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*O. Shmychkova, T. Luk'yanenko, L. Dmitrikova, A. Velichenko***ELECTROOXIDATION OF 4-CLORPHENOL ON MODIFIED LEAD DIOXIDE ANODES****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

The electrochemical oxidation of 4-chlorophenol on lead dioxide anodes micromodified by ions of iron group has been investigated. As follows from the data obtained, the rate of oxidation of organic substances on the anode materials involved is proportional to the number of reactive oxygen species in the near-electrode zone (OH⁻radicals) formed during the electrolysis as intermediates in water oxidation and participating in subsequent homogeneous chemical reactions with organic substrates in the bulk. The O1s peak on X-Ray photoelectron spectra was used to evaluate the amount of inert and labile oxygen-containing particles on undoped and doped PbO₂. Doping of lead dioxide with nickel leads to a significant increase in the number of labile oxygen-containing particles on the surface of the electrode, while iron modification leads to the opposite effect – an increase in the amount of inert oxygen-containing particles. The anodic oxidation of 4-chlorophenol yields a rather large number of intermediate products. The main intermediates include benzoquinone and maleic acid which was confirmed by high-performance liquid chromatography. The micromodification of lead dioxide with metal ions of iron group leads to a significant change in the electrocatalytic activity of oxide materials. The activity grows in the following sequence of modifying ions: PbO₂<Co–PbO₂<Fe–PbO₂<Ni–PbO₂.

Keywords: lead dioxide, nitrate electrolyte, 4-chlorophenol, oxygen-containing radicals, O1S peak.

The main requirements for anodic materials are their high electrocatalytic activity and selectivity towards the target process, as well as long life during exploitation [1–3]. Since the implementation conditions and the nature of the target process are very different, there is no universal anode material. However, this does not mean that the synthesis of anodes with given functional properties for specific tasks is chaotic and has no general regularities. In our opinion, the most rational approach is to use base material with a satisfactory averaged electrocatalytic activity and selectivity to a group of processes obtaining at high anodic potentials with oxygen-containing radicals participation. The distribution of oxygen-containing particles will depend not only on the electrocatalytic activity of the material in the target process, but also on its selectivity in several simultaneous reactions. That is to say, the detection of the relationship between the chemical composition of metal oxide materials, their physicochemical properties and electrocatalytic activity is of considerable interest in the applied aspect for the synthesis of efficient materials that will be used in conditional non-reagent systems of

electrochemical purification of wastewater from toxic organic compounds.

Having in mind that the challenge in PbO₂ research is the obtainment of an electrochemically active and durable material, we report and discuss in this work the electrodeposition of PbO₂ from a medium containing ions of iron group.

Although methanesulfonate is becoming the most popular electrolyte for PbO₂ electro-synthesis [4], we chose nitrate electrolytes because they are cheaper, easier to prepare and work with; their regeneration presents no particular difficulties, and PbO₂ obtained in this medium has satisfactory mechanical properties. In addition, we wanted to avoid the possible influence of the anion in an assessment of peculiarities of iron group ions effects; in this respect, the known specific adsorption of the methanesulfonate anion on oxides [5] would complicate the analysis of electrochemical results.

Material and methods

All chemicals were reagent grade. Electrodeposition of lead dioxide was studied in the nitrate electrolytes that contained 1 M HNO₃, 0.02 M Pb(NO₃)₂ and 0.01 M X(NO₃)₂ (X=Fe, Co, Ni).

Platinized titanium was used as a sheet. Titanium sheet was treated as described elsewhere [6–8] before platinum layer depositing. Lead dioxide coatings were electrodeposited at anodic current density 4 mA cm^{-2} and temperature $(293 \pm 2) \text{ K}$. The determination of modifying additive in anodic material was carried out with Graphite furnace atomic adsorption spectroscope (GF–AAS) model Analyst 800. Increasing the concentration of the ionic dopant in the deposition electrolyte leads to an increase in the content of modifying element in lead dioxide and grows in the following sequence: Ni^{2+} – Fe^{3+} – Co^{2+} . The content of the ion additives in the oxide does not usually exceed 0.1 wt.%. It is noteworthy that the energy of the adsorption interaction of iron group ions with lead dioxide increases in the same sequence as the content of the modifying elements in the oxide.

The surface morphology of lead dioxide anodes was studied by scanning electron microscopy (SEM) with SEM-106I microscope and by X-ray diffraction with Advance Bruker D8 diffractometer.

