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On the Influence of Composition and Structure of Carbon-Supported Pt-SnO₂ Hetero-Clusters onto Their Electrocatalytic Activity and Durability in PEMFC

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Abstract: A detailed study of the structure, morphology and electrochemical properties of Pt/C and Pt/x-SnO₂/C catalysts synthesized using a polyol method has been provided. A series of catalysts supported on the SnO₂-modified carbon was synthesized and studied by various methods including transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electrochemical methods, and fuel cell testing. The SnO₂ content varies from 5 to 40 wt %. The TEM images, XRD and XPS analysis suggested the Pt-SnO₂ hetero-clusters formation. The SnO₂ content of ca. 10% ensures an optimal catalytic layer structure and morphology providing uniform distribution of Pt-SnO₂ clusters over the carbon support surface. Pt/10wt %-SnO₂/C catalyst demonstrates increased activity and durability toward the oxygen reduction reaction (ORR) in course of accelerated stress testing due to the high stability of SnO₂ and its interaction with Pt. The polymer electrolyte membrane fuel cell current–voltage performance of the Pt/10wt %-SnO₂/C is comparable with those of Pt/C, however, higher durability is expected.

Keywords: PEM fuel cell; cathode catalysts; carbon support; catalyst stability; hybrid carrier; tin oxide; Pt-SnO₂ nanoclusters; accelerated stress testing

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are becoming a feasible candidate for applications in portable and automotive industries (especially in robotics and unmanned aerial vehicles [1]). Fuel cell performance is significantly determined by commonly used carbon-supported Pt-based nanostructured electrocatalysts [2,3]. The dissolution of platinum, the particles enlargement, and the carbon support corrosion are the main reasons causing a loss of activity and a decrease of the catalyst electrochemically active surface area (EASA) [3,4]. The main disadvantage of the carbon carrier is its oxidation under the fuel cell operating conditions and in start/stop modes. Because of the amorphous carbon structure, it is easily attacked by an acidic environment, which would be further accelerated by Pt [5]. The larger the Pt loading and the specific surface area of the Pt nanoparticles, the faster the degradation of the carbon support occurs [5–7]. Degradation of the support induces the using of high Pt loading $(0.4–5.0 \text{ mg cm}^{-2})$ to maintain high operational lifetime and high efficiency.



Metal oxides (SnO₂, for example) demonstrate high chemical and electrochemical stability, along with strong interaction with metal nanoparticles [8], showing great potential as an alternative carbon-free catalysts support material for PEM fuel cells [9]. Due to the low conductivity, these materials usually should be doped by conductive dopants (i.e., Sb, In, Nb, etc.) [10] after which is prone to be dissolved in acidic media at high cathodic and anodic potentials [11,12]. The promising strategy aimed to mitigate carbon supports limitations is using of carbon-based hybrid supports. One of the most attractive materials is a tin oxide (SnO₂) owing to its availability, cost-effectiveness, and non-toxicity [7,13–22]. The tin oxide-carbon composites are attractive due to their high oxidation resistance properties, as well as an improved electrochemical activity for the oxygen reduction reaction (ORR) as compared to Pt/C [23].

The uniformly distributed coating of tin dioxide on the carbon support surface can significantly improve the durability of the catalytic layers and reduce the degree of degradation of the catalyst. However, if the carbon surface is completely covered by the oxide phase, the semi-conductive behavior of tin oxide sharply decreases the electrical conductivity of the support [24]. Thus the formation of Pt-SnO₂ clusters [25] on the carbon support surface may improve the catalyst ORR activity and the catalyst durability maintaining high catalyst layer conductivity [24]. High durability of the Pt-SnO₂-based catalysts is attributed to the strong metal-support interaction (SMSI) that inhibits migration and agglomeration of the nanoparticles at the electrode surface [22,26–28].

In the previous study, the Pt-based catalysts supported on the SnO₂-modified carbon black were developed and studied in the ethanol oxidation reaction [29]. The used synthesis technique allowed to obtain the Pt-SnO₂ clusters in which SnO₂ provides protection of Pt active sites from the CO-poisoning and OH-adsorption [30] at high potentials giving better ethanol utilization at both low and high potentials.

The main goal of the presented study is the optimization of composition and structure of Pt-SnO₂ hetero-clusters on the carbon support as PEMFCs electrocatalysts in order to improve their catalytic activity and durability. Optimal SnO₂ content results in the formation of Pt-SnO₂ hetero-clusters with a uniform distribution over the carbon support surface which can provide higher Pt nanoparticles stability and carbon support durability in ORR. A series of catalysts with a SnO₂ content from 5 to 40 wt % was synthesized and studied by different approaches including transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical methods (cyclic voltammetry, accelerated stress testing in a three-electrode cell) in comparison with Pt/C. Comparable to the Pt/C benchmark PEMFC cathode performance of the designed catalysts is discussed as well which is important as there are only a few reports regarding the PEMFC performance using catalysts supported on the SnO₂-C hybrid supports [7].

2. Results and Discussion

2.1. Catalysts Characterization

Figure 1 shows TEM images of $Pt/x-SnO_2/C$ catalyst (where the catalyst mass content of Pt is 20 wt % and x = 5, 10, 20, 40 wt % is the mass content of tin dioxide in the composite support), 20wt %-SnO₂/C, and Pt/C. The actual Pt and Sn content of all catalysts was confirmed by EDS measurements (given in Table 1) and thermal gravimetric measurements. The obtained values of the Pt content correspond to the preliminary calculated before the synthesis.



Figure 1. TEM-images with individual particle distribution of, Pt/C (**a**,**b**); Pt/5wt %-SnO₂/C (**c**,**d**); Pt/10wt %-SnO₂/C (**e**,**f**); Pt/20wt %-SnO₂/C (**g**,**h**); and Pt/40wt %-SnO₂/C (**i**,**j**).

The particle size distribution data were obtained through the processing of the TEM images using the ImageJ software and considering more than 100 particles. A rather narrow particle size distribution for modified carbon-supported catalysts was obtained. The average particle size was ca. 2.7, 3.4, 3.2, and 3.6 nm for Pt/C, Pt/5wt %-SnO₂/C, Pt/10wt %-SnO₂/C, and Pt/20wt %-SnO₂/C, respectively. Due to the particle's agglomeration, the precious determination of particle size is not straightforward and

X-ray diffraction data additionally was used below. Particle size for tin dioxide-modified catalysts is close to those for Pt^{40}/C [31–33] catalyst but larger than the size of Pt/C catalyst particles and in a good agreement with previous study for $Pt^{20}/SnO_x^{-8}/C$ and $Pt^{20}/SnO_x^{-12}/C$ [29].

The morphology of all samples is characterized by the existence of the agglomerates consists of primary nanosized catalyst particles. However, the agglomeration degree increases significantly by increasing of tin oxide content. Pt/10wt %-SnO₂/C catalyst morphology is characterized with the most uniform distribution of Pt and tin dioxide particles on the carbon support surface. The average particle size for Pt/40wt %-SnO₂/C was ca. 4.6 nm which was the largest in comparison with other samples. The highest agglomeration degree was observed for this sample as well.

Catalyst	Pt, wt %	Sn, wt % 1	C, wt % ¹	O, wt % ¹	SnO ₂ , wt % 1
Pt/C	19.51	-	78.65	1.84	-
Pt/5wt %-SnO ₂ /C	20.05	4.09	72.84	3.02	5.3
Pt/10wt %-SnO2/C	19.79	8.42	67.71	4.08	10.7
Pt/20wt %-SnO ₂ /C	19.22	17.64	57.03	6.11	22.4
Pt/40wt %-SnO ₂ /C	20.51	30.89	37.62	10.98	39.2

Table 1. EDS elemental analysis data.

¹ Calculated using the Sn content.

Figure 2 shows the XRD-patterns of the catalysts on tin dioxide-modified carbon support. The spectra of both Pt/10wt %-SnO₂/C and Pt²/20wt %-SnO₂/C samples, in general, are particularly similar to those given in [16,34–36]. The diffraction peaks around 31 °, 39 °, and 61° refer to SnO₂ (110), (101), and (211) planes which is slightly grown in intensity with increasing tin content and are presented on the XRD pattern of the SnO₂²⁰/C support sample. Possible overlapping of the SnO₂ (110) plane reflection with the (002) plane of the hexagonal structure of Vulcan XC-72 should be considered. The diffraction peaks at ca. 46°, 53°, 81°, and 96° could be related to the (111), (200), (220), and (311) planes of Pt, respectively (all 2 theta angles are given with respect to the spectra obtained using the Co K α radiation). The presence of a rather small amount of alloyed Pt₃Sn (111) could be suggested due to the peak at ca. 46° in the Figure 2a inset which could be disguised by highly intensive Pt (111) reflection in case of supported catalysts.



