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COMPARATIVE STUDY OF Pt-BASED CATALYSTS SUPPORTED ON VARIOUS CARBON SUPPORTS FOR SOLID POLYMER ELECTROLYTE ELECTROCHEMICAL SYSTEMS

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Abstract: The comparative study of electrocatalysts synthesized by chemical reduction and pulsed magnetron-ion sputtering for polymer electrolyte membrane electrochemical systems are presented. Various carbon nanomaterials were used as supports of Pt nanoparticles: carbon black, nanotubes, nanofibers and reduced graphene oxide. The electrochemical studies of the obtained electrocatalysts as well as their testing in the fuel cell membrane-electrode assembly were carried out. The influence of supports morphology and the deposition approach of Pt nanoparticles on the electrochemically active surface area and activity of electrocatalysts, as well as the prospects of the magnetron-ion sputtering approach for electrocatalysts synthesis were studied and discussed.

Keywords: supported catalyst, reduce graphene oxide, carbon nanofibers, magnetron ion sputtering, PEM fuel cell

1. Introduction

An efficiency and a performance of polymer electrolyte membrane (PEM) electrochemical systems (fuel cells (FC) [1], oxygen concentrator [2], electrolysis cell for ozone production [3], reversible fuel cells [4-5] etc.) considerably depend on the structure and properties of the both the catalyst and the catalytic layer based on it. Carbon supported nanosized Pt particles are usually used as electrocatalyst for these devices. Therewith, the catalyst performance during its operation as a part of the cathode catalytic layer is determined by both the electrochemically active surface area (EASA) of the nanosized Pt particles and the capability of the reagent access to these particles, which in turn is governed by the structure of carbon support particles and the catalytic layer structure. In order to provide uniform distribution of the catalyst over the layer volume and to assist the reagent access to active electrocatalyst particles, the typical size of carbon support particles should not significantly exceed the Pt particles size (3–5 nm [6]). Therefore, the search for new nanosized carbon supports and methods of the Pt deposition, which allow to obtain the optimal structure of both the support and Pt nanoparticles from the point of view of catalyst activity and stability is necessary [7-11].

Pt deposited on a pretreated carbon black (for example, Vulcan XC-72R) by chemical reduction [11-12] is one of the common types of the catalyst for FC. The disadvantages of chemical synthesis methods, such as high-power consumption and multiple stages (high duration and complexity) of the process, aggregation of nanoparticles, losses during washing of the electrocatalyst, make us look for alternative approaches for the synthesis of electrocatalysts. One of these methods is the magnetron-ion sputtering (MIS) [7], which is free from the most of the above discussed disadvantages.

The aim of this work is to study alternative carbon support materials for electrocatalytically active Pt particles and new method of nanosized Pt particles deposition on these supports for FC. Pt catalysts supported on different nanostructured carbon materials synthesized by various methods were investigated. The structure of the synthesized catalysts was

studied by transmission electron microscopy (TEM). The electrochemical properties of the obtained catalysts were studied by cyclic voltammetry and quasi-stationary polarization curves at low potential scan rate [8] in a three-electrode glass cell, as well as in the polymer electrolyte membrane fuel cell.

2. Experimental

2.1. Used nanostructured carbon materials

In the present work the following carbon support materials were investigated: nitrogen-doped multi-walled carbon nanotubes (MWCNTs) (5 at.% N-MWCNTs), which were synthesized by decomposition of the 40% C₂H₄/60% NH₃ mixture using the Fe-containing catalyst at 700 °C [13]. Carbon nanofibers (CNF) provided by Grupo Graphenano (Spain) [14], Vulcan XC-72R carbon black (Cabot, USA) (the commonly used carbon support of PEMFC electrocatalysts) and reduced graphene oxide (RGO) [1, 15-16].

2.2. Synthesis of the catalysts supported on various carbon materials

Nanosized Pt particles were deposited on the carbon support by the chemical reduction approach (“polyol”, ethylene glycol reduction) [8] or MIS approach [7, 17]. These methods provide the deposition of Pt nanoparticles with the face-centered cubic lattice with the (111) plan prevailing confirmed by X-ray diffraction [18-19]. Our data for catalysts studied in presented work obtained using Röntgen (PW3040/60 X’Pert Pro) diffractometer are in a good agreement with the mentioned ones.

