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Application of the magnetron sputtering for nanostructured electrocatalysts synthesis[☆]



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ABSTRACT

Electrochemical systems with solid polymer electrolyte are considered to be the most promising for hydrogen energy and several branches of industry. Electrocatalysts are one of the key components of fuel cells and electrolyzers. Application of magnetron sputtering for their synthesis will allow replacing the multistage chemical methods, to decrease platinum loading and create new effective nanostructured electrocatalysts. This review presents the systematization of the available data on magnetron sputtering for electrocatalysts and protective coating synthesis. Moreover the review analyzes the influence of sputtering parameters on deposited films properties and proposes several strategies of optimization. There is special attention to nanocarbon support materials (graphene, carbon nanotubes).

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Introduction

Electrochemical systems with solid polymer electrolyte (or polymer electrolyte membrane -PEM) form the basis of developing hydrogen energy and now find application in other areas: space industry, aviation, submarine fleet. Electrolysers and fuel cells are promising for the development of autonomous systems based on renewable energy, emergency power supply systems, different modes of transport, and for hydrogen supply of various consumers (among the major analytical instrumentation, metallurgy, electronic industry, analytical chemistry, atomic energy, etc.). One of the key components of PEM electrolyzers and fuel cells are electrocatalysts and membrane-electrode assemblies on their basis. Acidic properties of the membrane (solid polymer electrolyte) and its high sensitivity to multivalent ions do not allow the use as electrode materials (electrocatalysts) of such metals as nickel, cobalt, iron and many others. Practically, taking into account high requirements to catalytic activity of materials, platinum metals (usually platinum for fuel cells and platinum, iridium and ruthenium and their oxides for electrolyzers) are used at present time [1]. The most common methods of synthesis of such catalysts are still chemical (reduction of appropriate metal compounds primarily in liquid and also in a gas phase) though they have some significant restrictions on the chemical and phase

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composition of synthesized catalysts (for example the inability to obtain some alloys). The chemical methods are characterized by multistage procedure, in particular, due to necessity of purification of the obtained catalyst from impurities; high energy consumption; the lack of environmental safety. Synthesis of catalysts by thermal decomposition of precursors also often requires the scrupulous catalyst purification, but, most significantly, increases the particle size of the catalyst and creates certain restrictions on the possible phase composition of the product.

Several publications confirming the possibility of electrocatalyst synthesis by magnetron sputtering of platinum appeared in the late 80s of the last century (first investigations, apparently, were started at the late 60s) [2,3]. These investigations got further development in the 90s [4,5]. For example Hirano et al. reported in 1997 about the synthesis of effective catalysts for PEM fuel cells. Using magnetron sputtering they decreased platinum loading up to 0.1 mg/cm² [5]. In the 21st Century interest to catalyst production by magnetron sputtering significantly increased: experimental and theoretical research on the influence of parameters of sputtering process, characteristics of carriers (including new nanomaterials) are carried out. A large number of foreign patents and publications dedicated to the electrodes production, including electrodes for PEM fuel cells, where magnetron sputtering was proposed to reduce the consumption of platinum (e.g. Ref. [6]), to create nano-structural electroctalyst layers [7–10], and also to produce corrosion resistant coatings for life-time increase [11,12] appeared. In Russia research activity in this promising area has also increased recently (see, e.g., [13-18]), yet this direction, from the point of view of the authors, receive insufficient attention. This review is an attempt to systematize the available data on magnetron sputtering application for the synthesis of electrocatalysts and production of corrosion resistant coatings, as well as a certain popularization of the above method developed in NRC "Kurchatov Institute" (earlier Institute of Atomic Energy name by I.V. Kurchatov).

Magnetron sputtering

Magnetron sputtering – cathodic sputtering of target material in magnetron discharge plasma – allows obtaining thin films and coatings on various supports. Dutch physicist F. Penning was the first to suggest using magnetron sputtering for the film deposition as early as 1935 [19]. Material sputtering in magnetron discharge was studied in several laboratories in the 1960s and in the 1970s various configurations of magnetron sputtering systems (MSS), including prototypes of modern planar magnetrons, were proposed [20,21]. Industrial application of this technology started at the end of the 1970s. Since then high-power impulse systems have been designed in addition to DC and RF classical variants. Development of new magnetrons is continuing now [22,23]. Many modern sputtering systems are fully automated and operate continuously.