Figure 2. Powder XRD-patterns for Pt/10wt %-SnO₂/C (**a**), Pt/20wt %-SnO₂/C (**b**) and 20wt %-SnO₂/C (**a**, inset). The interplanar distances are given above the lines.

Pt crystallite average diameter was calculated using Scherrer formula as

$$d = \frac{K\lambda}{\beta\cos\theta_{\beta}} \tag{1}$$

where *d* is the average crystallite size, nm; *K* is the Scherrer constant (depends on the crystallite shape; and equal to 0.94 for spherical particles with cubic symmetry), λ is the wave length of incident X-rays (0.178897 nm for Co-K α radiation used in this work), β is the full width of the strongest diffraction peak at half height (radians), θ_{β} is the Bragg angle at the position of peak maximum (degree).

The crystallite size of ca. 2.6, 3.15, 3.05, and 3.92 were obtained for Pt/C, Pt/5wt %-SnO2/C, Pt/10wt %-SnO2/C, Pt/20wt %-SnO2/C, and 20wt %-SnO2/C showing good correlation with the data obtained by TEM data analysis given above [37]. A difference in obtained values is due to any deviations from the assumptions accepted by both approaches (dislocations, non-spherical particles shape, particle agglomeration, etc.). Pt particle/crystalline size increase with increasing of the tin oxide content due to the particle agglomeration and the selective Pt reduction near the oxide particles located on the carbon support surface previously.

The increase in tin dioxide content provided a proportional decrease in porosity, specific surface area, and average pore diameter of the support compared with the Pt/C. In particular, the specific surface area decreased from $210 \text{ m}^2\text{g}^{-1}$ (pure carbon support) to $176 \text{ m}^2\text{g}^{-1}$ (support with 20 wt % of tin dioxide) and $145 \text{ m}^2\text{g}^{-1}$ (support with 40 wt % of tin dioxide). This trend is less pronounced for the low tin dioxide contents of ca. 0–10 wt %. Specific surface area decreasing leads to the worse Pt and tin dioxide particles distribution over the carbon support surface and catalyst EASA decreasing (as shown in the following sections).

The obtained XPS spectrums of studied catalysts contain Pt $4f_{7/2}$ /Pt $4f_{5/2}$ doublets suggesting metallic Pt⁰ and (at higher binding energy) PtO_{ads} and/or Pt(OH)₂ [27] due to partial surface oxidation of the Pt metal nanoparticles. The XPS spectrum of Pt²⁰/C and Pt²⁰/SnO₂¹⁰/C are given in Figure 3.



Figure 3. Pt $4f_{7/2}$ XPS spectrums of the Pt/C (a), Pt/5wt %-SnO₂/C (b), Pt/10wt.%-SnO₂/C (c) and Pt/20wt.%-SnO₂/C (d).

The binding energy of Pt $4f_{7/2}$ in Pt/10wt %-SnO₂/C and Pt/20wt %-SnO₂/C are given in Table 2 and exhibit a slight downshift (0.1 eV) compared to the Pt/C which is in a good agreement with the literature data [26]. This result confirms the electron transfer from Sn to Pt providing a more filled Pt d-band and the weaker chemisorption with oxygen-containing species, such as OH_{ads} [22,28]. Furthermore, the obtained Pt/10wt %-SnO₂/C and Pt/20wt %-SnO₂/C catalysts exhibits 0.5–0.55 eV higher Sn $3d_{5/2}$

binding energy (487.2 and 487.25 eV, respectively) than pure SnO_2 nanoparticles (486.70 eV [38]) which are in good agreement with [22,27], suggesting the electron transfer from tin oxide. The SMSI effect in the prepared Pt/x-SnO2/C catalysts induced by the formation of the Pt-SnO₂ clusters in which the electron donation from the oxide to Pt metal takes place enhances electron density on the latter and providing higher activity and stability of Pt nanoparticles [27]. The obtained results confirm that the SMSI effect exists but due to the low value of Pt $4f_{7/2}$ binding energy shift its influence is expected to be limited.

Catalyst	Pt 4f _{7/2}	Pt 4f _{5/2}
Pt/C	71.32	74.65
Pt/5wt %-SnO ₂ /C	71.21	74.61
Pt/10wt %-SnO ₂ /C	71.23	74.61
Pt/20wt %-SnO ₂ /C	71.20	74.62

Table 2. Analysis of the Pt 4f and Sn 3d photoemission lines for Pt/C and Pt/x- SnO₂/C catalysts.

2.2. Electrochemical Studies

Figure 4 presents the cyclic voltammograms (CVs) of Pt/SnO₂^x/C catalysts and Pt/C. The EASA value is 83, 55, 57, 51, and 27 m²g⁻¹ Pt of Pt/C, Pt/5wt %-SnO₂/C, Pt/10wt %-SnO₂/C, Pt/20wt %-SnO₂/C, and Pt/40wt %-SnO₂/C catalyst, respectively. The EASA values of Pt/5wt %-SnO₂/C and Pt/10wt %-SnO₂/C are in a good agreement with those taken from an average particle size (see Figure 1).



Figure 4. CVs for of Pt/C, Pt/5wt %-SnO₂/C, Pt/10wt %-SnO₂/C, Pt/20wt %-SnO₂/C and Pt/40wt %-SnO₂/C recorded in 0.5M H₂SO₄ solution at 25 °C (scan rate 20 mV s⁻¹).

In general, studied catalysts demonstrated well-defined hydrogen adsorption/desorption peaks in the potential region -0.20–0.20 V and the oxygenated species adsorption/desorption peaks at potentials ca. 0.6 and 1.0 V vs Ag/AgCl (sat.) electrode, which are in good agreement with the literature data for Pt-based catalysts [39,40]. Suppression of the currents in the hydrogen adsorption/desorption region is observed when the SnO₂ loading increases up to 20 wt %, which can be explained by the more facile adsorption of OH– species which hinders the hydrogen adsorption and by possible blockage of Pt sites [41]. The same phenomenon and/or defects, edge/corner sites, and various distribution of crystal orientations on the surface of Pt nanocatalyst may explain the fact that typical Pt crystal lattice peaks less pronounced and the hydrogen desorption wave shifts to more positive potentials with tin dioxide loading increasing as well [42].

At high concentrations of tin dioxide on the carbon support surface, the formation of large particles agglomerates is observed, which greatly enhances the catalyst structure irregularity. This is most pronounced for the catalyst supported on 40wt %-SnO₂/C which is characterized by a significant loss in EASA in comparison with Pt/C. The decrease of carbon black content and the ability of SnO₂ nanoparticles to fill all the sites suitable for Pt nanoparticle nucleation could also contribute to such deterioration of the Pt distribution and low EASA at high SnO₂ contents [29]. Due to the low EASA value the Pt²⁰SnO₂⁴⁰/C sample is not discussed in the following sections.

2.3. Durability Stress-Testing

The accelerated stress testing approach consisting of the potential cycling has shown itself to be the fastest and effective way to assess the corrosion resistance of ORR catalysts. The most intense dissolution of platinum is observed at a potential of 1.1 V and the potential cycling up to the values above this boundary leads to noticeable destruction of the carbon support providing the most severe degradation. There are various conditions for accelerated stress testing presented in the literature [43–48].

The carbon support corrosion is of prime importance for the long-term stability of the PEMFC electrocatalytic materials [45]. At potentials 0.6 < E < 1.0 V vs. SHE the carbon support oxidation is catalyzed by the presence of Pt nanoparticles [49,50]. From the other hand, at higher potentials Pt nanoparticles are prone to passivate, its dissolution is retarded and the carbon support corrosion is most important [46,51]. Thus, the durability stress testing (DST) approach at the potential range of 0.6-1.2 V vs. Ag/AgCl (sat.) electrode (described in Experimental Section) provides harsh conditions giving the carbon support corrosion as well as Pt nanoparticles degradation.

For all catalysts, there is a gradual decrease in the EASA values (Figure 5) with an increasing number of cycles associated with such degradation mechanisms as Pt dissolution/redeposition, agglomeration, detachment, and carbon corrosion [51–53]. The carbon-support corrosion is expected to be the prevailing degradation mechanisms due to the selected potential range of DST procedure. The pattern of the EASA decreasing is similar for all studied catalysts. The EASA retention values after DST is ca. 55, 62, 38.5, and 38.1% of the Pt/5wt %-SnO₂/C, Pt/10wt %-SnO₂/C, Pt/20wt %-SnO₂/C, and Pt/C, respectively.



Figure 5. The change in EASA values of Pt/20wt %-SnO₂/C, Pt/10wt %-SnO₂/C, Pt/5wt %-SnO₂/C and Pt/C in course of the DST: normalized (**a**) and absolute values (**b**) before and after DST.

The protective effect of tin dioxide coating is clear for the Pt/10wt %-SnO₂/C and Pt/5wt %-SnO₂/C (Figure 5) catalysts, due to the higher stability against carbon support degradation in comparison

with Pt/C. According to [24] the low electrocatalytic activity of Pt/SnO₂/C catalysts after DST can be either related to the degradation of the uncovered carbon or to the formation of an amorphous layer of tin oxide on the surface providing poor electrical conductivity. From the other hand, the weak stability against degradation of the Pt/20wt %-SnO₂/C could be related to the initially improper catalyst structure. Significant agglomeration and non-uniform distribution of SnO₂ particles, as well as the presence of carbon black defective structure (uncovered carbon) led to the heavy deterioration of electronically conductive network of the catalyst layer and to the sharp EASA decreasing (even faster than in the case of Pt/C). From the other hand, the formation of heterogeneous Pt-SnO₂ clusters may prevent platinum particle agglomeration, providing additional stabilizing effect [30].

Additional TEM studies of catalytic layers being aged were carried out after the DST (Figure 6).



Figure 6. SEM and TEM-images of Pt/5wt %-SnO₂/C (**a**–**c**), Pt/10wt %-SnO₂/C (**d**–**f**) and Pt/20wt %-SnO₂/C (**g**–**i**) catalytic layers after DST. Scale bar – 20 nm (**b**,**e**,**h**) and 10 nm (**c**,**f**,**i**). White circles show Pt-agglomerates.

Figure 6 shows pronounced agglomeration of platinum particles (marked with white circles) for all samples after DST. The average particle size for catalysts after DST was 5.2, 4.8 and 5.8 nm for Pt/5wt %-SnO₂/C, Pt/10wt %-SnO₂/C, Pt/20wt %-SnO₂/C, respectively. Significant changes in the catalysts structure after DST is observed for Pt/20wt %-SnO₂/C (as could be seen on Figure 6g,h,i). The catalyst is characterized by the rapid destruction of the catalytic layer structure and layer integrity leading to a

significant drop in EASA value. The initial non-uniform catalyst structure promotes the fast catalyst degradation even with the SnO₂ loading is high. According to [47], the durability behavior of various carbon supports in the corrosion process is determined not only by their surface area but also by the number of defective carbon sites. It could be suggested that the increasing of SnO₂ loading do not leads to higher carbon support coverage, but to the increasing of the particles size. All studied catalysts suffered from the degradation of carbon support defects and the Pt-SnO₂ cluster structure increases the stability of covered carbon and Pt particles but nor the uncovered carbon support. It could be suggested that the increasing of SnO₂ loading do not leads to the higher carbon support coverage, but to the increase to the higher carbon support. It could be suggested that the increasing of SnO₂ loading do not leads to the higher carbon support coverage, but to the increase of the particles size of SnO₂ loading do not leads to the higher carbon support. It could be suggested that the increasing of SnO₂ loading do not leads to the higher carbon support coverage, but to the increasing of the particles size (Figure 1). Finally, low SnO₂ content of ca. 5–10 wt % provides significant increasing of the catalyst stability due to the Pt-SnO₂ hetero-clusters formation, the uniform cluster dispersion and optimal catalyst layer structure.

2.4. Fuel Cell Testing

Figure 7 presents steady-state performance data of investigated PEMFC membrane electrode assemblies (MEAs). According to the polarization curves given in Figure 7 at low current densities the performance of Pt/10wt %-SnO₂/C catalyst is higher. This result could be related to the higher ORR activity of Pt-SnO₂ clusters [23] provided by the interaction of Pt and SnO₂. At high current densities the MEA ohmic losses dominates and the lower performance of the Pt/10wt %-SnO₂/C could be associated with higher catalytic layer resistance coming from the SnO₂ phase [24] lowering the EASA.



Figure 7. Steady-state performance data of MEAs (polarization curves (**a**) and power density vs. current density (**b**) curve) equipped with different cathode catalysts: Pt/C, Pt/10wt %-SnO₂/C and Pt/20wt %-SnO₂/C. Anode catalyst: Pt/C (40 wt % of Pt). Both anode and cathode with Pt loading is ca. 0.5 mg cm⁻². Membrane: Nafion[®] 212. Temperature: 40 °C. The cell is fed by dry hydrogen and air at relative humidity of 100%.

The worse performance of the $Pt^{20}SnO_2^{20}/C$ in comparison with $Pt^{20}SnO_2^{10}/C$ and Pt^{20}/C is related to the large SnO_2 content which leads to the significant particle's agglomeration degree, non-uniform distribution of Pt and SnO_2 particles. High SnO_2 content also may provide too dense catalytic layer with small sized pores and/or low porosity which hinders the oxygen diffusion to the Pt active sites [7].

The 5–10 wt % of SnO₂ content provides the appropriate catalytic layer structure with sufficiently high EASA, uniform dispersion of Pt-SnO₂ clusters, and high carbon support corrosion resistance. This result generally associated with the existence of SMSI which provide the increased stability of the catalyst and optimal catalytic nanoparticles morphology, higher EASA value and catalytic layer structure.

3. Materials and Methods

3.1. Preparation of Pt/SnO₂/C Catalysts

3.1.1. Preparation of SnO₂ Nanoparticles

The calculated amount of $SnCl_2 \cdot 2H_2O$ was dissolved in ethylene glycol (EG) solution contained small amount of DI water. The mixture was ultrasonicated and added to three-necked flask with EG under magnetic stirring. Magnetic stirring was maintained for half an hour at room temperature. After that, the obtained solution was rapidly heated up to 190 °C and boiled for 3 hours with constant magnetic stirring under atmospheric pressure until the color of the solution was changed to yellow indicating the formation of SnO₂ colloidal particles [16]. The obtained colloidal solution was cooled down to room temperature.

3.1.2. Preparation of SnO₂/C Composite Support

The x-SnO₂/C composite support was prepared according to the procedure described in [29]. In brief, the suspension of the calculated amount of the carrier (Vulcan XC-72, Cabot Corporation, Boston, MA, USA), DI H₂O and isopropyl alcohol was prepared by mixing. The obtained mixture was ultrasonicated and added dropwise to the colloidal dispersion of SnO₂/Sn particles under magnetic stirring. The colloidal solution was preheated to 50 °C. The particle adsorption on the support was carried out for 48 hours under constant stirring at atmospheric pressure. The mass content of SnO₂/Sn particles in the SnO₂/C composite varied from 5 to 40 wt %.

3.1.3. Preparation of Catalyst Pt/SnO₂/C

The preparation of the platinum electrocatalyst on carbon support was carried out using the polyol approach in ethylene glycol (EG) [54]. The aqueous solution of $H_2PtCl_6 2H_2O$ was used as the Pt nanoparticles precursor. The $H_2PtCl_6 2H_2O$ solution was added dropwise to the support (SnO₂/C or C) colloid solution under magnetic stirring. Magnetic stirring was maintained for half an hour using argon bubbling at room temperature. After that, the temperature gradually raised (1 °C/min.) up to 75 °C and the precursor adsorption process was carried out for 2 hours. Then the temperature was quickly raised up to 180 °C and the reduction of platinum was carried out for 1 hour. Then the mixture was cooled and a few drops of 2 M HCl solution were added in order to reduce the solution pH to ca. 6 and then the catalyst precipitation was filtered and washed using DI water. The resulting catalyst was dried in oven at 70 °C overnight.

3.2. Structural and Morphological Studies

The diffractograms were recorded using the D8 Advance (Bruker, Billerica, MA, USA) using Co K α - radiation at $2\vartheta = 20 - 120^{\circ}$ with a step of $\Delta 2\vartheta = 0.07^{\circ}$. A scanning/transmission electron microscope Titan 80–300 (Thermo-Fisher Scientific, Beverly, MA, USA) equipped with energy dispersive X-ray spectrometer (EDAX, Mahwah, NJ, USA) was used to study the supports and catalysts morphology. The XPS studies were performed using a PHOIBOS 150 (SPECS, Berlin, Germany) hemispherical analyzer (Al K α radiation) with 1486.61 eV photon energy at DE = 0.2 eV. The BET specific surface area of synthesized catalysts was determined using Tristar 3000 (Micromeritics, Norcross, GA, USA) in the relative pressure range from 10^{-6} to 0.99.

3.3. Electrochemical Studies

Catalytic inks were made by mixing of the electrocatalyst in 1:1 isopropanol/water solution with the following ultrasonication for a half of hour at room temperature. Then, the resulting catalytic ink aliquot was pipetted onto the smooth titanium foil electrode forming a thin catalyst layer. Then the titanium electrode was dried until complete removal of the solvent.

The cyclic voltammograms (CVs) were measured in N₂-saturated 0.5M H₂SO₄ at 25 °C using a conventional three-electrode glass cell. The measurements were performed using a Solartron 1285 (AMETEK, Inc., Berwyn, PA, USA) potentiostat. The catalyst's EASA was calculated using the hydrogen adsorption–desorption peaks at –0.15–0.2 V vs. Ag/AgCl (sat.) as described in [29,54].

Electrocatalysts were subjected to a DST [55] by cycling the potential in the range of 0.6–1.2 V vs. Ag/AgCl (sat.) electrode with a sweep rate of 100 mVs⁻¹ for 3000 cycles. A working 0.5M H₂SO₄ solution was pre-saturated with oxygen before DST cycles. CVs were measured initially and every 300 cycles. Before the CVs measurement, the working solution was purged with inert N₂. The degree of degradation of the cathode catalyst was estimated from the change in the EASA, calculated from the CVs.

3.4. Fuel Cell MEAs Fabrication and Testing

MEAs was prepared using Nafion[®] 212 (DuPont Inc., Wilmington, DE, USA) as the polymer electrolyte membrane and ELAT[®] LT 1400 W (NuVant Systems Inc., Crown Point, IN, USA) as anode and cathode gas diffusion electrodes (GDEs). The Pt⁴⁰/C was used as anode catalyst. The Pt²⁰/C, Pt/10wt %-SnO₂/C, and Pt/20wt %-SnO₂/C were used as cathode catalysts. The Pt loading of both anode and cathode electrocatalytic layers were 0.5 mg cm⁻². Catalytic layers were made through the catalytic inks air-spraying onto the GDE surface as described in [56] using 15 wt % Nafion[®] ionomer content. The MEA was clamped into the titanium test cell as described in [31,57]. MEAs testing was carried out using pure dry hydrogen and air at relative humidity of 100%. The cell temperature was 40 °C.

4. Conclusions

The influence of composition and structure of carbon-supported Pt-SnO₂ hetero-clusters onto their electrocatalytic activity and durability toward ORR in PEMFCs has been investigated. It was shown that formation of Pt-SnO₂ clusters has a significant impact on electrochemical performances, structure, and morphology of catalysts. The approaches used to prepare the SnO₂/C and Pt²⁰SnO₂*/C (where C is Vulcan XC-72 carbon black) hybrid supports and electrocatalysts significantly improved the carbon support stability and catalytic layers durability. XPS and TEM confirm the formation of Pt-SnO₂ hetero-clusters with a strong interaction between Pt and SnO₂ nanoparticles. The SnO₂ content of *ca*. 10 wt % ensures an optimal catalytic layer structure and morphology providing uniform distribution of Pt-SnO₂ clusters over the carbon support surface without significant particle agglomeration. The usage of higher SnO₂ content leads to the significant particle agglomeration and non-uniform distribution of SnO₂ particles leading to the lower EASA value and worse PEMFC cathode performance. Pt²⁰/SnO₂¹⁰/C catalyst demonstrates increased durability in course of accelerated stress testing due to the high stability of SnO₂ and its interaction with Pt. The EASA retention of Pt/10wt %-SnO₂/C and Pt/C is ca. 62 and 38.1%, respectively. These values correspond to the 35.3 and 31.2 m² g⁻¹ Pt, respectively. Moreover, the PEMFC cathode performance of the Pt/10wt %-SnO₂/C is comparable with those of Pt/C.

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