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MAGNETRON SPUTTERING SYNTHESIS OF ELECTROCATALYSTS

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Abstract: Magnetron sputtering is a well-known method of obtaining various coatings and surface modifications, but nowadays it is successfully used for the synthesis of electrocatalysts. One of the main advantages of the method is the possibility to vary the parameters during the process, such as the mode (direct current sputtering, pulsed medium-frequency sputtering, high radio frequency sputtering), potential supply to the sputtered substrate or catalyst carrier, pressure in the vacuum chamber, atmosphere composition, which allows to change the composition and structure of the obtained coatings and catalysts very widely. Changing the modes of sputtering makes it possible to create both dense (porous) protective/catalytic coatings and coatings with a very developed surface, i.e. for obtaining electrode materials.

Keywords: thin film electrode; proton exchange membrane; fuel cells; catalysts; carriers; magnetron.

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Introduction

Global energy consumption is increasing day by day and its cost of energy tends to grow over the last decade. This led to the need of renewable energy sources developing, where progress has been made in the transition to clean energy production. Electrochemical energy storage and conversion makes it possible to create a zero-carbon energy plants by utilizing renewable energy, including transport applications. In recent years, fuel cells and proton exchange membrane water electrolyzers are the most promising electrochemical systems. Proton exchange membrane (PEM) water electrolysis is a promising technology for obtaining hydrogen energy carrier, as it allows obtaining high purity hydrogen. PEM fuel cells have attracted much attention because they can convert hydrogen energy into electrical energy with high efficiency based on two key

electrochemical reactions: hydrogen oxidation reaction and oxygen reduction reaction. However, the practical application of fuel cells is still limited by the weak oxygen reduction reaction (ORR) kinetics and high potential [1]. To the best of our knowledge, ORR electrocatalysts to date are mainly composed of Pt nanoparticles, and to achieve high output voltage and sufficient power density, a significant amount of Pt is required, which accounts for a significant portion of the cost of PEM fuel cells. For this reason, it is imperative to develop low precious metal content electrocatalysts with high activity and stability, as the use of efficient and reliable electrocatalytic materials should effectively accelerate the aforementioned energy conversion reactions. However, the processes for obtaining electrocatalysts with excellent

performance usually involve undesirable chemical by-products and it is still difficult to proceed to mass production [2]. Among all the technologies for the production of nanomaterials, the magnetron sputtering is very promising, because it has a number of advantages, such as: ease of operation, environmentally friendly method, control of catalytic particle size and concentration (catalytical film thickness), and fast synthesis process. In addition, there is currently growing interest in the use of different materials synthesized by magnetron sputtering as electrocatalysts for electrochemical technologies.

Thin film electrocatalyst electrodes

Thin film electrodes are thin layers of electrocatalysts deposited on the surface of gas-diffusion layers (current collectors) to improve electrochemical reactions in various systems. They have a series of advantages that make them promising for electrochemical applications. For instance, thin film electrodes have a large surface area, which leads to high activity and stability of the reaction. Various synthesis methods such as chemical vapor deposition and magnetron sputtering allow control the film thickness, composition and structure.

Main applications of thin film electrodes: water electrolysis, fuel cells and supercapacitors. Thin films provide high stability, activity and selectivity, which helps to improve the efficiency of electrochemical systems. Added to this, they can have an important role in the development of lithium-ion batteries. Optimization of thin films structure and composition in these systems can lead to an increased stability as well as reduced cost of these devices.

The authors obtained [3] Ni-Mo, Au-Ni and Au-Mo thin film electrocatalysts by magnetron sputtering, where Au, Mo and Ni sputtering targets were placed at an equal distance from each other. The authors concluded that Ni-Mo, Au-Mo and Au-Ni had high activity in hydrogen evolution reaction (HER) as compared to the individual metal components. It was discovered, for the Ni-Mo alloy, the optimum activity was achieved at Ni content in the range of 60-70 at. %. These results are in

accordance with previous studies, which also indicated an optimum Ni content of about 60 at. % for Ni-Mo [4]. For Au-Mo, the activity was achieved at a Mo content of about 68 at. %. Au-Ni alloys were also studied and the optimum activity was achieved at a Ni content of about 35 at. %. However, problems were found in measuring the activity of the Au-Ni alloy due to film delamination and change in activity during the measurement process. The authors noted that the presence of high activity of the alloys may be due to an increase in the electrochemical surface area (ESCA) of the catalyst due to dissolution of one of the components during operation in the electrolyte.

