

Розглянуто процеси електросинтезу каталітично активної оксидної суміші на поверхні олова в лужних розчинах. Оригінальним кулонометричним методом визначено кількісний склад отриманих оксидних плівок. Показана сольова природа первинної електрохімічної пасивації олова з подальшим переходом в діоксид олова при потенціалі 3,0 В. Каталітична активність отриманих матеріалів показана на прикладі електроокиснення метил-трет-бутилового ефіру

Ключові слова: електросинтез, діоксид олова, олов'яний електрод, каталітична активність, склад оксидної суміші

Рассмотрены процессы электро синтеза каталитически активной оксидной смеси на поверхности олова в щелочных растворах. Оригинальным кулонометрическим методом определен количественный состав полученных оксидных пленок. Показана солевая природа первичной электрохимической пассивации олова с последующим переходом в диоксид олова при потенциале 3,0 В. Каталитическая активность полученных материалов показана на примере электроокисления метил-трет-бутилового эфира

Ключевые слова: электросинтез, диоксид олова, оловянный электрод, каталитическая активность, состав оксидной смеси

EXAMINING THE INFLUENCE OF ELECTROSYNTHESIS CONDITIONS ON THE COMPOSITION OF TIN-OXIDE CATALYST

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1. Introduction

A wide range of electron and chemical properties of metal oxides predetermines permanent interest of researchers in fundamental and applied fields. Oxides may exhibit properties of insulators, materials with metallic conductivity, and superconductors.

In chemical industry, oxides are used as auxiliary materials for dispersed metallic catalysts and often themselves exhibit a high catalytic activity. Catalytic reaction on oxides can occur with the participation of an oxygen atom of the catalyst lattice accruing oxygen from the gas phase. To implement such a mechanism of catalysis, oxygen content on the surface of a catalyst must be easily controlled.

Oxides are widely used as a working element in the solid-body gas sensors. Sensitivity of certain oxides to certain gases depends obviously on the chemical reactivity of these oxides.

Due to unique electrical and optical properties, tin dioxide can serve as a conductive material in microelectronics, lithium-ion batteries, solar cells [1]. Tin dioxide belongs to the class of materials that combines high electrical conductivity with optical clarity and is an important component in optoelectronic technology. Special chemical properties of SnO₂ determine its use as a material for devices of gas sensors and catalysts.

Depending on the conditions of synthesis, the composition, structure, and properties of oxides vary. Given this, it

is a relevant task to identify the influence of electrosynthesis conditions on the composition of tin-oxide catalyst.

2. Literature review and problem statement

The choice of method for the synthesis of tin oxides is determined by the desired properties of the resulting material. Hydro-thermal method was used in the synthesis of nanocrystalline photocatalysts with a SnO_2 matrix [2]. Thin films of nanocrystalline SnO_2 for ultracapacitors were obtained in phases. First, bivalent tin ions were oxidized in a solution of SnCl_2 with hydrogen peroxide. Then the hydrated tin dioxide was annealed at a temperature of 673 K for two hours [3]. Authors of [4] synthesized a SnO/SnO_2 photocatalyst using microwave radiation. Tin hydroxide, obtained by mixing the solutions of SnCl_2 and sodium hydroxide, was exposed to microwave treatment with a radiation frequency of 2.45 GHz. In [5], the influence of tin dioxide nanopowder synthesis conditions on the particle size was investigated. The SnO_2 nanopowder was synthesized as an anode material in lithium-ion batteries. The synthesis was conducted by sol-gel method using SnCl_2 . To obtain the tin dioxide powder, tin hydroxide sol was subjected to thermal treatment. Authors of [6] applied a sol-gel method in the synthesis of tin dioxide as an H_2S sensor. Optically transparent conductive tin dioxide-based films were synthesized employing a pyrolysis spraying of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in a non-aqueous medium [7].

