ELECTROCHEMICAL OXIDATION OF TOXIC ORGANIC AROMATIC SUBSTANCES

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The results of the study of electrochemical oxidation of salicylic acid on PbO_2-based anodes for effective wastewater treatment from organic pollutants as well as the influence of various modifying additives of lead (IV) anode on the process of mineralization of salicylic acid have been summarized. It is established that in the destruction of salicylic acid in the first stage there occurs the accumulation of aromatic hydroxylation products, and during the total destruction - the destruction of the aromatic system to form aliphatic compounds takes place.

In order to determine the influence of deposition conditions and the composition of the anode materials based on lead dioxide on their electrocatalytic activity in respect to the oxidation of organic toxicants salicylic acid was selected as model aromatics.

Electronic absorption spectra of solutions at different electrolysis time were taken to determine the time of the disappearance of intermediate aromatic products and a change in the concentration of the initial compound.

It is shown that the use of PbO_2, deposited from methanesulfonate electrolytes and modified electrodes significantly reduces the conversion time of salicylic acid in aliphatic products compared to lead dioxide anodes obtained by traditional technology from nitrate bath. The highest degradation rate occurs at the anodes modified by bismuth.

Salicylic acid is one of the most common pollutants of wastewater. This acid is used in many pharmaceutical and cosmetic preparations. It is known to be produced by hydrolytic deacetylation of acetylsalicylic acid (aspirin), which is a major source of accumulation in wastewater. Thousands of tons of pharmaceuticals consumed annually worldwide are used in veterinary medicine and in agriculture. Due to inefficient destruction of pollutants sewage plants, quite a number of these substances were found in soil and even water. This necessitates the development of powerful methods for oxidation to effectively remove drugs and their metabolites from wastewater [1].

Water purification from salicylic acid is possible through oxidative destruction. There are different ways of salicylic acid oxidation of which the electrochemical oxidation is considered the most promising [2-4]. It is proved that the efficiency of oxidation depends on the material of the anode. The use of oxides as electrode materials in most cases is advantageous compared to metal electrodes, this allows a lower cost electrode and ensures to control occurring electrochemical processes due to change of the composition of oxide during its synthesis.

The aim of our work was to study the electrochemical destruction of salicylic acid on lead (IV) oxide-based anode materials.

Research Methodology

All chemicals were reagent grade. Platinized titanium was used as a substrate. Titanium sheet was treated as described in [5] before platinum layer depositing. Lead dioxide coatings were electrodeposited at an anodic current density of 10 mA cm^{-2} from nitrate/methanesulfonate electrolytes that contained 0.1M HNO_3/CH_3SO_3H, 0.1 M $Pb(NO_3)_2/Pb(CH_3SO_3)_2$ and 0.1 M $Bi(NO_3)_3$, $Ce(NO_3)_3$ as dopants.

X-ray powder diffraction data were collected on a STOE STADI P automatic diffractometer equipped with a linear PSD detector (transmission mode, $2\theta/\omega$-scan; Cu $K\alpha_1$ radiation, curved germanium (1 1 1) monochromator; 2θ-range $6.000 \leq 2\theta \leq 102.945$ °2θ with step 0.015 °2θ; PSD step 0.480 °2θ, scan time 50 s/step).

Qualitative and quantitative phase analysis was performed using the PowderCell program. For selected samples with a relatively high degree of crystallinity the Rietveld refinement was carried out using the FullProf.2k (version 5.40) program.

The electrooxidation of organic compounds was carried out in a divided cell at j_a= 50 mA cm^{-2}. The volume of the anolyte was 1300 cm^3. Solution, containing phosphate buffer (0.25 M Na_2HPO_4 + 0.1 M KH_2PO_4) + 2×10^{-4} M organic compound, (pH=6.55) was used as an electrolyte. Stainless steel was used as a cathode. Modified lead dioxide electrodes were used as anodes. The electrode surface area was 2.5 cm^2.

Analyses of the reaction products were conducted by HPLC using a Shimadzu RF-10A xL instrument equipped with an Ultraviolet SPD-20AV detector and a 30 cm Discovery® C18 column. The formation of colored compounds during electrolysis was followed by UV-visible spectroscopy using a UV mini 1240 Shimadzu spectrometer.

The composition and structure of intermediates was confirmed by HPLC using a Shimadzu RF-10A xL instrument equipped with a Ultraviolet SPD-20AV detector and a 30 cm Discovery® C18 column.

Since the action of iron(III) chloride on monohydric and polyhydric phenols in aqueous neutral or weakly acidic solutions gives the characteristic color, which does not depend, however, on the structure of phenols [6], a qualitative analysis of diluting solution with 1% solution of iron(III) chloride was conducted.

It is known that salicylic acid gives violet, hydroquinone, while 2,3-dihydroxybenzoic and 2,5-dihydroxybenzoic acids give blue color. If there are complexing groups in the ortho position to the phenolic groups, the color with iron(III) chloride appears both in water and alcohol medium, resulting in formation of complex iron salts. These complexing groups include mainly carbonyl (aldehyde and ketone), carboxyl, hydroxyl and alkoxyl, and sulpho-groups [6].

Results and Discussion

Since the electrodeposition of lead(IV) oxide occurs through the formation of chemisorbed oxygen-containing particles, the presence in the electrolyte of ionic dopants which can be adsorbed or form oxygen-containing compounds with these particles on the surface of the electrode, leads to changes in kinetic regularities of PbO_2 formation and physicochemical properties of coatings. The electrodeposition rate is affected by the composition of the electrolyte.

The typical morphology of lead(IV) oxide that was deposited from nitrate and methanesulfonate electrolytes is shown on Fig. 1. As one can see (Fig. 1a), the PbO_2 obtained from nitrate solutions is represented by a set of large polycrystalline blocks with no significant preferences in crystallographic orientation [5]. The use of methanesulfonate electrolytes leads to significant changes in the morphology of the coating (Fig. 1b). In this case, polycrystalline blocks are not formed and the surface is a mixture of randomly oriented fine-grained crystals of nano and submicron size with a uniform surface. The specific electrode surface increases by several fold. A similar phenomenon was observed when the polyelectrolyte and surfactant particles were included in the growing PbO_2 deposit [7].

In order to determine the influence of deposition conditions and the composition of the anode materials based on lead dioxide on their electrocatalytic activity in respect to the oxidation of organic toxicants salicylic acid was selected as model aromatics.

According to [4], quite a number of intermediates are produced during anodic oxidation of salicylic acid. The primary intermediates include dihydroxybenzoic acids.
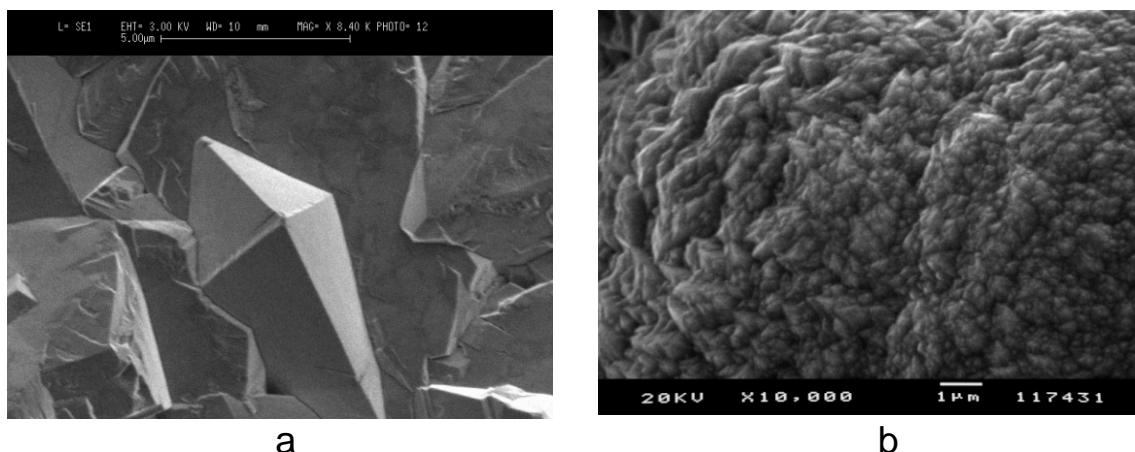

<div align="center">a   b</div>

Fig. 1. SEM micrographs of coatings, obtained from next solutions: a – 0.1 M Pb(NO$_3$)$_2$ +0.1 MHNO$_3$; b – 0.1M Pb(CH$_3$SO$_3$)$_2$ + 0.1M CH$_3$SO$_3$H

Electronic absorption spectra of solutions at different electrolysis time were taken in order to determine the time of the disappearance of intermediate aromatic products and a change in the concentration of the initial compound.

The initial solution of salicylic acid is characterized by a peak in the 290-300 nm region (Fig. 2). After 30 minutes of electrolysis the intensity of the peak decreases and a plateau at 250-270 nm appears due to the drop in the concentration of salicylic acid and the formation of intermediate aromatic products. Further increase in electrolysis time leads to the disappearance of the peak at 290-300 nm and reduced plateau at 250-270 nm due to the complete destruction of salicylic acid and intermediates. After 5.5 hours of electrolysis the complete conversion of aromatic compounds with the formation of only aliphatic products takes place.
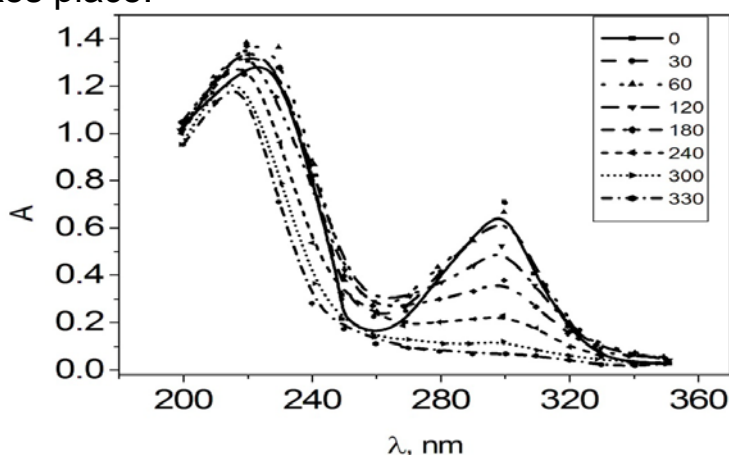

Fig. 2. The absorption spectra of salicylic acid solution (initial concentration 2 ×10^{-4}M) obtained at different time of electrolysis in a phosphate buffer on lead dioxide anode

Phenolic compounds are known to form intensely colored complex compounds with aqueous solutions of $FeCl_3$. And with the accumulation of hydroxyl groups in the ring as well as decarboxylation, the color of complexes changes from blue to purple then to blue or green [6]. We used this feature of phenol derivatives in order to deal with the products formed during oxidation. Salicylic acid forms a violet colored complex with $FeCl_3$. After 30 minutes of electrolysis the color of solution changed to blue-violet, indicating a partial destruction of salicylic acid and accumulation of 2,3-, 2,5-dihydroxybenzoic and trihydroxybenzoic acids. They give dark blue color with ferric chloride. After 2 hours the violet color completely disappeared and the solution became intensely blue, which, in our opinion, demonstrates the complete destruction of salicylic acid and hydroquinone accumulation, which is rapidly oxidized to benzoquinone. Over time, the color of the solution becomes blue, light blue and colorless, indicating the gradual destruction of aromatic products.

The process of oxidation of salicylic acid on lead dioxide anodes modified by bismuth lasts for 4 hours, which is 1.5 hours faster compared to nonmodified anodes, which is corroborated by kinetic studies. We have not seen the appearance of violet-blue color by using the qualitative reaction. After 30 minutes of electrolysis the solution was blue, after 60 minutes it was rich blue, and after 180 minutes the color almost disappeared.

Table 1 presents the phase composition of lead dioxide. In this case, structural factors play a significant role. The maximum electrocatalytic activity is achieved by increasing the proportion of α-phase, on the one hand, and increasing the crystalline zone of oxide on the other hand, which leads to increased amounts of oxygen-containing particles strongly bounded to the electrode surface that participate in the electrochemical oxidation of aromatic compounds [8].

Table 1. The phase composition of lead dioxide coatings depending on deposition conditions

Deposit	T/K	Content /wt.%/ α-PbO_2/β-PbO_2
PbO_2	282	59/41
PbO_2	298	90/10
PbO_2–Bi	282	5/95
PbO_2–Ce	298	83/17

The degradation rate is lower on lead dioxide anodes, modified by cerium ions. The complete destruction of aromatics ended after 5 hours. The test reaction for benzoic acid derivatives showed a similar color shift as in the case of anodes modified by bismuth.

Obviously, these processes proceed through the same intermediates and qualitatively are not different. But one can see different catalytic activity of modified and non-modified lead dioxide anodes.

The processes of electrochemical oxidation of the investigated organic compound on unmodified and modified lead dioxide electrodes occur qualitatively the same and differ only in the rate. This suggests the invariability of the mechanism of their oxidation on different materials that allows the correct comparison of their electrocatalytic activity.

Intermediates formed during the oxidation of salicylic acid depend on conditions of the oxidation. These intermediates are commonly α-, β-resorcinol acid, gallic acid, pyrocatechol, hydroquinone [4]. All of these compounds are oxidized to benzoquinones, which is further degraded into aliphatic acids – succinic, maleic, oxalic, etc. But the general stage of destruction of salicylic and sulfosalicylic acids is the aromatic nucleus hydroxylation and decarboxylation.

Hydroxylation occurs in the o- and p-position to the carboxyl group with the formation of isomeric dihydroxybenzoic acids. Decarboxylation of salicylic acid occurs on heating and leads to the formation of phenols.

Further oxidation leads to the formation of diketones and their oxidation through di- and monocarboxylic acid to carbon dioxide.

The rate of conversion of organic compounds depends on the nature of organics, on the one hand, and the nature of the anode material on the other hand. Experimental data show that there is no universal anode material on which the conversion rate would be maximized. In each case the choice of material was individual.

Conclusions

It has been found that the destruction of salicylic acid in the first stage occurs through the accumulation of aromatic hydroxylation products, and during the complete destruction – incineration to form aromatic aliphatic compounds.

It is shown that the use of PbO_2 deposited from methanesulfonate electrolytes and modified electrodes significantly reduces the conversion time of salicylic acid in aliphatic products compared to lead dioxide anodes obtained by the traditional technology from nitrate bath. The highest degradation rate occurs at the anodes modified by bismuth.

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