The magnetron sputtering system consisting of the DC laboratory installation (MIR-1), the bipolar power source APEL-SB5BP-1300 and a device for powder mixing during deposition process was used for the electrocatalytic layer deposition by MIS [18]. The parameters of the Pt pulse deposition onto different carbon supports are described in detail in refs. [17, 20].

Investigated catalysts synthesized by various approaches and their electrochemically active surface area (EASA) which were investigated by cyclic voltammetry are listed in Table 1.

Table 1. The list of studied catalysts

No	Catalyst	Mass content of Pt, wt. %	Method of Pt deposition	EASA, m ² g ⁻¹ Pt
1	Pt ⁴⁰ /MWCNTs	39.4	Chemical reduction	43
2	Pt ⁴⁰ /RGO	40.1	Chemical reduction	55
3	Pt ⁴⁰ /Vulcan XC-72R	39.7	Chemical reduction	49
4	Pt ²⁰ /CNF	20.2	Chemical reduction	76.6
5	Pt ²⁰ /Vulcan XC-72R	19.8	Chemical reduction	71.3
6	Pt ²⁰ /CNF (MIS)	20.5	MIS	43.3

2.3. Morphology and specific surface area studies

Specific surface area of carbon supports was measured by BET method using a porosimeter TRISTAR 3000 (Micromeritics, USA). Transmission electron microscopy (TEM) studies were done with TitanTM 80-300 S/TEM (FEI, USA) (80-300 kV, 0.07-0.08 nm space resolution). Samples were prepared through ultrasonication of catalysts in ethanol for 10 min. and the following deposition on perforated Lacey copper mesh covered with thin X-ray amorphous carbon layer.

2.4. Electrochemical studies

The electrochemical characteristics of the electrocatalytic layers based on the synthesized catalysts were studied by voltammetry at various potential scan rates in 1M H₂SO₄ solution using conventional three-electrode cell at 25 °C [8]. The scan rate for cyclic voltammetry and “quasi-stationary” polarization curves were 20 and 0.1 mV/s, respectively.

2.5. PEMFC testing of electrocatalysts

PEMFC membrane-electrode assembly (MEA) based on the obtained catalysts were fabricated using a Nafion 112 membrane (DuPont, USA) and Sigraset 10BB carbon paper (SGL CARBON GmbH, Germany) sheets, which were used as gas diffusion layers. The electrocatalytic layers were deposited on a microporous sublayer by air spraying of a catalyst ink. The catalyst ink in isopropyl alcohol with the addition of Nafion ionomer was prepared according to the procedure described in detail in ref. [16]. The 7 cm²-sized MEA is sandwiched between two flat titanium endplates. Titanium meshes were used as the clamping elements of the test cell monopolar plates [21]. MEA were tested using hydrogen and oxygen fed at the relative humidity of 100% at the pressure of 1 bar. The cell temperature during the test was 60 °C.

3. RESULTS AND DISCUSSION

3.1. Morphology studies of supports and synthesized catalysts

Morphology of synthesized catalysts was studied by TEM with high resolution. According to [13] N-MWCNTs have a bamboo-like structure with nitrogen in pyridine, pyrrole, graphite and oxidized states (according to X-ray Photoelectron Spectroscopy (XPS)). XPS spectrums of N-MWCNTs revealed that nitrogen is primary in pyridine and graphite states (55-57 %) and some molecular nitrogen is encapsulated inside the nanotubes.

TEM images of catalysts synthesized by chemical reduction supported on MWCNTs (A), Vulcan XC-72R (B), RGO (C, D) and CNF (E) as well as the CNF supported catalyst prepared by MIS method (F) are shown in Fig. 1.

Fig. 1 shows that the structure of the RGO is “crumpled” multilayer sheets. Herewith, the Pt particles are well defined, and their structure is quite similar for catalysts obtained by both synthesis approaches. The average size of Pt particles is ca. 4.5 nm for all electrocatalysts with 40 wt.% Pt and ca. 3 nm for electrocatalysts with 20 wt.% Pt. These results are in a good agreement with the EASA values obtained by cyclic voltammetry (Table 1).

