

Article

Pulse Electrolysis Technique for Preparation of Bimetal Tin-Containing Electrocatalytic Materials

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Abstract: Platinum–tin-containing materials are the most popular catalysts for processes occurring in fuel cells with direct ethanol oxidation. Pulse electrolysis based on the electrochemical dispersion of platinum electrodes under the influence of alternating pulse current in an alkaline electrolyte made it possible to introduce the tin component into the catalyst in the form of a dopant, an alloy with platinum, and in the form of an oxide phase and evaluate the effect of the form in which tin is present in the catalyst on its microstructural and electrocatalytic characteristics. The introduction of tin into the catalyst generally increases the rate of ethanol electrooxidation; however, with the most prominent effect observed when tin is present in form of an oxide.

Keywords: pulse electrolysis; direct ethanol fuel cell; platinum; tin; electrocatalysis; CO stripping



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1. Introduction

It is well-known that bi- or polymetallic nanostructures [1,2], including tin- and platinum-based nanostructures, are of great interest due to their potential application in fuel cell technologies with direct oxidation of liquid organic fuel [1,3,4]. Tin is known as the most active cocatalyst for the electrochemical oxidation of ethanol on platinum due to higher oxophilicity of Sn surfaces compared to Pt and other metals [5]. The incorporation of tin into a platinum catalyst changes the electrode's geometric and electronic structure, providing conditions required for complete ethanol oxidation to carbon dioxide [6].

When developing catalytic materials based on metal alloys, in particular, platinum-based alloys, considerable attention is paid to controlling the composition, size, and structure of catalytically active nanoparticles [2,7,8]. However, the preparation of bimetallic nanoparticles is often a technologically complex process that requires the use of high-temperature post-processing of materials, which can lead to sintering and coarsening of catalytically active particles.

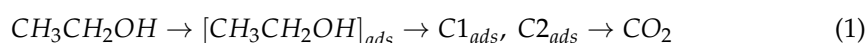
Tin can be included in the composition of Pt-containing materials in the form of adatoms [9], alloy [10], in the form of tin oxide as a support for Pt nanoparticles [11,12], and as a dopant of Pt nanoparticles [13,14]. Most of the methods for preparing bimetallic electrocatalysts based on platinum and tin belong to the group of bottom-up methods, which do not allow obtaining materials with the same crystallographic properties of the platinum component in order to assess the effect of the type of introduction of the tin component in the composition of a platinum-containing material.

Pulse electrolysis has already established itself as an effective method for obtaining both materials based on platinum nanoparticles [15] and tin oxides [16,17] for various applications by dispersion of metal electrodes under the influence of alternating pulse current in aqueous electrolytes. At the same time, due to the highly nonequilibrium conditions that arise in the near-electrode region when alternating pulse current is applied to the electrodes, pulse electrolysis made it possible to obtain non-hydrated crystalline products that do not require high-temperature post-processing techniques. In addition,

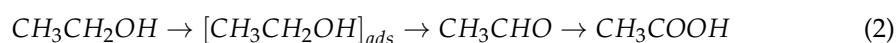
the crystallographic properties of platinum nanoparticles obtained under the conditions of pulse electrolysis are practically independent of the properties of the support [18].

In the technology of low-temperature fuel cells (LTFCs), not only hydrogen fuel cells, but also fuel cells with direct liquid fuel oxidation are attracting much attention. A large amount of research has been devoted to the study of methanol as a fuel [19–21]. However, the toxicological properties of methanol have been among the limiting factors for the use of methanol in real energy systems based on fuel cells. From this point of view, ethanol seems to be a more attractive type of fuel for LTFCs [22,23], the production of which is possible in large quantities in the processes of biomass fermentation [24].

Studies of the electrooxidation of ethanol on platinum with the identification of adsorbed intermediates and elucidation of the reaction mechanism using various methods, such as differential electrochemical mass spectrometry, Fourier-transform infrared spectroscopy, electrochemical thermal desorption mass spectroscopy [25–30], established the general mechanism of ethanol oxidation, and it was shown that in an acidic medium, the process can proceed either to CO_2 through the formation of stable C1_{ads} , C2_{ads} intermediates (hereinafter, C1_{ads} is denoted as CO):



or partially to formic acid:

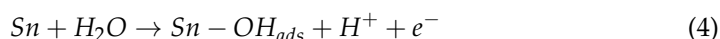


It is known that tin is a good promoter of the electrochemical oxidation of ethanol on Pt-containing catalysts since tin and its oxides are more oxophilic than platinum group metals [31]. In the presence of tin in the catalytic system, the oxidation of ethanol proceeds according to a bifunctional mechanism [32] and consists in:

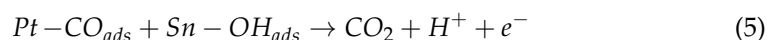
1. the adsorption of organic particles on platinum:



2. the adsorption of oxygen-containing particles on the tin component, or tin in the oxide form can itself be a source of oxygen-containing particles:



3. the chemical interaction of particles of organic nature and oxygen-containing particles:



As already noted, tin can be included in the composition of Pt-containing catalysts in the form of adatoms, a dopant, an alloy with platinum, and a tin oxide, as a support or a component of a support for Pt nanoparticles. It should be noted that there are very few works in which a comparative assessment of the effect of the method of introducing tin or tin oxides into the Pt-based catalytic system was carried out [33]. In addition, traditional chemical methods for the synthesis of Pt-containing materials, including those containing tin in a different form, are severely limited due to the influence of the composition and properties of the support (pure carbon, carbon/metal oxide composite) and the properties of the initial precursors of Pt–Sn alloys on the microstructural and, as a consequence, electrochemical characteristics of the active catalytic phase (platinum). From this point of view, pulse electrolysis makes it possible to evaluate the influence of the composition and properties of the tin component while maintaining the microstructural characteristics of the platinum component.

2. Results and Discussion

2.1. Composition and Microstructure Characterization

To obtain platinum–tin-containing materials under the conditions of pulse electrolysis, three synthesis strategies were used (Figure 1) with the introduction of the tin component:

1. in the form of tin hydroxide, which made it possible to obtain materials based on tin-doped platinum nanoparticles [13] (strategy 1, Figure 1),
2. in the form of a dispersed tin oxide into the electrolyte, which made it possible to obtain Pt/SnO₂/C materials [11,18] (strategy 2, Figure 1),
3. in the form of a platinum–tin alloy Pt₃Sn supported onto carbon black (strategy 3, Figure 1).

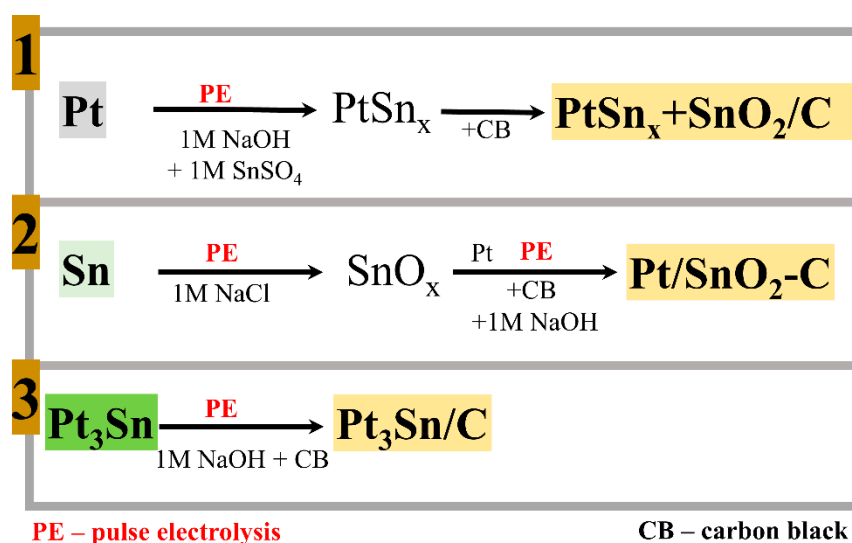


Figure 1. Strategies for obtaining platinum–tin-containing materials under pulse electrolysis conditions: strategy 1—introduction of the tin component in the form of a platinum-doping element, strategy 2—introduction of the tin component in the form of tin dioxide into the SnO₂/C hybrid support, strategy 3—introduction of the tin component as an alloy with platinum.

