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Modified lead dioxide for organic wastewater treatment: Physicochemical properties and electrocatalytic activity

OLESIA SHMYCHKOVA[1], TATIANA LUK’YANENKO[1], LARISA DMIRTIKOVA[2] and ALEXANDER VELICHENKO[1]*

[1]Ukrainian State University of Chemical Technology, 8, Gagarin Ave., 49005 Dnipro, Ukraine and [2]Oles Honchar Dnipro National University, 72, Gagarin Ave., 49010 Dnipro, Ukraine

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Abstract: An investigation on lead dioxide electrodeposition from methanesulfonate electrolytes additionally containing Ni^{2+} is reported. It is shown that the lead dioxide electrodes micromodified by nickel have different physicochemical properties *vs*. nonmodified PbO_2-anodes, that are formed during the deposition. The electrocatalytical reactivity of the electrodes involved in comparison to both the oxygen evolution, as well as to the electrooxidation of 2,4-dichlorophenoxyacetic (2,4-D) acid is investigated. The processes of electrochemical oxidation of 2,4-D on various materials occur qualitatively with the same mechanism and differ only in the reaction rate. It is shown that the Ni-PbO_2-anode possesses the highest electrocatalytic activity: the destruction rate of 2,4-D on it increases 1.5 times in comparison with the unmodified lead dioxide. The chemical oxygen demand (*COD*) of a 0.4 mM solution of 2,4-D, determined by the dichromate method, is 90.0 mg dm^{-3} which is 94 % of the theoretical value.

Keywords: methanesulfonate electrolyte; oxygen evolution; 2,4-D; direct anodic oxidation.

INTRODUCTION

Wastewater treatment is recognized as one of the priorities of modern science, particularly in industry, where chemical methods using reagents are widely applied.[1,2] Alternative to the traditional methods of water purification from toxic aromatics are electrochemical technologies, which should be classified as conditionally non-reagent. The electrochemical destruction of toxic pollutants is achieved both by the direct transfer of the electric charge between organic compounds and electrode, and in secondary chemical reactions, where the oxidant is an oxygen-containing radical, which is formed during the electrolysis from water molecules. Such methods are of great advantage for water purification from a

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*Corresponding author E-mail: velichenko@ukr.net

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wide range of organic substances of various types, for example, for phenolic compounds and pesticides.[3–6]

It is recognized,[7,8] that for complex reactions involving organic compounds, the electrode material determines the general direction of the reaction, as well as the nature of intermediates. These two ways of the catalytic action of the electrode material, namely on the rate and selectivity of many reactions, are of great importance for the practical application of such reactions in electrolysis. For most processes, there is a problem of selecting the optimal material for a catalyst electrode, which must satisfy a number of requirements: *i*) to have electronic conductivity; *ii*) to be stable toward corrosion in the conditions of processes; *iii*) not to lose activity for long-term use and, above all, *iv*) to have a low cost. Only a small amount of materials, including metal oxide catalysts, meets the listed requirements. For this purpose, the oxide electrodes, micro-modified with additives of various ions, are of considerable interest for the study, since their activity can vary widely while preserving the basic properties of the material.

As it is well known,[9] there are two zones on PbO_2 surface: hydrated, consisting of Pb^{2+} associated with the corresponding number of hydroxyl ions, and crystalline, in which the ions of Pb^{4+} in the crystal lattice are bound to the O^{2-}.

We believe that the introduction of ions into cation vacancies in the hydrated oxide zone, or at the sites of its crystalline lattice will allow one to control the amount of inert and labile oxygen-containing particles, which in turn will provide the ability to control the electrocatalytic activity and the material selectivity.

The distribution of oxygen-containing particles will depends not only on the electrocatalytic activity of the material in the target process, but also on its selectivity if several reactions are simultaneous. That is, the detection of the relationship between the chemical composition of metal oxide materials, their physicochemical properties and the electrocatalytic activity is of considerable interest in the applied aspect for the creation of efficient materials that will be used in conditional non-reagent systems of the electrochemical wastewater purification from toxic organic compounds.

In a recent work by our group,[10] we have investigated the chemical properties of these systems, deposited from nitrate medium, as well as the nucleation regularities, and kinetics of the electrodeposition of coatings. However, due to the limitations on the mechanical strength, in nitrate solutions it is not possible to obtain coatings with a thickness greater than 100 microns. Considering this, we proposed the methanesulfonate electrolytes in which PbO_2 composite coatings are up to 2 mm thick to be used, with satisfactory mechanical properties that can be prepared.[11]

Herein, we report further important details on the effect of the deposition conditions on the composition, the physicochemical properties and the electrocatalytic activity of Ni modified PbO_2-based materials, obtained from methanesulfonate electrolytes. One of the objects of our work was to develop a system with given electrocatalytic properties by changing the quantity of the oxygen-containing particles adsorbed on the electrode surface.

EXPERIMENTAL

Chemicals

The ultrapure acids were obtained from Merck and all other chemicals from Sigma–Aldrich.

Equipment

The determination of the modifying additive in anodic materials was carried out with grafite furnace atomic adsorption spectroscope (GF-AAS) model Analyst 800. The content of nickel in the synthesized PbO_2 does not exceed 0.01 wt.%.

Surface morphology of materials involved was studied by scanning electron microscopy (SEM) with SEM-106I microscope. X-ray powder diffraction data were collected on a STOE STADI P automatic diffractometer equipped with linear PSD detector (transmission mode, $2\theta/\omega$-scan; $CuK\alpha_1$ radiation, curved germanium (1 1 1) monochromator; 2θ-range 6.000–102.945° with the step of 0.015°; PSD step 0.480°, scan time 50 s/step).

Qualitative and quantitative phase analysis was performed using the PowderCell program. For the selected samples with relatively high degree of crystallinity the Rietveld refinement was carried out using 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 formation of coloured compounds during electrolysis was followed by UV–Vis spectroscopy using a Kontron Uvikon 940 spectrophotometer.

Analyses of the reaction products were conducted by HPLC using a Shimadzu RF-10A xL instrument equipped with Ultraviolet SPD-20AV detector and a 30 cm Discovery® C18 column.

Methods

Lead dioxide coatings were electrodeposited on platinized titanium at anodic current density 10 mA cm^{-2} from methanesulfonate electrolytes that contained 0.11M CH_3SO_3H, 0.1 M $Pb(CH_3SO_3)_2$ and 0.1 M $Ni(NO_3)_2$ as dopant.

The volume of anolyte was 130 cm^3. Solution, containing phosphate buffer (0.25 M Na_2HPO_4 + 0.1 M KH_2PO_4)+0.1–0.4 mM organic compound, (pH 6.55) was used as the electrolyte. Stainless steel was used as the cathode. Modified lead dioxide electrodes were used as the anodes. The electrode surface area was 2.5 cm^2. Ag/AgCl reference electrode was used.

The changing of the concentration of the organic substance during the electrolysis was measured by sampling (volume of 5 cm^3) at regular intervals and measuring the optical density of the solution in the ultraviolet and visible region (wavelength range 200–570 nm). Solution, containing phosphate buffer, was used as reference solution.

The chemical oxygen demand (*COD*) was determined by the dichromate method. Samples (5 cm^3) were taken from a cell in a round-bottom flask, 11 cm^3 of water, 1 cm^3 of 0.04 M $HgCl_2$ (to mask chloride ions), 0.8 cm^3 of 0.1 M $AgNO_3$ (as catalyst), 10 cm^3 of H_2SO_4 (concentrated) and 1 cm^3 of 0.1 g-equiv. dm^{-3} of $K_2Cr_2O_7$. The contents of the flask were heated in a sand bath until it was boiling, which was maintained for an hour. After this, the excess of potassium dichromate was measured by the amperometric titration with 0.017 N ammonium iron(II) sulfate, at amperometric titration unit with two indicator platinum electrodes at E = 0.2 V. The reference experiment was conducted the same way, by disposing distilled water instead of organic compound. Concentration of chlorides was determined by the photometric method using mercuric rhodanide.