Electrosynthesis is a manageable and well-reproducible method for the formation of thin layers of tin oxide [8]. It is known that the electrochemical technique of applying alloys [9] and composites [10–12] makes it possible to control the thickness and composition of the obtained deposits. Synthesis of oxides by the electrochemical method also enables obtaining films with a predetermined composition, thickness, and structure. Factors that affect the electrosynthesis process include the composition of a solution, parameters of electrolysis, and the availability of specialized additives [13].

Electrosynthesis of tin dioxide is actively used in the formation of anodes of lithium-ion power sources [14]. In [15], authors investigated electrical and structural characteristics of the nanoporous tin dioxide, synthesized as an anode of sodium-ion batteries. Forming the nanostructured SnO_2 thin films in [16] was conducted by the anodic treatment of a copper electrode in the presence of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and HNO_3 in the solution. It is shown that the oxide structure depends on the electrosynthesis potential. Grain size grows with an increase in the potential from 2.0 V to 2.4 V. Tin dioxide, synthesized at 2.0 V, is formed in the shape of nanopyramids with a side length of 200–250 nm. Electrosynthesis at 2.4 V leads to the formation of nanoplates with a thickness of 800 nm. It was established that SnO_2 in the form of nanopyramids possessed a larger number of active centers. This predetermines greater reactivity during interaction with lithium ions in lithium power sources.

In [17], authors explored photoelectric properties of the porous tin oxide synthesized by electrochemical method. It was found that the photoelectric effect of oxide film depends on the duration of anodic treatment of tin in a solution of NH_4OH . Authors of [18] have shown that the nanoporous tin dioxide, synthesized during anodic treatment of tin in 0.5 M NaOH proved to be more a more effective photoelectrode in comparison with powder SnO_2 . It was established in [19] that during anodic treatment of tin in the NaOH

solution at a voltage of 5–15 V, there formed the nanoporous tin dioxide with a pore size of 10–60 nm. The film thickness of SnO_2 increases with an increase in treatment time, voltage, and alkalinity of the solution. Applying oxalic acid as a working solution leads to the formation of anode deposition of tin oxide with a Sn:O ratio equal to 1:1 [20, 21]. It is expected that such a nanoporous tin oxide can be used as a gas sensor or a catalyst. Further thermal treatment of tin oxide contributes to the oxidation of Sn^{2+} into Sn^{4+} [22]. The resulting SnO_2 powder is characterized by high photocatalytic activity.

An analysis of the scientific literature shows [17–22] that the electrosynthesis of tin oxides is a promising and highly-technological technique for obtaining catalytically active materials. At the same time, an issue on the ratio of SnO and SnO_2 in the obtained deposits is still not studied well. In this regard, it appears relevant to examine dependence of the composition and properties of tin oxides on the conditions for performing electrosynthesis.

3. The aim and objectives of the study

The aim of present work is to establish the influence of electrosynthesis conditions on the composition and properties of a tin-oxide catalyst. This will make it possible to develop a new technology for the predictable synthesis of tin oxides with a specified composition with the desired catalytic activity towards anodic oxidation reactions.

To achieve the set aim, the following tasks have been solved:

- to obtain dependences of the composition of tin oxide mixture of varying degrees of oxidation on the magnitude of anode potential, and to establish a formation mechanism of these oxides;
- to determine catalytic activity of the tin-oxide catalyst in relation to the anode decomposition reaction of methyl tert-butyl ether.

4. Materials and methods for examining the electrosynthesis, structure, and catalytic activity of tin oxides

The research was conducted in a KOH solution of variable concentration. We used a face tin electrode, pressed into a Teflon housing, as a working electrode. A mercury oxide alkaline electrode whose potential is equal to 0.25 V was applied as the comparison electrode in alkaline solutions. The values of potentials were converted to a hydrogen scale. Electrochemical studies were conducted in a standard three-electrode cell. Instruments included the impulse potentiostat PI-50-1.1 (Belarus), programmer PR-8 (Belarus), and a two-coordinate potentiometer N-307/1 (Belarus).

PH indices of solutions were controlled using the universal ionomer EV-74 (Belarus).

Determination of the oxide mixture composition was performed in line with the original methodology using coulometry [23]. The oxide film was reduced in a solution containing 0.01 mol/l of KCl and tartrate buffer at pH 3.5. Under these conditions, chemical dissolution of tin and tin oxides is excluded. The process was conducted at potentials –0.2 V and –0.7 V, corresponding to the reduction of Sn(II) and Sn(IV), respectively [24].

Oxidation of methyl tert-butyl ether (MTBE) was carried out in a cell with separate cathode and anode spaces.

We used steel 3 as the cathode. In all experiments, starting concentration of MTBE in electrolytes was 0.04 mol/l.

A change in the concentration of MTBE during its anodic decomposition was performed using the gas-liquid chromatograph Shrom-5 (Czech Republic). To plot a calibration chart, we used standard MTBE solutions with concentrations of 2, 5, 6, 8, 10 ml/l of MTBE (Fig. 1).

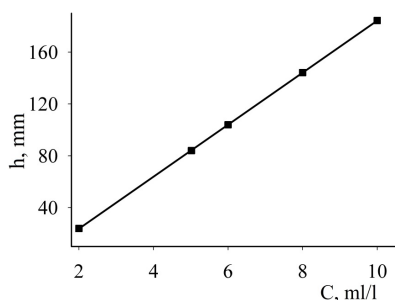


Fig. 1. Dependence of chromatographic peak height on the concentration of standard MTBE solutions

The Sn(SnO_x) surface morphology study was performed using the raster electron microscope REMMA 102-02 (Ukraine). Accelerating voltage was 20 kV, resolution – 5 nm.

5. Results of examining the influence of electroynthesis conditions on the composition of tin-oxide catalyst

In order to establish mechanism for the formation of oxide compounds of tin in the electroynthesis process, we obtained anode voltammogram on the tin electrode (Fig. 2). A decrease in the anodic current density on plots KF and FG is caused by the adsorption blocking of electrode's surface by the hardly-soluble tin compounds.

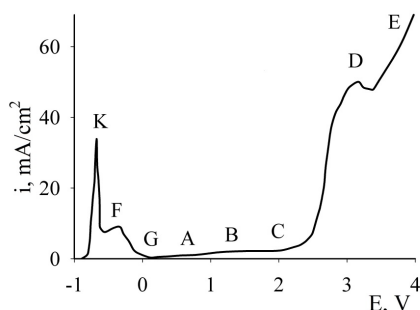
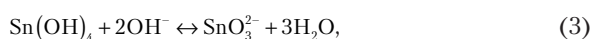
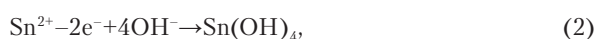


Fig. 2. Volt-ampere dependence, registered on the tin electrode in a 0.5M KOH solution. Linear potential sweep speed is 10 mV/s

Coulometric study into the composition of electroynthesis products at electrode's potential –0.3 V (plot FG, Fig. 1) showed that the molar ratio of Sn(II)/Sn(IV) in this case is equal to unity (Table 1). An analysis of the processes that might occur under the specified conditions of electroynthesis allowed us to make up the following reaction pathway:



Thus, at potential –0.3 V, tin surface is coated with a thin layer of SnSnO₃.

Table 1

Results of coulometric analysis of oxide films on tin

Potential of oxide film formation, V	Sn(IV):Sn(II), % (mol)
–0,3	50:50
0	45:55
+1.0	41:59
+3.0	59:41

Fig. 1 shows that the morphology of the tin electrode surface, treated in a 0.5M KOH solution at $E = -0.3$ V, is an amorphous structure.

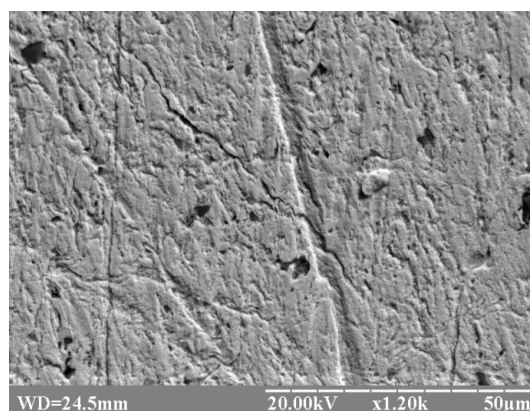


Fig. 3. Microphotograph of the tin electrode surface, treated in a 0.5 M KOH solution at $E = -0.3$ V

A further increase in the anode potential contributes to a transition into the region of passive state of the electrode (–0.2–1.0 V). In this region (plot GA), current is virtually zero.