Magnetron sputtering is important not only for industrial application but also for science and technology research. This technique has been used in NRC "Kurchatov institute" since the mid-1980s. Wide experience in deposition of amorphous and polycrystalline films of metals, alloys, intermetallic compounds with necessary structure, protective and functional properties has been gained [24–27], Fig. 1 (left). Method of catalytic layers deposition by magnetron sputtering has been developed and surface Raney catalysts [28] and new effective catalysts for various processes have been synthesized [29]. Development of these works resulted in the creation of catalytic membrane reactors [30]. Carbon supports were considered closely: coating deposition added catalytic properties and improved thermal and chemical stability [31].

Solving some problems important for hydrogen energy development (e.g. encapsulation of hydride forming powders, synthesis of catalysts on granules) needs various films/coatings (including Pt, Pd ones) on disperse carriers [32]. One sample of coated granules is shown in Fig. 1 (right). Special device producing pseudoboiling powder layer was used for uniform deposition on granules and powders. Later on new devices for prevention of powder aggregation were designed. Preliminary experiments on deposition of Cu and Ni on carbon powders showed the possibility of carbon nanomaterials and carbon based nanocomposites coating.

Promising prospects of magnetron sputtering for electrocatalysts synthesis were confirmed by experimental data obtained in the 2010–2012s [13,14]. This technique has high productivity, is ecologically clean and allows reducing platinum loading and obtaining particles with required size. It is necessary to note that catalysts production can be easily scaled as various Russian and foreign companies produce vacuum coating systems with modern MSS. Thus technology of electrocatalysts synthesis by magnetron sputtering can be introduced in Russia and other countries.

Influence of sputtering parameters on the composition, structure and protective/catalytic properties of the deposited coating

Influence of the main sputtering parameters (working gas type and pressure, MSS power, substrate bias potential, targetsubstrate distance et al.) on the grain size, film morphology and catalytic properties should be taken into account for the effective electrocatalysts synthesis. Here we briefly review some experimental results important for the deposition of nanostructured coatings with desired properties.

Silver deposition on Si substrate was studied in Ref. [33]. The target-substrate distance, deposition time and sputtering current appeared to be the main parameters determining the particle size. With decreasing the target-substrate distance from 20 to 10 cm the grain size of Ag nanoparticles increased from 3.8 to 5.9 nm. The authors explained this effect by the increase in the deposition rate and the total amount of deposited Ag. The target-substrate distance also affected the shape and the distribution of particles – high deposition rate resulted in nonuniform size, shape and distribution of Ag particle's position. When the sputtering current was increased from 50 to 150 mA, nanoparticles became larger and formed wormlike morphology due to coalescence. These results are consistent with mechanisms of thin film formation by DC magnetron sputtering.



Fig. 1 – Typical columnar structure of Ni sputtered on the porous substrate (left). Cu-coated LaNi₅ granules and powder (right).

The influence of DC power and gas pressure on the morphology of platinum films and their catalytic activity toward the oxygen reduction was studied in Ref. [34]. Optimal sputtering parameters were determined. High argon pressure (68 mTorr) and low sputtering power (100 W) proved to ensure large active surface and increased catalytic activity of Pt films deposited on glass substrates upon 25 nm Ti layer. The increase in applied power from 100 to 1000 W resulted in the target potential increase by 90 V. Higher argon ions acceleration leads to increased kinetic energy and longer mean free pass of sputtered platinum particles. This reduces the probability of Pt particles collisions with Ar ions so these particles hit the substrate with more energy. The probability of surface rearrangement increases. Dense layers are formed. The decrease in Ar pressure also results in longer mean free pass. Platinum particles with increased kinetic energy form compact films.

The influence of the sputtering parameters L (targetsubstrate distance), F_{Ar} and F_{ox} (the flow rates of Ar and O_2 , on the composition, correspondingly) structure, morphology and electrochemical properties of iridium oxide films was studied in Ref. [35]. These films were deposited by reactive magnetron sputtering on hydrophobic carbon paper with 50 nm Ti sublayer. The combination of 100 W power, L = 78 mm, F_{Ar} = 40 sccm, F_{ox} = 8–12 sccm proved to be the optimal one. The excellent catalytic activity in the oxygen evolution reaction has been demonstrated for iridium oxide films sputtered under these conditions. The influence of Ar pressure on the surface structure and morphology of sputtered Pd films has been studied recently [36]. The pressure of argon gas was varied in the range 5 \times 10⁻³–1 \times 10⁻¹ mbar (applied power was 100 W, target-substrate distance 78 mm, glass with 25 nm Ti layer was used as a substrate), Table 1.