RESULTS AND DISCUSSION

Phisycochemical properties of Ni–PbO_2 synthesized from methanesulfonate bath

It follows from the above results that the systems based on lead dioxide obtained from methanesulfonate electrolytes are of considerable practical interest and are worth of detailed studies. Considering this, we performed an investigation of the phase composition and the texture of obtained materials. A comparison of the XRD spectra reported in Fig. 1 (a and b) shows that the nickel doping causes some changes in the texture of the PbO_2 coating. Both reflection patterns show that in all cases the deposits consist of a mixture of α- and β-phases of PbO_2. In the doped sample case, the degree of crystallinity of the coatings

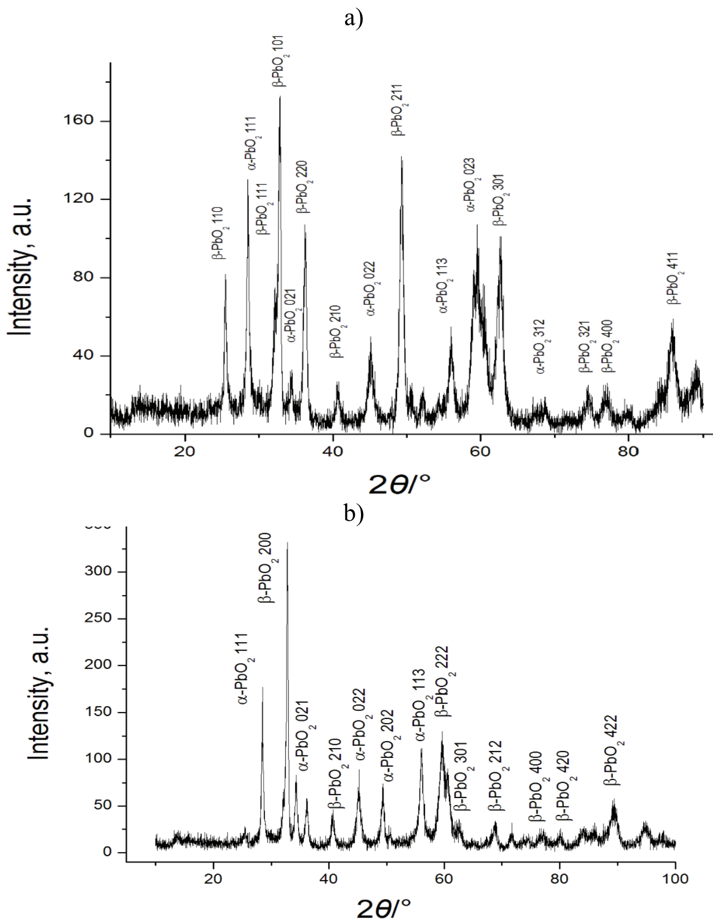

Fig. 1. X-Ray diffractogramms of surfaces of PbO_2, deposited from 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H (a) + 0.01 M $Ni(NO_3)_2$ (b).

increases, as evidenced by the increase of the peaks intensity and sharpness on diffractogramms. For the most intensive $\beta(200)$ peak, the average size of particles in Ni–PbO$_2$, according to Scherrer's equation, yield particle dimensions of 16.5 nm.

The data on the surface morphology of the PbO$_2$-based materials were obtained by scanning electron microscopy. As one can see from the obtained results (Fig. 2), which are in agreement with XRD results, the morphology of Ni-doped PbO$_2$ is more regular, with better oriented crystals of bigger size. Typical morphology of lead dioxide electrodeposited from methanesulfonate electrolyte is displayed on Fig. 2a. PbO$_2$ surface is a mixture of randomly oriented crystals. Polycrystalline clusters sizes vary in the 0.5–4 μm range. A similar morphology was observed during the incorporation of surfactants and polyelectrolytes in the growing PbO$_2$ deposit.[12]

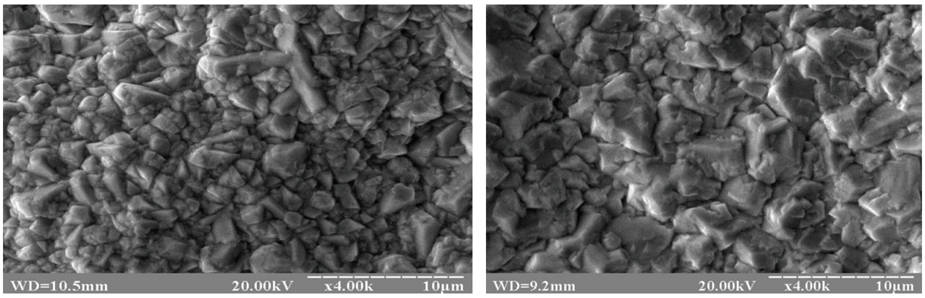

Fig. 2. SEM micrographs of PbO$_2$-coatings surfaces, obtained electrochemically at j_a = 10 mA cm^{-2} from next solution: 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H+X M $Ni(NO_3)_2$, where X = 0 (a); 0.01 (b);10000×.

As it is seen from Fig. 2b, when lead dioxide is modified by nickel ions the surface crystallinity grows and more marked aggregates can be observed.

We now consider the influence of electrodeposition conditions on the state of lead dioxide surface layer.

SEM/EDAX experiments were performed to evaluate the amount and the distribution of nickel in electrodeposited PbO$_2$. Unfortunately, it was impossible to reveal nickel because of its low amount in the deposit.

To get further insights in the effect of doping, XPS method was employed. The investigation was focused mainly on the detailed analysis of O1s region. Results are not shown, but the obtained spectra are characterized by two peaks: the one of lower binding energy (528 eV) refers to strongly bound oxygen of the crystal lattice, whereas the one of higher binding energy (530 eV) was assigned to the weakly bound oxygen-containing particles (adsorbed OH-groups and water).

Similar to the Ni-doped coating, obtained from the nitrate bath,[10] the sample synthesized from methanesulfonate medium reveals a significant increase in the number of labile oxygen-containing particles. Since the amount of adsorbed oxygen-containing particles on the electrode affects the electrocatalytic activity of anodes, the next step of our investigation was to establish the relationship between the composition of the anode material and its electrocatalytic activity in oxygen transfer reactions.

Electrocatalytic activity of nickel-doped lead dioxide

Having in mind that the processes of oxidation of organic substances and the oxygen evolution in most cases proceed simultaneously, we investigated the dependence of the overvoltage of the oxygen evolution reaction on the electrodes involved.

According to the mechanism proposed by Pavlov *et al.*,[13] the oxygen evolution occurs at active sites located in a hydrous layer on PbO_2. Oxygen evolution proceeds through the following elementary steps:

$$PbO(OH)_2 + H_2O \rightarrow PbO(OH)_2\cdots(OH^\bullet) + H^+ + e^- \quad (1)$$

$$PbO(OH)_2\cdots(OH^\bullet) \rightarrow PbO(OH)_2 + O + H^+ + e^- \quad (2)$$

$$2O \rightarrow O_2 \quad (3)$$

As has been proven by Trasatti and Lodi,[14] if oxygen evolution reaction (OER) is limited by a second electron transfer (electrochemical desorption), an increase of the bond strength of chemisorbed oxygen will lead to an increase of OER overvoltage.

According to our results (Fig. 3), the oxygen overpotential on modified electrodes is practically the same as on non-modified PbO_2-electrode. The Tafel slope is 301.4 and 301.6 mV/dec for non-modified and for Ni-doped PbO_2, respectively. Such phenomenon can be manifested for several reasons, one of which

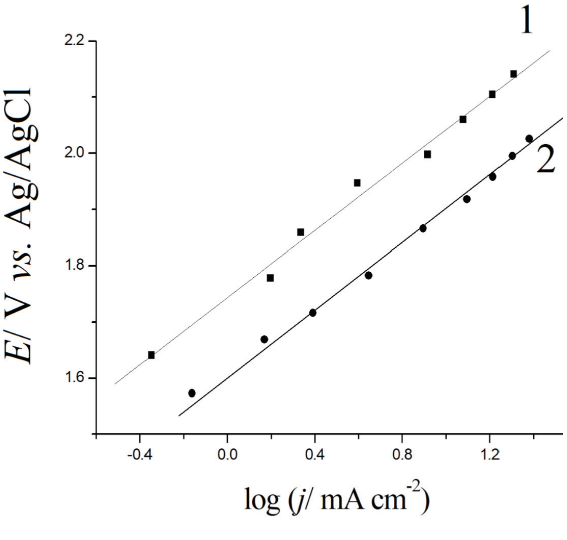

Fig. 3. Polarization curves for oxygen evolution on lead dioxide anodes, electrodeposited from solutions: 1.0–0.1 M $Pb(CH_3SO_3)_2$ + 0.11 M CH_3SO_3H; 2 – 0.1 M $Pb(CH_3SO_3)_2$ + 0.11 M CH_3SO_3H + 0.01 M Ni^{2+} at $j_a = 10$ mA/cm^2. Supporting electrolyte: 1.0 M $HClO_4$.

is the effect of the semiconductor component of the transition layer. Since the deposition of lead dioxide is carried out on platinized titanium, and the content of platinum is low, the platinum coverage is non-complete, *i.e.*, there is a partial oxidation of the titanium substrate during the deposition of PbO_2, which leads to the formation of TiO_x type oxides, which are n-type semiconductors and contribute to the thickness of the space charge layer. In the case of modified coatings, the additional effect is exerted by Ni active sites, which reduce the degree of filling with the oxygen-containing particles participating in the oxygen evolution process. Since the slope can increase, because of adsorption, as it was observed in the case of bismuth,[15,16] in our case nickel, apparently contributes to the incurporation of $CH_3SO_3^-$ into lead dioxide.[17]

Modification of lead dioxide by Ni^{2+} as in the system[10] reduces the oxygen evolution overpotential, and we did not observe the slope decrease with the increase of Ni^{2+} content in the oxide. This allows one to assume that the reaction of electrochemical desorption (the second electron transfer)[14] remains the rate-limiting step. Since PbO_2 modification by Ni^{2+} leads to a significant increase in the amount of labile surface oxygen-containing species, an increase in the catalytic activity of the oxide, in respect to the oxygen evolution reaction, is quite natural.

We investigated the degradation of aromatic compounds, namely 2,4-dichlorophenoxyacetic acid (2,4-D). This is a pesticide widely used in agriculture because of its low cost and high efficiency. This herbicide belongs to the moderate toxicity class of pesticides. Methods for chemical, photocatalytic and photochemical oxidation[4,6] are used to mineralize 2,4-dichlorophenoxyacetic acid. Electrochemical conversion methods of 2,4-D are also actively used, such as reducing electrochemical dechlorination and direct electrochemical oxidation.[2] A significant number of publications in the last decade are devoted to secondary oxidation of 2,4-D in the process of electro- and photoelectro-Fenton in H_2O_2–Fe^{2+}, H_2O_2–Fe^{2+}–UV systems, which allow the production of OH-radicals in the solution.[3,18–20] The hydroxyl radical is known to be the one of the most effective oxidants for 2,4-D, but in the Fenton process, the oxidation of a pesticide is accompanied by the reaction of formation of complexes of Fe^{3+} with products of 2,4-D oxidation (aliphatic acids), which makes it difficult to completely mineralize the pesticide.

The interaction of $OH^\bullet$ with pesticides results in: *i*) reactions with the proton cleavage, *ii*) redox process or *iii*) the electrophilic addition to double bonds. Addition of O_2 to radical organic compounds leads to formation of $OH^\bullet$ that initiates further oxidative degradation of pesticides to CO_2 and H_2O.

The simplest and, at the same time, effective electrochemical method of oxidation of 2,4-D by $OH^\bullet$ is direct anodic oxidation. In this case, the oxidation of the pesticide occurs through the generation of absorbed on the electrode surface hydroxyl radicals, which are formed by oxidation of water.

The initial solution of 2,4-D is characterized by the absorption maxima at 230 and 285 nm (Fig. 4). At the beginning of electrolysis, the optical density is reduced at 230 nm, while during the formation of the intermediate product 2-chlorobenzoquinone the appearance of the plateau is at 250–270 nm. Further oxidation of the pesticide results in the disappearance of peaks at 230 and 285 nm and the absence of absorption in the region of 250–270 nm, which indicates a complete conversion of 2,4-D and aromatic products of its oxidation into aliphatic compounds, after 3 h of electrolysis. The complete destruction of aromatic compounds, with the formation of only aliphatic products of electrolysis occurs on the Ni–PbO_2 anode after 2 h of electrolysis, and on the unmodified PbO_2-anode after 3 h. Thus, the modification of PbO_2 anodes increases the degradation rate of 2.4-D by 1.5 times. It should also be noted that the processes of the oxidation of a pesticide on the unmodified and modified lead dioxide precede qualitatively the same and differ only in the rate of destruction.

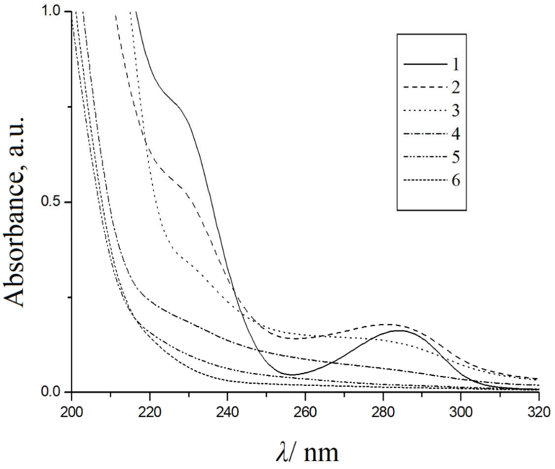

Fig. 4. The absorption spectra of 2,4-D solution (initial concentration 0.1 mM) obtained at different electrolysis duration in a phosphate buffer on Ni–PbO_2 anode. Electrolysis duration, h: 1−0; 2−0.5; 3−1; 4−1.5; 5−2; 6–3.

In most works on wastewater treatment with oxidative methods, not the kinetic parameters of oxidation of the initial organic compounds, but the generalized *COD* index, which reflects the ability to oxidize both the primary substrate and the intermediate products of its degradation, is used to evaluate the efficiency of the processes. The nature of the change in the total amount of the pesticide and its intermediate products in the electrolysis process was determined by the *COD* change (Fig. 5). The theoretically calculated *COD* of 0.4 mM 2,4-D is 96.0 mg dm^{-3} in accordance with the reaction equation:

$$2C_8H_6Cl_2O_3 + 15O_2 \rightarrow 16CO_2 + 4H_2O + 4HCl \qquad (4)$$

The *COD* of a 0.4 mM solution of 2,4-D, determined by the dichromate method, is 90.0 mg dm^{-3} which is 94 % of theoretical. It can be seen from Fig. 5, that during the electrolysis a uniform decrease in the concentration of organic substances in the electrolyte solution occurs. Within 8 h of electrolysis, a complete destruction of the pesticide occurs in a solution containing 0.4 mM 2,4-D, as evidenced by the *COD* value of 24 mg dm^{-3}.

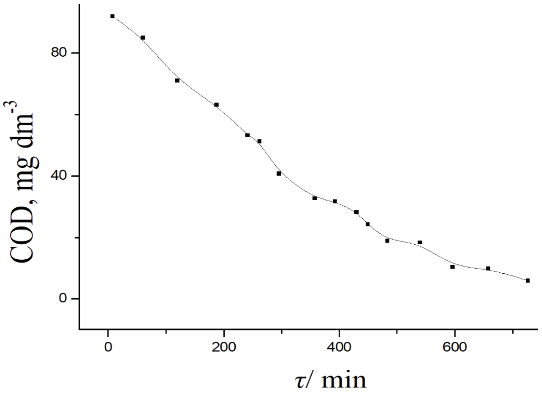

Fig. 5. The *COD versus* the electrolysis duration in a 0.4 mM 2, 4-D on a Ni–PbO$_2$-anode.