XPS studies were carried out using a PHI 5000 spectrometer with monochromatic AlK_{α} radiation for excitation. The BE value of C(1s) due to adventitious carbon and residual solvent is $285.0 (\pm 0.3) \text{ eV}$.

The electrooxidation of organic compounds was carried out in a divided cell at $j_a = 50 \text{ mA cm}^{-2}$. The volume of anolyte was 130 cm^3 . Solution containing phosphate buffer ($0.25 \text{ M Na}_2\text{HPO}_4 + 0.1 \text{ M KH}_2\text{PO}_4$) + $0.1 \times 10^{-3} \text{ M}$ organic compound (pH 6.55) was used as an electrolyte. Stainless steel was used as a cathode. Lead dioxide electrodes modified by iron group ions were used as anodes. Electrode surface area was 3 cm^2 .

The analyses of the reaction products were performed by HPLC using a Shimadzu RF–10A xL instrument equipped with a Ultraviolet SPD-20AV detector and a 30 cm Discovery[®] C18 column. Ozone analysis was carried out mostly by iodometric titration [9]. In some cases, the results were checked by the spectrophotometric method. The formation of

colored compounds during electrolysis was followed by UV-visible spectroscopy using a Kontron Uvikon 940 spectrometer.

Results and discussion

Structural parameters and chemical composition

Almost all the anode processes occurring in aqueous solutions at high anodic potentials (oxygen and ozone evolution, oxidation of inorganic and organic compounds), due to the similarity of mechanisms and the participation of oxygen-containing radicals in them, are conventionally combined into a single group of the so-called oxygen transfer reactions. At the same time, the nature and energy of oxygen-containing particles can vary dramatically. In the latter case, depending on the bond strength with the surface of the electrode, the oxygen-containing particles are divided into two large groups: inert (localized in the crystalline zone of oxide) and labile (associated in the hydrated zone) [10].

It is widely recognized that the electrocatalytic activity of oxide materials is influenced by two groups of factors: structural and chemical [1–3,7–9]. Since in most cases they are interconnected, it is very difficult to divide them. However, in particular cases, their influence on electrocatalytic activity and selectivity towards the target process may differ significantly.

A typical texture of lead dioxide deposits deposited from nitrate electrolytes is shown in Fig. 1. According to scanning electron microscopy (SEM) micrographs, the lead dioxide surface is a set of large polycrystalline blocks with a negligible predominant crystallographic orientation.

The comparison of the electrocatalytic activity of PbO_2 -based materials with the morphology of the resulting deposits indicates that there is no direct relationship between the above-mentioned parameters. At the same time, an increase in the surface of the electrode due to the reduction of the size of the polycrystalline blocks, in general, is a positive factor, since it allows increasing the total

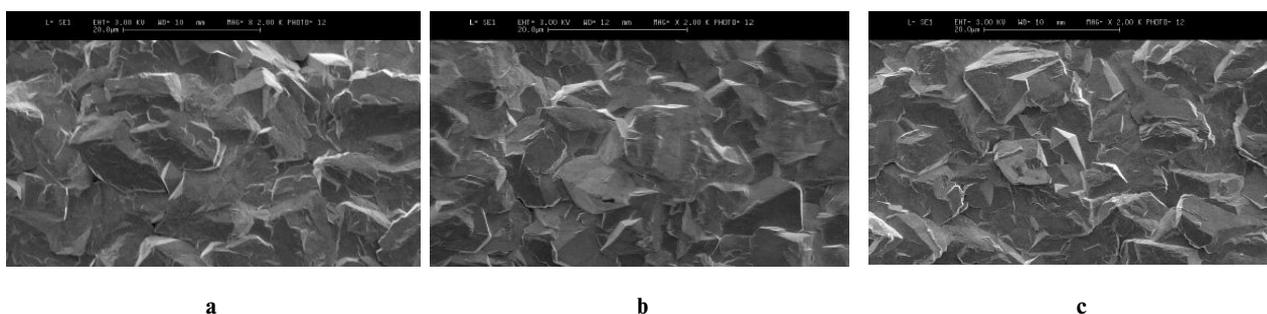


Fig. 1. SEM images of the surface of PbO_2 deposited from $0.1 \text{ M HNO}_3 + 0.1 \text{ M Pb}(\text{NO}_3)_2$ solution which additionally contained $\text{X}(\text{NO}_3)_2$, where X is Fe (a), Co (b) or Ni (c). $j_a = 4 \text{ mA cm}^{-2}$

current at the anode with a fixed geometric surface.