The region of voltammogram (plot ABCD) consists of two sections, which correspond to the activation of the anodic process.

The first section corresponds to the interval of potentials from 1.0 to 2.2 V (plot ABS, Fig. 4). The area of current limit is observed here. A possible reason for this effect can be the occurring post-oxidation process of the mosaic structure of tin oxides. However, the coulometric analysis revealed that the relative content of Sn(IV) in oxide mixture at 1.0 V is less than at –0.3 V (Table 1), and is 42 % (mol).

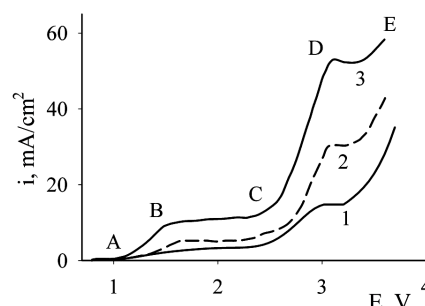


Fig. 4. Voltammograms, registered on tin ($V = 10$ mV/s) in the KOH solutions: 1 – 0.1 M, 2 – 0.5 M, 3 – 1.0 M

Thus, activation on plot AB (Fig. 4) is not related to an increase in the proportion of Sn^{4+} compounds in the volume of an oxide film. Apparently, in this case, there is no oxidation of the primary SnSnO_3 salt film. An increase in the electrode's anode potential obviously results in the intensified oxidation process of a matrix metal with the salt film being saturated with the Sn^{2+} ions.

It should be noted that there is a release of oxygen in the region of potentials, corresponding to plot ABC (Fig. 4). This becomes possible due to the course of the following sequential processes. Electrooxidation of hydroxide-ions leads to the formation of hydrogen peroxide:



The latter catalytically decomposes into tin dioxide with the formation of oxygen:



The equilibrium potential of reaction (5) at pH 13 is 0.985 V, which is close to experimental data. Thus, the onset of activation corresponds to the potentials approximately equal to 1 V (Fig. 4). The second activation section of the anodic process (plot CD) is probably due to the electrooxidation processes of OH^- -ions and water.

As a result of the course of anodic reaction there occur diffusion limitations in the delivery of OH^- -ions to the electrode surface. This leads to a higher proportion of current being used to electrooxidize the water by reaction:



The course of reaction (7) determines a partial dehydration of the oxide film, which affects the composition of the oxide mixture.

Coulometric study into oxide films formed at a potential equal to 3.0 V showed (Table 1) that the content of Sn(IV) was 59 % (mol), Sn(II) – 41 % (mol). That is, the film contains 18 % (mol) of Sn(IV) , which is not included in the composition of SnSnO_3 . Reduction of pH of the near-electrode layer due to reaction (7) contributes to the transition of SnO_3^{2-} ions into thermodynamically-stable form of SnO_2 . Therefore, this region of potentials matches the onset of a process of converting SnSnO_3 into SnO_2 .

It is noteworthy that at a potential equal to 3.0 V there is a maximum of anode current (Fig. 4). The emergence of this maximum may be related to a change in the ohmic resistance as a result of dehydration and enrichment of the resulting film with tin dioxide. Thus, the formation of an oxide film with elevated content of tin dioxide occurs when electrosynthesis at a potential of 3.0 V.

6. Discussion of results of examining the influence of electrosynthesis conditions on the composition and catalytic activity of the tin-oxide catalyst

Tin dioxide and composite materials based on it are actively used in electrochemical technologies when creating semiconductors with strong electrocatalytic properties. It would seem advisable to establish the dependence of catalytic activity of oxide films on tin on the conditions of a catalyst synthesis. The research was conducted employing the

substance MTBE, which is an effective additive to gasoline. This substance is dangerous for the environment with one of the most efficient techniques for its destruction being the electrooxidation on metal-oxide electrodes.