Ir-Ru thin-film electrocatalysts, which were tested as a part of the membrane electrode assembly (MEA) for a PEM water electrolyzer, were obtained in [5]. The Ir-Ru film thickness was 280 nm with Ir and Ru loading of 158 and 256 $\mu\text{g cm}^2$, respectively. The results showed that this electrocatalyst has a superior activity of 1 A cm^{-2} at 1.606 V and stability of 1.3 $\mu\text{V h}^{-1}$ at 1 A cm^{-2} for 500 h as compared to the reference electrocatalyst.

Magnetron sputtering allows stable production of nanomaterials for electrocatalysts for electrochemical systems [6]. Among all the technologies for the production of nanomaterials, magnetron sputtering is characterized by its environmental friendliness and relatively low cost. Nanostructured catalysts of Pt obtained by this technology for use in the ORR have been described in detail in [7–14]. Recently, the work of Jason A. revealed that etching of Ir_xCo_y deposited films dramatically increases the mass activity and stability of IrO_x [14].

In [15], the authors considered the NbO_2 sublayer. Initially, an NbO_2 layer was deposited on carbon nanotubes (CNT) by sputtering a target was sputtered by radio-frequency (RF) magnetron sputtering. After that, platinum was deposited on the surface. The authors investigated the obtained electrocatalysts by cyclic voltammetry in 0.1 M HClO_4 . It was shown that the electrocatalyst with a 0.2 nm thick NbO_2 sublayer has a higher stability (loss of ESCA is 12.3% after 10000 cycles) compared to Pt/CNT (loss of ESCA is 47.3%),

because the NbO₂ sublayer contributes to the reduction of corrosion of CNT.

The Pt-TiO₂ supported on multi-walled carbon nanotubes (MWCNT) electrocatalyst with enhanced activity and stability in alkaline medium was obtained in [16]. Pt nanoparticles were deposited by magnetron sputtering on TiO₂-decorated MWCNT. The authors observed high mass activity of the modified electrocatalysts (124 A g⁻¹) as compared to the reference Pt/C electrocatalyst (62 A g⁻¹) in 0.1 M KOH solution, respectively.

Selective electrooxidation of alcohols (methanol, ethanol, isopropanol) is of

significant importance for solving energy and chemical problems [6,17,18]. Since pure platinum is not an optimal catalyst for such processes, eighteen thin-film Pt-M alloys obtained by magnetron sputtering were studied in [19]. Their studies in the methanol oxidation reaction showed that Sn, In, Fe, Zn, and Ru-based alloys had the highest activity.

In [20] MoS₂ films with complex highly developed structure were obtained by RF magnetron sputtering by varying Ar pressure in the system (Fig.1). Such material is competitive with platinum in the hydrogen release reaction.

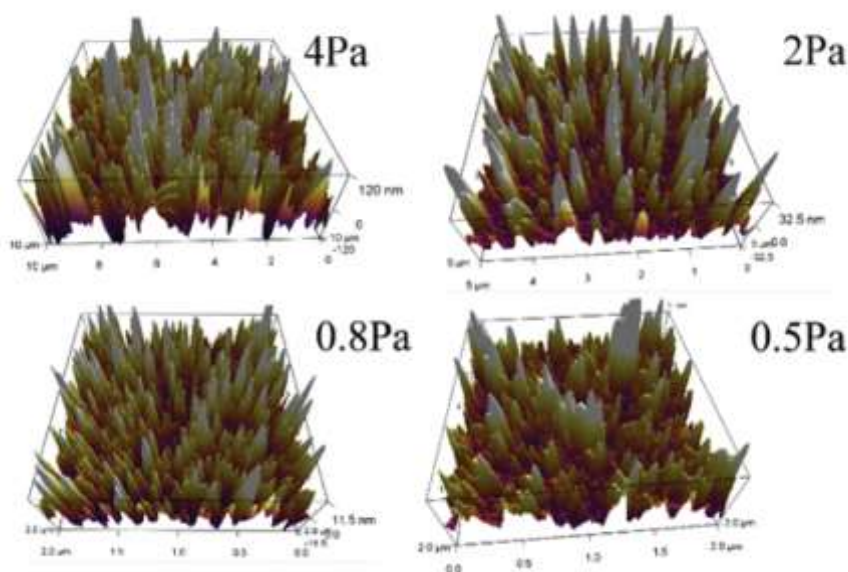


Fig. 1. AFM images of MoS₂ films prepared under different sputtering pressures [20].

A highly efficient ORR catalyst of PtCu (with Cu content from 95 to 99.5 at. %) subjected to Cu etching was obtained in [21]. It was shown that catalysts with lower Cu:Pt ratio have the highest specific activity but have relatively low ESCA. Subjecting the samples to accelerated stress tests, it was found that nanostructured Pt Cu networks without substrate are relatively stable within high potential cycling.

Later, a similar method was used to create an electrocatalyst from a nanoporous Pt-CoO film, followed by etching of CoO. In this work [22] the authors investigated the electrocatalyst for degradation by accelerated stress testing method developed by Fuel Cell Commercialization Conference of Japan (FCCJ)

and compared it with a reference Pt/C electrocatalyst. During accelerated stress testing of the electrocatalysts, a loss of electrochemically active surface area equal to 45 % is observed.

However, the observed trend of ESCA loss during accelerated stress testing is different. While under the conditions used for the Pt/C catalyst a more or less continuous exponential decrease of the electrochemically active surface area was observed, with the Pt-CoO electrocatalyst it occurs in the first 600 cycles and afterwards the degradation becomes slower.

PtNi thin film catalyst (10 nm) obtained by sputtering of two targets at direct current showed higher activity in the oxygen reduction reaction than Pt [23].

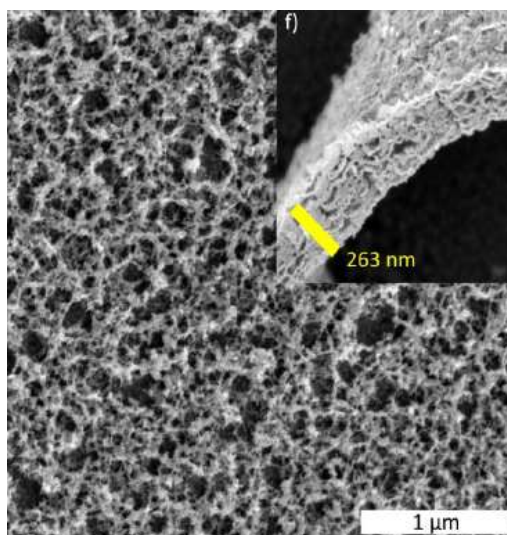


Fig. 2. Scanning electron microscope (SEM) top view of Pt-CoO film [22].

The authors noticed that during the electrochemical tests in liquid electrolyte at high potentials (1.3 – 1.5 V), Pt nanoparticles were dissolved, which leads to the growth of nanoparticles due to Ostwald ripening and, on the other hand, to the leaching of Ni from the surface. Indeed, using instead of platinum its alloys with 3d transition metals (usually Ni, Co, Cu) not only reduces the content of Pt, but also increases the activity in the ORR, because the surrounding atoms of the second component of the alloy modify the electronic structure of Pt atoms on the surface. But base metal gradually dissolves in the acidic medium, and, as a general rule, the ORR activity starts to decrease. This occurs even in the case of preliminary partial etching of the base metal component. Stability can be improved by using alloys of Pt with rare earth metals (REM) [24].