The *COD* data accurately correspond to the electronic absorption spectra of 2,4-D of the same initial concentration (Fig. 6). It is noteworthy that in many cases the oxidation of phenolic organic substances, with an increase in their initial concentration, produces coloured intermediate products during electrolysis. In the UV spectra of solutions, the absorption maxima and the shape of the absorption bands shifts, which slows down the rate of destruction such compounds.[21] As can be seen from Figs. 4 and 6 in the case of 2,4-D, this effect is not observed, *i.e.*, with an increase in the initial content of the pesticide by 4 times, the time of its decomposition to aliphatic acids also increases in 4 times.

Since halogenated derivatives are formed during the decomposition of organic molecules, an important stage in the detoxification of 2,4-D type is the process of their dehalogenation. The character of the change in the concentration of

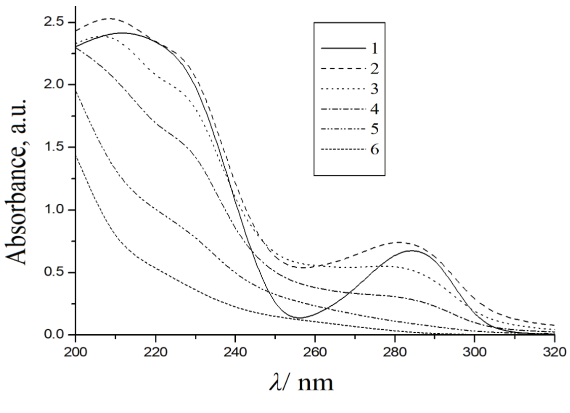

Fig. 6. The absorption spectra of 2,4-D solution (initial concentration 0.4 mM) obtained at different electrolysis duration in a phosphate buffer on Ni–PbO$_2$ anode. Electrolysis duration, h: 1–0; 2–2; 3–3; 4–4; 5–6; 6–8.

chloride ions over time was studied in the oxidation of 2,4-D on the Ni–PbO_2-anode. The process of destruction of the herbicide to CO_2 and H_2O can be described by the reaction:

$$C_8H_6Cl_2O_3 + 13H_2O \rightarrow 8CO_2 + 2Cl^- + 32H^+ + 30e^- \quad (5)$$

As the herbicide itself and its intermediate aromatic fragments are oxidized, chloride ions are accumulated in the solution and after 2 h of electrolysis, when no more aromatic intermediates are detected on the electronic absorption spectra (see Fig. 4), the concentration of Cl^- reaches a maximum concentration of 0.19 mM, which is 95 % of the value theoretically calculated from the reaction (2). Thus, by the time of the slower process of the destruction of aliphatic acids to CO_2 and H_2O, the dechlorination process is already complete. Further, the concentration of Cl-ions remains constant, which indicates the stability of the chlorides in the solution under the experimental conditions and the absence of their oxidation with the formation of Cl_2.

Analysis of the obtained results suggests that the concentration of 2,4-dichlorophenol, 4,6-dichlororesorcinol, formed at the initial stage of 2,4-D decomposition, decreases rapidly and the main intermediate product, on the decomposition of which is spent most of the time, is 2-chloro-1,4-benzoquinone.

The comparative estimate of the 2,4-D conversion rate is made from the current efficiency (*CE*) value calculated by the formula:[22]

$$CE = \frac{COD_{t_1} - COD_{t_2}}{1000C} \quad (6)$$

where COD_{t_1} and COD_{t_2} are the chemical oxygen demand at the initial and final moment of electrolysis, C is the amount of electricity passed through the cell during this period. Results are displayed in Table I.