Given this, very promising is the considered electrosynthesis of catalytically-active oxide layer on the surface of a metal that is homogeneous with a given oxide. In such systems, the regeneration of an oxide layer is implemented, which provides the possibility to prolong operation life of the catalyst.

The electrooxidation of ether was conducted at the anode potential 3.0 V. At this potential, the most complete regeneration of an oxide layer on the electrode surface takes place.

Dependence of change in the concentration of MTBE on the duration of anode process is shown in Fig. 5. Curve 1 corresponds to the destruction of MTBE on the tin electrode without anodic pre-treatment. Because the electrooxidation was performed at an electrode potential equal to 3.0 V, at the same time with the destruction of MTBE, the oxide layer formation took place on the surface of tin. This naturally contributed to the intensification of the target process.

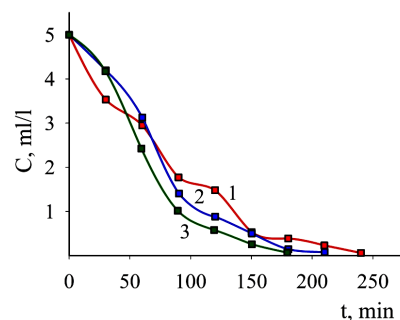


Fig. 5. Dependences of MTBE concentration on the duration of electrolysis in a 0.5M KOH solution: 1 – tin electrode, oxidized by oxygen in the air; 2 – tin electrode treated in 0.5M KOH at $E=3.0$ V; 3 – tin electrode treated in 0.5M KOH at $E=3.0$ V with subsequent thermal treatment at 100 °C

The oxide catalyst, obtained in advance by electrosynthesis, speeds up this process (Fig. 5, curve 2). Thermal treatment of the oxide catalyst has a positive effect on the catalytic activity of oxide mixture (Fig. 5, curve 3). This is obviously due to the partial dehydration of the film and an increase in the content of SnO_2 . In addition, the loss of water may contribute to an increase in the porosity of film and, consequently, the active surface of the catalyst. Based on mutual arrangement of curves in Fig. 5, one can assume that the decomposition process of MTBE speeds up with an increase in the content of SnO_2 in a catalyst layer.

Based on the results of conducted research, we can argue about significant catalytic activity of the oxide films formed on the surface of tin using the electrosynthesis method. Thus, the starting concentration of MTBE is reduced by 98 % within 180 minutes, while only 73 % of MTBE is decomposed over the same time on a nickel electrode [25].

7. Conclusions

1. Studies into the influence of electrosynthesis conditions on the composition of tin oxides have shown that the mechanism of anodic process is the most important. Under the proposed mechanism for the formation of oxide

film on tin, the resulting products of SnO_3^{2-} are bound by the intermediate Sn^{2+} and form a stable compound SnSnO_3 . By using the original coulometric technique, we determined the composition of oxide mixture, obtained at different values of potential. It is established that at a potential of 3.0 V the ratio of $\text{Sn(IV)}:\text{Sn(II)}$ is equal to 59:41. We detected and characterized a maximum of anode current on the tin electrode in alkaline medium at an electrode potential of 3.0 V. It was established that the height of this maximum depends on the concentration of KOH. The emergence of maximum is related to the dehydration of oxide film due to the electrooxidation of

crystalline water and an increase in the ohmic resistance of the film. Based on data on the composition of the oxide mixture, we proposed a tin surface treatment method at a potential of 3.0 V.

2. The oxide mixtures, formed on tin as a result of electrosynthesis, possess catalytic activity. It is shown that the acceleration of the reaction of MTBE electrooxidation occurs at an increase in the oxygen-containing compounds of tin on the surface of electrode. It was established that the kinetic characteristics of electrode reactions that proceed on the oxide anodes depend on the technique for preliminary preparation of electrodes.

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