In addition, the electrocatalysts morphology shown in fig. 1 suggests that all considered support materials have quite similar characteristic dimension of primary particles (directly on the surface of which Pt particles are located). Carbon black particles have a sphere shape with the diameter of up to 0.1 µm, CNF size is ca. 0.05-0.1 µm and the “crumpled” multilayer sheet (flake) of RGO has a typical thickness of ca. 0.05 µm and length of a few µm, which can be explained by RGO sheets agglomeration due to Van-der-Waals interaction [22].

Specific surface area of Vulcan XC-72R, CNF, MWCNTs and RGO measured by BET is ca. 220–230, 130–150, 175–186 and 260–280 m²/g, respectively. Support particles in electrochemical systems (electrolysis and fuel cells) form large agglomerates, and Pt particles mainly located on the agglomerates surface participate in electrochemical reactions. The EASA values of active Pt particles deposited on RGO and carbon black are quite similar (Table 1) despite the significantly larger RGO specific surface area. It can be assumed that mainly Pt nanoparticles located on the RGO flake outer surface participate in electrochemical reactions. Thus, the size of the RGO flake of ca. 100-200 nm should be taken as the characteristic dimension of a such RGO agglomerate [16, 23].

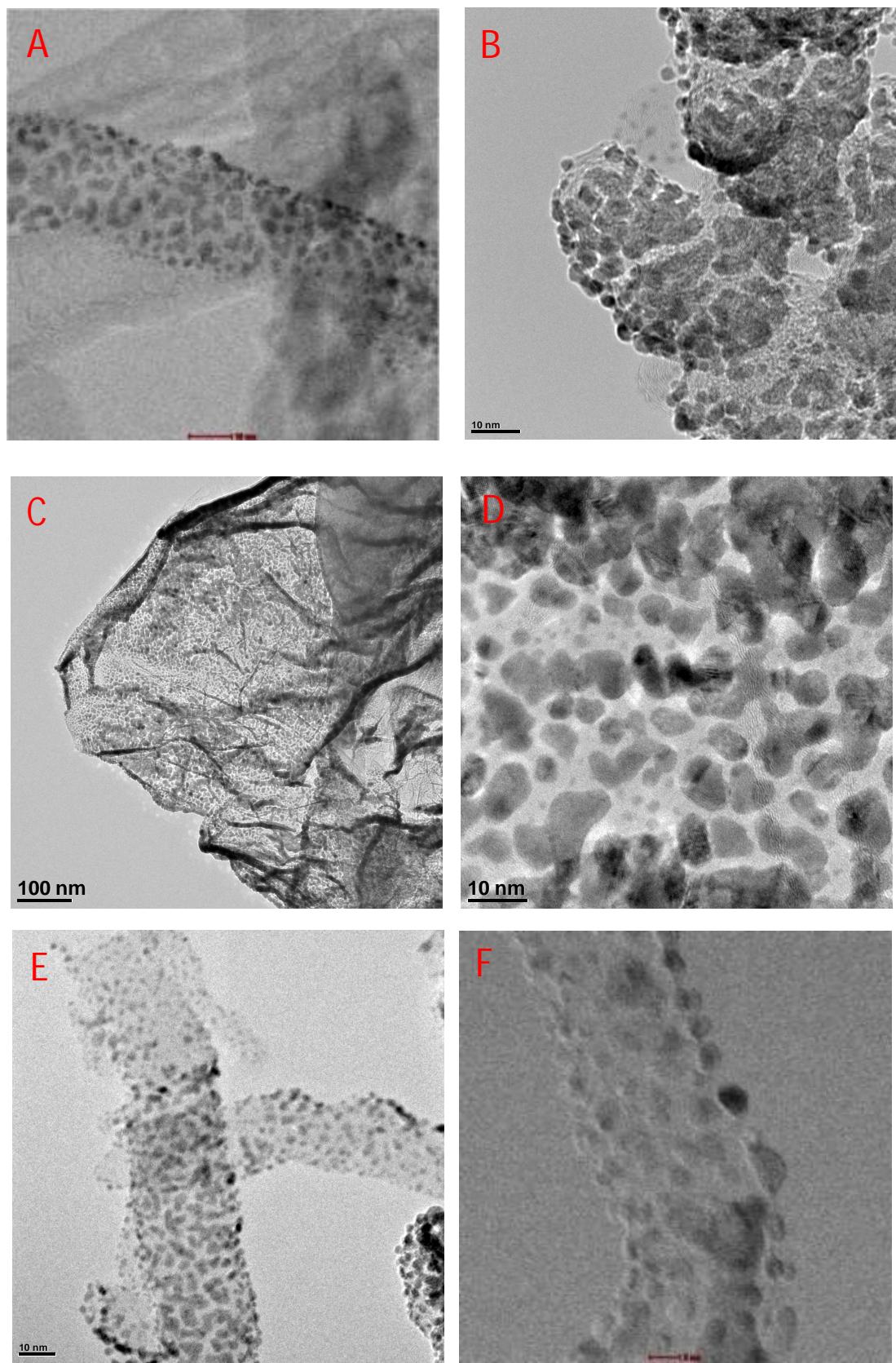


Fig. 1. TEM images of Pt⁴⁰/MWCNTs (A), Pt⁴⁰/Vulcan XC-72 (B), Pt⁴⁰/RGO (C, D), Pt²⁰/CNF (E) and Pt²⁰/CNF (MIS) (F).

3.2. Electrochemical studies

The results of cyclic voltammetry (CV) studies of electrocatalysts based on various supports (MWCNTs, Vulcan XC-72R and RGO) synthesized by chemical reduction are shown in Fig. 2.

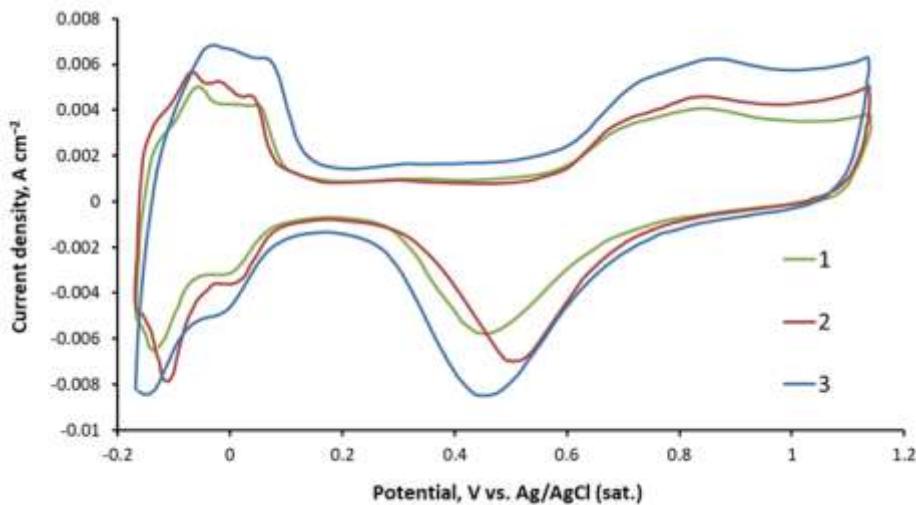