Electrocatalysts of this type have been successfully obtained by magnetron sputtering. The authors showed [25] that Pt₃Y alloy thin films deposited by sputtering a Pt target with 5 Y inserts exhibit a specific activity of 13.4 ± 0.4 mA cm⁻², 7 times higher in ORR than polycrystalline form of Pt, and a mass activity an order of magnitude higher than for Pt nanoparticles. This is the highest activity for the deposited material without further thermal or chemical treatment. Detailed studies of the 27 nm thick Pt₃Y film showed that after testing in the electrolyte, the film structure became inhomogeneous- a top layer consisting of several Pt monolayers was formed on the

surface of Pt₃Y film. Probably, this explains the high activity. In [26], the deposition of Pt₃Y film electrocatalysts by magnetron sputtering was carried out at a higher than usual pressure of the working gas (27 Pa, Ar/He=1). This made it possible to obtain not a dense film, but a layer of Pt₃Y alloy from nanoparticles was 10–12 nm in size. The excellent characteristics of the electrocatalyst from several deposited layers of Pt₃Y were due to a small size of nanoparticles, the porosity of the catalytic layer and the growth of kinetic activity in the ORR.

Pt, Pt₃Y, Pt₅Tb and Pt₅Gd catalyst films of 60 nm thickness was deposited by magnetron sputtering on microporous gas diffusion layers [26]. The specific activity at 0.9 V of Pt₃Y and Pt₅Gd catalysts is 2.5 times higher, and Pt₅Tb is 2 times higher than that of Pt catalysts. Electrochemical and physical investigations have shown that a platinum catalyst layer is formed on the catalyst surface due to etching of rare earth metals in acidic medium, and so thin that it does not affect the composition of the film catalyst. Apparently, Pt₅Tb is less stable in the working environment of fuel cells with solid polymer electrolyte, and a thicker top platinum layer is formed, which slightly reduces the activity. Nevertheless, all the studied alloys are promising for use as ORR catalysts.

Wide variation of composition and structure of the obtained samples is achieved by using several targets from different materials/composite targets [12,27–29]. The use of C-Pt, PtNi_x/C and Mo-Ir for magnetron

sputtering of composite targets allowed to obtain the corresponding composite nanostructured catalysts with reduced consumption of platinum group metals, which showed high stability in resource tests in the electrolysis cell [27,28].

Platinum-carbon composites with a platinum particle size of about 3 nm were obtained by depositing a layer of carbon substrate by magnetron sputtering followed by platinum vapour deposition [30]. It was shown that using composite targets targets platinum-

carbon and palladium-carbon [29,31], the structure of coatings strongly depends on the sputtering modes: DC sputtering with cathodic potential supply on the titanium substrate gave a dense layer structure, and when using pulse sputtering mode, porous layers with appreciable electrocatalytic activity were formed. At the same time, increasing the pulse frequency from 10 kHz to 100 kHz increased the specific surface area almost 2 times and gave a sufficiently high electrochemical activity.

