presence of PAn on the surface of the electrodes and showed the presence of impurities of metal sulfates, which are part of the WEs, in the polymeric film.

1. Introduction

Electrically conducting polymers (ECP) are relatively new class of polymers [1, 2] the most famous representative among which is the polyaniline (PAn). Polyaniline is an conductive polymer with a wide range of physicochemical properties [1]. As electrodes during the electrochemical synthesis of polyaniline, including also in the form of nanostructured films, the metals of various nature are used [1-4]. Such films posse anticorrosion protection properties regard to the active metals and alloys on them base, and also are used widely for various applications [3]. Therefore, the studies of nanostructured PAn films deposited on various substrates is an urgent scientific problem [5].

The most common usable methods after chemical synthesis are the electrochemical methods of PAn obtaining, namely galvanostatic

(GS), potentiostatic (PS), and potentiodynamic (PD) mode [1-4]. Galvanostatic polymerization of aniline (An) makes easy to control the properties of the PAn's films, namely molecular weight of polymer and the thickness of deposited coatings. Potentiostatic mode of polymerization in turn permits to control by the reactivity of electrochemically active intermediates of the starting monomer's oxidation during reaction. Polymerization in potentiodynamic mode (cyclic voltammetry), which is carried out under cyclic scanning of the electrode potential allows to control in real time both of An oxidation and redox conversions of deposited PAn [6]. Cyclic voltammetry is actively used for the determination of mechanisms of An oxidation, redox reactions of PAn, mechanisms of ion exchange in films of PAn [16], as well as for the researches of the stability of PAn's film's [17], dispersions and composites [18], capacitive characteristics [19–23] or electrical activity of PAn's films [23] and others.

2. Experimental

2.1 Materials

Aniline (99.5%) of the "Aldrich" company was distilled in a vacuum. Solutions of sulfuric acid (H2SO4) were prepared from the standard titrimetric substance of Cherkasy State Plant of Chemicals Production. Distilled water was used as the solvent. Ethanol was distilled under normal conditions. Samples (size ~2.0 × 0.2 cm) of polycrystalline aluminum (Al-electrode, purity 99.995%) and Al-based AMA of $Al_{87}Ni_8Y_4Dy_1$ composition (AlNiYDy-electrode) were used as the WE in the form of plates with the thickness ~40 μm and active surface ~0.2 cm^2.

2.2. PAn films electrochemical deposition

There are two different sides in the AMA ribbon obtained by the flow turning method, namely contact side (which adjacent to the cooling drum) with developed (defective) surface and the external side (which is in contact with the atmosphere of helium) having a smooth surface. In the presented work, the films of PAn were deposited at one time on both sides of the AMA samples, which were used as the working electrode (WE) together with aluminium polycrystalline sheets.

WEs were previously washed with ethanol and were air-dried for 5 min. Electrodeposition of PAn was performed from air-free argon for 10 min 0.25 M aqueous solution of An in 1.0 M H_2SO_4 simultaneously on both sides of the electrodes at the potential scanning rate 25 mV/s within (−200)−(+1200) mV. The films of PAn on the WEs were formed for 75 cycles of the potential scanning. Electrodes with the coated films of PAn were washed with distilled water and dried at room temperature.

2.3. Instrumental methods

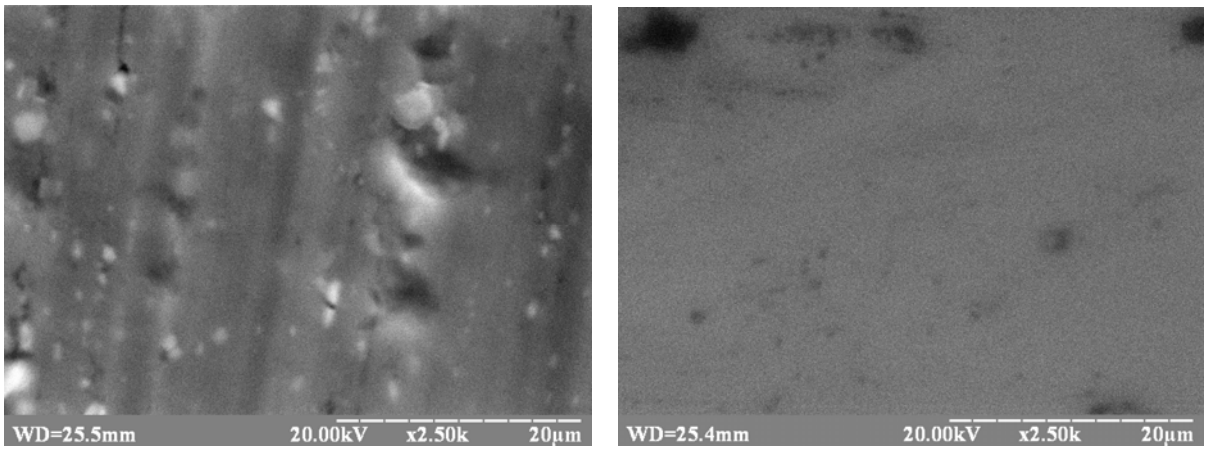
The deposition of PAn's films was carried out in PD mode with electrochemical-electrochemiluminescent analyser CVA-1 accordingly to three-electrodic scheme with Ag/AgCl reference electrode of EVL-1M4 model. All values of the electrode potentials in this work are given in relation to this reference electrode. Cyclic voltammogramms were recorded on a personal computer. Platinum plate (99.9%) with the size of 1 × 1 cm was used as the auxiliary electrode.

The structure of the synthesized PAn films was studied using X-ray diffraction method (XRD) and Fourier-transform infrared spectral (FTIR) analysis. The diffractograms of the samples were received with the use of DRON-3 diffractometer (Cu–Kα radiation, λ = 1.54060 Å). FTIR spectra of the samples were recorded with the use of spectrophotometer NICOLET IS 10 ATR in reflection mode. The microscope-microanalyzer REMMA-102-02 was used for receiving of scanning electron microscopy (SEM) images. XRD and FTIR analysis, electrochemical impedance spectroscopy (Bode plot) and scanning electron microscopy of PAn's films was performed directly on the surface of WEs.

3. Results and discussion

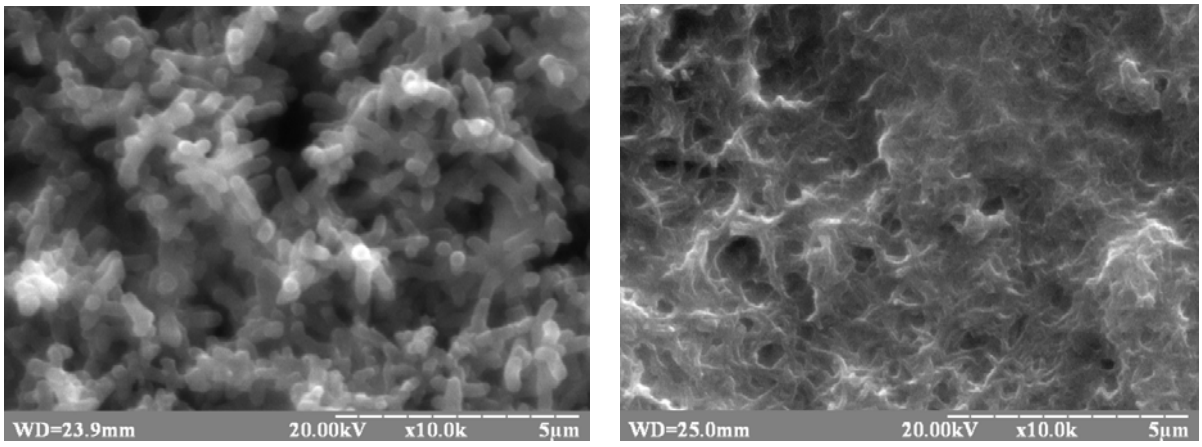
The surfaces of the working Al (*a*) and AlNiYDy (*b*) electrodes are shown in Fig. 1. The SEM images indicates that surface of the Al-electrode is more inhomogeneous, while the surface of AlNiYDy is smooth, due by above noted features of the processes of their manufacture.