Optimal sputter regime (100 W, 8 \times 10^{-2} Ar pressure) ensured the deposition of Pd layers with highly developed surface, Fig. 2.

The influence of sputtering parameters on the properties of ferromagnetic films deposited on nonporous substrates (e.g. SiO_2) has been studied in Refs. [37–39]. It was shown that argon pressure had noticeable effect on film texture. It can be connected with some energy process both on the substrate surface during deposition and in the space between target and substrate. Mean free pass at high pressure is significantly lower. Sputtered particles energy decreases on the way to substrate due to their collisions with argon atoms and ions therefore migration ability of atoms on the substrate surface and grain size are changed. The decrease in argon pressure results in the grain size increase and the transformation from column microstructure to quasihomogeneous film.

The effect of substrate bias in the range from -400 to +300 V on the structure and magnetic properties of the films were studied in details. In particular it was shown for Ni that at negative bias ion bombardment produced many defects which acted as nucleation centers on the substrate and film surfaces. High density of defects on the surface results in the decrease of adatom mean free pass therefore nucleation rate increases and the critical cluster size decreases. Moreover ion bombardment can break clusters during their formation thus clusters consisting of two atoms are formed preferably which leads to certain film texture.

In the case of positive bias the substrate surface is irradiated by electrons. Electron bombardment promotes fast and intense heating of the substrate which increases adatom migration ability. Probability of other clusters formation rises. It is noted that the effect of positive bias on the film structure depends on argon pressure.

Table 1 — Influence of Ar pressure on the deposition rate and Pd crystallite size.						
P _{Ar} (mbar)	$5 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$4 \cdot 10^{-2}$	8·10 ⁻²	$1 \cdot 10^{-1}$
Sputter rate (nm/min)	7.8	7.5	7.34	6.9	4.5	3.2
Crystal size (nm)	33.0	27.5	22.0	18.0	17.5	19.0



Fig. 2 – SEM image of Pd film at $P_{Ar} = 8 \cdot 10^{-2}$ mbar. Based on Ref. [36].

Densification and partial destruction of columnar structure was observed in Ref. [40] at negative substrate bias. This effect is probably connected with resputtering due to intensive ion bombardment. Densification and decrease of the grain size was also obtained at nitrogen addition to the working gas. Studies on pulse ion implantation (surface bombardment by 1–30 keV argon ions) confirmed the coating densification [41,42]. This effect was especially obvious at high enough energy and doses leading to appreciable coating resputtering (Fig. 3).

It has been previously shown that substrate bias is the important parameter for porous substrates. This parameter allows control of the energy of ions at the substrate during deposition and determines Pt penetration inside the electrode [43].

Leakage into the vacuum chamber before deposition is also an important parameter [44] as it influences the quantity of impurities which can be introduced into the coating.

Synthesis of catalysts on porous supports

Magnetron sputtering allows obtaining films and coatings on various supports. However support materials for electrocatalysts fabrication have specific features. Carbonaceous porous materials and porous titanium are commonly used. Carbon support has large specific surface and high electric conductivity. Support structure influences the catalytic layer microstructure thus affecting the electrochemical properties. Catalytic particles (Pt or other precious metal) are deposited on the surface of carbon supports therefore surface morphology has a significant effect on catalytic metal dispersion. The traditional support is carbon black (e.g. Vulcan XC-72). Recently carbonaceous nanomaterials such as carbon nanofibers (CNF), carbon nanotubes (CNT), graphene, mesoporous carbon, aerogels and others have attracted great interest [45-47]. Perspective support based on carbon nanocages (a kind of spherical nanocarbon with a graphitic shell and a hollow interior) has been investigated in Ref. [48]. Pt catalysts deposited on this support possess not only high activity but also long-term stability. Specialists believed that new generation of electrocatalysts can be designed on the base of graphene. Technologies of graphene industrial production are progressing rapidly and proposals for commercial use are increasing. Nobel Prize winner K. Novoselov refutes the opinion of some specialists that we are decades away from commercial graphene production [49]. US-based Bluestone Global Tech has the capacity to produce 20-200 square meters of graphene per day. In 2013 Bluestone Global Tech decided to open a new graphene production plant in UK. Commercial graphene production began in Poland at the end of 2013. This country hopes to occupy 30-40% of the world market. Companies and Universities of China, Japan, South Korea (Samsung especially) actively work on graphene commercialization.