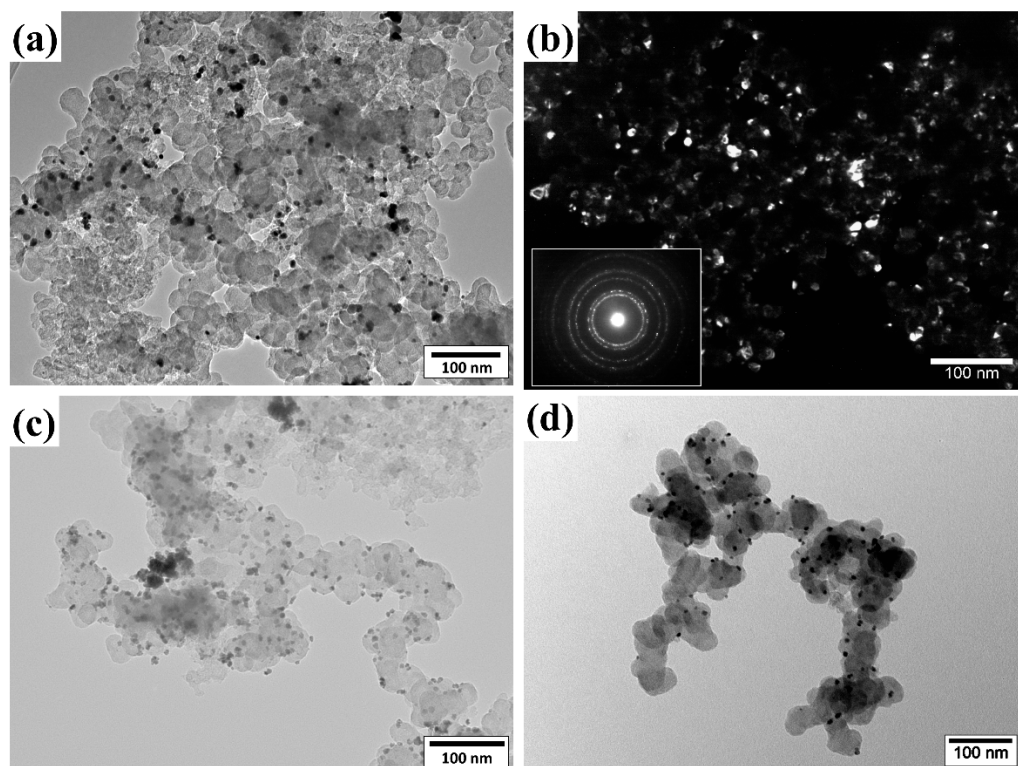
X-ray phase analysis of the Pt₃Sn/C (Figure S2) and PtSn_x (Figure S3a) [13] materials obtained under the conditions of pulse electrolysis showed they were characterized by an increase in the unit cell parameter in comparison with the Pt nanoparticles in Pt/C (Table 1) due to the doping of platinum with tin in the case of PtSn_x [13] as well as the formation of alloy nanoparticles in the case of the Pt₃Sn/C material. The obtained results are in good agreement with the cell parameter data for Pt₃Sn as reported in [34]. It is important to note four main points here:

1. the composition of the platinum–tin alloy nanoparticles obtained as a result of the dispersion of the Pt₃Sn alloy electrodes (strategy 3) corresponds to the composition of the initial alloy electrode: using energy-dispersive X-ray spectroscopy (EDS) (Figure S1), it was found that the atomic ratio of the elements in a dispersed electrode is as follows: Pt:Sn = 3:1;
2. the PtSn_x-based material (strategy 1) was characterized by the presence of SnO₂ in its composition, the concentration of which in relation to the PtSn_x particles was 11 wt.%, while EDS mapping of PtSn_x + SnO₂/C showed a fairly uniform distribution of the Pt, Sn, O, and C elements (Figure S3b);
3. Pt/C and Pt/SnO₂/C (strategy 2) were characterized by the same platinum unit cell parameters (Table 1, Figure S4);
4. 3D spectra of the Pt₃Sn/C material (XPS analysis, Figure S4) demonstrate the presence of both an oxidized tin surface and tin in the metallic state.

Table 1. Crystallographic parameters of the Pt-based and Sn-containing materials prepared via pulse electrolysis technique.

Sample	a, Å	D (XRD), nm	D (TEM), nm
Pt/C	3.9131	7.3 ± 1.0	10.4 ± 1.0
PtSn _x + SnO ₂ /C	3.9174	5.6 ± 0.6	-
Pt/SnO ₂ /C	3.9131	7.3 ± 1.0	8.0 ± 0.8
Pt ₃ Sn/C	4.0047	5.7 ± 0.8	7.6 ± 0.7

Studies of the Pt/C, Pt/SnO₂/C, and Pt₃Sn/C materials by transmission electron microscopy (TEM) show that nanoparticles of the platinum-containing phase are rather uniformly distributed over the surface of carbon black or carbon black + tin dioxide composite support (Figure 2a,c,d). Studies of the PtSn_x + SnO₂ material by scanning transmission electron microscopy (STEM) (Figure 2b) show that PtSn_x particles are fairly evenly distributed over the surface of the tin oxide phase. This phase is probably a mixture of crystalline tin dioxide, the presence of which was confirmed by XRD. In addition, the SAED results (inset in Figure 2b) clearly show at least four main diffraction rings that can be indexed to the (111), (200), (220), and (311) reflections of the FCC structure. These results confirm the crystallinity of the PtSn_x + SnO₂ sample.

**Figure 2.** TEM images of Pt/C (a), Pt/SnO₂-C (c), Pt₃Sn/C (d), and a STEM image of PtSn_x + SnO₂ (b).

The obtained results for the composition and microstructure of bimetallic materials synthesized under the influence of alternating pulse current showed promising results for the application of pulse electrolysis with the addition of tin in platinum-containing materials in the form of a dopant or as an oxide phase in the composition of a hybrid support or as an alloy of tin with platinum.

2.2. Electrocatalytic Properties

In this regard, the electrocatalytic properties of materials were studied using the example of electrochemical oxidation of CO and ethanol in acidic media.

Figure 3a demonstrates the anodic scan of the CV curves of the Pt/C and platinum–tin-based materials in 0.5 M H₂SO₄ during the CO stripping process. In the general case, the introduction of tin into the composition of a platinum-containing material led to an increase in electrocatalytic activity of synthesized materials (current density at 0.6 V at platinum–tin-containing materials ($j_{0.6V}$) was higher than on Pt/C) and contributed to a decrease in the overvoltage of the CO electrooxidation process (potential of the CO electrooxidation peak (E_{peak}) for platinum–tin-containing materials was shifted to the cathode potential relative to Pt/C) (Figure 3b). Full CVs of the CO stripping process on the Pt/C and platinum–tin-based materials are shown in Figure S6.

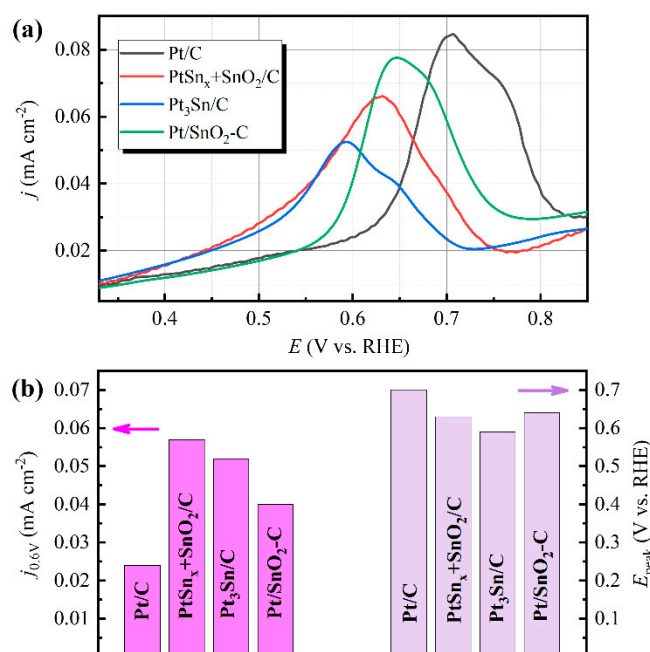


Figure 3. Anodic scan of the CV curves of the Pt/C and platinum–tin-based materials in 0.5 M H₂SO₄ during the CO stripping process; scan rate, 0.02 V s⁻¹ (a); current density at 0.6 V vs. RHE and potential of the CO electrooxidation peak of CO during the CO stripping process (b).

The value of the electrochemically active surface area (ECSA) determined by CO stripping practically did not depend on the presence of tin in the composition of the material (Table 2).

Table 2. Electrocatalytic properties of the Pt-based and Sn-containing materials prepared via the pulse electrolysis technique.

Sample	CO Stripping			Ethanol Electrooxidation			
	ECSA, m ² g ⁻¹	$j_{0.6V}$, mA cm ⁻²	E_{peak} , V	$j_{0.6V}$, mA cm ⁻²	j_{peak} , mA cm ⁻²	E_{onset} , V	E_{peak} , V
Pt/C	13.1 ± 1.3	0.024	0.70	0.046	0.406	0.77	0.93
PtSn _x + SnO ₂ /C	12.3 ± 1.2	0.057	0.63	0.083	0.84	0.62	0.90
Pt/SnO ₂ /C	13.1 ± 1.5	0.040	0.64	0.113	1.19	0.62	0.86
Pt ₃ Sn/C	13.5 ± 1.5	0.052	0.59	0.62	0.64	0.61	0.90

The CVs of the Pt/C and platinum–tin-based materials have a typical shape for Pt-containing materials (Figure 4a) and are characterized by ethanol oxidation peaks in the potential range of 0.6–1.0 V and 0.8–0.4 V at the anode and cathode scans, respectively. In general, all tin-containing materials demonstrate a significant decrease in both the potential for the onset of ethanol oxidation (E_{onset}) and the potential for the peak of ethanol oxidation (E_{peak}) compared to Pt/C (Table 2). Thus, regardless of the state and method of introduction, the presence of tin in the composition of the Pt-containing material contributed to a decrease in the overvoltage of the electrooxidation of ethanol on platinum and increased the electrocatalytic activity of the material. The highest electrocatalytic activity, expressed by the rate of ethanol oxidation at a potential of 0.6 V ($j_{0.6V}$) and at oxidation peak potentials (j_{peak}), was demonstrated by the Pt/SnO₂/C material.