The analysis of the SEM images of electrodes modified by polymeric layer (Fig. 2) shown that porous PAn films formed by rod-like aggregates (Fig. 2, *a*) deposited on the aluminium electrode, while films with closed fibrillar structures has been detected on the amorphous alloys electrode (Fig. 2, *b*).



a *b*

Figure 1: SEM images of the surfaces of crystalline aluminium (*a*) and amorphous $Al_{87}Ni_8Y_4Dy_1$ (*b*) electrodes. Magnification ×2 500.

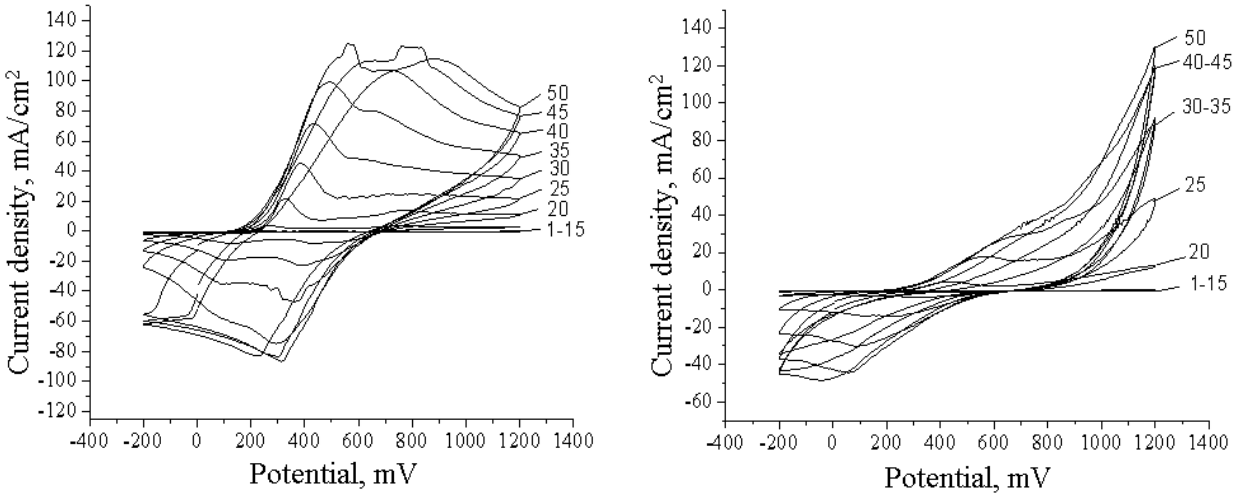


a *b*

Figure 2: SEM images of the surfaces of PAn films deposited on crystalline aluminium (*a*) and amorphous $Al_{87}Ni_8Y_4Dy_1$ (*b*) electrodes. Magnification ×10 000.

CV curves of the PAn deposition on the surface of different working electrodes in potentiodynamic mode are shown on Fig. 3. The form of the received CV curves is different, but the current density, which corresponds to An oxidation is the same practically, which may

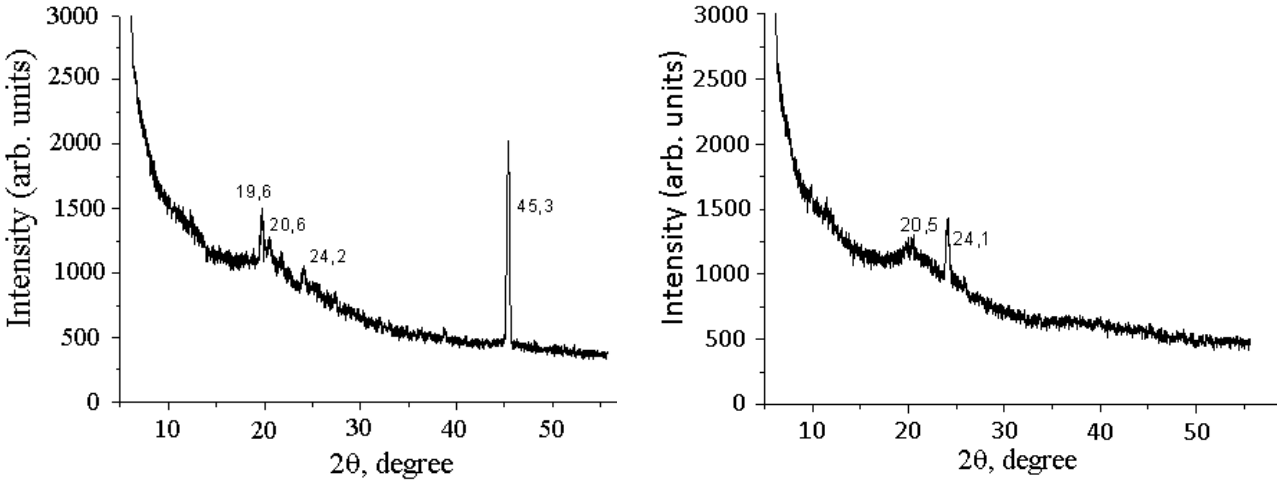
indicate on the identical thickness of the PAn films formed on the surfaces of different WE.