Fig. 3 – Structure of platinum coating on Ti before and after ion implantation (Ar⁺, 10^{16} ion/cm², E = 10 keV). Based on data from Refs. [41,42].

Graphene-carbon composites are also promising Pt supports. Increased electrochemical activity has been obtained using macroporous carbon-graphene [50], CNT-graphene [51]. Due to unique hierarchical architecture PtRu nanoparticles with diameters 2–4 nm on N-doped CNT/graphene hybrid support showed an improved electrocatalytic performance compared to conventional CNTs and commercial catalysts [52].

Some other hybrid supports, for example with TiO_2 or ceria addition are also of interest. Effective catalysts $Pt/TiO_2/gra$ phene and Pt/TiO_2 coated carbon nanofibers have been synthesized [53]. $Pt/CeO_2/graphene$ [54] and $Pt/CeO_2/CNT$ [55] exhibited remarkable electrocatalytic activity.

Novel materials described above certainly should be used as supports of electrocatalysts synthesized by magnetron sputtering. Several investigations are known by now. In one of the first research nanocomposites with high electrochemical activity were produced by sputtering Pt nanoparticles onto vertically aligned CNx nanotubes [56].

Magnetron sputtering was used for deposition PtRu catalysts on carbon nanotubes and N-doped carbon nanotubes [45], Pt nanoparticles on CNT (here ion liquids were used for immobilization) [57]. Electrocatalysts Pt/CeO₂CNT [58] and Pt on the mixture CNT/Vulcan XC-72 [7] were synthesized by RF magnetron sputtering. Carbon nanofibers also can be used as supports: efficient Pt-sputtered electrodes for direct methanol fuel cell have been produced on carbon nanofibers directly grown on the carbon paper [59].

Excellent electrocatalysts for methanol oxidation have been produced by sputtering of Pt nanoclusters of various thickness on porous graphene nanoflakes [60], Fig. 4.

Magnetron sputtering of Pt on the vertically aligned carbon nanotubes resulted in fabrication of the low cost, large area and high performance electrocatalysts [8]. (PECVD method was used to grow aligned CNT on the Al foil). Pt loading was substantially reduced (down to $35 \,\mu g \, cm^{-2}$) compared with the traditional Pt/C catalysts. SEM and TEM images of Pt/CNT show that the deposition depth is around 500 nm from CNT tops and the most part of Pt nanoparticles are dispersed on the 200 nm depths (Fig. 5).



Fig. 4 – Pt nanoclusters with thickness of 2.1 nm sputtered on porous graphene nanoflakes. Based on Ref. [60].

Multi-walled CNT (MWCNT) on a glassy carbon plate were used as supports in Refs. [9,10,61]. Efficient catalysts for oxygen reduction have been produced by magnetron sputtering of Pt and Pd. Additional effect of heat treatment of sputtered Pd nanolayers on catalytic activity was studied in Ref. [10]. The Pd/CNT composite annealed in Ar at 500 °C during 30 min proved to be the most effective one. After heat treatment continuous metal film was converted into 2–12 nm Pd nanoparticles (Fig. 6). By authors opinion these composites can be an alternative to Pt-based catalysts.

Synthesis of unique all-carbon hierarchical support for PEMFC was reported in Ref. [62]. CNT were grown on carbon paper (to catalyze CNT growth, Al and Fe were deposited onto carbon paper by magnetron sputtering), then graphene was grown on CNT using PECVD. The cathode based on this support was obtained by magnetron deposition of only 19 nm Pt layer (0.04 mg/cm²), Fig. 7.