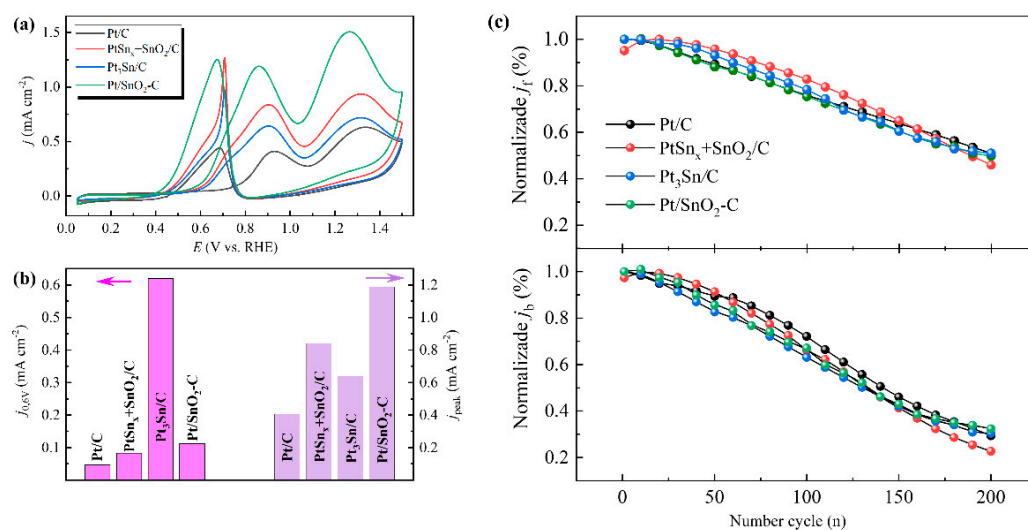


Figure 4. CV curves of the Pt/C and platinum–tin-based materials in the 0.5 M H₂SO₄ + 0.5 M C₂H₅OH electrolyte; scan rate, 0.02 V s⁻¹ (a); current density at 0.6 V vs. RHE and current density of the anodic peak of ethanol electrooxidation (b); normalized current density of the ethanol electrooxidation peaks on the forward (j_f) and back (j_b) scans of the CVs during the accelerated stress test (c).

It should be noted that among the platinum–tin-containing materials in which tin was incorporated into the composition of the platinum crystal lattice in various ways—doping with tin (PtSn_x) and alloy (Pt₃Sn)—the highest electrocatalytic activity was demonstrated by the PtSn_x + SnO₂/C material, which is characterized by the presence of tin oxide in its composition in the form of SnO₂ at 11 wt.%. Based on the obtained results, it can be concluded that the presence of tin in the oxide phase form has a greater effect on the anodic electrocatalytic processes occurring on Pt-containing materials.

It should also be noted that the rate of degradation of Pt/C and platinum–tin-based materials, which is a change in the current density of the peak of ethanol oxidation on the forward and back scans of CV under accelerated stress testing conditions for all the studied materials, had a similar character (Figure 4c). However, higher current densities of ethanol oxidation in the presence of tin give hope for the prospects of using platinum–tin-based systems in ethanol fuel cells.

Thus, regardless of the state in which tin is in platinum–tin-containing materials, in which both the platinum and tin components are obtained under pulse electrolysis conditions, such materials demonstrate an increased electrocatalytic activity in the ethanol electrooxidation reaction in comparison with Pt-containing materials obtained by a similar method and which do not contain tin. In this case, the oxide phase of tin demonstrated the greatest contribution to the increase in the electrocatalytic activity of Pt-containing materials in the ethanol electrochemical oxidation process. In the general case, it should be noted that the electrocatalytic activity of platinum–tin-containing materials obtained under

pulse electrolysis conditions is comparable to the electrocatalytic activity of materials of similar composition obtained by other laboratory methods (Table S1).

3. Materials and Methods

3.1. Electrocatalyst Preparation

To prepare the Pt/C material, two platinum foil electrodes with the same geometric dimensions were placed in a suspension of carbon support Vulcan XC-72 in 1 M NaOH. Alternating pulse current was applied to the Pt electrodes; the current shape is shown in Figure 5. Under the influence of alternating pulse current, electrochemical dispersion of platinum electrodes to platinum nanoparticles occurred, which were simultaneously deposited on a carbon support.

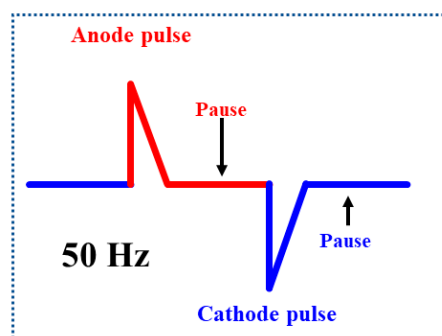


Figure 5. Alternating pulse current profile used during pulse electrolysis.

