

Electrocatalysis of Polyaniline Formation by PbO₂ in Acetonitrile

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ABSTRACT: Electrocatalytic effects on electropolymerization of aniline were investigated. It was determined that surface catalysis by β -PbO₂ causes formation of higher amounts of polyaniline than catalysis by α -PbO₂ and Pb²⁺ ions. β -PbO₂ surfaces decreased the upper potential limit of

aniline electropolymerization about 400 mV. The catalytic effect of PbO₂ is highly dependent upon the crystal structure of PbO₂. Dry conductivity values of polyaniline samples obtained under different conditions were also compared. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 599–605, 2003

INTRODUCTION

Electropolymerization of aniline in acetonitrile can be enhanced by the availability of protons in the medium.^{1,2} Anilinium cation radicals that initiate and propagate polyaniline formation can be generated chemically as well as electrochemically under these conditions. In addition to this autocatalytic behavior, we have reported the catalytic action of cupric ions and thiophene cation radicals during the formation of the polyaniline that results in a considerable improvements in the conductivity values of electrodeposited film.^{3,4} Cogenerating of cupric ions or thiophene cation radicals, together with aniline cation radicals, causes chemical oxidation of the oligomeric and polymeric species of aniline as well as the oxidation of the monomer. This catalytic process apparently causes a higher degree of conjugation in the polymer obtained.

PbO₂ has proven to be a good anode material for many chemical oxidations due to its electrical resistivity, good chemical stability, and high oxygen overpotential.⁵ PbO₂ anodes that may be readily electrodeposited are cheaper than platinum and able to withstand prolonged high positive potentials more effectively than graphite that undergoes degradation. Two forms of PbO₂ are present. α -PbO₂ has an orthorhombic, β -PbO₂ has a tetragonal structure.⁶ Lead dioxide shows electrical conductivity similar to that of the metals. α -PbO₂ has a lower electron mobility and higher electron concentration compared to those of β -PbO₂. The effect of the electron mobility overcompensates that of the electron concentration so that the

conductivity of α -PbO₂ is almost one order of magnitude lower than that of β -PbO₂.⁷ In O₂ evolution, the β -form is known to be much more electrocatalytically active than the α -form.⁸ The phase composition of PbO₂ may depend on many parameters such as solution composition, temperature, current density, mass transport conditions, and the choice of the substrate. α and β -PbO₂ may be distinguished from each other by means of X-ray diffraction patterns that are extensively used to estimate the proportions of the polymorphs in a mixture of the two.⁹ The degree of the crystallinity or the amount of amorphous form can be estimated by the halfwidth of the diffraction lines. The halfwidth decreases as the degree of crystallinity increases.¹⁰

Recently, we have reported the results of a constant current deposition of PbO₂ layers in acetonitrile medium.¹¹ The polymorphic composition and degree of crystallinity can be controlled by the water content and electrolyte contents of the electrolysis solution and by the applied current density value. The highest conductivity was measured for the PbO₂ deposits that were produced with water content of 6 M and 100 mM Pb(ClO₄)₂ solutions in acetonitrile/0.1 M tetrabutylammonium perchlorate (TBAP) with an applied current density of 4 mA/cm². The degree of the crystallinity and the conductivity of electrodeposited PbO₂ reached its maximum values under these conditions. It is the aim of this study to use these surfaces as electrodes in polyaniline formation.

EXPERIMENTAL

The procedure used to purify acetonitrile (Merck) has been described elsewhere.¹² Aniline (Merck) was vacuum distilled and kept at -10°C in darkness. Tetrabutyl ammonium perchlorate (TBAP) was prepared by

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TABLE I
Change of Charge Passed during the Electrooxidation of Polyaniline with Crystal Structure of PbO₂ When Water Concentration in Electrodeposition Solution of PbO₂ is Changed

Water Conc. in Acetonitrile for Electrodeposition of PbO ₂ (mol/L)	Crystal Structure of PbO ₂			Charge Passed during the Electrooxidation of Polyaniline (C × 10 ⁴)
	%α	%β	Conduc.(S/cm)	
0.3	5	95	16	2.0
1.0	5	95	114	4.5
2.0	2	98	116	5.6
4.0	2	98	170	11.1
6.0	1	99	300	17.3
8.0	2	98	230	12.7
15.0	4	96	21	4.2
25.0	3	97	23	4.1
55.5	3	97	22	2.1

Current Density was 4 mA/cm², Pb(ClO₄)₂ Conc. was 100 mM for Electrodeposition of PbO₂. Potential range for electropolymerization of Aniline was -0.4 ± 1.9 V.

