



Agnieszka Martyla^{1*}, Maciej Kopczyk¹, Monika Osińska-Broniarz¹, Piotr Marciniak², Robert Przekop³

¹ Institute of Non-Ferrous Metals, Division in Poznan, Central Laboratory of Batteries and Cells, ul. Forteczna 12, 61-362 Poznan, Poland

² Poznan Science and Technology Park of Adam Mickiewicz University Foundation, ul. Rubież 46, 61-612 Poznan, Poland

³ Centre of Advanced Technologies, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznan, Poland

*Corresponding author. E-mail: agnieszka.martyla@claio.poznan.pl

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NANOCOMPOSITE ELECTRODE MATERIALS IN ALCOHOL OXIDATION REACTIONS

This paper presents an electroactivity comparison of Pt/SnO₂ nanocomposites with different metal phase precursors in a methanol oxidation reaction. One of them is a water solution of hexachloroplatinic acid and the second is the platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (known as Karstedt's catalyst). The Pt/SnO₂ system has a broad range of applications in various sectors of industry. It is a very popular heterogeneous and electrochemical catalyst as well, especially in fuel cells. This effect is due to the presence of platinum. As the most expensive component of the catalyst it is still a barrier to its widespread use, hence, the constant search for new, cost-effective methods of obtaining this kind of systems. The aim of the research was to obtain a highly active Pt/SnO₂ catalyst with a low metal concentration in an electrochemical system. The small size of the Pt crystallites should result in high activity of the Pt/SnO₂ system. We proposed two synthesis methods of the platinum catalyst based on the sol-gel technique and tin(IV) acetate as the SnO₂ precursor in conjunction with the use of inorganic and organic sources of the metallic phase. The presented method of SnO₂ synthesis allows for obtaining nano-support and in the next step - a nano-catalyst. The system structures were investigated using TEM and XRD techniques to describe their thermal structural evolution. To study the influence of the metallic phase precursor, we used cyclic voltammetry (in acidic media), which is the best method to check the activity of the electrocatalyst. The results showed high electrocatalytic activity of the nanocomposites, irrespective of the metal phase source. The systems obtained from an organosilicone precursor demonstrate high temperature stability.

Keywords: sol-gel, composite, electrocatalyst

NANOKOMPOZYTOWE MATERIAŁY ELEKTRODOWE W REAKCJACH UTLENIANIA ALKOHOLI

Prezentowana praca zawiera porównanie elektroaktywności kompozytów Pt/SnO₂ w reakcji utleniania metanolu. Kompozyty te pochodzą z dwóch różnych prekursorów. Jednym z nich jest wodny roztwór kwasu sześciochloroplatinowego, a drugim kompleks platyna(0)-1,3-divinylo-1,1,3,3-tetrametylodisiloksan, zwany też katalizatorem Karstedta. Układ Pt/SnO₂ ma szerokie spektrum zastosowań jako katalizator w procesach reformingu węglowodorów, katalizator w ogniwach paliwowych. Jednak wysoki koszt platyny stanowi barierę w ich powszechnym stosowaniu. W pracy proponujemy dwie metody otrzymywania takiego układu wykorzystujące technikę zol-żel i octan cyny jako prekursor SnO₂ oraz dwa rodzaje prekursorów fazy metalicznej. Otrzymane układy zostały zbadane za pomocą cyklicznej woltamperometrii, która jest najlepszą techniką sprawdzenia elektroaktywności. Ponadto, przeprowadzono badania kompozytów za pomocą technik XRD oraz TEM, które wykazały istotne zależności między ich strukturą a obróbką termiczną. Rezultaty badań wskazują na wysoką aktywność elektrochemiczną kompozytów Pt/SnO₂ niezależnie od rodzaju prekursora. Kompozyty otrzymane z wodnego roztworu kwasu sześciochloroplatinowego dają wyższe wartości prądowe, z kolei te uzyskane z prekursora krzemooorganicznego wykazują wyższą stabilność temperaturową.

Słowa kluczowe: zol-żel, kompozyt, elektrokatalizator

INTRODUCTION

Platinum (Pt) has currently been regarded as the best catalyst for fuel cell electrochemical reactions. However, its high commercial cost and scarcity hinder its advantages. Moreover, pure Pt is not the most efficient anodic catalyst for fuel cells due to the fact that the Pt surface is known to be rapidly poisoned by strongly adsorbed species coming from the dissociative adsorption of ethanol [1]. To circumvent the limitation of bulk

noble metal catalysts, good support materials are being explored for the dispersion of these nanoparticles such as carbon-based materials [2, 3] and conductive polymers [4, 5]. The use of support materials could not only reduce the cost of noble metals but also improve the efficiency and poisoning tolerance of electrocatalysts [6].