Fig. 2. Cyclic voltammetry curves of (1) $\text{Pt}^{40}/\text{MWCNTs}$, (2) $\text{Pt}^{40}/\text{Vulcan XC-72R}$ and (3) $\text{Pt}^{40}/\text{RGO}$.

The cyclic voltammetry curves of the electrocatalysts qualitatively coincide, showing clear hydrogen adsorption/desorption peaks in the potential range from -0.17 to 0.2 V (vs. SSCE (sat.)), using which EASA of electrocatalysts was calculated (Table 1). Some difference in a CV curves shape could be attributed to the difference in Pt particles surface structure (different Pt crystal faces distribution) [18]. At potentials of 0.2 – 0.6 V (rel. SSCE (sat.)) the RGO-supported catalyst demonstrates higher current density, i.e. the RGO support provides a higher double layer capacity, which is due to a defective multilayer flake structure of RGO and includes the contribution of the “inner” layers. Larger double layer capacitance could also be explained by larger amount of oxygen-containing functional groups [24], a significant part of which was not reduce during the synthesis and can serve as additional Pt nanoparticles nucleation sites during the synthesis. The latter also could explain more uniform distribution of Pt nanoparticles over the RGO surface and higher $\text{Pt}^{40}/\text{RGO}$ EASA.

Carbon nanotubes are often characterized by the lack of active sites for catalytic nanoparticles, which leads to insufficient dispersion of Pt particles and their agglomeration during synthesis [25]. The $\text{Pt}^{40}/\text{MWCNTs}$ EASA is ca. $43 \text{ m}^2 \text{ g}^{-1}$ Pt, slightly lower than the one of $\text{Pt}^{40}/\text{Vulcan XC-72R}$ ($49 \text{ m}^2 \text{ g}^{-1}$ Pt), which is assumed to be associated with nitrogen atoms, which contributes to a better dispersion and lower size of Pt nanoparticles [20].

The CV curves of electrocatalysts synthesized by chemical reduction and MIS are shown in Fig. 3. EASA of electrocatalysts synthesized by chemical reduction on Vulcan XC-72R and CNF supports are almost the same, but EASA of samples synthesized by the MIS method is 1.65–1.75 times lower.

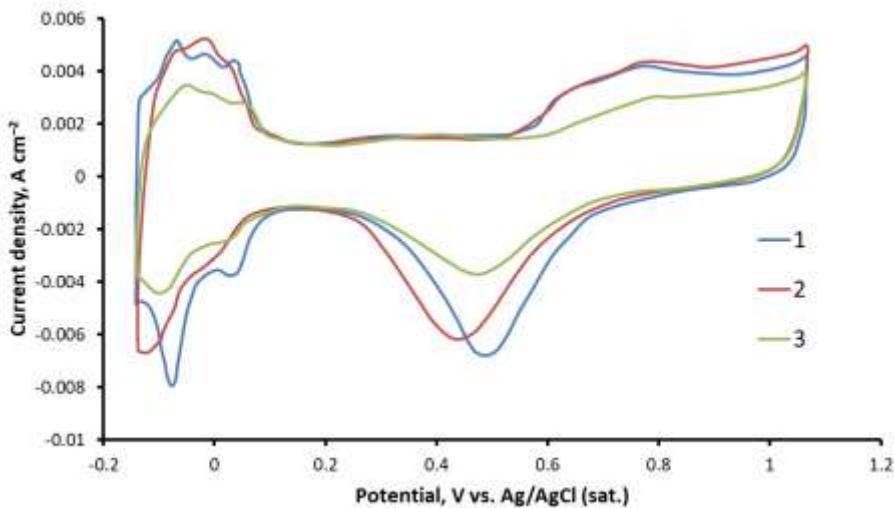


Fig. 3. Cyclic voltammetry curves of electrocatalysts: (1) Pt²⁰/CNF, (2) Pt²⁰/Vulcan XC-72R and (3) Pt²⁰/CNF (MIS).

Electrocatalysts activity in oxygen evolution reaction (OER) could be compared through the quasi-stationary polarization curves. According to the fig. 4 A the current density of Pt⁴⁰/MWCNTs, Pt⁴⁰/Vulcan XC-72R, Pt⁴⁰/RGO and Pt²⁰/CNF (MIS) at 1.25 V (vs. SSCE(sat.)) is ca. 0.6, 0.46, 0.64 and 0.69 A g⁻¹ Pt, respectively, and the Tafel slope is ca. 226.1, 299.7, 212.5 and 190.8 mV dec.⁻¹, respectively (fig. 4 B).

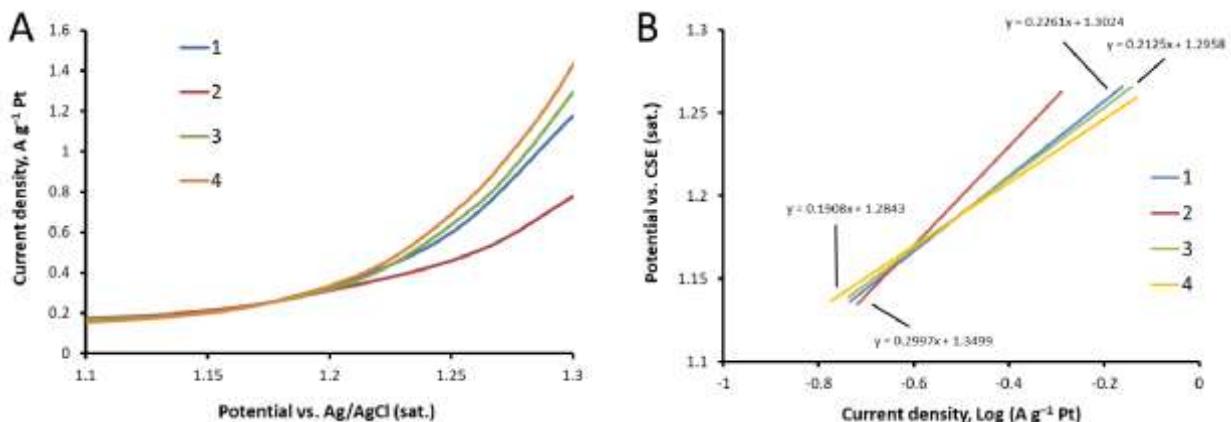


Fig 4. Quasi-stationary polarization curves (A) and Tafel curves (B) of (1) Pt⁴⁰/MWCNTs; (2) Pt⁴⁰/Vulcan XC-72R; (3) Pt⁴⁰/RGO and (4) Pt²⁰/CNF (MIS) at anodic potentials.

Obtained current densities indicate low OER rate which is typical for Pt-based catalysts [26]. Significantly lower Tafel slope of Pt⁴⁰/Vulcan XC-72R could be described by strong oxidation of the carbon support under high anodic potential in the presence of Pt [27]. This effect is less pronounced in the case of catalysts supported on the MWCNTs and RGO due their high stability [25].

The OER Tafel slope of the Pt²⁰/CNF (MIS) catalyst is ca. 190.8 mV dec.⁻¹ which is significantly higher than the one of catalysts synthesized by chemical reduction approach. It could be related to the stronger interaction of Pt nanoparticles with the support due to its intercalation into the carbon support [28]. Thus, instead of the lower EASA the activity of the catalysts prepared by the MIS approach is particularly same as the activity of chemically prepared catalysts. Due to the possible support particles agglomeration during the synthesis and electrode coating the MIS approach provide the preferred deposition of Pt particles on the outer agglomerate surface which provides the better access for the electrochemical reaction.

The quasi-stationary polarization curves of Pt⁴⁰/MWCNTs, Pt⁴⁰/Vulcan XC-72R, Pt⁴⁰/RGO and Pt²⁰/CNF (MIS) are shown on fig. 5.

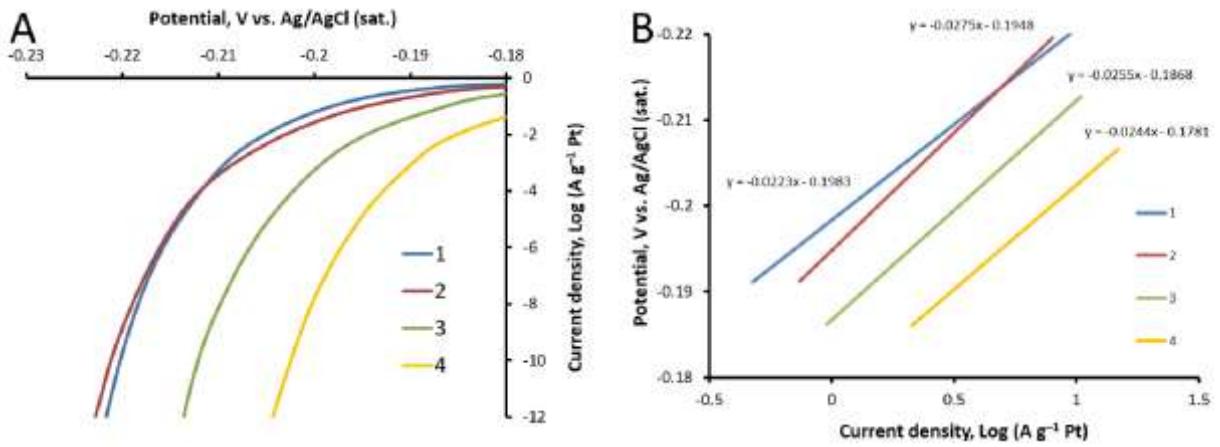


Fig. 5. Quasi-stationary polarization curves (A) and Tafel curves (B) of (1) Pt⁴⁰/MWCNTs, (2) Pt⁴⁰/Vulcan XC-72R, (3) Pt⁴⁰/RGO and (4) Pt²⁰/CNF (MIS) at cathodic potentials.

The specific activity of the Pt⁴⁰/MWCNTs, Pt⁴⁰/Vulcan XC-72R, Pt⁴⁰/RGO and Pt²⁰/CNF (MIS) in hydrogen evolution reaction (HER) is 1.22, 1.58, 3.24 and 7.81 A g⁻¹ Pt, respectively (fig. 5 A). The Tafel slope of Pt⁴⁰/MWCNTs, Pt⁴⁰/Vulcan XC-72R, Pt⁴⁰/RGO and Pt²⁰/CNF (MIS) is ca. 22.3, 27.5, 25.5 and 24.4 mV dec.⁻¹, respectively (fig. 5 B). These Tafel slope values are quite similar and slightly lower than typical for Pt/C electrocatalysts (30 – 40 mV dec.⁻¹ when the limiting reaction step is Tafel step or Heyrovsky step, respectively [29]). The reason of the obtained Tafel slopes may be the specific interaction of Pt nanoparticles with carbon support. Pt⁴⁰/RGO and Pt²⁰/CNF (MIS) demonstrate higher HER activity due to the higher EASA and Pt-carbon support interaction. Moreover, the high activity of Pt²⁰/CNF (MIS) could be related to the preferred location of Pt nanoparticles over the outer support particles agglomerates surface.

3.3. PEMFC testing

The performance of PEMFC catalytic layers depends not only on the EASA of Pt nanoparticles and their specific activity, but also on the catalytic layer structure, which affects the layer conductivity (both ionic and electronic) and the layer permeability to reagents and reaction products [18].

The performance of PEMFC with MEAs based on various cathode electrocatalysts are shown in Fig. 6. The current density of the MEA equipped with Pt⁴⁰/MWCNTs, Pt⁴⁰/Vulcan XC-72R, Pt⁴⁰/RGO and Pt²⁰/CNF (MIS) cathode catalysts at voltage of 0.7 V is ca. 1.02, 1.1, 1.12 and 0.925 A cm⁻², respectively, and maximum output power density is ca. 0.84, 0.88, 0.91 and 0.75 W cm⁻², respectively. The MEA performance with the cathode catalytic layer based on Pt²⁰/CNF (MIS) is lower in comparison with other MEAs and, therefore, its maximum power density is 12 - 20% lower even at a similar cathode Pt loading. This result could be ascribed to the fact that at the same Pt loading the layer thickness is higher when the catalyst Pt percentage is lower, which leads to increasing mass transfer losses as well as to decreasing of its proton and electron conductivity [30].

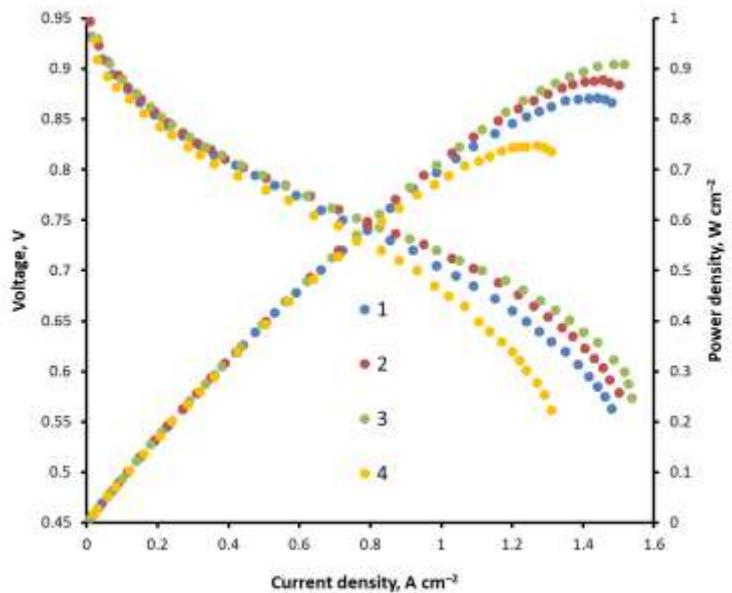


Fig. 6. The performance of the PEMFC with different cathode catalysts: (1) Pt⁴⁰/MWCNTs, (2) Pt⁴⁰/Vulcan XC-72R, (3) Pt⁴⁰/RGO и (4) Pt²⁰/CNF (MIS). The anode catalyst is Pt⁴⁰/Vulcan XC-72R. The Pt loading on the cathode and anode is 0.4 mg cm⁻¹ and 0.2 mg cm⁻¹, respectively. The pressure of H₂ and O₂ is 1 bar. The gas relative humidity is 100%. The working temperature is 60 °C.

