

## NANOMATERIALS IN PROTON EXCHANGE FUEL CELLS

G. Ya. Gerasimov

UDC 621.352.6

*The present paper considers the state of the art of investigations on the use of nanomaterials in the technology of preparing proton exchange fuel cells. This technology has great prospects for use in transport facilities, as well as in stationary and portable electronic devices. The unique properties of nanostructures permit creating new effective catalysts, polymer membranes, and hydrogen storage systems — key elements of the above technology, which upgrades markedly the efficiency of energy conversion in devices created on its basis and decreases their cost.*

**Keywords:** fuel cells, proton exchange membranes, nanomaterials, carbon nanostructures, electrochemical reaction, catalysts, hydrogen storage systems.

**Introduction.** Problems of environmental pollution with combustion products of organic fuels have stimulated rapid development of alternative technologies of energy production and conversion. Among them is, in particular, the technology of preparing fuel cells realizing direct conversion of the chemical energy of the fuel to electric energy without using the low-efficiency combustion process [1]. In the works connected with the above topic, primary consideration is given to the investigation of proton exchange fuel elements (PEFCs) [2]. This type of energy converters is considered to be the most promising for use in transport facilities, as well as in stationary and portable electronic devices. For the electrolyte in PEFCs, solid polymer membranes are used [3]. Compared to other types of fuel cells, PEFCs having the same weight produce more energy and operate at a lower temperature (below 100°C) [4].

An important stimulus for the development of the technology of preparing fuel cells is motor transport. PEFC-based electric motors burning mainly hydrogen are fairly rapidly promoted to the world automobile market and can provide, in the nearest future, strong competition with traditional internal combustion engines [5]. Unlike accumulator motors, they permit covering long distances without refuel. At present the leader in the strategy of fuel cell vehicles is the California market [6]. Estimates made by the company "CaFCP" (California Fuel Cell Partnership) show that at the end of 2017 up to 50,000 fuel cell vehicles are expected on the roads in California, and a proper network of hydrogen filling stations will be set up thereby. To date, practically all large producers of vehicles have announced that they are developing cars of a new type [7]. A hydrogen transport infrastructure is also being created in Europe, where the appearance of a commercially available fuel cell electromobile is expected at the end of 2015 [8].

The late advances in obtaining and investigating new functional materials and systems of nanometer size, whose main characteristic is the exhibition of quantum properties, open up wide possibilities for their practical application in various spheres of human life [9, 10]. From the point of view of the technology of fuel cells, the unique properties of nanostructures are used to develop new effective catalysts, membranes, and hydrogen storage systems [11–15]. The development of new types of PEFCs based on nanomaterials will make it possible to upgrade considerably the energy conversion efficiency of these devices and decrease their cost.

The generally used catalyst for electrochemical oxidation of hydrogen in PEFCs is platinum (Pt) and its alloys with other metals sputtered on the surface of commercial carbon. To decrease the amount of platinum and increase its catalyst activity, Pt nanoclusters and hyperfine layers on PEFCs electrodes are used [14]. On the other hand, the application of various nanostructures, including carbon nanotubes (CNTs) and graphene layers as a support for finely dispersed Pt particles, leads to a higher activity of the electrochemical reaction and a higher productivity of the fuel cell compared to a catalyst sputtered on commercial hydrogen [15]. An important role in the development of PEFCs is also played by the development of new nanostructured membranes [16] and mobile hydrogen storage systems based on nanomaterials [17]. In particular, graphing

---

Institute of Mechanics, M. V. Lomonosov State Moscow University, 1 Michurinskii Ave., Moscow, 119192, Russia; email: gerasimov@imec.msu.ru. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 88, No. 6, pp. 1498–1511, November–December, 2015. Original article submitted December 11, 2014.

functionalization of ion tracks in polymer films leads to the formation of electrolyte ion-track membranes highly permeable for H<sup>+</sup> ions [18].

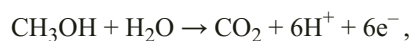
The present paper presents a comprehensive review of various applications of nanomaterials in the technology of producing fuel cells for motor transport. Because of the rather large number of publications on this subject, the present review gives references only to the most typical works on each of the considered fields of application of the above materials.

**Fuel Cell Engines.** The fuel cell generates electric current in the sequence of electrochemical reactions, omitting the low-efficiency process of organic fuel combustion proceeding with large energy losses. The basic diagram of the hydrogen fuel cell is shown in Fig. 1. On the anode side of the PEFC molecular hydrogen diffuses to the surface of the anode catalyst where it dissociates into protons and electrons. Protons pass through the electrolyte membrane to the cathode, and electrons close the circuit through the external electric circuit, since the membrane is made from the electroinsulating material. On the cathode side of the PEFC, electrons and protons react with molecular hydrogen on the surface of the cathode catalyst to form water molecules. A fairly detailed analysis of the electrochemical and transport processes in PEFCs was carried out in [15], where the operating characteristics of various kinds of membranes were considered.

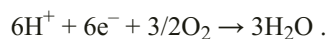
The proton-exchange membrane is the key element of the PEFC system. Attempts to gain an insight into the complex and interrelated transport and electrochemical processes inside the membrane stimulated numerous theoretical and experimental investigations [20]. Figure 2 shows the supposed mechanism of proton transport through a chemically stable proton-exchange membrane made from Nafion (material based on sulfonated polytetrafluoroethylene developed by DuPont). At present researchers are actively searching for ways of increasing the proton conductivity of the membrane [21] and decreasing the electron conductivity [22] and permeability of the fuel in the PEFC and attaining for it a low electroosmotic resistance coefficient [24], good chemical and mechanical stability [25], and a low cost [26]. Numerical calculations were used mainly to estimate the influence of various performance and geometric parameters of the PEFC on its performance [27–29].

Direct methanol fuel cells (DMFCs), in which methanol is used as a fuel, are a variety of PEFCs. The general scheme of the electrochemical reactions on the electrodes of DMFCs can be given in the following form:

anode:



cathode:



Methanol is supplied to the anode side of the fuel cell in the composition of a weak aqueous solution, so that at a high concentration it tends to diffuse through the polymer membrane to the cathode side of the fuel cell and react with oxygen, thus decreasing the efficiency of the oxidation process (the so-called crossover effect). Such devices can be regarded as the most suitable mobile energy sources, since they operate at low temperatures and high energy densities of methanol, which is in the liquid state under any ambient conditions [30]. A review of the state of the art of the investigation of the transport processes in DMFCs is given in [31].

The hydrogen fuel cell engine consists of four basic units: a fuel cell stack, an air feed system, and a fuel feed and control system regulating heat and water flows [32]. The fuel cell stack represents a battery of elementary elements (anode, polymer membrane, cathode) bundled by bipolar plates into a flat technological configuration. The stack operates at a pressure of 2.5 atm and a temperature of 80°C to provide a total energy conversion efficiency of 50% in terms of the lowest hydrogen combustion heat. The control system consists of two coolant loops and a water loop. The high-temperature coolant loop supplies the cooling liquid (aqueous solution of ethylene glycol) to the fuel cell stack, carrying the excess heat away to the air cooling battery, as well as provides heating of reagents arriving at the cathode and anode. The low-temperature coolant loop incorporates a shell-and-tube condenser and an electric motor cooling system. The water loop uses deionized water to humidify the heat and oxidizer flows.

The state of the art of investigations as applied to the technology of fuel cells for motor vehicles was reviewed in [33]. The review includes the technological aspects of the problem, an economic analysis, a comparative analysis of various types of hydrogen motors, as well as environmental concerns. The technological aspects are connected with the consideration of the problem of durability of the proton-exchange membrane [34], the search for new potential hydrogen production methods [35, 36], and the development of reliable onboard fuel storage systems [37].

In recent years, the problems of degradation and durability of the proton-exchange membrane have been increasingly attracting the attention of researches [38]. Various factors influence the performance characteristics of the fuel cell, in whose

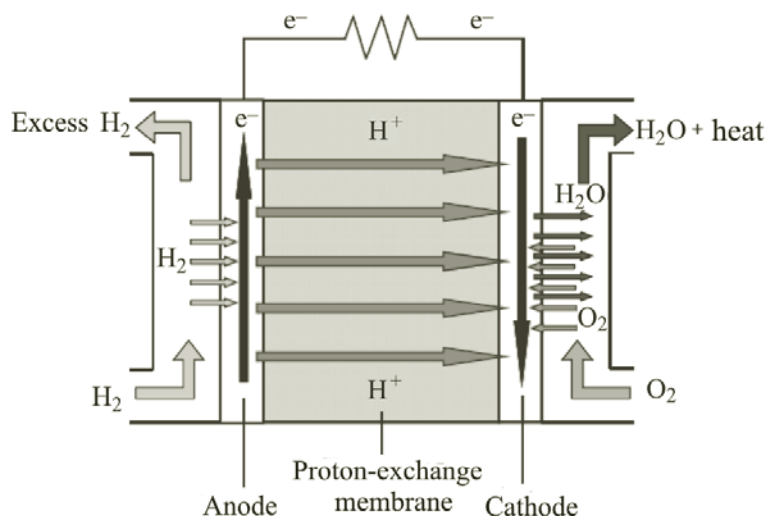


Fig. 1. Principle of operation of the hydrogen fuel cell [2].

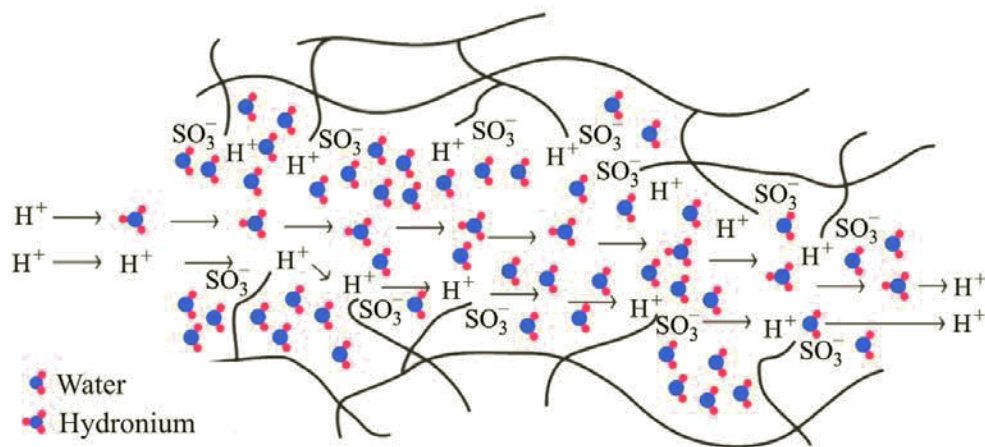


Fig. 2. Schematical representation of the mechanism of proton transport in the nafion membrane of the fuel cell [20].

structure irreversible changes take place, leading to a degradation of its kinetic and transport properties. Among them are, in the first place, the lamination and cracking of the catalytic layer of the fuel cell taking place in the process of its operation (Fig. 3). Among the main reasons for the appearance of such defects are the influence of fuel contaminants [39], the effect of the temperature and relative humidity [40], the cyclic character of the current load [41], as well as the problems of start-up and shutdown of the engine [42] and fuel and air starvation [43]. A fairly comprehensive review of the current investigations of the degradation of fuel cells was presented in [44].

The problem of hydrogen fuel production, storage, and distribution is one of the main problems of the development of hydrogen fuel cell motor vehicles. Hydrogen is available directly at gas-filling stations or at large-scale production plants from which it is piped or trunked to gas-filling stations. In the latter case, it can be supplied in the form of compressed gas or in the liquid form [45]. Among the main methods of industrial hydrogen production are reforming of the vapor-methane mixture (about 50% of the world demand for hydrogen), reforming of oil refining products or waste gases of chemical plants (about 30%), coal and biomass gasification (about 18%), and electrolysis of water (3.9%); the other technologies constitute 0.1% [46]. An important factor in effective operation of hydrogen fuel cell vehicles is the development of reliable onboard hydrogen storage systems [47]. Variants of such storage include the use of metal hydrides [48], carbon nanostructures [49], compressed gas [50], and liquid organic carriers [51].

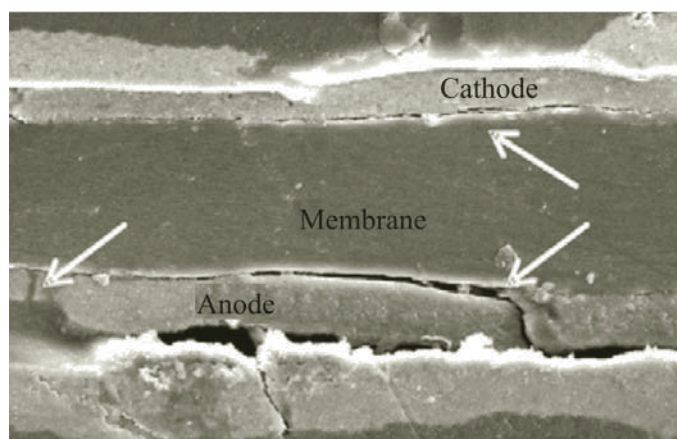


Fig. 3. Structural changes in the proton-exchange membrane taking place in the process of its operation [34].

The change in the energy consumption and emission of pollutants into the environment due to the changeover to hydrogen fuel cell vehicles was considered in [52]. As estimates show, in this case the total amount of the main types of pollutants, including nitrogen oxides, volatile organic compounds, solid particles, ammonia, and carbon oxide emitted into the atmosphere, will be much lower. On the other hand, as was noted in [53], these emissions should be divided into total and urban ones to differentiate their location, since pollutants are formed mainly by fuel production, which is concentrated, as a rule, in rural areas. Therefore, converting motor vehicles to hydrogen fuel, for example, by coal processing will lead to an increase in the total amount of pollutants emitted into the atmosphere [54].

**Catalysts Based on Nanomaterials.** One of the main problems of commercializing fuel cell motor vehicles is the development of active, reliable, and inexpensive catalysts [55]. The catalysts most generally used for electrochemical oxidation of hydrogen and methanol in PEFCs consist of nanoparticles of Pt or its alloys with other metals (Co, Ni, V, Fe, Cu, Pd, W, Ag, Au) sputtered on a carbon support [11]. The mechanism of the oxidation process is rather complicated and is still not clearly understood [56]. The scheme of methanol conversion on the surface of a bimetal Au–Pt anode catalyst in DMFCs is shown in Fig. 4. The process includes the absorption of the  $\text{CH}_3\text{OH}$  molecule on the Pt particle, its dehydrogenization, and the formation of an intermediate  $\text{CO}_{\text{ads}}/\text{Pt}$  compound with subsequent transport of  $\text{CO}_{\text{ads}}$  to the active center of the neighboring Au particle. At the final stage, desorption of the intermediate compounds occurs and the end product is formed.

The methods of fine catalyst precipitation on the support surface can be subdivided into chemical, electrochemical, and physical ones. The chemical methods use colloidal processes, as well as the processes of impregnation-reduction, chemical vapor deposition (CVD), and reverse micelles. A fairly simple chemical method for forming a catalytic layer on a carbon surface with the use of colloidal precipitation was proposed in [57], where  $(\text{NH}_4)_2\text{WO}_4$  reacts with  $\text{H}_2\text{PtCl}_6$  to form  $(\text{NH}_4)_2\text{PtCl}_6$  and  $\text{H}_2\text{WO}_2$ . Precipitation of  $(\text{NH}_4)_2\text{PtCl}_6$  on the support surface leads to the formation of Pt nanoparticles with sizes varying over a rather narrow range. In the impregnation-reduction methods, the carbon support is impregnated with water and/or an organic medium containing a metal precursor with its subsequent reduction in the presence of a reduction agent, for example, organic alcohol [58]. A catalyst for fuel cells with upgraded electrochemical properties was obtained in [59] by dispersing Pt nanoparticles on the surface of CNTs by the CVD method. Particles synthesized by such a method have a size of the order of 1 nm, which is much smaller than the corresponding value for the commercial catalyst obtained by the impregnation-reduction method. The reverse micelle method was used in [60] to improve the homogeneity of Pt/Ni bimetal nanoparticles synthesized on an alumina support.

The method of electrochemical reduction of Pt nanoparticles on a porous and highly developed surface of a carbon support (carbon black, CNTs) is an alternative method for making electrodes for PEFCs that permits localizing metal particles in certain areas of the electrode surface and decreasing the thickness of the catalytic layer [61]. The procedure of electrolytic deposition can be carried out with the use of potentiostatic or galvanostatic methods [62] including pulse or direct techniques [63]. The galvanostatic pulse electrodeposition method is the most convenient for controlling the current distribution and, therefore, it is easier to follow the changes in the size of particles and the alloy composition by varying such experimental

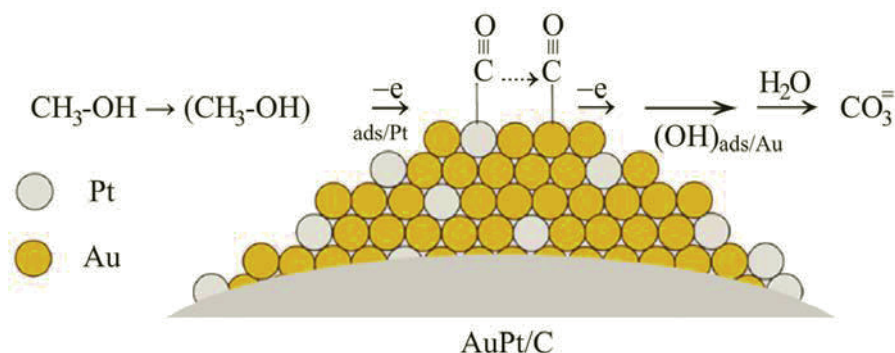


Fig. 4. Schematical representation of the electrolytic oxidation of methanol on the AuPt/C catalyst [56].

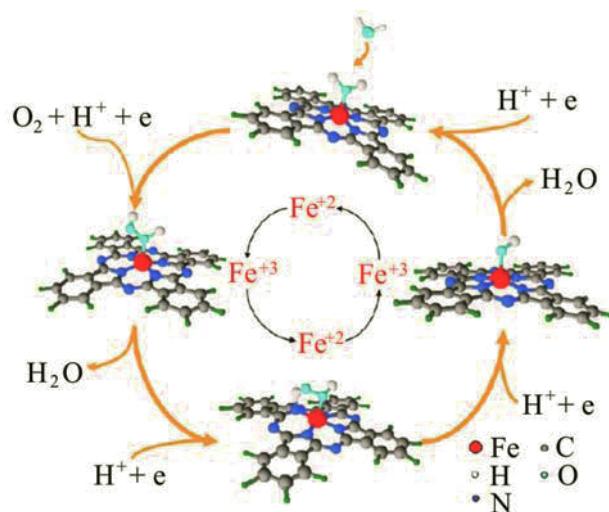


Fig. 5. Hypothetical model of the main stages of the oxygen reducing reaction on graphene doped with Fe and N atoms [11].

parameters as the on/off time and the peak current density [64]. At present, the possibilities of using the electrochemical method for electrolytic deposition of metal nanoparticles on supports from carbon structures are being explored [66–67].

Of the physical methods, the sputter deposition method is used most commonly. It permits obtaining an ultralow level of the catalyst surface density (of the order of  $5 \mu\text{g Pt}/\text{cm}^2$  by contrast with the commercial catalyst whose density reaches  $300 \mu\text{g}/\text{m}^2$ ). The catalyst is localized thereby on the outer surface of the support and has a high activity at methanol oxidation [68]. The advantages of this method over the CVD method are the simpler procedure of obtaining the catalyst (absence of the reducer and deflocculant, absence of heat treatment in the hydrogen atmosphere) and a lower cost of the product due to the decrease in the catalyst layer thickness, which in turn facilitates its entering the market [69]. Among the physical methods are also the plasma deposition method [70], the laser ablation method [71], and the radiation methods for obtaining and modifying the surfaces on polymer electrolytic membranes [72–74].

The high cost of platinum catalyst and the progress in nanotechnology and material science have stimulated in recent years numerous investigations on the synthesis of new alternative catalysts based on base metals featuring high activity and durability [11]. Special consideration was given to the cathode catalyst, since the oxygen reducing reaction is most likely responsible for the voltage drop in the fuel cell. For this reaction, promising catalysts from chalcogenides of base metals [75], carbides of transition metals [76], nitrides [77], and organic-metal compounds [78] were developed. A review of the recent investigations on these lines is given in [79].

Although CNTs and graphene are usually used as a support for metal nanoparticles, it has been found recently that carbon nanostructures upon surface modification acquire electrochemical activity for the oxygen reducing reaction in alkaline

and acid media [11]. Figure 5 shows a diagram of the main stages of the above catalytic reaction on the surface of graphene doped with nitrogen and ferrum atoms. To obtain graphene doped with nitrogen atoms, in [80] the CVD method was used for a mixture of methane and ammonia. The obtained nanostructure acts as a metal-free electrode having a much higher electrolytic activity, a longer stability, and a greater tolerance for the crossover effect than the platinum catalyst. A review of works on doped carbon nanomaterials used as effective cathode catalysts in fuel cells is given in [81]. Carbon nanomaterials can also be functionalized by the physical absorption process. As was shown in [82], some polyelectrolytes are capable of taking electrons from atoms of the carbon lattice in CNTs, thus initiating the appearance on it of a positive charge, which leads to the demonstration of the catalytic activity of the lattice.

**Nanostructured Supports for the Catalyst.** The performance and service life of the fuel cell are largely determined by the material of the support for the anode and cathode catalysts [11]. The most important thing thereby is the type of the material, since it determines the dispersion and stability of metal nanoparticles, as well as the electronic properties, the mass transfer, and the ohmic resistance in the catalyst layer [83]. At present catalysts for PEFCs are made from platinum or its alloys deposited on the surface of coal black. However, recent investigations show that Pt nanoparticles deposited on a support from other kinds of carbon, such as carbon nanofibers, CNTs, and graphene, demonstrate higher electrocatalytic properties [15, 84]. Although the main mechanisms of enhancing the catalyst activity are not quite clear in this case, it may be assumed that a certain contribution to the improvement of the catalytic properties of nanoparticles is also made by the electronic properties of the carbon structures under consideration. Figure 6 shows highly dispersed Pt nanoparticles of size of the order of 2–3 nm deposited on supports from carbon nanofibers and CNTs. These images were obtained with the use of a transmission electron microscope (TEM) [85].

Carbon nanotubes have a large specific area, a high corrosion resistance, a good electronic conductivity, and a high stability [86, 87]. Catalysts are precipitated on the surface of CNTs by various methods of reducing salts of Pt (II), including microemulsion, CVD, and electrochemical methods [88]. In the last few years, for the oxygen reducing reaction in DMFCs, new types of supports with enhanced catalytic properties have been developed on the basis of polyphosphazene-coated nanotubes [88] doped with phosphorus atoms [90], decorated with tungsten nitrides [91], and hybridized with the use of indium-tin oxide (ITO) [92] and other compounds. Carbon nanotubes are also used to obtain supports consisting of a combination of various carbon materials. Figure 7 schematically represents the isomultidimensional structure containing direct and spiralled CNTs, as well as the carbon support Vulcan XC-72 [93]. As measurement data show, the above structure used as a support for the cathode catalyst not only improves the catalytic activity in the proton membrane, but also intensifies the mass transfer processes in it.

Graphene occupies a special place among the carbon nanomaterials owing to the much higher ratio of the surface area of this material to its mass. A review of works devoted to the investigation of the application of graphene as a support for the catalyst in fuel cells is given in [94]. Systematic and comparative analyses of the effect of the structure, composition, and adsorption properties of various carbon nanomaterials (graphene, CNTs, Vulcan XC-92) on the electrocatalytic activity and stability of the Pt–Ni nanocatalyst for methanol oxidation were performed in [95]. The obtained results show that the support from graphene improves the reaction properties of the catalyst and increase its durability. Methods of obtaining a catalytic layer on the graphene surface also influence the quality and performance of the fuel cell [96]. The hyperfine layer of Pt particles deposited on the surface of a porous graphene structure by a combination of CVD and magnetron deposition methods [12] demonstrated an exceptionally high catalytic activity for the methanol oxidation reaction at an ultralow metal consumption. Doped graphene supports are also capable of enhancing the reaction properties of the catalyst and provide its stable performance [97].

Of the other types of nanomaterials used as a support for depositing a catalytic layer, filamentary crystal structures are noteworthy [98, 99]. They are obtained by annealing organic red pigment deposited in a vacuum by the sputtering method. The support of this type consists of one layer of crystal organic whiskers of length about 1  $\mu\text{m}$ , diameter of the order of 50 nm, and numerical surface density  $5 \cdot 10^9 \text{ cm}^{-2}$  [100]. The thermal, chemical, and electrochemical stability of the given material permits using it in DMFCs [101].

**Membranes Based on Nanomaterials.** Nanostructured materials are also used in developing less expensive and effective membranes for fuel cells. The majority of commercial membranes are made from nafion (material based on sulfonated polytetrafluoroethylene, commercial name "DuPont Nafion") [102]. This material features high ionic conductivity and low permeability for a gas with good chemical, mechanical, and thermal strength. Nevertheless these fluorine-containing membranes are expensive and ineffective at temperatures below 0°C or above 80°C because of the water evaporation from the membrane structure. Under real conditions the operating temperature of membranes may exceed 100°C in both hydrogen

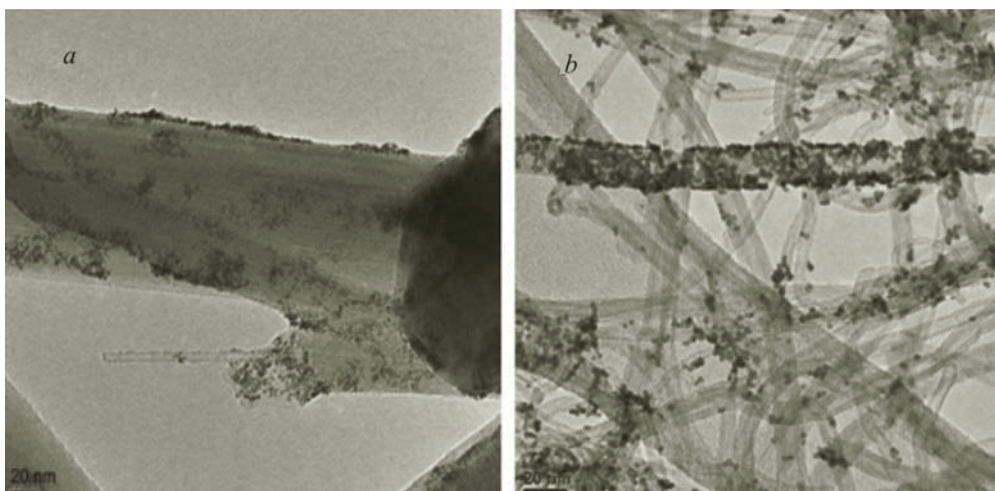


Fig. 6. TEM images of platinum nanoparticles deposited on nanofibers (a) and nanotubes (b) [85].

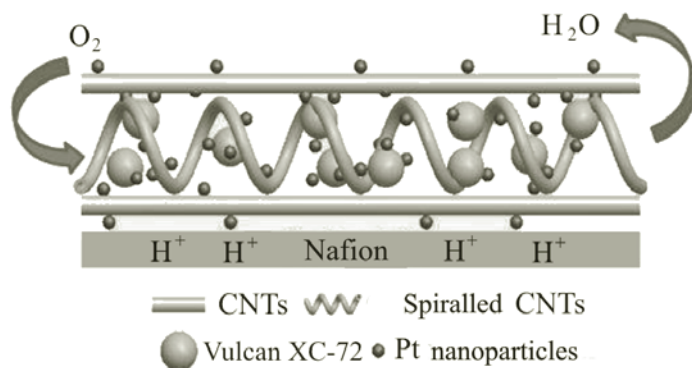


Fig. 7. Structure of the combined carbon support for the cathode Pt catalyst of the fuel cell [93].

and methane fuel cells, which calls for the development of new classes of membranes [2]. An overview of investigations on the development of nanostructured membranes for fuel cells is given in [103].

The first approximation to the improvement of the properties of membranes is the use of nanocomposite hybrids. The addition of nanocrystalline ceramic materials to nafion [104] improves the membrane characteristics of the fuel cell, increasing the operating temperature of hydrogen fuel cells to 130°C and of fuel cells with direct oxidation of methanol to 145°C. A new reinforcing porous ceramic support for use in fuel cells was developed in [105]. It consists of hygroscopic silica (SiO<sub>2</sub>) nanoparticles bound to one another by silicate and polymer binders interspersed in the sulfonated polysulfone layer. This unusual ceramic material possesses high mechanical strength, has a well-developed nanoporous structure, is highly hydrophilic, and shows a good ability to hold water.

Promising materials for preparing membranes are carbon nanostructures and their derivatives. The effect of using graphene oxide nanosheets functionalized by sulfonic acid as an inorganic filler for the nafion membrane was investigated in [106]. This novel nanocomposite material demonstrates a marked (fourfold) increase in the proton conductivity as compared to the nonmodified membrane and can be considered as a potential substitute for the nafion membrane for working conditions with a low humidity (30%) and a high temperature (120°C). The nanocomposite based on sulfonated ketone polyester interspersed with multilayer CNTs functionalized by sulfonic acid was obtained in [107] as a new material for preparing PEFCs membranes.

Possible candidates for replacing usual nafion membranes in fuel cells are also ion-track membranes whose advantage, apart from the absence of the necessity of humidification, is their high proton conductivity and stability under extreme

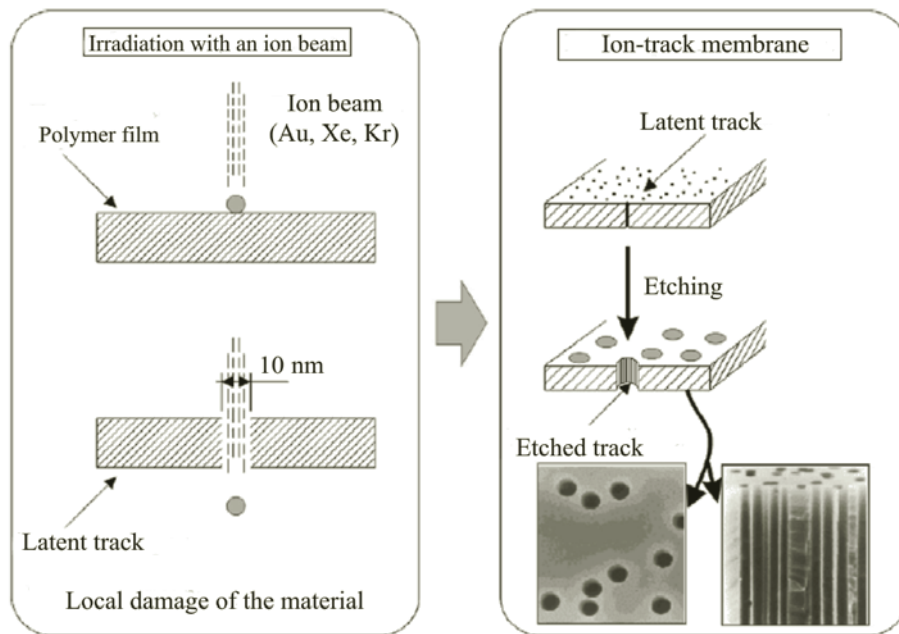


Fig. 8. Scheme of preparing ion-track membranes [110].

conditions [108]. The ion-track technology is based on the irradiation of thin films of various materials by accelerated heavy ions [109]. Heavy ions, passing through the substance, create in it latent tracks of diameter of the order of 5–10 nm with a high damage density [110]. Etching [111] and grafting functionalization [18] of ion tracks in polymer films lead to the formation of electrolyte membranes highly permeable for  $H^+$  ions used in fuel cells. The process is schematically represented in Fig. 8. Ion-track membranes have a lower crossover of methanol, a good proton conductivity, a smaller ability for ion exchange, as well as exceptional mechanical properties as compared to nafion membranes [112].

**Nanomaterials in Hydrogen Storage Systems.** Although hydrogen is recognized as a promising energy carrier for motor vehicles, the wide introduction of hydrogen technologies strongly depends on the possibilities of compact storage of hydrogen. At present accumulating materials or technologies of hydrogen storage that would satisfy all requirements of the advancing market of fuel cell vehicles are lacking [113].

Hydrogen can be stored in the form of a compressed gas, a cryogenic liquid, or a solid material [114]. The simplest solution of the problem from the point of view infrastructure requirements is the technology of gaseous hydrogen storage at a high pressure which holds the leading position among the other technologies [115]. An overview of the state of the art of investigations on the cryogenic storage of liquid hydrogen is given in [116]. Solid-state devices are potentially the most convenient and safe, since this storage technology presupposes the presence of temperatures and pressures close to the corresponding parameters of the environment [117]. An attempt to classify the known materials used for hydrogen storage was made in [118].

The materials for solid hydrogen storage can be divided into several categories in terms of the strength of the hydrogen bond (chemical and physical adsorption, as well as the intermediate quasi-molecular bond) [17]. In the case of chemisorption, the  $H_2$  molecule dissociates into separate atoms, migrates into the material, and combines with it chemically with an energy from 2 to 4 eV. Because the binding energy in chemisorption is high, hydrogen desorption occurs at higher temperatures. This category of materials includes elementary metals and intermetallic hydrides having a large volume of hydrogen. The review given in [119] considers the main properties of metal hydrides, including the specific storage density of hydrogen, the process kinetics, the cyclic behavior, the toxicity, and the response to pressure and temperature variations. At present the focus of much attention of researchers is the group of nanostructured Mg-based hydrides, in which the hydrogen volume reaches 7.6 weight percent [120]. Structures of various compositions and configurations are considered. In particular, in [121] the sorption properties of  $MgH_2$  in a multilayer structure consisting of nanoparticles of size of the order of 50 nm were investigated. In [122], a  $MgH_2$ - $TiH_2$  nanocomposite, in which the desorption temperature of hydrogen is more than



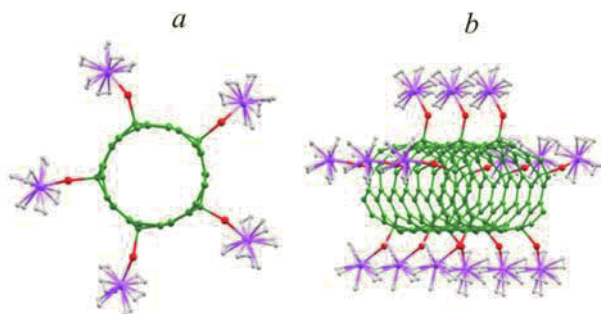


Fig. 9. Atomic structure of Ti-hydroxyl complexes attached to CNTs [129]: a) cross-sectional view; b) general view.

100°C lower than in the commercial MgH<sub>2</sub> composite, was synthesized. Among the other solid-state materials with chemical adsorption of hydrogen LiBH<sub>4</sub>, whose hydrogen storage capacity is equal to 18.5 weight percent, stands out [123].

The physical adsorption of hydrogen in porous materials is also an effective hydrogen storage mechanism. This mechanism has the advantages of fast process kinetics, low adsorption heat, and complete reversibility. The investigation of the adsorption capacity of various nanostructured carbon materials is one of the current strategic lines in developing hydrogen storage systems [124]. The problems, the distinguishing features, and the apparent contradictions between the carbon-based hydrogen storage technologies were considered in [125]. Of the other porous materials, the best candidates for H<sub>2</sub> adsorption are metal-organic compounds, since they consist of light atoms and have a well-developed porous structure [126]. The latest advances in the development of new microporous silicon structures, aluminosilicates, and their related materials were analyzed in [127].

The transition of H<sub>2</sub> molecules from the state of physical adsorption on nanostructured carbon materials to the state of chemisorption was investigated in [128] with the example of C<sub>20</sub> fullerenes and C<sub>19</sub>B fullerenes doped with boron atoms by the methods of the density functional theory. The most convenient hydrogen adsorbents among the carbon nanomaterials are carbon nanotubes. A review of investigations of the possibilities of various types of CNTs for hydrogen accumulation is given in [49]. Figure 9 shows the structure of CNTs decorated with Ti-hydroxyl complexes. As numerical estimates show, the gravimetric density of hydrogen in such a nanostructure is equal to 5.5 weight percent [129]. The ability of carbon nanostructures to adsorb molecular hydrogen is also inherent in graphene and its derivatives. Investigations of the properties of graphene with Ca atoms adsorbed on its surface show a value of 7.7 weight percent for the gravimetric density [130].

**Conclusions.** Due to their unique electronic, mechanical, and chemical properties nanomaterials have a large potential for use in the technology of preparing fuel cells with a proton-exchange membrane. One of the most important problems for commercialization of this technology is the production of active, reliable, and inexpensive catalysts based on nanomaterials, as well as nanostructured supports for the catalyst. Nanostructured materials are also used to prepare cheap and effective proton-exchange membranes, including ion-track membranes. Wide use of the above technology of preparing fuel cells strongly depends on the possibilities of hydrogen accumulation. From the technological point of view the most convenient and safe hydrogen storage technology is the use for these purposes of solid-state devices. This group of hydrogen accumulators includes Mg-based hydrides, new microporous silicon-based structures, as well as various nanostructured carbon materials.

## REFERENCES

1. S. M. M. Ehteshami and S. H. Chan, The role of hydrogen and fuel cells to store renewable energy in the future energy network — potentials and challenges, *Energy Policy*, **73**, No. 1, 103–109 (2014).
2. A.-C. Dupuis, Proton exchange membranes for fuel cells operated at medium temperatures materials and experimental techniques, *Prog. Mater. Sci.*, **56**, No. 3, 289–327 (2011).
3. H. Zhang and P. K. Shen, Recent development of polymer electrolyte membranes for fuel cells, *Chem. Rev.*, **112**, No. 5, 2780–2832 (2012).

4. J. M. Andújar and F. Segura, Fuel cells: History and updating. A walk along two centuries, *Renew. Sustain. Energy Rev.*, **13**, No. 9, 2309–2322 (2009).
5. B. G. Pollet, I. Staffell, and J. L. Shang, Current status of hybrid, battery and fuel cell electric vehicles: From electrochemistry to market prospects, *Electrochim. Acta*, **84**, 235–249 (2012).
6. C. Dunwoody, Transition to a commercial fuel cell vehicle market in California, *Fuel Cells Bull.*, **2009**, No. 11, 12–14 (2009).
7. Hyundai FCEV out next spring, concept cars shown by Toyota, Daihatsu and Honda, *Fuel Cells Bull.*, **2013**, No. 12, 2 (2013).
8. A. Zubaryeva and C. Thiel, Analyzing potential lead markets for hydrogen fuel cell vehicles in Europe: Expert views and spatial perspective, *Int. J. Hydrogen Energy*, **38**, No. 36, 15878–15886 (2013).
9. B. Brushan (Ed.), *Springer Handbook of Nanotechnology*, Springer, Berlin (2010).
10. A. I. Gusev, *Nanomaterials, Nanostructures, Nanotechnologies* [in Russian], Nauka–Fizmatlit, Moscow (2007).
11. A. Rabis, P. Rodriguez, and T. J. Schmidt, Electrocatalysis for polymer electrolyte fuel cells: Recent achievements and future challenges, *ACS Catal.*, **2**, No. 5, 864–890 (2012).
12. N. Shang, P. Papakonstantinou, P. Wang, and S. R. P. Silva, Platinum integrated graphene for methanol fuel cells, *J. Phys. Chem. C*, **114**, No. 37, 15837–15841 (2010).
13. R. A. Varin, T. Czujko, and Z. S. Wronski, *Nanomaterials for Solid State Hydrogen Storage*, Springer, New York (2009).
14. W.-D. Lee, D.-H. Lim, H.-J. Chun, and H.-I. Lee, Preparation of Pt nanoparticles on carbon support using modified polyol reduction for low-temperature fuel cells, *Int. J. Hydrogen Energy*, **37**, No. 17, 12629–12638 (2012).
15. Y. Li, J. Song, and J. Yang, Graphene models and nanoscale characterization technologies for fuel cell vehicle electrodes, *Renew. Sustain. Energy Rev.*, **42**, 66–77 (2015).
16. H. Chen, G. R. Palmese, and Y. A. Elabd, Membranes with oriented polyelectrolyte nanodomains, *Chem. Mater.*, **18**, No. 20, 4875–4881 (2006).
17. P. Jena, Materials for hydrogen storage: Past, present, and future, *J. Phys. Chem. Lett.*, **2**, No. 3, 206–211 (2011).
18. M.-C. Clochard, T. Berthelot, C. Baudin, et al., Ion track grafting: A way of producing low-cost and highly proton conductive membranes for fuel cell applications, *J. Power Sources*, **195**, No. 1, 223–231 (2010).
19. K.-D. Kreuer, S. J. