



Synthesis of Hybrid Nanocomposite Based on PbO₂ and Polyaniline Coated onto Stainless Steel by Cyclic Voltammetry

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A hybrid nanocomposite based on PbO₂ and polyaniline (PbO₂-PANi) coated onto stainless steel by cyclic voltammetry was investigated. It was found that PbO₂ exists in both α and β -modifications by X-ray diffraction and cyclic voltammogram, but it leans toward β -form. The adsorption of N-H group as well as the presence of benzenoid and quinonoid ring vibrations on IR-spectrum asserts that polyaniline was successfully co-electrodeposited with PbO₂ and created a composite of nanostructured PbO₂-PANi. This was clearly evidenced by SEM and TEM images. Its thermal stability was higher than that of lead dioxide alone due to the presence of polyaniline in composite matrix resulting particle size in nano range which affected significantly by scan rate during synthesizing process.

Key Words: PbO₂-PANi composite, Cyclic voltammetry, Co-electrodeposition, Nanostructure.

INTRODUCTION

Currently, there is a big considerable interest in fabricating nanostructured organic-inorganic hybrid materials which based on conducting polymers [polyaniline, polypyrrole, poly(N-vinylcarbazole), polythiophene] and inorganic components (such as clay, carbon materials, metal oxides)¹⁻⁴. These materials were prepared by various synthetic techniques and possessing well-defined intercalation properties for electrocatalytic effects and electro-analytical applications. Among them, lead dioxide polyaniline composite may be significantly considered as a good electrocatalytic material for oxidation reaction of organic compounds due to following reasons:

Firstly, polyaniline (PANi) is a non-toxic, inexpensive and environmental stable conducting polymer. It has an excellent electrocatalytic activity for oxidation process such as methanol oxidation because of having nanostructure⁵. Otherwise, PANi could affect the formation of α -PbO₂ and β -PbO₂ structures⁶ that may be leading to improving the electrocatalytic activity of that hybrid organic-inorganic material (PANi-PbO₂).

Secondly, PbO₂ is the cheapest metal-oxide material for anode process such as ozone production⁷ or decomposition of organic compounds⁸. It is a favourite electrocatalytic material in view of its high electrical conductivity, large oxygen overpotential and chemical inertness in applications for electrocatalytic oxidation⁹⁻¹¹.

Because of both above mentioned reasons, in this work, we tried to synthesize nanostructured PbO₂-PANi composites

by cyclic voltammetry on stainless steel and characterize their physicochemical properties.

EXPERIMENTAL

Analytical grade nitric acid, Cu(NO₃)₂, Pb(NO₃)₂ and ethylene glycol (Merck) were used without any purification. Aniline (Merck) was fresh distilled under-water vacuum condition at about 120 °C before using. The cyclic voltammetric method was applied to electrosynthesize PbO₂-PANi composite and PbO₂ as well for comparison. Electrodeposition of those layers was carried out by cyclic voltammetry on electrochemical workstation system IM6 from Zahner Elektrik unit (Germany) in the voltage range from 1.2-1.7 V *versus* Ag|AgCl| saturated KCl electrode. The current-potential curves (Fig. 2) obtained by the application of a triangular impulse of potential was shown in Fig. 1.

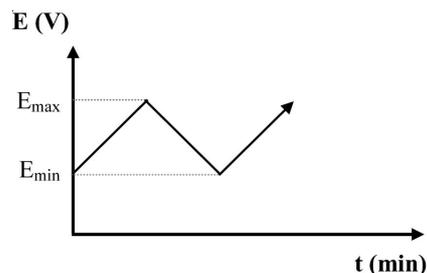


Fig. 1. Variation of applied potential with time in cyclic voltammetry shows the maximum (E_{max}) and minimum (E_{min}) potentials. The scan rate $|dE/dt| = v$