The Pt₃Sn/C material was obtained in a similar way: two Pt₃Sn foil electrodes were electrochemically dispersed under the influence of alternating pulse current in a suspension of carbon support Vulcan XC-72 in 1 M NaOH.

To prepare PtSn_x particles containing a catalyst, two platinum foil electrodes with the same geometric area were placed in a suspension of carbon support Vulcan XC-72 in a 1 M NaOH + 1 M SnSO₄ electrolyte and subjected to alternating pulse current. Carbon support Vulcan XC-72 was added to the PtSn_x particles at the stage of preparation of the catalytic ink.

The Pt/SnO₂/C electrocatalyst was prepared via electrochemical dispersion of two platinum foil electrodes in a suspension of carbon support Vulcan XC-72 and SnO₂ particles in 1 M NaOH. Loading of SnO₂ in the final Pt/SnO₂/C electrocatalyst was 15 wt.%.

Pt, Pt₃Sn, PtSn_x loading in the electrocatalysts was 20.0 ± 2.0 wt%. Pt loading was controlled by the duration of synthesis, taking into account that the rate of dispersion of platinum under the conditions of pulse electrolysis was 10.0 ± 1.0 mg (cm^{−2} h^{−1}). The average density of alternating pulse current was 1.0 A cm^{−2}. Electrochemical synthesis of materials under conditions of pulse electrolysis was carried out with continuous stirring and cooling of the electrolyte. After synthesis, the Pt/C and platinum–tin-containing electrocatalyst suspension was filtered, washed many times with distilled water, and dried at 80 °C.

3.2. Composition and Microstructure Studies

XRD patterns were obtained by using an ARL X'TRA powder diffractometer, a Thermo Scientific diffractometer equipped with a Cu Kα source operating at 40 kV and 40 mA. XRD data were collected in the 2θ range of 30–90° using the step scan mode with a step size of 0.03 deg and a step time of 1.8 s. The instrumental resolution function was determined in a special diffraction experiment with LaB6 powder (NIST SRM660a). The average size and the unit cell parameter of Pt-containing nanoparticles were determined by refining the X-ray diffraction pattern by the Rietveld method using the spherical harmonic technique [35].

The transmission electron microscopy measurements were made on a JEOL JEM 1400 microscope at an accelerating voltage of 120 kV in the light field. Samples were prepared

by dispersion in ethanol and exposed to ultrasound for 10 min. A droplet with suspended particles was applied onto copper meshes covered with a carbon film (Holey Carbon Grid).

The chemical composition of the Pt₃Sn electrodes was examined using an EDAX Norton system 6 attached to the SEM unit.

3.3. Electrochemical Measurements

The “catalytic ink” contained the synthesized electrocatalysts, 10% Nafion® DE-1020 solution and isopropanol. All the electrochemical measurements were carried out in a standard three-electrode cell. The preparation of the working electrode included dropping catalytic ink onto a glassy carbon plate and drying the electrode in the air. A platinum wire was used as the counter electrode. An Ag/AgCl electrode was used as a reference electrode. All the potentials were then recalculated on the scale of a reversible hydrogen electrode (RHE). Before starting all the electrochemical measurements, the working electrode was cycled 30 times in 0.5 M H₂SO₄ over a potential range of 0.05–1.5 V, scan rate of 0.02 V s^{−1} (Figure S7).