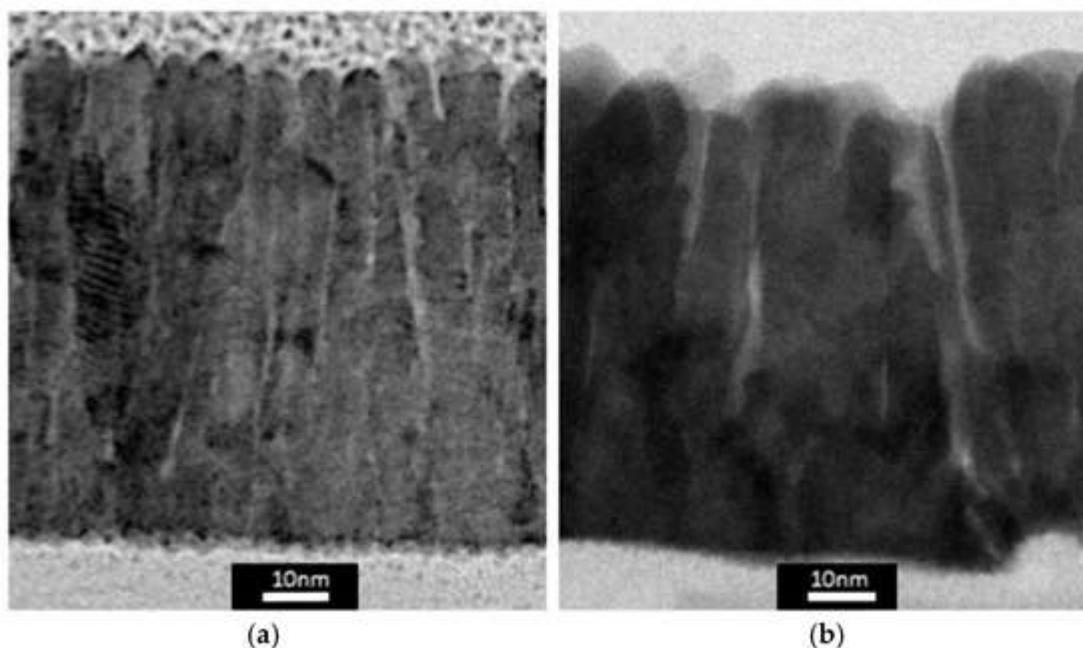


Fig. 3. Scanning transmission electron microscopy (STEM) images of the samples produced by Pt-C and Pt targets sputtering using pulsed magnetron sputtering regime (frequency 100 kHz). (a) Pt-C film deposited on Ti substrate. (b) Pt film deposited on Ti substrate [31].

It may be supposed that the current density increases at 100 kHz along with reduced pulses duration inhibit large globule growth and lead to highly homogenous fine grain/pillar structures with a developed surface area and an increased porosity. In this case, the sputtered platinum-carbon layers had a more porous structure compared to pure platinum (Fig. 3). The efficiency of pulsed sputtering mode for magnetron sputtering using such a composite target to produce nanosized platinum particles (1-5 nm) with high specific surface area on a carbon gas diffusion layer was also shown in [12].

However, it is not only the deposition of platinum group metals but also other active materials what is of obvious interest. Recent

research [32] has shown that it is possible to increase the electrochemical resistance of porous titanium, as well as to improve the catalytic activity of electrodes with Ir on its basis by depositing a porous sublayer of nanosized particles of TiN by magnetron sputtering of Ti in Ar atmosphere with N and/or N/O₂. Electrochemical impedance spectroscopy measurements show that the deposition of the sublayer leads to a decrease in the overvoltage of the anodic reaction (due to an increase in the contact surface of the current collector with the catalytic layer), but the increase in the total resistance and ohmic losses in the porous sublayer has a negative effect on the MEA characteristics at high current densities. Accelerated stress testing has also shown a

slight increase (6-7%) in the lifetime of the current collectors.

Magnetron sputtering is of significant interest for the production of thin-film electrodes for batteries, such as Si [33]. This method is relevant for obtaining solid electrolytes for solid-state batteries. Thus, in [34, 35] RF magnetron sputtering of Li_3PO_4 target in N atmosphere produced LiPON thin films. In [36], a thin film solid Li_3PO_4 electrolyte were synthesized by this method and deposited on a film electrode. The selected sputtering mode allowed avoiding crystallization of the electrolyte, which ensured a high electrical conductivity of more than $1 \times 10^{-6} \text{ S cm}^{-1}$, close to the conductivity of LiPON. Other solid electrolytes, such as Li-V-Si-O, are also being produced by magnetron sputtering [37], as well as other components of solid-state batteries (buffer layers of LiCoO_2 microcrystals [38]). Studies are ongoing to obtain high-temperature yttria-stabilized zirconia (YSZ) thin-film electrolytes [39], NiO/YSZ thin-film NiO/YSZ [40].

In general, the production of thin film electrodes by magnetron sputtering is a promising technology for improving the stability and efficiency of electrochemical systems, as this method allows to control of the film structure, including composition, thickness and morphology, which in turn helps to optimize the catalytic properties of the film and tailor it for specific electrochemical reactions.

Dispersed carriers

The magnetron sputtering method can be used for dispersed catalysts production and, for example, provide an additional increase in the activity and stability of Pt on carbon-based catalysts by modifying carriers (including reduced graphene oxide (RGO)) with nitrogen or sulphur atoms in situ in a vacuum chamber prior to Pt deposition [41].