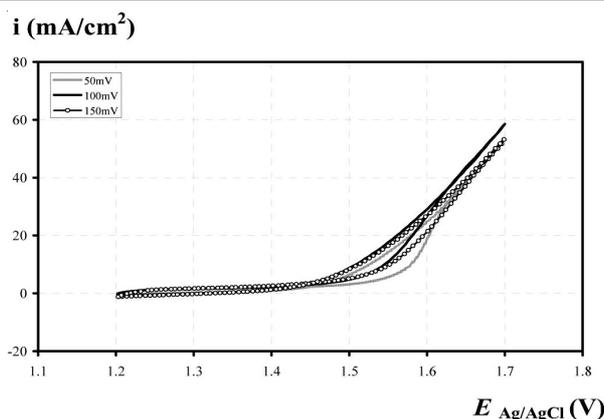


Fig. 2. Current-potential curves in the preparing stage of PbO_2 -PANi electrode from solution of $0.5\text{M Pb(NO}_3)_2 + 0.1\text{M HNO}_3 + 0.05\text{ Cu(NO}_3)_2 + 0.1\text{M ethylenglycol} + 0.005\text{M aniline}$ at different scan rates

General procedure: Firstly, the stainless steel electrode (Φ 7 mm) was mechanically polished with smooth sand paper, washed and rinsed by distilled water, then it was electrochemically treated in 60 g/L NaOH alkaline solution. The next step was electrodeposition of PbO_2 -PANi composites on above treated stainless steel electrodes by cyclic voltammetric technique from prepared solution of $0.5\text{M Pb(NO}_3)_2 + 0.1\text{M HNO}_3 + 0.05\text{M Cu(NO}_3)_2 + 0.1\text{M ethylene glycol} + 0.005\text{M aniline}$, which purged with argon to remove oxygen. Scan rate was varied from 50-150 mV/s in the above given potential area and the film thickness was kept stable at 300 cycles during synthesis process. After finishing, those films were washed by distilled water, immersed in acetone to remove the excess of aniline and then brought to characterize their physicochemical properties.

Detection method: The structure of film layer was carried out by infrared spectrum on IMPACT 410-Nicolet unit. The surface morphology of coatings was examined by SEM on an equipment FE-SEM Hitachi S-4800 (Japan) and TEM on a Jeol 200CX (Japan). The analysis of crystalline structure of those layers were performed by using an X-ray diffractometer D5000-Siemens (Germany) and an electrochemical workstation IM6 (Zahner-Elektrik, Germany). The thermal stability was analyzed by a thermal detector (Shimadzu TGA 50Hz, Japan).

RESULTS AND DISCUSSION

X-Ray diffraction: Fig. 3 shows X-ray pattern of samples from a to c for PbO_2 -PANi composites at different scan rates and d for PbO_2 at 100 mV/s. In the cases of a, b and c, it was found that the first peak located at 2θ degree of near 30 corresponding to α - PbO_2 modification as reported by previous workers^{12,13}. The second peak strongly oriented at 2θ of 62.4° indicated $\beta(301)$ - PbO_2 ¹⁴. Three peaks appeared on the diffractogram d at 2θ degrees of 32; 49.2 and 62.4 are signals for β - PbO_2 modification. No signal for α - PbO_2 modification was observed in this case. In another word, β structure was mainly formed due to using acid medium without aniline for synthesis.

One can observe that β - PbO_2 modification for the case of PbO_2 -PANi composites has more strongly orientation at 2θ of 62.4° in comparison with PbO_2 alone. It can be explained by the presence of PANi in composite matrix.

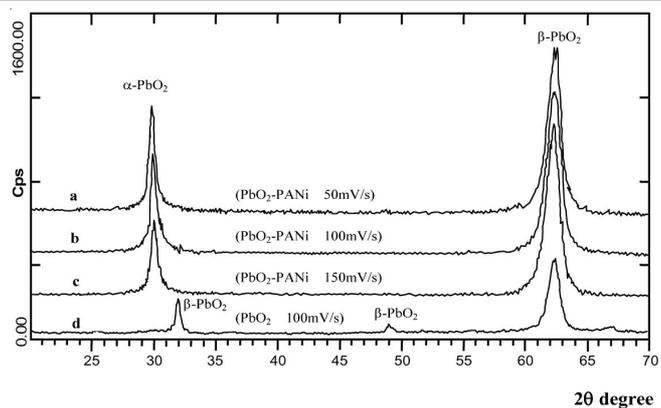


Fig. 3. X-Ray diffractograms of PbO_2 and PbO_2 -PANi composites prepared by cyclic voltammetric method (300 cycles) in acid medium at different scan rates

Morphology: There was a distinct difference on Fig. 4 between SEM micrographs of both PbO_2 -PANi composite and PbO_2 alone. It can be seen that the SEM image of PbO_2 (d) represented a typical pyramid shape of only β - PbO_2 modification which was compact together, similar to the result of Morales *et al.*¹⁵, but herein, there was a difference of the size of particles.