Electrochemical cycling performance tests were implemented in a three-electrode cell in 0.5 M H₂SO₄ containing 0.5 M C₂H₅OH deaerated with N₂ over a potential range of 0.05–1.5 V. Comparison of the CVs was carried out after preliminary cycling of the working electrode for 20 cycles. The electrochemically active surface area (ECSA) of the electrocatalysts was determined by CO stripping. CO was preliminarily adsorbed on the working electrode at a potential of 0.3 V (RHE) in the deaerated 0.5 M H₂SO₄ electrolyte. Then, CO was removed from the electrolyte by purging the electrolyte with N₂, and the CV of the electrode was measured from 0.3 V. A CO desorption peak was observed in the first cycle. Based on the charge used for CO desorption, the surface area of platinum-containing particles was calculated as follows:

$$ECSA = \frac{Q_{CO}}{Q_m \times g_{Pt}} \quad (6)$$

where Q_{CO} is the charge passed during CO oxidation, g_{Pt} is the mass of the Pt-containing phase on the working electrode, and $Q_m = 420 \mu\text{C cm}^{-2}$ [36] is the charge required for the desorption of a CO_{ads} monolayer.

An accelerated stress test was carried out in 0.5 M H₂SO₄ containing 0.5 M C₂H₅OH deaerated with N₂ over a potential range of 0.05–1.5 V, scan rate of 0.02 V s^{−1}. Every 10th cycle was recorded.

4. Conclusions

Pulse electrolysis makes it possible to introduce tin into the composition of Pt-containing catalysts in the form of a dopant, an alloy with platinum, or as part of a tin oxide–carbon hybrid support. Electrochemical dispersion of platinum electrodes in 1 M NaOH containing tin ions ensures the formation of a multicomponent PtSn_x + SnO₂ material. When platinum is dispersed in a suspension containing carbon support and SnO₂ particles, Pt/SnO₂/C materials are formed. As a result of the dispersion of the Pt₃Sn alloy in 1 M NaOH under the conditions of pulse electrolysis, Pt₃Sn particles are formed, the composition of which is similar to that of the dispersed alloy, and in the presence of a carbon support in the electrolyte, it is possible to obtain the Pt₃Sn/C material in one stage.

Platinum–tin-containing materials obtained under the conditions of pulse electrolysis demonstrated high electrocatalytic activity in the electrooxidation of ethanol compared to the Pt/C material regardless of the method of introducing the tin component into them. However, among all the platinum–tin-containing materials, the maximum electrocatalytic activity was shown by materials in which tin was present in the form of tin oxide in the composition of the hybrid support. The result obtained may be due to the fact that SnO₂ has a greater effect on the process of ethanol electrooxidation as a result of the greater oxophilicity of tin oxide compared to the tin component in the form of an alloy with platinum or a doping element.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12111444/s1>, Figure S1: Results of the study of the Pt₃Sn electrode by the method of energy-dispersive X-ray spectroscopy; Figure S2: XRD powder pattern and Rietveld refinement plot of a synthesized carbon-supported Pt₃Sn sample. Red dots—observed intensity; black solid line—intensity estimated by the Rietveld refinement; blue line—difference between the experimental and calculated intensities; green tick marks correspond to the Fm3m unit cell of platinum; Figure S3: XRD powder pattern and Rietveld refinement plot of a synthesized carbon-supported PtSn_x sample. Red dots—observed intensity; black solid line—intensity estimated by the Rietveld refinement; blue line—difference between the experimental and calculated intensities; brown tick marks correspond to P42/mnm unit cell of the SnO₂ phase, green tick marks correspond to the Fm3m unit cell of platinum; Figure S4: XRD powder pattern of Pt/C and Pt/SnO₂/C; Figure S5: Sn 3D spectra of the tin-containing materials prepared via pulse electrolysis, blue line—Sn(IV), red line—Sn(0); Figure S6: CO stripping of the Pt/C and platinum-tin-based materials in 0.5 M H₂SO₄, scan rate, 0.02 V s^{−1}; Figure S7: CV curves of the Pt/C and platinum-tin-based materials in 0.5 M H₂SO₄, scan rate, 0.02 V s^{−1}; Table S1: Comparison of the electrochemical properties of platinum–tin-based materials. References [37–41] are cited in the supplementary materials.

Author Contributions: Investigation, A.K., M.K., I.L. and T.M.; writing—original draft preparation, A.K.; writing—review and editing, N.S.; supervision, N.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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