As mentioned above, the magnetron sputtering method can be used to obtain stable and active electrocatalysts. However, in this case the point is about the deposition of catalytically active materials on 2D planar carriers (e.g., on gas diffusion layers of carbon paper, fabric, porous titanium). In some cases, substrates having an ordered 3D structure,

including composite substrates, are used. For example, platinum nanoparticles were deposited by magnetron sputtering on vertically aligned carbon nanofibers (CNF) obtained on a flat substrate (methanol oxidation reaction [42]), TiO_2/CNT [16], on a substrate made of a network of nitrogen-doped CNT (cathode catalyst for CO_2 reduction for Li- CO_2 batteries [43]). However, as mentioned above, an important direction of electrochemistry remains the production of catalysts on dispersed carriers. The use of magnetron sputtering method for this purpose has its own peculiarities, because in order to ensure uniform application of metal nanoparticles on powders which having friability and tendency to aggregation, it is necessary to use special stirring devices. Various variants of vibration devices creating a powder pseudo-boiling layer, devices with polygonal drums were developed, which allowed achieving positive results. The works in this direction continue.

Platinum nanoparticles were synthesized on Vulcan XC-72 (Pt content from 32 to 40 wt. %) by magnetron sputtering with readily replaceable targets 67 mm in diameter and 4 mm in thickness with different bias voltages applied in [44]. Vulcan XC-72 powder (0.55-0.65 g) was loaded into a cap with a diameter of 115 mm and wall height of 25 mm. The sputtering was carried out by vibrating the cup along a vertical axis with a frequency of 2-3 Hz and amplitude of 0.5-1.0 mm with simultaneous rotation around this axis at a speed of about 10 rpm. Before sputtering, the chamber was evacuated to a pressure of $\sim 5 \times 10^{-5}$ Torr and filled with the Ar. The morphology of the electrocatalysts was analyzed by transmission electron microscopy (TEM), which showed that platinum was uniformly distributed on the carrier surface and the particle size was from 3 to 4 nm. The different catalysts were studied as cathode catalysts in PEMFC. Test results showed that the use of Pt/Vulcan-XC-based MEA (Pt content of 37 wt. %) has better characteristics (cell voltage was 0.55 V at a current density of 1 A/cm^2) as compared to other samples. Probably, the favorable effect is mainly due to the bias voltage applied to obtain the sample.

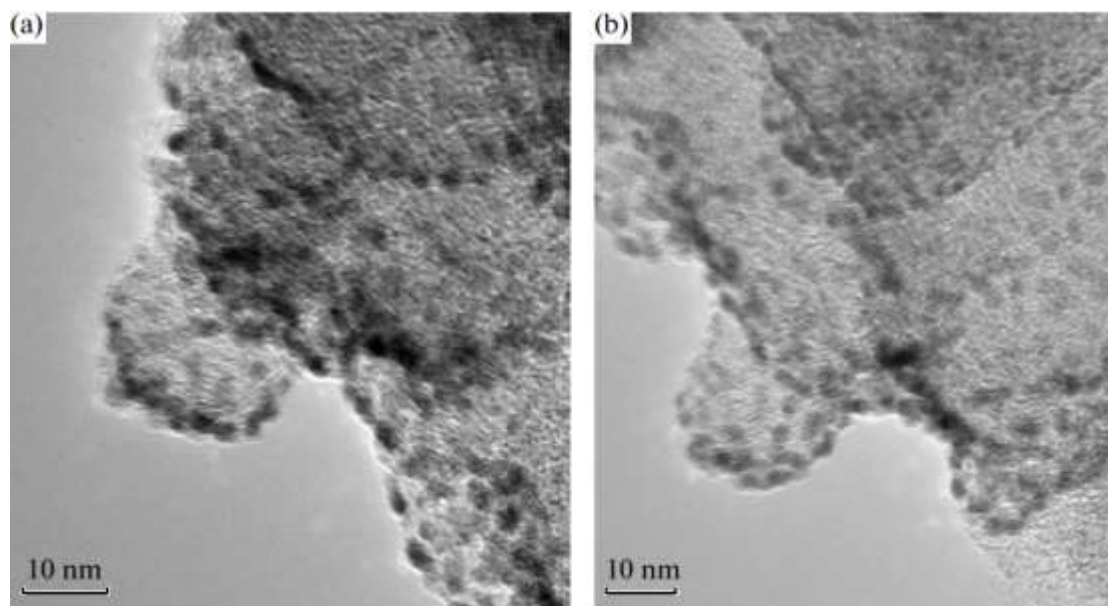


Fig. 5. TEM images of Pt³⁹/Vulcan XC (a) and Pt³²/Vulcan XC (b) [44].