From the point of view of the possible influence of the bond strength of oxygen-containing radicals adsorbed on the electrode surface during processes occurred at high anodic potentials, structural parameters such as the texture and phase composition of PbO₂-based materials may be more important. These factors can also have a secondary effect on the chemical composition of the surface of PbO₂ by changing the number and nature of cation vacancies as well as the nature and surface concentration of oxygen-containing compounds. It is important to note that according to data obtained from X-Ray diffractograms, in contrast to nitrate solutions, the use of methanesulfonate electrolytes of various compositions allows wide varying of the phase composition of the coating.

An increase in the current density from 4 to 10 mA cm⁻² does not practically affect the phase composition and texture of the coatings, while the growth of acid content in both nitrate and methanesulfonate solutions from 0.1 M to 1.0 M leads to a significant increase in the amount of α -phase in coatings up to 25 and 90%, respectively. It should be noted that the phase composition of PbO₂ deposited from nitrate and methanesulfonate electrolytes practically does not differ at low acidity. However, at an acid concentration of 1.0 M in an electrolyte in mixed nitrate-methanesulfonate electrolytes, the maximum amount of α -phase is only 44%, which is 2 times lower compared to the content in coatings obtained from methanesulfonate bath (90%). Since the nitrate ion is not adsorbed on the surface of the electrode and does not form complex compounds with Pb²⁺, the only fact of influence may be an additional presence of sodium ions in a solution. Possibly, the latter influences the coordination of water and its structure in the near-electrode layer or the hydration of methanesulfonate ions, which in turn can affect the nature of oxygen-containing radicals involved in the formation of PbO₂.

It is necessary to take into account that when depositing coatings of a small thickness, certain influence on its texture and phase composition can reveal the nature of the substrate. This effect is manifested for a short time, and then the deposition is carried out on the lead dioxide.

As concerns the phase composition of coatings, all investigated samples contained two phases: α -PbO₂ and β -PbO₂ with various preferred orientation depending on type of the dopant. The difference was observed only in the ratio of these two phases and also in the degree of crystallinity.

Let's consider the influence of electrodeposition

conditions on the chemical composition of lead dioxide. As it is known, in almost all cases, there are deviations from the ideal stoichiometry of PbO₂ and the actual chemical formula of PbO₂ was experimentally established by detection of Pb(II) [11] and structural water [12] within the lattice. Investigations have also confirmed that there is a relationship between the hydrogen content in PbO₂ and its electrochemical activity.

The chemical composition of PbO₂-based materials may be altered by adding dopants to the electrolyte. In the first case, it should also be taken into account the secondary effect of dopants on the coordination and bond strength of oxygen-containing particles in the hydrated and crystalline oxide zones.

In the first place, we consider the possibility of changing the chemical composition of materials based on PbO₂ via their micromodification with dopants. According to the model based on deviations from the ideal stoichiometry of PbO₂ that is imputed to the occurrence of lead cation disorder in the crystallographic structure, with cation vacancies forming interfaces (internal surfaces) between crystallographic ally ordered areas [11], each missing Pb⁴⁺ ion would be compensated by Pb²⁺ and OH⁻ ions, and the chemical composition is described by the formula $\text{Pb}^{4+}_{(1-x-y)}\text{Pb}^{2+}_y\text{O}^{2-}_{(2-4x-2y)}\text{OH}^{-}_{(4x+2y)}$. Especially in the case of electrochemically deposited films, the coefficients x and y can have high values [11]. This structure of the lead dioxide provides a number of possibilities for its modification by dopants, which are capable as a result of introduction into the base oxide to replace as Pb⁴⁺ and Pb²⁺ ions or oxygen-containing ions O²⁻ and HO⁻. The replacement of one and the other, will lead to a change in the bond strength of oxygen-containing particles with the surface of the electrode, which in turn can cause a significant change in the electrocatalytic activity of the materials based on lead dioxide in advanced oxidation processes.

In all cases, the amount of additive in the oxide does not reach even 0.1% which indicates some difficulties in its localization in PbO₂ due to the small amount of Pb²⁺ ions in the hydrated zone and geometric inconsistency. An additional complication is the mismatch of ion charges of lead and ionic additives, which necessitates the reorganization of oxygen-containing ions to comply with the principle of electroneutrality.