SEM and TEM images of as-grown and Pt-deposited hybrid are shown in Fig. 8. An average diameter CNT with leaf-like graphene features is 100 nm. The detail investigations confirmed high sp^2 content in this hybrid. New support combines the advantages of both an ultra-high density of active graphene edges and the porous structure of CNT. Pt/hybrid electrocatalyst showed superior performance compared to a commercial Pt/V XC-72.

It should be noted that electrocatalysts on commercial carbon supports are also produced by magnetron sputtering. Porous carbon paper was used in Ref. [63]. The influence of Ar pressure (0.05, 0.1 and 0.5 mbar) on the structure and electrocatalytic properties of Pt films was studied. Films deposited at low Ar pressure had uniform surface. At 0.5 mbar number of collisions between particles and Ar increases and mean free path of Pt decreases. Due to the loss of kinetic energy Pt atoms nucleate before reaching the support. As a result conical nanopillar structure favorable for electrodes performance is formed (Fig. 9).

Mechanisms of interaction between metal particles and support are still not quite clear. The authors of review on carbon materials for electrocatalysts [46] note that controlling metal nanoparticles growth is still a bottleneck in catalyst synthesis.

Deposition of atoms by magnetron sputtering is coupled with diffusion which is generally anomalous in a porous medium. The goal of study [64] was to characterize "diffusion-deposition" process in a porous carbon medium. Pt was sputtered on the porous layer of a few tens of microns thick composed of Vulcan XC 72 and PTFE particles on the carbon cloth. The specific area was $15 \text{ m}^2/\text{g}$ before and about 13 m²/g after Pt deposition. The diffusion process was studied at argon pressures of 0.5 and 5 Pa leading to a mean kinetic energy of Pt around 7 and 0.04 eV. The depth profile was studied by Rutherford backscattering spectroscopy. Since all Pt atoms cannot be adsorbed inside pores immediately the Pt layer on the surface grows and act as a screen from the plasma. Amount of Pt mass in the porous medium as a function of time is shown in Fig. 10. The diffusion coefficient in the porous support and the flux at the interface (carbon surface z = 0) decrease with time due to the Pt layer deposition on the surface. Some fitted Pt depth profiles in porous



Fig. 5 - SEM and TEM images of Pt on CNT. Data are from Ref. [8].



Fig. 6 – SEM images of Pd/MWCNT before (left) and after (right) annealing (500 °C, 30 min). Based on data from Ref. [10].

carbon at different deposition times are presented in Fig. 11. Data in Figs. 10 and 11 correspond to P = 0.5 Pa, but these effects are also observed at 5 Pa.

For better understanding of the growth of catalytic clusters/films on carbon porous supports simulations of Pt–Pt interactions at the atomic level have been carried out [65]. MD simulations confirm the previous experimental data and the model of Pt penetration in the porous medium [64]. Support of amorphous carbon spheres with diameter 0.3–1.3 nm (2.26 g/ cm², porosity of 60%) and the result of Pt deposition are shown in Fig. 12. Molecular simulations can be useful for the optimization of catalysts synthesis especially on the porous supports.

Investigating of mechanisms of particle growth during deposition on the supports is very important for the efficient catalysts production. Adhesion and nanocluster formation depend on the energy distribution of the deposited particles. This distribution is determined by the energy of sputtered particles and slowing down processes due to collisions with atoms and ions of the gas. The average kinetic energy of sputtered atoms is in the range 3–10 eV (up to 30 eV according to some data). These atoms can thermalize before reaching



Fig. 7 – Schematic illustration of Pt/graphene/GNT cathode fabrication and the comparison of the new cathode and the conventional one. Data are from Ref. [62].



Fig. 10 – Pt distribution in the porous carbon calculated as a function of time (loglog plot) [64].

cluster surface [66]. The mechanisms of Pd nanoclusters formation by magnetron sputtering have been studied in this work. The mixture of argon and helium was used. The size of clusters decreases with increasing He flow rate from 5 to 25 cm³/min (at a constant Ar flow of 40 cm³/min) because three-body collisions occurs more frequently. Besides, He stream is extracted out of the vacuum chamber more effectively than Ar and nucleation time decreases.



Fig. 8 – SEM image of the graphene/CNT hybrid support (left), TEM image at higher magnification (center), SEM image of the Pt/graphene/CNT (right). Based on data from Ref. [62].