In [45], using DC magnetron sputtering, platinum atoms were introduced onto the powder of graphite-like carbon nitride $g\text{-C}_3\text{N}_4$. Due to some stabilization of nitrogen atoms between Pt atoms, no agglomeration occurred. Stirring during the process ensured dispersion of platinum nanoparticles in the whole volume of the powder (0.5 wt. % Pt per 1 $g\text{-C}_3\text{N}_4$). The authors [46] suggested another option for the synthesis of an efficient Pt/C catalyst for PEM fuel cells. Firstly, a monodisperse layer of spherical carbon nanoparticles with a diameter of 50 nm was prepared from Vulcan XC-72 carbon black using special treatment, and then a uniform layer of 3 nm platinum nanoparticles was deposited on these spheres by DC sputtering of platinum. The electrochemical surface area increased by 34% as compared to a commercial Pt/C catalyst with the same platinum content. Moreover, MEA tests showed that the nominal specific capacity of the new catalyst under H₂/Air test conditions was 26.7% higher than that of the commercial Pt/C catalyst.

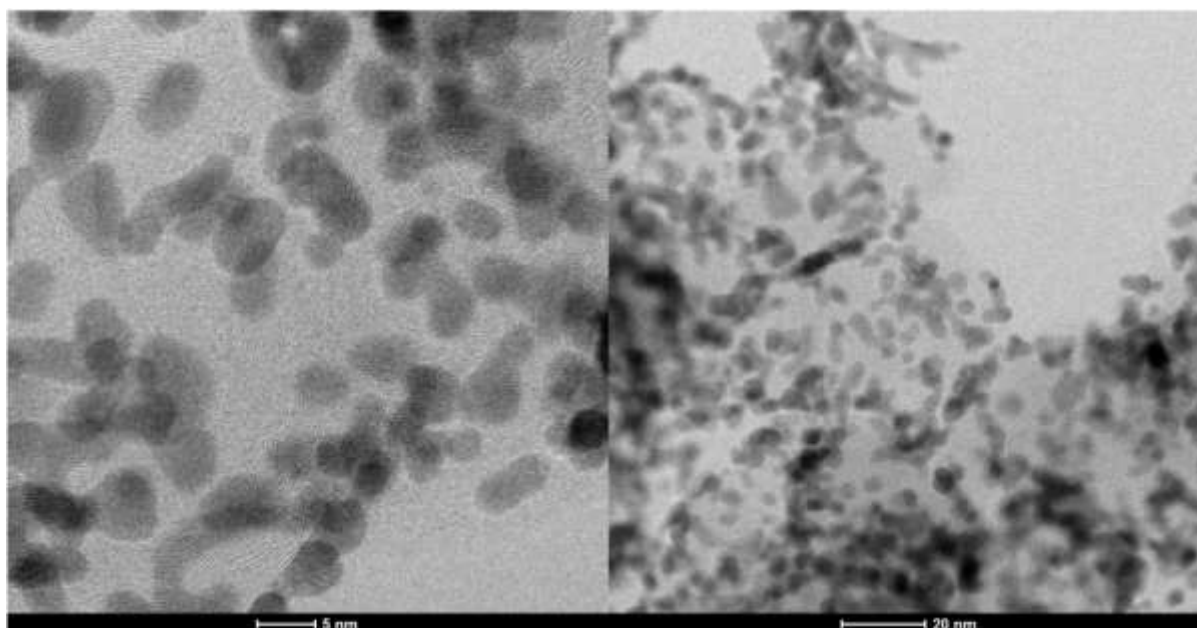


Fig. 6. TEM images of 40 wt. % of Pt on XC-72 added by 1% of RGO [48].