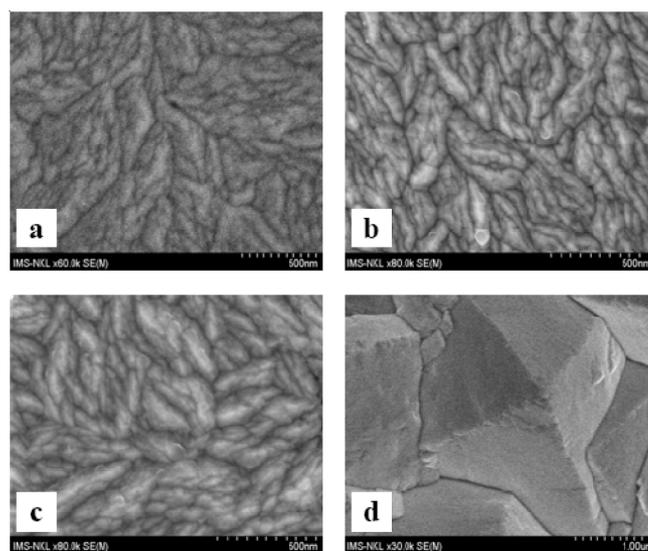


Fig. 4. SEM images of PbO_2 and PbO_2 -PANi composites prepared from acid medium by CV-method with 300 cycles. (a) PbO_2 -PANi at 50 mV/s; (b) PbO_2 -PANi at 100 mV/s; (c) PbO_2 -PANi at 150 mV/s; (d) PbO_2 at 100 mV/s

The SEM images of PbO_2 -PANi composites (from a to c) showed that a clearly mix of both PANi and lead dioxide in fine structure, which is evidenced by TEM images on Fig. 5. In comparison with PbO_2 alone under the same prepared condition (300 cycles, 100 mV/s), that composite had a structure in nano range due to co-deposition of PANi. The best uniform morphology was found for composite obtained from condition of 300 cycles at 100 mV/s.

Through SEM and TEM image observations, it showed that nanostructured PbO_2 -PANi composites have been synthesized by cyclic voltammetric method in acid environment at room temperature, to which belonged available both α - PbO_2 and β - PbO_2 modifications resulting by X-ray diffractograms.



Fig. 5. TEM images of PbO₂-PANi composites prepared by cyclic voltammetric method with 300 cycles at scan rate of 100 mV/s from acid medium

It can suggest that a suitable synthesis parameters for obtaining an optimal composite layer should be 300 cycles and 100 mV/s.

Cyclic voltammogram: A cyclic voltammogram on Fig. 6 was taken in cathodic direction at a scan rate of 100 mV/s in 0.5M H₂SO₄ for the sample (prepared by 300 cycles at 100 mV/s from acid medium) which have the more uniform nanostructure of all. It shows that two peaks like as reported by Thanh *et al.*¹⁶ at 1.258 and 1.180 V *versus* Ag/AgCl reference electrode corresponding to reduction of β - modification and α -PbO₂ to lead sulfate, respectively. It explained that not only β -modification but also α -modification of PbO₂ was successfully formed due to presence of PANi in composite matrix.

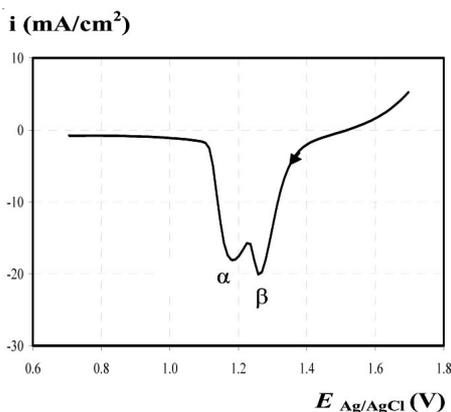


Fig. 6. Voltammogram of PbO₂-PANi composite in cathodic direction at scan rate of 100 mV/s in 0.5M H₂SO₄ (sample prepared by cyclic voltammetric method with 300 cycles at 100 mV/s)