To get further insight into the effects of doping, we investigated the surface layers by X-ray photoelectron spectroscopy (XPS). The XPS spectra of doped PbO₂ deposited from nitric solutions have been discussed in detail in our previous publication

[7,12,13]. The XPS spectra showing the reported Pb $4f_{7/2}$ and Pb $4f_{5/2}$ binding energies and peak separation of ~ 5 eV both in the absence and in the presence of dopants, can be assigned to Pb(IV) [7,8,12,13]. The XPS investigation was focused mainly on the detailed analysis of O element. O1s region reveals peaks at 528.9 and 530.2 eV assigned to the lattice oxygen and to weakly bound oxygen species: adsorbed OH^- and water. Doping of lead dioxide with nickel leads to a significant increase in the number of labile oxygen-containing particles on the surface of the electrode, while iron modification leads to the opposite effect: an increase in the amount of inert oxygen-containing particles [7,12,13]. Most likely, such a significant difference in the properties of PbO_2 modified by the metals from iron group is caused by strong differences in the bond strength between the hydroxyl groups and the oxygen-containing compounds of iron, cobalt and nickel. Unfortunately, due to the low content of the modifying elements, we failed to identify the nature of the surface compounds of iron, cobalt and nickel by XPS.

Oxidation of 4-chlorophenol

It is widely recognized [2,6,9,10] that the electrochemical oxidation of most organic and inorganic substances at high anode potentials occurs with the participation of oxygen-containing particles chemisorbed on the electrode formed during the anodic ionization of water. At the same time, these same particles also participate in the reactions of oxygen and ozone evolution, which proceed simultaneously to the oxidation of organic compounds [2,6]. In order to determine the nature of the electrocatalytic activity in the oxidation of organic substances, we have chosen phenolic compounds, in particular, 4-chlorophenol and anode materials based on lead dioxide. This choice was due to the fact that the electrochemical oxidation processes of phenolic compounds at various electrodes have been fairly well studied, so the main focus can be only on clarifying the role of the anode material.

It must be taken into account that the process of oxidation of organic substances is not necessarily a direct electrochemical process. There is a strong possibility that it may occur via oxidants formed in the primary electrochemical reaction (for example, hydroxyl radicals or ozone). In fact, such a process is a secondary chemical process. It should also be noted that it is not always taken into account that the oxygen evolution reaction on the electrode can occur simultaneously with other oxygen transfer reactions, such as the oxidation of organic or inorganic compounds [2,9,10].

According to the literature data [14], the anodic oxidation of 4-chlorophenol results in a large number of intermediate products. The main intermediates include benzoquinone and maleic acid. A rather simple and convenient way to estimate the electrocatalytic activity of an electrode material is measuring the time of disappearance of aromatic intermediates, which can be determined from the UV spectra of solutions at different times of electrolysis.

Fig. 2 shows data on the conversion of chlorophenol in a sulfuric acid solution on PbO_2 at a current density of 50 mA cm^{-2} and the formation of benzoquinone during electrolysis.

According to the data of high-performance liquid chromatography, 1,4-benzoquinone (BQ) is the main aromatic intermediate, while only maleic acid was mainly detected in solution during prolonged electrolysis.

It should be noted that benzoquinone is a toxic compound, therefore, additional time is required for its conversion to aliphatic compounds during electrolysis. According to the literature [3,6,9], it is easily oxidized on various oxide materials. As follows from Fig. 3, the concentration of benzoquinone reaches a maximum after 100 minutes of electrolysis during the oxidation of chlorophenol in sulfuric acid solutions under our conditions.

Since benzoquinone is an important aromatic intermediate of chlorophenol oxidation, we performed electrolysis of solutions containing benzoquinone as an initial compound. According to the data obtained, benzoquinone oxidized faster than chlorophenol.