The Pt⁴⁰/CNF catalyst with particle size from 4 to 6 nm was synthesized by magnetron sputtering in an impulse mode for high-temperature PEM fuel cell based on polybenzimidazole (PBI) doped by H₃PO₄ [47]. Magnetron sputtering was carried out in Ar atmosphere at discharge power 70 W with bias voltages applied. The MEA tests showed a power density of about 300 mW/cm² in both MEAs for Pt⁴⁰/Vulcan XC-72 and Pt⁴⁰/CNF at 0.5-0.6 V. However, after stability tests, it was found that the degradation of Pt⁴⁰/Vulcan XC-72 was found to be higher compared to Pt⁴⁰/CNF. Oxidation experiments were also carried out on the electrocatalysts in air at 350 °C. The mass loss of Pt⁴⁰/CNF was only 6-10

wt. %, while the mass loss of Pt⁴⁰/Vulcan XC-72 reached 45-50 wt%.

The authors in [48] conducted studies by adding RGO (from 0 to 6 wt%) to the electrocatalytic composition based on Pt⁴⁰/Vulcan-XC obtained by pulsed sputtering mode for magnetron sputtering as a cathode electrocatalyst of a PEM fuel cell. TEM images showed that the platinum nanoparticles are uniformly distributed on the carrier surface and have a rather small size in the range of 3.1 ± 0.6 nm. The addition of RGO to the active layers of the fuel cell showed that the addition of 1 wt. % improves its performance. In particular, the maximum specific power is increased by about 8.5 wt. %.

Conclusions

Magnetron sputtering is one of the promising methods for the production of catalyst nanomaterials, as it is ecologically friendly and allows producing catalysts of high purity, controlling particle size and/or thickness of catalytic coatings, and easing operation. In this review, various examples were provided to show the diversity of morphology of nanomaterials obtained by this synthesis method. It can be observed that magnetron sputtering offers great opportunities for the development of electrocatalysts and their

processing, such as the introduction of heteroatoms into the structure of the catalyst itself. Especially important that the technology permits to obtain catalyst particles on dispersed carriers (powders) which are very important for PEM fuel cells and electrolyzers.

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ELEKTROKATALİZATORLARIN SİNTEZİ ÜÇÜN MAQNETRON SƏPİLMƏ

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Xülasə: Maqnetron səpilmə müxtəlif örtüklərin alınması və səth modifikasiyası üçün məlum üsuldur, lakin hazırda bu üsuldən elektrokatalizatorların sintezində uğurla istifadə olunur. Üsulun əsas üstünlüklərindən biri prosesin parametrlərini dəyişmək imkanındır: rejim (birbaşa cərəyan ilə səpilmə, impulsu orta tezlikli səpilmə, yüksək tezlikli səpilmə), səpilən substrata və ya katalizator daşıyıcısına potensialın verilməsi, vakuum kamerasında təzyiqliq, atmosfer meydana gələn örtüklərin və katalizatorların tərkibini və strukturunu çox geniş şəkildə dəyişməyə imkan verən kompozisiya. Səpilmə rejimlərinin dəyişdirilməsi elektrod materiallarının alınması üçün həm sıx (məsaməli) qoruyucu-katalitik örtüklər, həm də çox inkişaf etmiş səthə malik örtüklər yaratmağa imkan verir.

Açar sözlər: nazik təbəqəli elektrod; proton mübadilə membranı; yanacaq elementi; elektrokatalizatorlar; daşıyıcılar; maqnetron.

МАГНЕТРОННОЕ РАСПЫЛЕНИЕ ДЛЯ СИНТЕЗА ЭЛЕКТРОКАТАЛИЗАТОРОВ

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Аннотация: Магнетронное распыление - хорошо известный метод получения различных покрытий и модификации поверхности, но в настоящее время он успешно применяется для синтеза электродов. Одним из основных преимуществ является возможность

варьировать параметры процесса: режим (распыление постоянным током, импульсное среднечастотное распыление, высокочастотное распыление), подачу потенциала на распыляемую подложку или носитель катализатора, давление в вакуумной камере, состав атмосферы, что позволяет очень широко изменять состав и структуру получаемых покрытий и катализаторов. Изменение режимов напыления позволяет создавать как плотные (пористые) защитно-каталитические покрытия, так и покрытия с очень развитой поверхностью, т.е. для получения электродных материалов.

Ключевые слова: тонкопленочный электрод; протонообменная мембрана; топливный элемент; электрокатализаторы; носители; магнетрон.