Fig. 9 — AFM images of Pt films deposited at different Ar pressures: (a) 0.05 mbar, (b) 0.1 mbar, (c) 0.5 mbar. Data are from Ref. [63].

the support if the distance is rather long or sputtering gas pressure is high enough. Particles with nonthermal energies and inert gas ions influence the growth of clusters/film.

The growth of clusters may involve two processes: embryo formation via three-body collisions (2 sputtered atoms and an atom of inert gas which takes away excess kinetic energy) and nucleation of large clusters by two-body collisions (nanocluster-nanocluster) and accepting new atoms arriving to the Interestingly, the critical cluster size can be decreased by increasing the surface defect density. Nanoparticles of gold with diameters of 5–30 nm were obtained in Ref. [67] depending on sputtering conditions (especially kinetic energy of the particles) and density of defects on MWCNT surface. Density of defects was changed by heat pretreatment.

Results of the combined molecular dynamics and experimental study of platinum cluster growth on porous carbon are



Fig. 11 – Pt depth profiles in porous carbon support depending on deposition times. z = 0 corresponds to the carbon layer surface. Data from Ref. [64].

Magnetron sputtering for the deposition of catalytic particles on powder supports

Application of the magnetron sputtering for the deposition of catalytic particles on powder supports have some peculiarities and is rather difficult task. Powders have high flowability and at the same time they can form agglomerates; due to the large specific surface area powder is the source of intensive gas evolution; however it is necessary to ensure uniform deposition, large active area of the catalyst, strong adhesion, minimal loading of precious metals. Powder stirring during the process of deposition is required for uniform coating. As noted above the team of authors achieved significant progress. At the beginning of these investigations (2004–2006s) a vibration exciter producing pseudoboiling powder layer was used. Special cup was fabricated and placed into the vacuum



Fig. 12 – Support of amorphous carbon spheres with diameter 0.3–1.3 nm (left), molecular modeling of Pt deposition (center), Pt depth profile (right), points – experiment, line – theory. Based on data from Ref. [65].

presented in Refs. [23,68]. The authors used the simple model in which the mean kinetic energy was calculated according to a modified Thompson formula [69,70] for atoms traveling through an argon plasma.

Platinum clusters were deposited under the following conditions: power 530 W, target voltage 700 V, target current 0.78 A; carbon and $Pt_{0.01}C_{0.99}$ targets were used. The target-to-substrate distance was 6.5 cm. Targets were 45° tilted with respect to the porous carbon support. Data obtained by Rutherford backscattering spectroscopy showed that 90% of Pt atoms were localized in the first 200 nm depth of the support. Results of molecular modeling for Pt atoms deposited on the support with three different kinetic energies are presented in Fig. 13. Energy of 1 eV corresponds to low argon pressure therefore to low energy loss of sputtered atoms. Energy of 0.1 eV is typical for resistive or electron beam evaporation, and E = 0.026 eV corresponds to Pt atoms deposited by magnetron sputtering at 5 Pa Ar and 300 K.

Experimental data and MD simulations showed the possibility of the synthesis of effective catalyst for FC by plasma sputter deposition. Such catalyst consists of very small amorphous platinum clusters fitting closely the surface morphology [23]. chamber (e.g. Ref. [32]). Later on the system was modernized to improve stirring; in particular two crossed spirals were added in the cup near its bottom [13–16]. Other variants of magnetron system modernization for powder coating were presented by the authors of [71,72]. Pt–Ru alloy was sputtered from the composite target and deposited on carbon support using a powder sample holder in the form of the wheel in Ref. [71]. It was noted that the close control of the sputtering parameters such as power, gas pressure, sputtering time *etc* was necessary for the deposition of catalyst particles with required sizes, surface composition and structure. The authors succeeded in selecting these parameters and produced the electrocatalyst for the direct methanol oxidation which showed superior performance compared to a commercial one.

Hemispherical gold nanoparticles of 2–3 nm were deposited by magnetron sputtering on alumina granules [72]. The system consisting of two stainless rotating cups (with support powder in the inner cup) tilted 45° from vertical was used, Fig. 14. Process parameters were as follows: power 11 W, Ar pressure 15 mtorr (2×10^{-5} atm).