Like for chlorophenol, the conversion rate of benzoquinone was higher at 0°C than at 25°C . Thus,

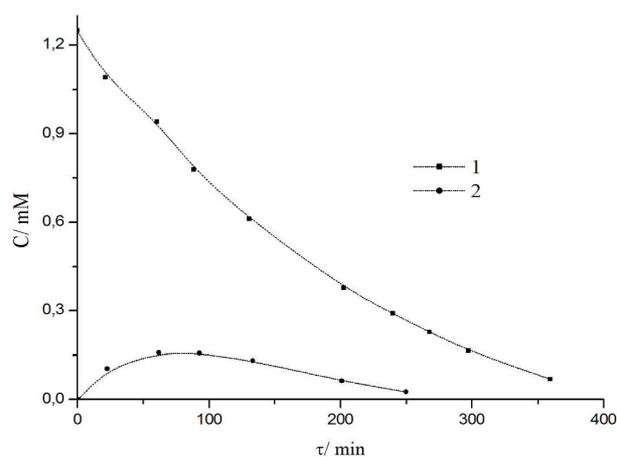


Fig. 2. Change of concentration of 4-chlorophenol (1) and benzoquinone (2) solutions during electrolysis in 1 M H_2SO_4 at 50 mA cm^{-2} . Temperature 273 K

under identical experimental conditions and with an initial benzoquinone concentration of 1.2×10^{-3} M, about 95% of the initial compound was oxidized after 2 hours of electrolysis at 50 mA cm^{-2} and 0°C , while at 25°C the conversion rate was only 65%.

As the decrease in solution temperature leads to a significant increase in ozone current efficiency [9], one of the possible reasons for increasing the rate of oxidation of chlorophenol and benzoquinone at low temperatures is a secondary chemical oxidation of organic substances by electrochemically generated ozone. However, this reason is hardly the main and the only one. As follows from the obtained data, the rate of ozone formation decreases considerably with increasing temperature as compared with the oxidation of benzoquinone. In addition, it should be taken into account that adding new portion of chlorophenol or benzoquinone to the solution leads to an almost complete inhibition of ozone evolution. The data obtained allow making an assumption that there is no direct relationship between the processes of electrochemical oxidation of phenols and ozone evolution. Most likely, the adsorption of phenols on the surface of the electrode blocks the active sites on which oxygen-containing particles highly bonded to the surface are formed, that was described in detail in our previous article [9].

The maximum conversion rate of chlorophenol is observed in a phosphate buffer solution at pH 7. The observed phenomenon can hardly be due to the dissociation of chlorophenol, since such a process is usually observed at a pH of more than 9. This is most likely due to a change in the ratio of various forms of adsorbed oxygen-containing particles during

the adsorption of phosphate ions to surface of PbO_2 .

Fig. 3 shows the electronic absorption spectra of solutions obtained at different duration of electrolysis (the initial concentration of 4-chlorophenol was 1 mM). The initial solution of chlorophenol is characterized by two peaks at wavelengths of 230 and 280 nm. At the first time of the electrolysis, a peak decrease at 230 nm is observed as well as a slight increase in the peak at 280 nm and the appearance of the plateau at 250–270 nm, which is due to a decrease in the concentration of chlorophenol and the accumulation of benzoquinone in the solution. A further increase in the electrolysis duration leads to the disappearance of peaks at 230 and 280 nm as well as to the site decrease at 250–270 nm due to a decrease in the concentrations of both chlorophenol and benzoquinone. After 4 hours of electrolysis, the complete destruction of aromatic compounds occurs with the formation of only aliphatic products (in particular, maleic acid). It should be noted that the processes of electrooxidation of 4-chlorophenol on unmodified and modified lead dioxide electrodes proceed qualitatively via the same way and differ only in the rate of process.

As one can see from Fig. 4, the micro-modification of lead dioxide with metal ions of iron group leads to a significant change in the electrocatalytic activity of oxide materials. The activity grows in the following sequence of modifying ions: $\text{PbO}_2 < \text{Co-PbO}_2 < \text{Fe-PbO}_2 < \text{Ni-PbO}_2$. With the exception of oxide modified with iron, the strength of the bond of chemisorbed oxygen-containing particles to the surface of the electrode decreases in this same sequence. This suggests that labile oxygen-