TABLE II
Change of Charge Passed during the Electrooxidation of Polyaniline with Crystal Structure of PbO₂ When Current Density for Electrodeposition of PbO₂ Is Changed

Current Density for Electrodeposition of PbO ₂ (mA/cm ²)	Crystal Structure of PbO ₂			Charge Passed during the Electrooxidation of Polyaniline (C × 10 ⁴)
	%α	%β	Conduc.(S/cm)	
2.5	4	96	210	14.8
4.0	1	99	300	17.3
10.0	3	97	195	11.2
25.0	2	98	102	11.7
50.0		100	93	12.7
100.0		100	22	2.8

Water Conc. was 6 M and Pb(ClO₄)₂ conc. was 100 mM for Electrodeposition of PbO₂. Potential range for electropolymerization of aniline was -0.4 ± 1.9 V.

TABLE III
Change of Charge Passed during the Electrooxidation of Polyaniline with Crystal Structure of PbO₂ When Current Density for Electrodeposition of PbO₂ Is Changed

Pb ²⁺ Conc. in Electrodeposition Solution (mol/L)	Crystal Structure of PbO ₂			Charge Passed during the Electrooxidation of Polyaniline (C × 10 ⁴)
	%α	%β	Conduc.(S/cm)	
50.0	39	61	47	4.1
75.0	3	97	300	13.0
100.0	1	99	300	17.3
150.0	12	88	125	4.9
200.0	68	32	14	2.2

Water conc. was 6 M, and current density was 4 mA/cm² for electrodeposition of PbO₂ (Potential range for electropolymerization of aniline was -0.4 ± 1.9 V).

TABLE IV
Change of Charge Passed during the Electrooxidation of Polyaniline with Crystal Structure of PbO₂ When Acid Concentration in Electrodeposition of PbO₂ Is Changed

Acid Conc. in Acetonitrile (mol/L)	Crystal Structure of PbO ₂			Charge Passed during the Electrooxidation of Polyaniline (C × 10 ⁴)
	%α	%β	Conduc.(S/cm)	
0.0	1	99	300	17.3
0.1	4	96	183	12.6
1.0	16	84	17	5.2
2.0	28	72	13	3.8

Water conc. was 6 M, Pb(ClO₄)₂ conc. was 100 mM, and current density was 4 mA/cm² for electrodeposition of PbO₂. Potential range for electropolymerization of aniline was -0.4 V. ± 1.9 V.

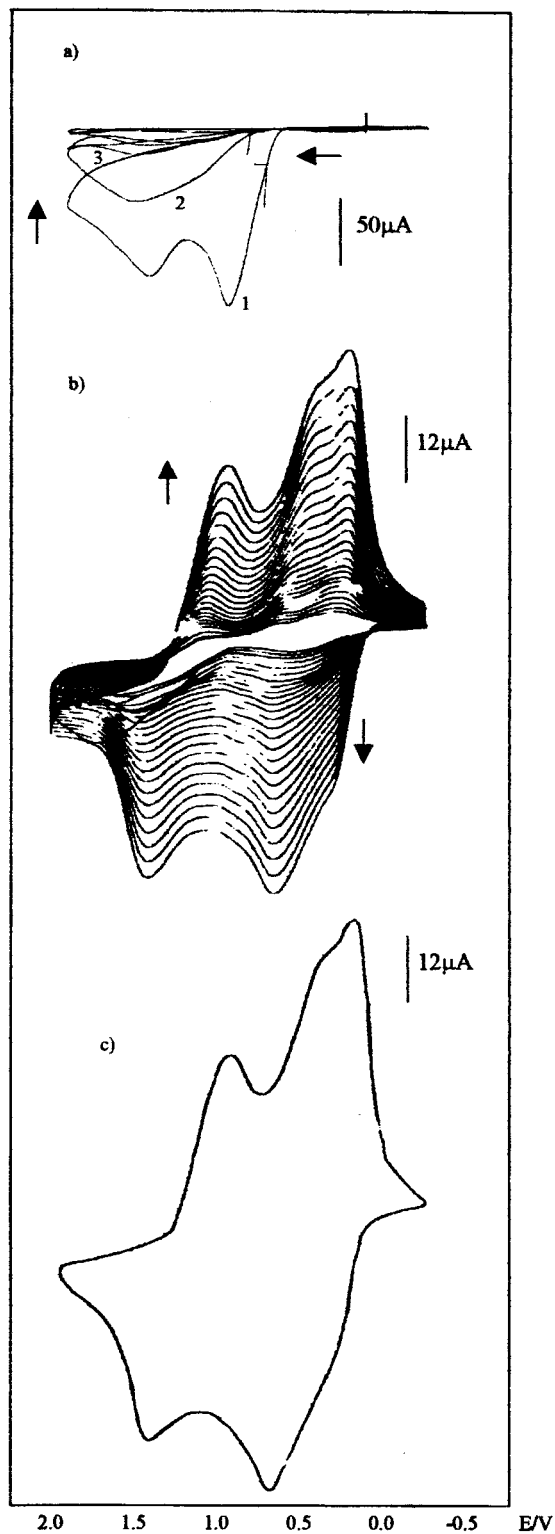


Figure 1 (a) Multisweep cyclic voltammograms during the oxidation of aniline in the electropolymerization solution. (b) Multisweep cyclic voltammograms taken during the growth of polyaniline. (c) Cyclic voltammogram of the polyaniline film in a blank solution (working electrode was β -PbO₂. Potential range was -0.4 ± 1.9 V).

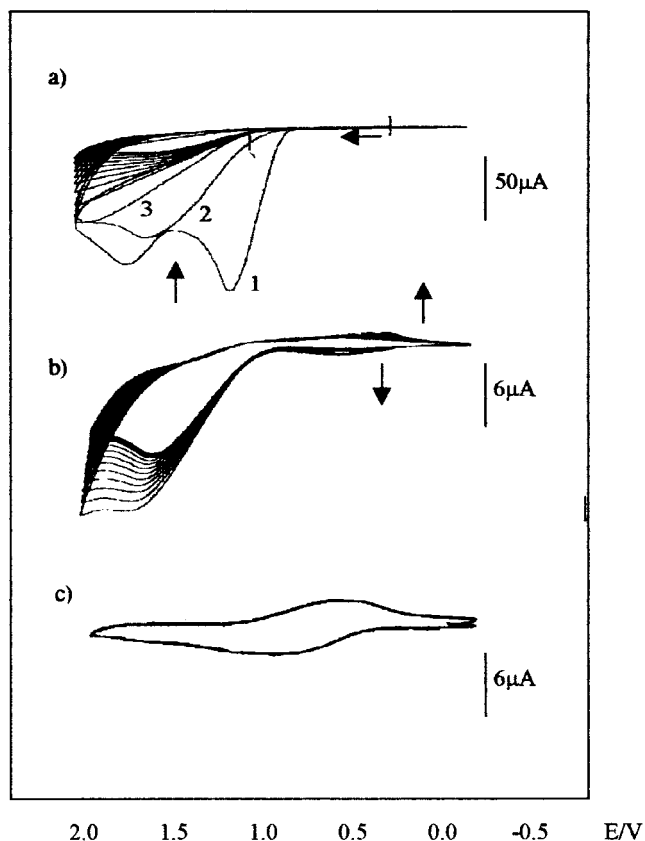


Figure 2 (a) Multisweep cyclic voltammograms during the oxidation of aniline in the electropolymerization solution. (b) Multisweep cyclic voltammograms taken during the growth of polyaniline. (c) Cyclic voltammogram of the polyaniline film in a blank solution (working electrode was Pt and potential range was -0.4 ± 1.9 V).

reacting concentrated perchloric acid solution (Analar) with a 40% aqueous solution of tetrabutylammonium hydroxide (Aldrich). It recrystallized from ethanol several times and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120°C. Lead perchlorate [Pb(ClO₄)₂] was prepared by concentrated perchloric acid with lead monoxide (Analar). All electrochemical experiments were carried out under a nitrogen (BOS) atmosphere. The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode [Ag,AgCl(sat)] and the counter electrode (Pt spiral). The acetonitrile + 0.1 M TBAP solution in the reference electrode compartment was saturated with AgCl. The working electrode was a platinum disk (0.0132 cm²). Pt foil (3 cm²) electrode was used for electrodeposition of PbO₂ and for preparing polyaniline macrosamples for conductivity measurements. Lead wire was used as a working electrode for electrooxidative production. The electrodes were rinsed with acetonitrile and dried before use.

Polyaniline samples were prepared by the successive potential cycling, and could be easily peeled off

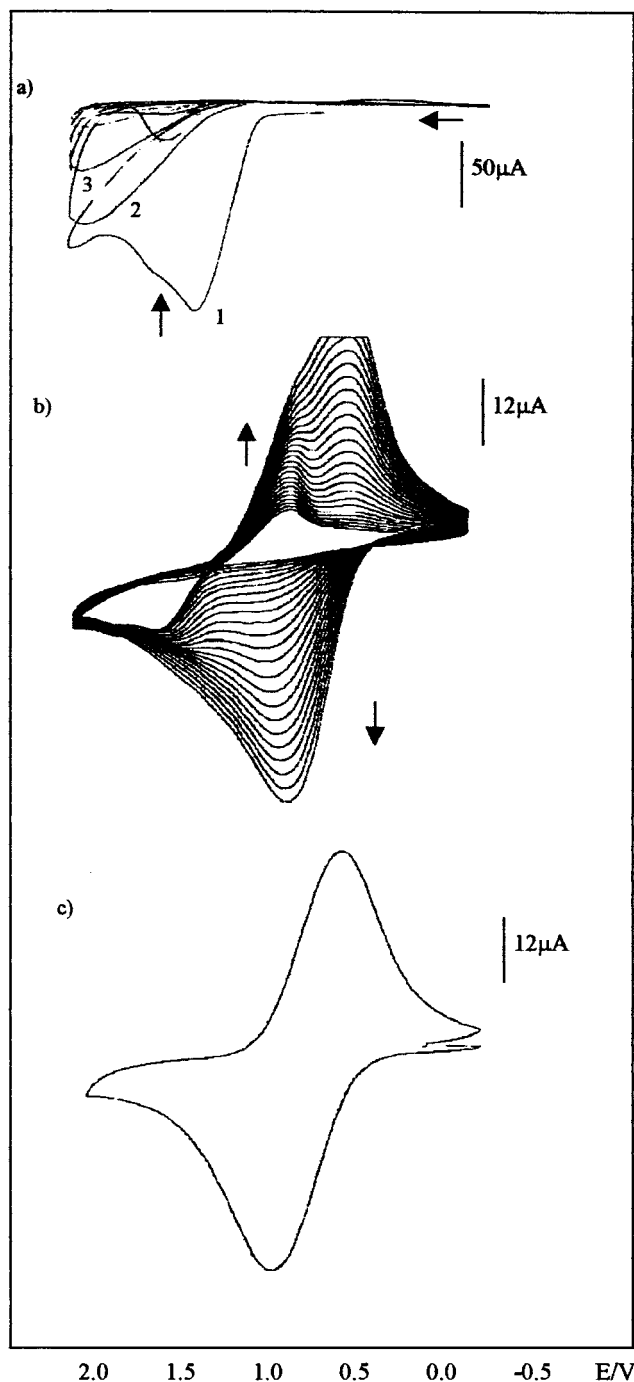


Figure 3 (a) Multisweep cyclic voltammograms during the oxidation of aniline in the electropolymerization solution. (b) Multisweep cyclic voltammograms taken during the growth of polyaniline. (c) Cyclic voltammogram of the polyaniline film in a blank solution (working electrode was β - PbO_2 , and potential range was -0.4 ± 1.9 V).

from the hard PbO_2 surfaces. Polyaniline films were washed with acetonitrile and vacuum dried for 1 h; dry pellets were prepared from the films under a pressure of 5 tons cm^{-2} for conductivity measurements. The dry conductivity values were measured using the four-probe measuring technique at room

temperature. The ohmic contact to the films was made with Au-plated four probe tips, and at least 10 different current values were used in the measurement of the potential drops. The atomic absorption method was used to determine whether any conducting lead dioxide was incorporated into polyaniline films. It was found that these films contained 0.1–0.2% lead, which is not a significant amount to contribute to the dry conductivity values of polyaniline films.

The 99% β - PbO_2 layer on the Pt surface was deposited from a solution that had 100 mM $\text{Pb}(\text{ClO}_4)_2$ and 6 M water in acetonitrile/0.1 M TBAP at a 4.0 mA/cm^2 current density. The 100% (pure) β - PbO_2 surface was electrodeposited from 6 M H_2O and 100 mM $\text{Pb}(\text{ClO}_4)_2$ solution in acetonitrile/0.1 M TBAP with a current density of 50.0 mA/cm^2 . The 100% (pure) α - PbO_2 film was prepared using 100 mM aqueous $\text{Pb}(\text{ClO}_4)_2$ solution containing saturated amount of PbO with a current density of 4 mA/cm^2 .

Electropolymerization solution was prepared by adding 100 mM aniline to acetonitrile/0.1 M TBAP. Blank solution contained acetonitrile and 0.1 M TBAP.

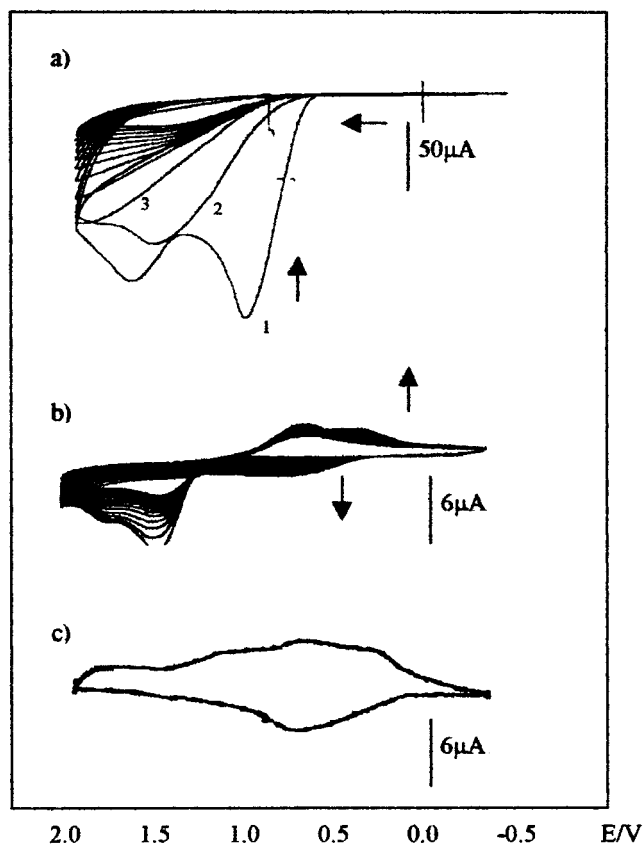


Figure 4 (a) Multisweep cyclic voltammograms during the oxidation of aniline in the electropolymerization solution. (b) Multisweep cyclic voltammograms taken during the growth of polyaniline. (c) Cyclic voltammogram of the polyaniline film in a blank solution (working electrode was α - PbO_2 , and potential range was -0.4 ± 1.9 V).

TABLE V
Comparison of the Polyaniline Growth Rate
on Different Surfaces

	Increase in Oxidation Peak Current of Polyaniline Film (μA)			
	99% β -PbO ₂ Surface	β -PbO ₂ Surface	α -PbO ₂ Surface	Pt Surface
Between 1 th and 10 th cycles	2,4	2,8	—	—
Between 10 th and 20 th cycles	12.1	11.4	0.76	0.63
Between 20 th and 30 th cycles	23.9	18.9	1.33	1.11
Between 30 th and 40 th cycles	26.1	22.4	1.84	1.53
Between 40 th and 50 th cycles	26.4	22.5	1.83	1.51
Between 50 th and 60 th cycles	26.3	22.4	1.83	1.52

The electrochemical instrumentation consisted of a PAR model 173 potentiostat–galvanostat coupled to a PAR model 175 universal programmer and a PAR model 179 digital coulometer, and also a PAR model 273 potentiostat–galvanostat.

Lead analysis was carried out by Shimadzu (AA-6800) atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Electrode performance of the PbO₂ surfaces is known to be strongly dependent upon its phase composition and the degree of crystallinity. When the polymorphic composition and degree of crystallinity of PbO₂ electrodes were changed by controlling the parameters such as water concentration, electrolyte contents of the electrolysis solution, the applied current density value, and the amount of the acid; the amount and the degree of oxidation of the corresponding polyaniline formed changed accordingly. To compare polyaniline amounts formed; charge passed during the second oxidative cycles of the cyclic voltammograms in blank solution was used, because there was no apparent loss of electroactivity of the film during the first scan. The results of this comparison are listed in Tables I, II, III, and IV. It was determined from these results that the 99% β -PbO₂ film produced the maximum amount of polyaniline.

Figures 1(a) and 2(a) shows the multicycle electrooxidation voltammograms of aniline on the 99% β -PbO₂ electrode and platinum electrode in the electropolymerization solution. Figures 1(b) and 2(b) show the cyclic voltammograms during the growth of films in electropolymerization solution. Multisweep scans in Figures 1(a) and 2(a) clearly show that a faster decrease in the current density in cyclic voltammograms of aniline is observed, and Figures 1(b) and 2(b)

show that faster growth of the polyaniline film occurs on the 99% β -PbO₂ compared to that on the Pt surface. This is further supported by the comparison of the yields of polyaniline formation from the charges or the peak intensities of the blank cyclic voltammetric peaks in Figures 1(c) and 2(c).

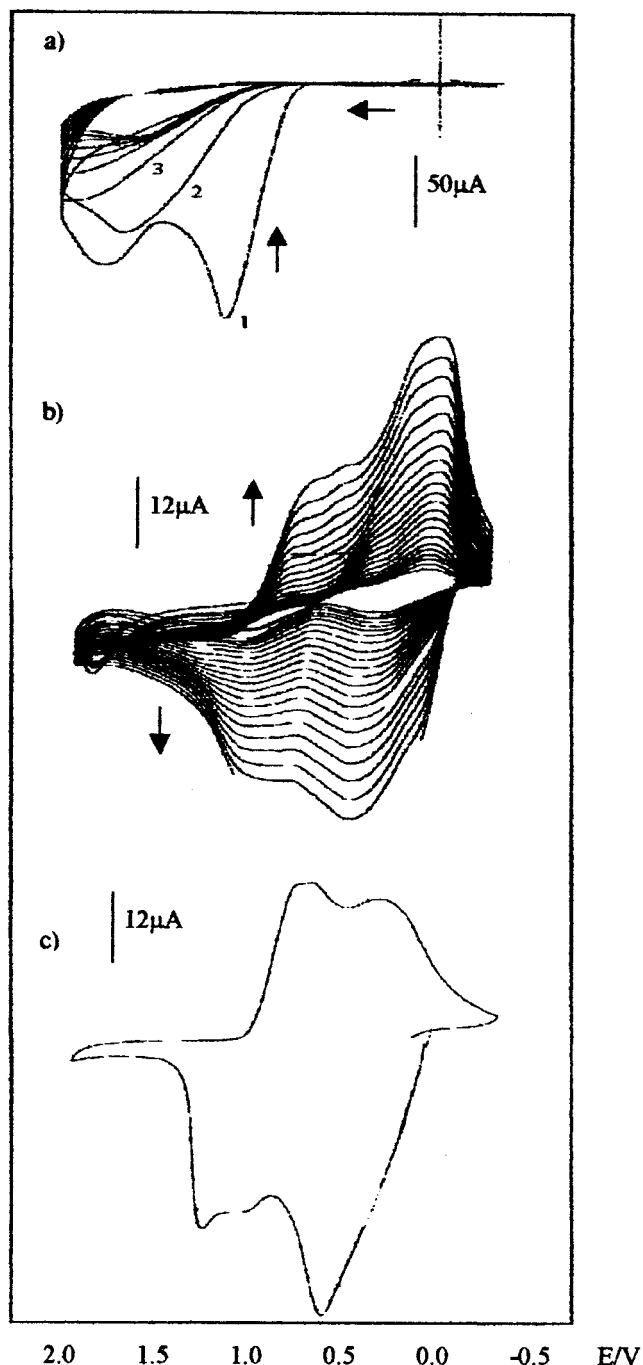


Figure 5 (a) Multisweep cyclic voltammograms during the oxidation of aniline in the electropolymerization solution. (b) Multisweep cyclic voltammograms taken during the growth of polyaniline. (c) Cyclic voltammogram of the polyaniline film in a blank solution (4 mM Pb²⁺ in electropolymerization solution, and potential range was -0.4 ± 1.9 V).

TABLE VI
Charge Comparison during the Electrooxidation of Polyaniline and Conductivity Values

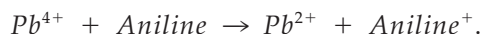
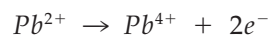
Catalyst	Charge Passed in Blank Solution within the Potential Range Indicated (C × 10 ⁴)					Dry Conductivities (S/cm)
	-0.4 ± 1.9 V	-0.4 ± 1.8 V	-0.4 V ± 1.7 V	-0.4 ± 1.6 V	-0.4 ± 1.5 V	-0.4 V ± 1.9 V
Surface catalysis						
%99 β-PbO ₂	17.3	9.8	5.3	1.5	1.0	0.88
Pure β-PbO ₂	12.7	4.1	—	—	—	0.085
Pure α-PbO ₂	1.3	—	—	—	—	—
Pt	1.1	—	—	—	—	0.17
Solution Catalysis						
1 mM Pb ²⁺	2.4	1.2	—	—	—	—
2 mM Pb ²⁺	5.9	3.3	—	—	—	—
4 mM Pb ²⁺	10.8	5.5	—	—	—	0.34

To understand the role of the type of the two polymorphs on the polyaniline formation pure α-PbO₂ and pure β-PbO₂ deposits were prepared electrolytically. Figures 3(a) and 4(a) shows the multicycle electrooxidation voltammograms of aniline on the pure β-PbO₂ electrode and the pure α-PbO₂ electrode in the electropolymerization solution. Figures 3(b) and 4(b) show the cyclic voltammograms during the growth of films in the electropolymerization solution. Figures 3(c) and 4(c) are the cyclic voltammograms of the respective grown polyaniline films in a blank solution. It is clear that the pure β-PbO₂ surface is a much better electrocatalyst for polyaniline formation than pure α-PbO₂ surface. This is evident from a faster decrease in current intensity of the cyclic voltammograms of aniline during electropolymerization and faster growth of polyaniline film on the β-PbO₂ surface [compare Figs. 3(a) and 4(a), 3(b) and 4(b)]. In other words, the initial nucleation of polyaniline formation occurs much faster on β-type surfaces than on α-PbO₂ and Pt surfaces. However, the heterogeneous catalytic effect does not extend beyond the first few layers on the polyaniline formation. This is probably because of the porous structure of the polyaniline formed on the PbO₂ surface. This is easily seen when one compares the current increases on the 99% β-PbO₂, β-PbO₂, α-PbO₂, and Pt surfaces during the various cyclic scans (Table V). The peak currents increase in successive potential cycles during the growth of the polyaniline films. The increase in peak current on the α-PbO₂ surface is about 1.2 times that on the Pt surface after the tenth cycle. On the other hand, the increase in peak current on β-type surfaces is about 15–22 times that on the Pt surface after the tenth cycle. Autocatalysis by polyaniline itself also has an important contribution to the polyaniline growth,² but this process occurs on Pt and α-PbO₂ surfaces as well. It is apparently a minor contribution to the growth compared to that caused by the surface catalysis on the β-type surfaces.