a *b*

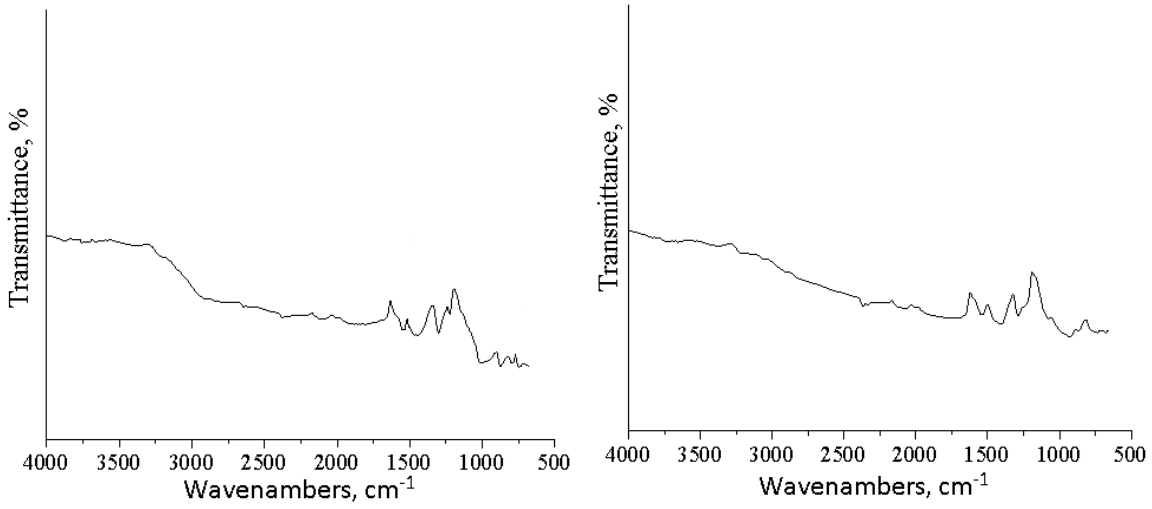
Figure 3: CV curver of PAn deposition in potentiodynamic mode on the surface of Al (*a*) and $Al_{87}Ni_8Y_4Dy_1$ (*b*) WEs

The the diffraction peaks at 2θ = 20.6 and 24.2° (Fig. 4, *a*) and 2θ = 20.5 and 24.1° (Fig. 4, *b*) on the received X-ray diffraction patterns of the samples indicates that the PAn deposited respectively on the surface of Al and AlNiYDy working electrodes is crystalline [6, 7]. Peaks at 2θ = 19.6 and 45.3° has been referred to Al.



a *b*

Figure 4: XRD patterns of PAn PAn films deposited on the surface of Al (*a*) and $Al_{87}Ni_8Y_4Dy_1$ (*b*) WEs



a *b*

Figure 5: FTIR spectra of PAn films deposited on the surface of Al (*a*) and $Al_{87}Ni_8Y_4Dy_1$ (*b*) WEs

Table 1 – The main characteristic bands and wavenumbers of the vibrations of atomic groups of the PAn samples

Зразок	Wavenumbers of the vibrations of atomic groups, cm^{-1}							
	N=*Q*=N_v	N−*B*−N_v	C−N_v	C−$N^{+\bullet}{}_v$	C−$N^{+}{}_v$	SO_4^{2-}	B–NH–Q or B–NH–B	C−H_n
Al/PAn	1538.5	1435.3	1286.1	1208.6	1133.7	1002.9	931.2	779.8
AlNiYDy/ PAn	1539.8	1404.4	1281.5	1212.1	1067.9	1002.3	926.5	723.5

The form of FTIR spectra (Fig. 5) and position of characteristic bands (Table 1) confirms that PAn deposited on the surface of used WEs are in the form of emeraldine salt of sulfuric acid [8].