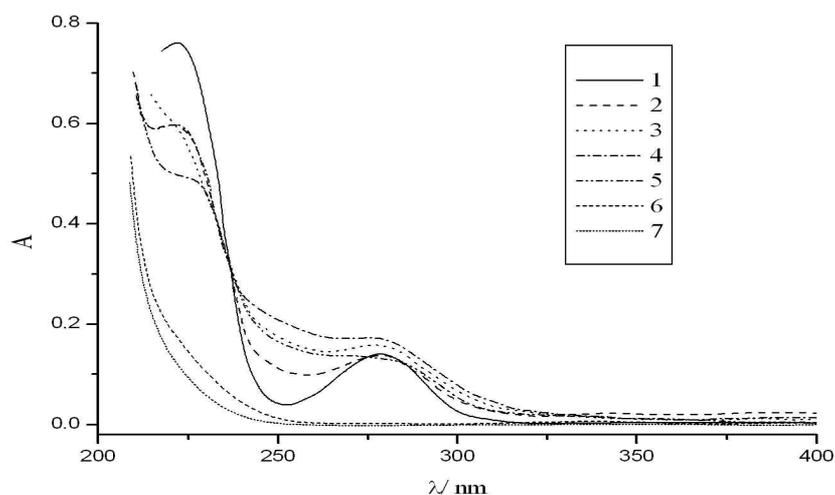


Fig. 3. The electronic absorption spectra of $0.5 \text{ M Na}_2\text{SO}_4 + 1.2 \text{ mM 4-chlorophenol} + \text{phosphate buffer solution}$ at different electrolysis duration on the nonmodified PbO_2 anode, where electrolysis duration is (h): 1 – 0; 2 – 0.5; 3 – 1.0; 4 – 1.5; 5 – 2.0; 6 – 3.0; 7 – 4.0. Temperature 293 K

containing particles take part in the electrochemical oxidation of organic substances at high anode potentials. The creation on the electrode surface of an additional number of active centers on which such particles are generated, in particular, by micromodifying the oxide with various ionic additives, will lead to an increase in the electrocatalytic activity of the material.

An increase in the content of a dopant in the deposition electrolyte leads to an increase in the electrocatalytic activity of the material (Fig. 5). This

is due to an increase in the number of active sites due to an increase in the content of modifying ions in lead dioxide.

Conclusions

As follows from the data obtained, the rate of oxidation of organic substances on the anode materials involved is proportional to the number of reactive oxygen species in the near-electrode zone (OH-radicals) formed during the electrolysis as intermediates in water oxidation and participating in subsequent homogeneous chemical reactions with

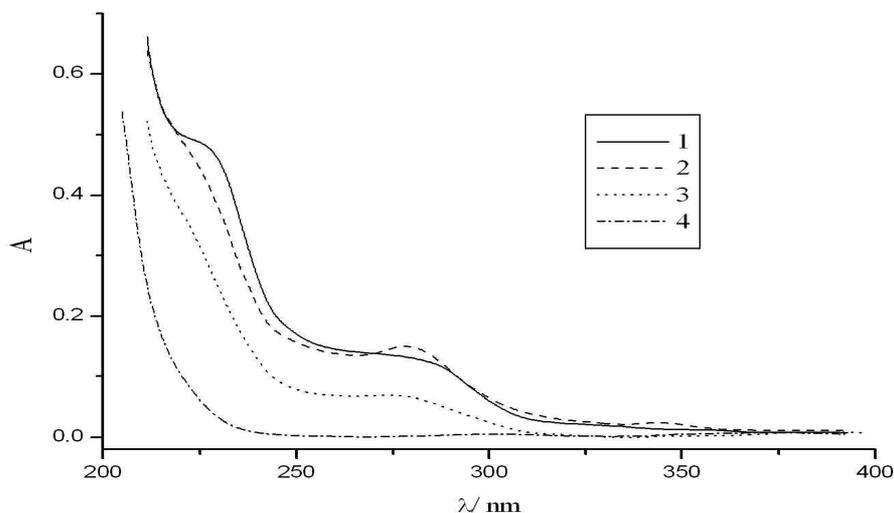


Fig. 4. The electronic absorption spectra of 0.5 M Na_2SO_4 +0.1 mM 4-chlorophenol+phosphate buffer solution on different electrodes at 50 mA cm^{-2} after 2 hours of electrolysis, where 1 – PbO_2 ; 2 – Co-PbO_2 ; 3 – Fe-PbO_2 ; 4 – Ni-PbO_2 . Temperature 293 K