Later these researches sputtered gold nanoparticles on other supports, for example on WO_3 (specific surface area 5 m²/g) and activated carbon (specific surface area



Fig. 13 – Results of molecular modeling for Pt atoms deposited on porous carbon support with three different kinetic energies. Data from Ref. [68].



Fig. 14 – Hemispherical gold nanoparticles deposited on alumina granule and schematic representation of the chamber. Based on data from Ref. [72].

1100 m²/g) [73]. Two teflon stir bars were put into the inner cup to promote mixing. Many small gold nanoparticles with average diameter of 2.1 nm were formed on WO_3 surface. Gold nanoparticles on the surface of activated

carbon were even smaller (with average diameter of 1.7 nm). It is interesting that a substantial number of single atom species were observed on the surface of this support.



Fig. 15 – The polygonal barrel-sputtering system for powder samples. Based on [75].

The polygonal barrel-sputtering system (Fig. 15) was successfully used for deposition on various powder supports in Refs. [74–76].

However at Pt deposition on carbon nanofibers the authors faced with a problem – the large CNFs aggregates with sizes of 5–15 mm were formed and about 40% of CNFs remained unmodified. The problem was solved when pieces of bent columnar stainless steel were placed into the barrel with nanofibers. As a result CNFs coated with highly dispersed Pt nanoparticles (1.7–3.5 nm) were obtained successfully, Fig. 16 [74].

Possibility of method optimization

The method of magnetron sputtering permits to apply very small amount of catalytic active material in the controlled process. Optimization of the method additionally allows decreasing the size of produced particles and platinum loading and increasing catalytic activity. It can be achieved in different ways. Process parameters are of course very important and due to their optimization in NRC "Kurchatov Institute" platinum particles on different carbon carriers with



Fig. 16 – TEM image of the nanofiber coated with Pt nanoparticles. Data from Ref. [74].

dimensions of 3-5 nm and specific surface up to $120 \text{ m}^2/\text{g}$ were obtained (Fig. 17) [42].

At the same time one can use sputtering of a composite target or simultaneous sputtering of several targets, for example, from Pt and carbon [47,77–79]. In Ref. [78] original structure schematically shown on Fig. 18 was obtained.

During co-sputtering of Pt—C anisotropic growth of carbon columns and platinum clusters on their surface can be observed. The growth of clusters is controlled by their distribution on the surface, nucleation, surface diffusion and coalescence processes.

Co-sputtering of Pt, Ru and C permits not only to decrease a particle size but also to obtain Pt–Ru alloy with higher catalytic activity [80-82]. Electrocatalyst Pt–Ru/TiO₂/C was obtained [83] in a similar manner: first, by reactive sputtering TiO₂/C was received, and then by co-sputtering of targets Pt–Ru was deposited on the carrier. In Ref. [84] PdPt (10 wt % Pt) target was used for decrease of platinum loading.

In recently published [85] co-sputtering of the two targets was also used but with an individual control of sputtering power to ensure the necessary components ratio. As the result Pt_2Si catalyst was synthesized for the first time and it appeared to be significantly more efficient in reaction of ethanol oxidation in comparison with Pt. It must be emphasized that it is very difficult to obtain Pt–Si compounds by traditional method, so one more advantage of magnetron sputtering was demonstrated in this research – the possibility of applying of different alloys and silicides.

Authors of [86] offered their own optimization of the deposition process for production of the necessary surface structure: direct current magnetron with a power 200 W, distance between the target and the substrate 15 cm, Ar pressure $\sim 3 \times 10^{-6}$ atm. The substrate with a catalyst carrier was placed perpendicular to a particle flux and also under a small angle (the angle between the substrate surface normal and the deposition flux was 0° and 87°). In the first case the Pt formed a continuous layer that approximately replicated the rough surface morphology of the carrier and in the second case separated Pt nanoparticles were obtained (Pt atoms were nucleated preferentially on raised areas of the carrier surface



Fig. 17 – Pt deposited on graphene nanotubes. Data are from Ref. [42].



Fig. 18 – Schematic drawing of the PtC composite showing cluster's evolution in depth (B: surface). Data are from Ref. [78].

and then a vertical growth of particles took place due to continuous rotation of the substrate, Fig. 19).