Conclusions

Thus, the results of the studies indicates the influence of the nature (morphology and composition) of used working electrodes on the properties of PAn films formed on their surface. In particular, the morphology of the PAn films can changes from rod-like aggregates (on the aluminium electrode) to closed fibrillar structures (on the Al87Ni8Y4Dy1 electrode). In the same time, the crystallinity of the PAn produced on the AMA electrode is higher in comparison to crystallinity of samples deposited on the aluminium electrode.

References

[1] Ćirić-Marjanović G. Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications // Synth. Met. 2013. Vol. 177. P. 1–47.

[2] Kuntyi O., Yatsyshyn M., Zozulya G., Dobrovets'ka O., Reshetnyak O. Electrochemical synthesis of metallic nanoparticles and nanocomposite / O. Kuntyi, O. Reshetnyak (Eds.). Lviv: Publishing House of Lviv Polytechnic National University. 2019. 288 p. (in Ukrainian).

[3] Yatsyshyn M. M., Boichyshyn L. M., Demchyna I. I., Nosenko V. K. Electrochemical Oxidation of Aniline on the Surface of an Amorphous Metal Alloy $Al_{87}Ni_8Y_5$ // Russ. J. Electrochem. 2012. Vol. 48. P. 502–508.

[4] Reshetnyak O. V., Yatsyshyn M. M. Chapter 8. Corrosion Protection of Aluminum and Al-Based Alloys by Polyaniline and Its Composites / Computational and Experimental Analysis of Functional Materials // Oleksandr V. Reshetnyak, Gennady E. Zaikov (Eds.) [Series: AAP Research Notes on Polymer Engineering Science and Technology]. – Toronto, New Jersey: Apple Academic Press, CRC Press (Taylor & Francis Group). 2017. P. 287–329.

[5] Hnizdiukh Yu. A., M.M. Yatsyshyn M. M., Reshetnyak O. V. Chapter 12. Surface Modification of Polymeric Materials by Polyaniline and Application of Polyaniline/Polymeric Composites / Computational and Experimental Analysis of Functional Materials // Oleksandr V. Reshetnyak, Gennady E. Zaikov (Eds.) [Series: AAP Research Notes on Polymer Engineering Science and Technology]. – Toronto, New Jersey: Apple Academic Press, CRC Press (Taylor & Francis Group). 2017. P. 423–472.

[6] Yatsyshyn M. M., Boichyshyn L. M., Demchyna I. I., Hnizdiukh Yu.A. Chapter 2. Morphology of Polyaniline's Films Electrochemically Deposited on the Surface of Al-Based Amorphous Metal Alloys / Computational and Experimental Analysis of Functional Materials // Oleksandr V. Reshetnyak, Gennady E. Zaikov (Eds.) [Series: AAP Research Notes on Polymer Engineering Science and Technology]. – Toronto, New Jersey: Apple Academic Press, CRC Press (Taylor@ Francis Group). 2017. P. 61–91.

[7] Yatsyshyn M. M., Boichyshyn L. M., Koval'chuk E. P., Demchyna I. I. Serkiz, R. Ya., Demchenko P. Yu. The morphology of the polyaniline films on the surface of $Al_{87}Ni_8Y_5$ amorphous metallic alloy // Chem., Phys. Texnol. Surf. 2012. Vol 3. P. 74–81.

[8] Yatsyshyn M. M., Demchyna I. I., Mudry S. I., Serkiz R. Ya. Morphology of the Deposited Electrochemically in Potentiodynamic Mode on the

Surface of $Al_{87}Ni_8(REE)_5$ Amorphous Metallic Alloys Polyaniline Film // PCSS. 2013. Vol. 3. P. 593–601.