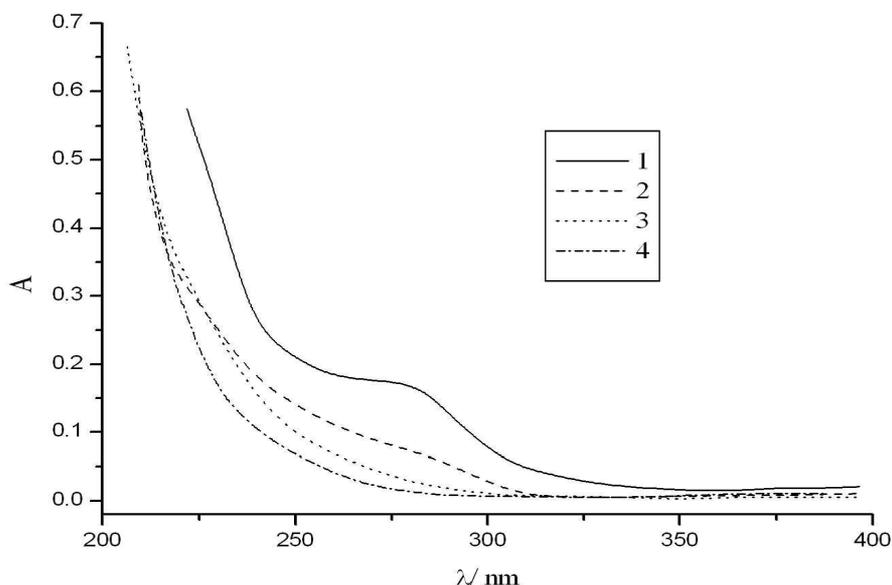


Fig. 5. The electronic absorption spectra of 0.5 M Na_2SO_4 +0.1 mM 4-chlorophenol+phosphate buffer solution on different electrodes at 50 mA cm^{-2} after 1.5 hours of electrolysis, where 1 – PbO_2 ; 2 – Ni-PbO_2 (0.01 M $\text{Ni}(\text{NO}_3)_2$); 3 – Ni-PbO_2 (0.03 M $\text{Ni}(\text{NO}_3)_2$); 4 – Ni-PbO_2 (0.1 M $\text{Ni}(\text{NO}_3)_2$). Temperature 293 K

organic substrates in the bulk.

The micromodification of lead dioxide with ionic additives leads to a significant increase in the electrocatalytic activity with respect to direct anodic oxidation of 4-chlorophenol. The micromodification of lead dioxide with metal ions of iron group leads to a significant change in the electrocatalytic activity of oxide materials. The activity grows in the following subsequence of modifying ions: $\text{PbO}_2 < \text{Co-PbO}_2 < \text{Fe-PbO}_2 < \text{Ni-PbO}_2$. The data obtained suggest that an analogous increase in activity should be observed with respect to other reactions with oxygen transfer of a similar type, in particular, the oxidation of natural and synthetic organic substances.

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ЕЛЕКТРООКИСНЕННЯ 4-ХЛОРФЕНОЛУ НА МОДИФІКОВАНИХ ДІОКСИДНОСВИНЦЕВИХ АНОДАХ

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Досліджено електрохімічне окислення 4-хлорфенолу на діоксидносвинцевих анодах, мікрomodифікованих іонами групи Феруму. Як впливає з отриманих даних, швидкість окислення органічних речовин на анодних матеріалах пропорційна числу активних форм кисню в навоколелектродній зоні (ОН-радикали), що утворюються під час електролізу як проміжних сполук у процесі окиснення води та беруть участь в подальших однорідних хімічних реакціях з органічними субстратами. Пік O_1s на рентгенівських фотоелектронних спектрах був використаний для оцінювання кількості інертних і лабільних оксигеновмісних частинок на немодифікованому та модифікованому PbO_2 . Допування плюмбум діоксиду Ніколом приводить до значного збільшення кількості лабільних оксигеновмісних частинок на поверхні електрода, тоді як модифікація Ферумом приводить до протилежного ефекту – збільшення кількості інертних частинок, що містять кисень. Анодне окислення 4-хлорфенолу приводить до досить великої кількості проміжних продуктів. Основні проміжні сполуки включають бензінон і малеїнову кислоту, що підтверджується високоефективною рідинною хроматографією. Мікрomodифікація плюмбум діоксиду металевими іонами групи Феруму веде до суттєвої зміни електрокаталітичної активності оксидних матеріалів. Активність зростає в наступному ряду модифікуючих іонів: $\text{PbO}_2 < \text{Co-PbO}_2 < \text{Fe-PbO}_2 < \text{Ni-PbO}_2$.

Ключові слова: плюмбум діоксид, нітратний електроліт, 4-хлорфенол, оксигеновмісні радикали, O_1s пік.

ELECTROOXIDATION OF 4-CLORPHENOL ON MODIFIED LEAD DIOXIDE ANODES

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Keywords: lead dioxide; nitrate electrolyte; 4-chlorophenol; oxygen-containing radicals; O1s peak.

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