In several articles authors offer to use high-power impulse magnetron sputtering (HiPIMS). High-power impulses are applied to a target and result in the high degree of ionization not only gas atoms but also the sputtered atoms of the target. A negative voltage bias supply to a support controls the energy of ions coming to the surface. It could be useful in the case of atom deposition deep in the pores of the carrier [87,88]. Nanoclusters of PtPd and PtAu were synthesized using HiPIMS in Ref. [87]. This magnetron installation had a specificity: metal clusters were obtained in the first chamber with a relatively high argon pressure (0.3 mbar), and then through an aperture they were transported to a high vacuum chamber (0.003 mbar), where they were deposited on a support. Authors of [88] confirmed that the use of HiPIMS increased penetration of Pt into microporous carbon - a dense layer limiting this process was not formed on the surface.

One of the technological approaches which can improve the quality of nanocoatings is an ion assistance implemented by the impact of a directed flow of the working gas ions on the surface of the deposited coating [44]. In such a case, part of the ions energy is transferred to the atoms of a surface layer which results in the increase in atoms mobility, desorption of impurity atoms, relaxation of internal stresses and assists in creation of more regular structure of the coatings. Authors of [44] used the Hall type system of ion purification for ion assistance.

Note that the application of ion implantation for the controlled modification of the electrode surface layer has been studied in NRC "Kurchatov Institute" since 1990s. In one of the first publications [89] it was shown that modification of platinum coating on the surface of porous titanium electrode by ion implantation (argon ions were used) resulted in a significant increase of the coating adhesion and increase of the electrode stability. Recent studies of the same team [42] confirm that the introduction of platinum atoms in the surface layer of the support by impulse implantation allows to improve the corrosion resistance of the coating significantly.

Conclusions

Analysis of the information obtained recently and from earlier publications showed that the usage of ion magneton sputtering method could provide production of efficient electrocatalysts. The method gives possibility to deposit a very small amount of catalytic active material in a controlled high purity process. Moreover, from the point of view of the green chemistry, application of magnetron sputtering would permit to refuse from using of toxic chemical reagents. The method allows decreasing the size of deposited particles and platinum metals consumption due to the application of composite targets, co-sputtering of several targets, various modes of voltage bias supply to a support, placement of the support with a carrier at definite angle and so on.

With the development of the ion magnetron sputtering method for electrocatalyst production it is necessary to pay attention to the perspective catalyst carriers mentioned above, especially carbon nanotubes and graphene. However the deposition of catalytically active particles with necessary size, structure and surface on a dispersed carrier and/or porous



Fig. 19 – Formation of Pt films and separated particles depending on the support position. Data are from Ref. [86].

carrier has its own features and is a complicated problem. In each case it is necessary to find the optimal combination of different process parameters such as power, working gas pressure, distance between target and support, bias potential on support and so on. These parameters influence on the kinetic energy of the deposited particles, energy of gas ions which are acting on the surface. From the authors point of view impulse supply of the bias voltage to the support is rather perspective as it strongly decreases probability of electric arcs generation (more efficient is to use bipolar power supply) and excludes local overheating of the support surface. The bottleneck of the synthesis of catalysts on carbon support is a control of nanoparticle growth on a porous carrier. Modeling of the deposition process by molecular dynamic methods is useful for the understanding of catalyst clusters formation at atomic level depending on the process parameters.

Analysis of publications showed that for electrocatalyst synthesis not only direct current but also high-current pulsed magnetron sputtering could be used.

Carrier modification (doping, annealing, gas ions treatment) is also useful. For example by annealing before spraying one can change the density of defects on the carrier surface which influences cluster formation process. Gas ions treatment of the carrier and deposited particles can be done before, during and/or after deposition process.

It is worth to underline that magnetron sputtering allows the synthesis of electrocatalysts based on compounds and alloys which cannot be produced by traditional methods, in particular Pt₂Si. Using reactive magnetron sputtering one can synthesize electrocatalytically active sulphides, for example RuS_2 [90]. Moreover the method permits to obtain active electrocatalyst without platinum metals. A catalyst from tantalum oxide nanoparticles appeared to be an efficient cathode material for fuel cells (in the process of an oxygen reduction). The sputtering of tantalum target was conducted over short periods (1–5 min) with addition of small amount of oxygen into the chamber. The obtained electrocatalyst had similar efficiency as a platinum one [91]. The investigation of such possibilities also deserves attention.

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