It was also observed that the phase composition of the PbO₂ electrodes causes the formation of different

polymeric forms of aniline. Pure β-PbO₂ electrode caused the formation of mostly quinoid rings (partially oxidized form of polyaniline); however, when the amount of β-content decreased, mostly benzenoid rings (partially reduced form of polyaniline) was obtained^{1,2} (compare Figs. 1 and 3).

Solution catalysis of the polyaniline formation by Pb²⁺ ions was also studied to compare surface catalysis with solution catalysis. Pb²⁺ (1 mM), 2 mM Pb²⁺, and 4 mM Pb²⁺ were added to the electropolymerization solution, respectively. After 4 mM Pb²⁺, a precipitate occurred in the electropolymerization solution due to reaction of Pb²⁺ with aniline. It was determined that more polyaniline was formed with increasing amounts of Pb²⁺ in the solution, but it never exceeded the amount of polyaniline formed on the 99% β-PbO₂ and the pure β-PbO₂ electrodes. Figure 5(a) shows the multicycle electrooxidation voltammograms of aniline in the 4 mM Pb²⁺/electropolymerization solution. Figure 5(b) shows the cyclic voltammogram during the growth of film in the 4 mM Pb²⁺/electropolymerization solution. Figure 5(c) is the cyclic voltammogram of the grown polyaniline film in a blank solution. During the electrooxidation of aniline, Pb²⁺ ions were oxidized to form Pb⁴⁺ ions. As a result of the electro-generated Pb⁴⁺ ions, aniline cation radicals were produced electrochemically as well.



It is interesting to note that the reduced form of polyaniline is always obtained during the solution catalysis by Pb²⁺ ions.

The fact that polyaniline has a porous structure is also evidenced by the results obtained with solution catalysis by Pb²⁺ ions. These ions diffuse through the pores of the polyaniline and are oxidized on the underlying Pt surface. Electrochemically generated Pb⁴⁺ ions oxidize the aniline and its oligomers, producing

the necessary cation radicals for polymer chain propagation. Because the PbO_2 surface is not completely covered by the polymer, porous structure prevails and catalytic centers are available during the whole period of polymer growth.

The upper positive limit for the polyaniline formation during a cyclic potential scan was also determined for both surface and solution catalysis. With increasing the β content of PbO_2 , this upper potential limit decreased. It decreased considerably with respect to platinum during the formation of polyaniline with the 99% β - PbO_2 (about 400 mV). During the solution catalysis of polyaniline film formation on the Pt surfaces by Pb^{2+} ions, the upper value of the potential for film formation decreased only for about 100 mV. The summary of a detailed comparison is presented in Table VI.

The dry conductivity values of polyaniline films under different conditions are also given in Table VI. The dry conductivity of polyaniline obtained on 99% β - PbO_2 is about five times greater than that obtained on the Pt surface. This means more conducting polyaniline chains are obtained on the 99% β - PbO_2 surface and excludes the surface area affect. If the faster growth of polyaniline were due to the greater surface area, one would expect to obtain similar dry conductivity values on the α - PbO_2 surface, which probably has a similar surface area. Even the catalysis caused by Pb^{2+} ions in solution produces polyaniline chains on the polymer-coated Pt surface with a dry conductivity value twice of that on the bare Pt surface.

The dry conductivity values of polyaniline films are also strongly affected by the phase composition and the degree of crystallinity of the PbO_2 surfaces and the oxidation state of the polyaniline formed. The pure

β - PbO_2 surface has a lesser degree of crystallinity than that of the 99% β - PbO_2 . In addition, the pure β - PbO_2 causes the formation of mostly polypyrroligrafin and polyemeraldine, as seen from the respective cyclic voltammograms.² Because of these two additional effects the dry conductivity value of polyaniline obtained on the pure β - PbO_2 is much less than that on the 99% β - PbO_2 .

It can be concluded from the above results that the β -type PbO_2 surfaces show an electrocatalytic effect on the electropolymerization of aniline. The 99% β - PbO_2 surface acts as a better electrocatalyst than the pure β - PbO_2 surface. It was also shown that the surface catalysis of the polyaniline formation by β -lead dioxide electrodes is more effective than the solution catalysis by Pb^{2+} ions.

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