Infrared spectrum: Fig. 7 shows the spectrum of the PbO₂-PANi composite prepared by cyclic voltammetry in acid medium at scan rate of 100 mV/s. It exhibits clearly the presence of benzoid and quinoid ring vibrations at 1626 and

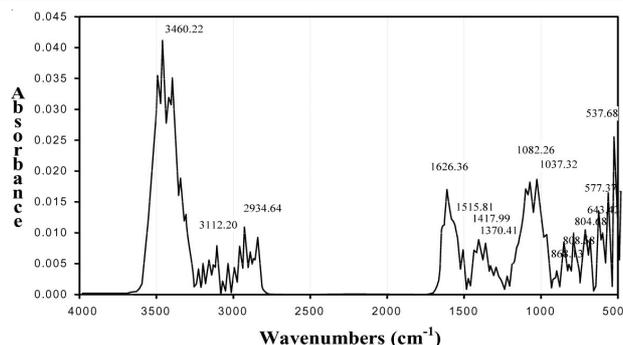


Fig. 7. IR-spectrum of PbO₂-PANi composite (prepared by cyclic voltammetric method at scan rate of 100 mV/s from acid medium)

1515 cm⁻¹, respectively. The band from 3500-3300 cm⁻¹ is assigned to the N-H stretching mode, from 3112-2850 cm⁻¹ (aromatic C-H), from 1417-1370 cm⁻¹ (-N=quinoid=N-). The signals at 1082 and 1037 cm⁻¹ were determined due to the C-N⁺ group. The peaks over 800 cm⁻¹ were confirmed due to the absorption of the N-H group. These vibration signals were similar in reported literatures^{17,18} which explained that PANi in emeraldin form was existed in composite matrix due to co-electrodeposition with PbO₂.

Thermal analysis: The physical dehydration of both materials occurred at temperature range from 300 to 450 °C. The decomposition masses at 575 °C were about 5.2 and 4.8 % for PbO₂ and PbO₂-PANi composite, respectively. From temperature of 575 to 900 °C, the decomposition per cent of composite was 2.785 %, a little less in comparing to lead dioxide alone (3.461 %). It means that this composite was more thermal stable than lead dioxide due to presence of PANi in composite matrix.

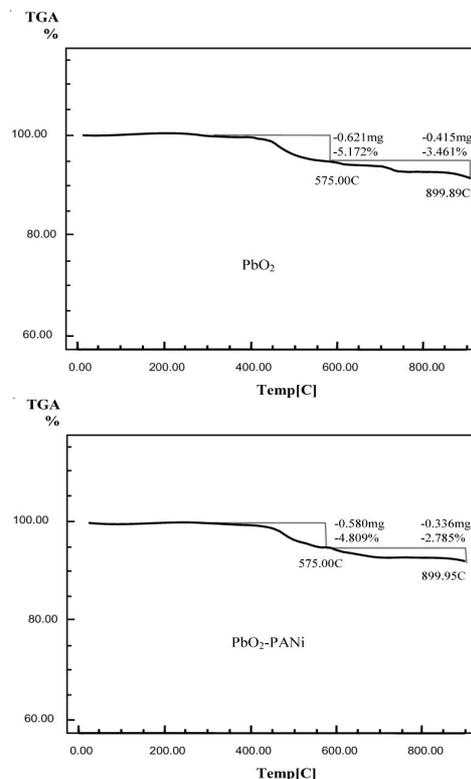


Fig. 8. TG diagrams of PbO₂ and PbO₂-PANi composite prepared by cyclic voltammetric method with 300 cycles at scan rate of 100 mV/s from acid medium

Conclusion

The present experimental results clearly indicate that nanostructured PbO₂-PANi composites have been successfully gained by cyclic voltammetric technique. The best uniform one among them was found at a scan rate of 100 mV/s (300 cycles) from acid medium under room temperature, in which both α -PbO₂ and β -PbO₂ modifications were formed simultaneously. The conducting polyaniline matrix containing lead dioxide formed together as a composite that having nanostructure and better thermal stability in comparing to lead dioxide alone.

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