The result for MEA based on Pt⁴⁰/MWCNTs, Pt⁴⁰/Vulcan XC-72R and Pt⁴⁰/RGO is in good agreement with the catalysts EASA values (Table 1). However, the performance of the MEA based on the magnetron-ion sputtered catalyst is higher than expected considering its low EASA value. It is consistent with the hypothesis made above that the Pt nanoparticles of the MIS prepared catalyst are better accessed for electrochemical process.

Conclusions

Carbon supports described in presented work (MWCNT, carbon black Vulcan XC-72R and CNF) have quite close values of characteristic dimension of ca. 20–60 nm and BET specific surface are of ca. 130–230 m² g⁻¹. Primary support particles forms agglomerates. Pt nanoparticles located on the outer surface of support agglomerates mainly take part in electrochemical reactions. RGO is a flake structured material (agglomerated sheets) with high aspect ratio (length-to-thickness ratio) and thus its characteristic dimension should be taken equal to 100–200 nm. The chemical reduction synthesis approach allows to obtain electrocatalysts with better Pt nanoparticles dispersion and higher EASA. From the other hand the mass specific activity of Pt²⁰/CNF (MIS) in OER is higher than the one of Pt⁴⁰/MWCNTs, Pt⁴⁰/Vulcan XC-72R, Pt⁴⁰/RGO. The capability of covering mainly the outer surface of carbon support agglomerates with Pt nanoparticles when the MIS approach used is suggested. This approach allows to increase the noble metal utilization which confirms by studies in both liquid electrolyte media and PEMFC. The higher stability of catalysts supported on MWCNT, CNF and RGO at high anode polarization is demonstrated as well. Further study and optimization of magnetron-ion sputtering of metals over the carbon support powders is necessary.

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СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ ПЛАТИНОВЫХ КАТАЛИЗАТОРОВ НА РАЗЛИЧНЫХ УГЛЕРОДНЫХ НОСИТЕЛЯХ ДЛЯ ТВЕРДОПОЛИМЕРНЫХ ЭЛЕКТРОХИМИЧЕСКИХ СИСТЕМ

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Представлены результаты сравнительного исследования электрокатализаторов для электрохимических систем с твердым полимерным электролитом, синтезированные методами химического восстановления и импульсного магнетронно-ионного распыления. В качестве носителей наночастиц Pt использовались различные углеродные наноматериалы: углеродная сажа, нанотрубки, нановолокна и восстановленный оксид графена. Проведены электрохимические исследования полученных электрокатализаторов и их тестирование в составе мембранны-электродного блока топливного элемента. Изучено влияние морфологии носителя и метода нанесения наночастиц Pt на электрохимически активную поверхность электрокатализатора, а также перспективность применения метода магнетронно-ионного распыления для синтеза электрокатализаторов.

Ключевые слова: катализатор на носителе; восстановленный оксид графена, углеродные нановолокна; магнетронно-ионное напыление; топливный элемент с твердым полимерным электролитом.

**BƏRK POLİMERLİ ELEKTROKİMYƏVİ SİSTEMLƏR ÜÇÜN MÜXTƏLİF KARBON
DAŞIYICILAR ÜZƏRİNĐƏ Pt KATALİZATORLARIN MÜQAYİSƏLİ TƏDQİQİ**

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Məqalədə bərk polimerli elektrokimyəvi sistemlər üçün kimyəvi reduksiya və maqnetron-ion səpilmə metodları ilə sintez olunmuş elektrokatalizatorların tədqiqinin nəticələri verilib. Pt nanohissəcikləri üçün daşıyıcı kimi müxtəlif karbon nanomateriallar istifadə olunub: duda, nanoborular, nanoliflər, reduksiya olunmuş qrafen oksidi. Alınan elektrokatalizatorlar yanacaq elementinin membran-elektrod blokunun tərkibində yoxlanılıb. Daşıyıcının morfolojiyasının və Pt nanohissəciklərinin çökdürmə metodlarının elektrokatalizatorun aktiv səthinə təsiri və elektrokatalizatorların sintezində maqnetron-ion səpilmə metodunun tətbiqinin perspektivliyi öyrənilib.

Açar sözlər: elektrokatalizator, qrafen oksidi, nanoborular, nanoliflər, maqnetron-ion səpilmə metodu, bərk polimerli elektrolitli yanacaq elementi