TABLE I. The conversion rate of 2,4-D

Compound	Conversion time, h	COD_{t_1}	COD_{t_2}	CE
2,4-D	18	90.03	12.2	0.022

The characteristic of the oxidizability of organic compounds in electrochemical methods is the instantaneous current efficiency (*ICE*). We found that during the first two hours of electrolysis the *ICE* value increased sharply. This indicates that the oxidation process proceeds relatively quickly. This period is characterized by the decomposition of 2,4-D with the formation of phenol, resorcinol and hydroquinone, which, as has been found, oxidize much more rapidly on lead dioxide than 2,4-D itself. Therefore, we assume that after the decomposition of 2,4-D with the formation of the above listed intermediates, a large contribution to the process of electrochemical oxidation is the direct adsorption of these compounds on the PbO_2-anode surface. The decrease in the instantaneous current efficiency indicates the accumulation in the solution of weakly adsorbed and slowly oxidized aliphatic products, which leads to a decrease in the rate of their decomposition.

CONCLUSION

The investigated $Ni–PbO_2$ anodes, synthesized from methanesulfonate solution are of considerable interest in the applied aspect for the production of efficient materials that will be used in conditional non-reagent systems of electrochemical wastewater purification from toxic organic compounds. It is shown that the lead dioxide electrodes micro-modified by nickel have different physicochemical properties *vs*. unmodified PbO_2-anodes that are formed during the deposition. The obtained deposits consist of the mixture of α- and β-phases of PbO_2. In the doped sample case, the degree of crystallinity of the coatings increases, as evidenced by the increase of the peaks intensity and sharpness on diffractogramms. The morphology of Ni-doped PbO_2 is more regular, with better oriented crystals of bigger size. The coatings revealed a significant increase in the amount of labile oxygen-containing particles on the electrode surface, which in turn enhances the electrocatalytic activity of electrodes. The slope for oxygen evolution is 301.4 and 301.6 mV/dec for the unmodified and for the Ni-doped PbO_2, respectively. The use of the electrocatalysts involved, allows reducing the incineration time of 2,4-D by 1.5 times compared to unmodified anodes. The *COD* of a 0.4 mM solution of herbicide, determined by the dichromate method, is 90.0 mg dm^{-3} which is 94 % of the theoretical.

ИЗВОД

МОДИФИКОВАН ОЛОВО-ДИОКСИД ЗА ТРЕТМАН ОРГАНСКИХ ОТПАДНИХ ВОДА: ФИЗИЧКО–ХЕМИЈСКЕ СВОЈСТВА И ЕЛЕКТРОКАТАЛИТИЧКА АКТИВНОСТ

OLESIA SHMYCHKOVA[1], TATIANA LUK'YANENKO[1], LARISA DMIRTIKOVA[2] и ALEXANDER VELICHENKO[1]

[1]*Ukrainian State University of Chemical Technology, 8, Gagarin Ave., 49005 Dnipro, Ukraine* и [2]*Oles Honchar Dnipro National University, 72, Gagarin Ave., 49010 Dnipro, Ukraine*

Испитивано је електрохемијско таложење олово-диоксида из метансулфонатног електролита коме су били додати Ni^{2+}. Показано је електроде од олово-диоксида микро-модификоване никлом ($Ni–PbO_2$) имају различите физичко–хемијске особине у поређењу са немодификованим анодама које су добијене таложењем олово-диоксида истим поступком. Испитана је електрокаталитичка активност ових електрода за реакције издвајања кисеоника и оксидације 2,4-дихлорфеноксисирћетне киселине (2,4-D). Реакција оксидације 2,4-D на различитим материјалима се одиграва по квалитативно истом механизму, али различитим брзинама. Електроде од $Ni–PbO_2$ су показале већу електрокаталитичку активност: брзина разлагања 2,4-D на њима је била 1,5 пута већа него на немодификованој електроди. Хемијска потрошња кисеоника (*COD*) раствора 2,4-D концентрације 0,4 mM, одређена дихроматном методом, износила је 90,0 mg dm^{-3}, што је 94 % од теоријске вредности.

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