Tin(IV) oxide was reported to be able to enhance the activity of a platinum catalyst for methanol and ethanol

electrooxidation [7-9]. The lattice structure of the tin(IV) oxide substrate allows for easy manipulation of pore size, making it a favorable material. This is important since the substrate is covered with nanosized platinum particles. Being able to control the pore size distribution can help make the process more effective owing to even platinum distribution over the entire surface of a desired concentration [10]. For these reasons, searching for new, simple and effective synthesis methods of highly active electrocatalysts is still a challenge.

The purpose of this work was to prepare Pt/SnO₂ catalyst systems from an H₂PtCl₆·6H₂O solution and Karstedt's catalyst as the platinum precursors with different metal phase concentrations and to investigate the effect of the precursor on the thermal stability and electrocatalytic activity in the oxidation of methanol.

EXPERIMENTAL PROCEDURE

1. Organic platinum precursor

The tin(IV) oxide precursor was tin(IV) acetate. 1.6 g of tin(IV) acetate was added to a mixture of 48 cm³ of isopropanol and 8 cm³ of methanol and immersed in an ultrasonic bath at 323 K until the tin(IV) acetate dissolved. Increasing amounts of a xylene Pt(dvs) catalyst solution were added to the tin acetate alcohol solutions, corresponding to 13 and 26 mg of Pt to obtain samples containing 1.87 and 3.74 wt.% Pt - series A. After Pt(dvs) dosing, the systems were dispersed in an ultrasonic bath at 323K for 24 hours. In these conditions, with no water added, an SnO₂ gel is formed by subsequent processes of transesterification, condensation, hydrolysis and esterification. Next, the resulting gel was dried in vacuum for 48 h at a temperature of 293 K. Series of samples containing 1.87 and 3.74 wt.% Pt were heated in air atmosphere for 4 hours at temperatures of 373, 473, 573, 673, and 773 K using a temperature gradient of 20K/min.

2. Inorganic platinum precursor

The tin(IV) oxide precursor was tin(IV) acetate. 1.6 g of tin(IV) acetate was added to 48 cm³ of isopropanol and 8 cm³ of methanol and immersed in an ultrasonic bath at 323K until the tin(IV) acetate dissolved. Increasing amounts of H₂PtCl₆·6H₂O solution were added to the tin acetate alcohol solution: 1.35, 2.7 and 5.4 cm³ respectively, corresponding to 28.12, 56.24 and 112.55 mg of Pt to obtain samples containing 4.1, 8.2 and 16.4 wt.% Pt - series B. After H₂PtCl₆·6H₂O dosing, the systems were dispersed in an ultrasonic bath at 323 K for 12 hours.

PHYSICOCHEMICAL CHARACTERISTICS

The cyclic voltammetry (CV) experiment was performed in a Swagelok two-electrode cell with the application of an ECLAB V10.12 VMP model 0.3 potentiostat/galvanostat by Bio-Logic, in the range of

potential from -0.5 to 1.0 V. The scan rate of 0.05 mVs⁻¹ was applied. The catalyst powders were suspended in a solution of PVdF-HFP in acetone with graphite and applied onto a stainless steel electrode. The electrolyte contained 1 mol/dm³ H₂SO₄ and 0.5 mol/dm³ CH₃OH. Phase identification was performed using an X-ray diffraction (XRD) powder diffractometer (Philips, PW 1050) using CuKα lamp radiation and an Ni filter. The X-ray spectra were recorded in the angular range of 5÷80° [2theta]. Imaging the surface was performed with a Transmission Electron Microscope - TEM (JOEL JEM 1200 EX).

RESULTS AND DISCUSSION

The electrocatalytic activity of the composite catalysts was evaluated by CV [11, 12.]. In this work, we compared the effect of the metal phase precursor by the ΔI parameter. Its value is equal to the amplitude of oxidation and reduction current (1):

$$\Delta I = I_{ox} + |I_{red}| \quad (1)$$

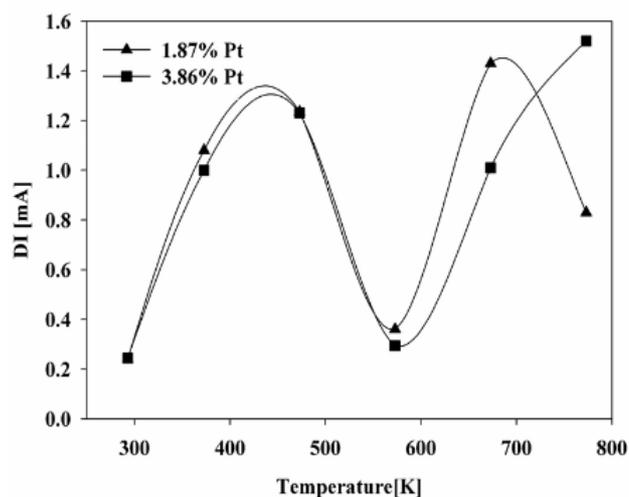


Fig. 1. Sum of oxidation current and absolute value of reduction current as function of temperature - Pt from organosilicone precursor (series A)

Rys. 1. Suma wartości prądowych w funkcji temperatury - Pt z prekursora krzemorganicznego (seria A)

The plots in Figure 1 the present values of the ΔI of systems obtained from Pt(dvs) as a function of temperature. We can observe comparable activity of both systems in the methanol oxidation reaction which is independent of the platinum content. The composites dried at room temperature show relatively low electrocatalytic activity. The maximal electrocatalytic activity for 430 K seems to be related to the decomposition of Karstedt's complex, which occurs at about 400 K in oxidative atmosphere. We suppose that small Pt clusters are stabilized by the formation of SiO₂. In the decomposition reaction of Karstedt's complex, silica and platinum form (Fig. 2).

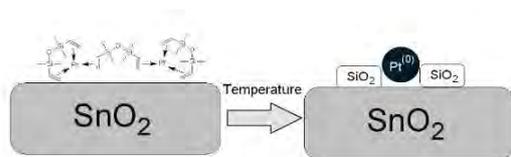


Fig. 2. Pt cluster formation mechanism in A system

Rys. 2. Mechanizm powstawania klastrow Pt w układzie A

The electrochemical activity of the composites after heat treatment at 393 K is related to Karstedt's complex in the surrounding SnO_2 gel. As a result of complex decomposition, small clusters of Pt are formed and we can observe them in TEM micrographs (Fig. 3). The heat treatment caused a change in the crystallite morphology and support grains. After heat treatment at 473 K, the particle size is very small, similar to the microscope image of Karstedt's complex after evaporation of the solvent from the solution [11]. With an increase in heating temperature, the SnO_2 nanoparticle size slightly rises. We observed Pt crystallites smaller than 1 nm. In this method, decomposition of the metal precursor and formation of nanocrystalline SnO_2 occur simultaneously. This method of simultaneously obtaining metal nanoparticles and formation of the oxide simultaneously we called in an earlier work the *one-pot* method. The use of this method in both cases is that the synthesis affects the variable activity of the electrocatalytic as a function of the temperature of the heat treatment.

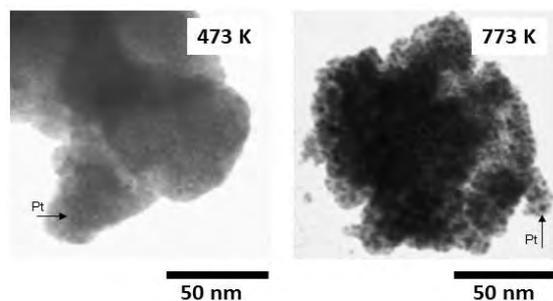
Fig. 3. TEM micrograph of 1.87% Pt/ SnO_2 system obtained from organic precursor after heat treatmentRys. 3. Zdjęcia TEM układu 1,87% Pt/ SnO_2 pochodzącego z organicznego prekursora po obróbce termicznej

Figure 1 shows a decrease in electrocatalytic activity above 460 K. It seems to be related to changes in the SnO_2 support, not to a change in Pt dispersion. The minimal electrocatalytic activity observed circa 580 K corresponds to the maximum mass loss from DTG curves [11]. This temperature range overlaps the end of gel support formation.

In the results of our research, we observe two phenomena. The first is the change in the platinum chemical form: both the of precursors, Karstedt's complex and hexachloroplatinic acid, undergo thermal decomposition which is reflected in the change in electrochemical activity. The second phenomenon is gradual formation of the porous structure of tin oxide which is not

fully understood or described. The application of these two effects results in variable electrochemical activity as a function of temperature. The literature data indicate the role of structural factors such as nanoparticle orientation in catalytic activity and the increase in activity can be caused by the formation of a system in which the support phase starts to play an important role [13, 14]. From this point of view, we see visible growth in electrochemical activity. However, a too high temperature of heat treatment also causes negative phenomena, such as sintering of the metallic phase and the support. Furthermore, these effects are also dependent on the concentration of the metal phase. In our case, this resulted in different activity as a function of temperature only in the case of high concentrations of platinum (Fig. 4).

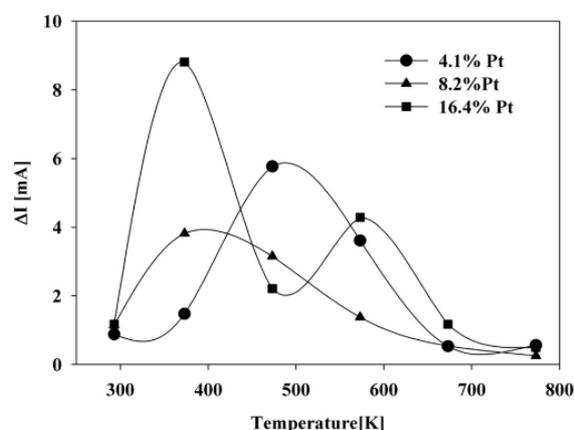


Fig. 4. Sum of oxidation current and absolute value of reduction current as function of temperature - Pt from inorganic precursor (series B)

Rys. 4. Suma wartości prądowych w funkcji temperatury - Pt z nieorganicznego prekursora (seria B)

The plots in Figure 4 present the ΔI values of all the systems from hexachloroplatinic acid as a function of temperature. Observing the ΔI curves, we found a dependence between the electroactivity of the electrode composites and distribution of the subsequent stages of metal precursor decomposition during heat treatment [15]. The hydrated hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) is inactive in electrochemical processes. The activity of these systems increases after removal of the coordinating water [12], most pronounced for high platinum content systems. The plots and collected data show that the Pt oxidation state is a determining factor of its activity and for systems in which platinum is at the II or IV oxidation state [12, 16]. The complex nature of the plot systems is a result of the previously described processes occurring simultaneously during the formation of the carrier and requires a detailed study.

With an increase in the processing temperature, the system activity decreases because of Pt sintering. Larger agglomerates of Pt - visible on the TEM micrograph (Fig. 5) - have lower activity in the methanol oxidation reaction. For the samples treated at temperatures above

573 K, a significant decrease in activity is observed. The use of the Pt divinyl complex affects the size of the metallic Pt clusters. The use of hexachloroplatinic acid and the incipient wetness impregnation method results in Pt crystallites larger than 2.5 nm at the same loads.

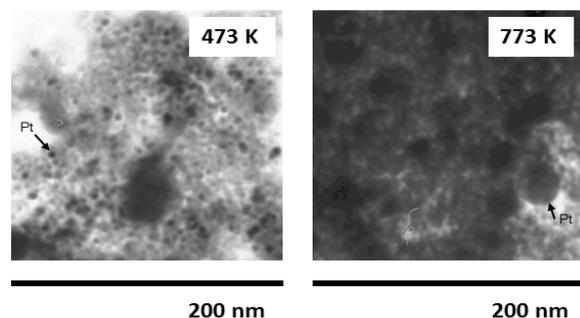


Fig. 5. TEM micrograph of 4% Pt/SnO₂ system obtained from inorganic precursor after heat treatment

Rys. 5. Zdjęcia TEM układu 4% Pt/SnO₂ pochodzącego z nieorganicznego prekursora po obróbce termicznej

The presence of platinum was confirmed by means of TEM micrographs. XRD studies were also conducted. Figure 6 presents the diffraction patterns for systems with a maximum loading of platinum obtained from the organic precursor. The XRD analysis of the composite showed temperature dependence only in the preparation of the composite materials. There are no noticeable platinum reflexes. We believe that it is related to the small size of the platinum crystallites which cannot be detected [17] by the XRD method and in such concentrations. The particle size is very small, which is approximately similar to the microscope image of Karstedt's complex after evaporation of the solvent from the solution [18].

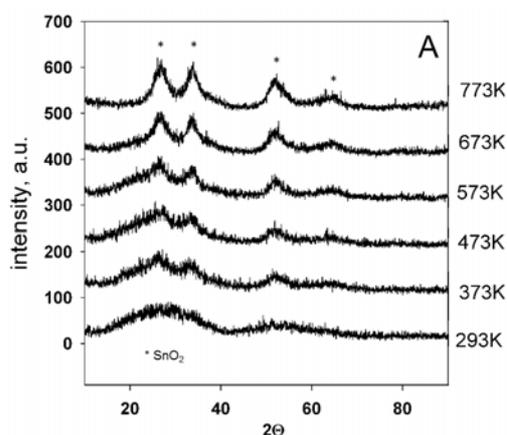


Fig. 6. Diffractometric patterns of 3.87% Pt/SnO₂ system from precursor A after heat treatment

Rys. 6. Dyfraktogramy układu 3,87% Pt/SnO₂ z prekursora A po obróbce termicznej

For both systems (Figs. 6 and 7), the XRD diffractogram presents reflections from the tetragonal crystallographic phase (cassiterite) of SnO₂. For higher temperatures, the diffraction peaks become progressively

more intense and sharp. Miller indexes are indicated on each diffraction peak. The reflection peaks at ~26° (2θ)/{110}, ~33° (2θ)/{101} at ~51° (2θ)/{211}, at ~65° (2θ)/{301} can be readily indexed to a tetragonal rutile structure of SnO₂ (PDF 4+ Card File No. 04-003-5853).

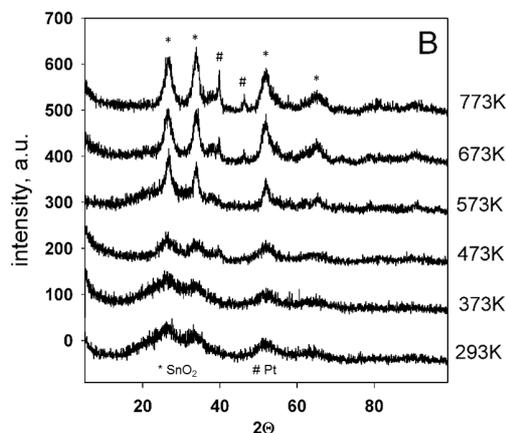


Fig. 7. Diffractometric patterns of 16.4% Pt/SnO₂ system precursor B after heat treatment

Rys. 7. Dyfraktogramy układu 16,4% Pt/SnO₂ z prekursora B po obróbce termicznej

Only for the composite with 16% Pt (Fig. 7) from the water medium can we observe the reflexes of platinum crystals or its compounds. This is probably a confirmation of the high dispersion and stabilization of platinum in the tin dioxide gel structure. The Pt/SnO₂ nanocomposite formation mechanism is presented in Figure 8.

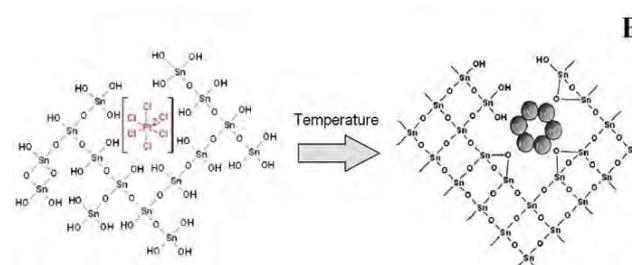


Fig. 8. Pt/SnO₂ nanocomposite formation mechanism in B system

Rys. 8. Mechanizm tworzenia nanokompozytu Pt/SnO₂ w układzie B

CONCLUSIONS

Pt/SnO₂ composite systems were obtained from two different precursor solutions. Our results show that Pt deposited on SnO₂ support can be used as an electrocatalyst for methanol oxidation.

In the composite electrode from Karstedt's catalyst, the presence of small amounts of SiO₂ formed after the decomposition of the Pt complex stabilizes the platinum nanoparticles in the SnO₂ gel structure.

In case of the systems obtained with the use of hexachloroplatinic acid, we observed that heat treatment affected the final form of the metal. This phe-

nomenon causes different shapes of voltammetric curves, which makes them difficult to compare. The hydrated hexachloroplatinic acid is not active in electrochemical processes. The activity of the system increases rapidly after heat treatment, which removes the coordinating water. This nanocomposite allows one to obtain higher current values and better activity than the composite from the organic precursor.

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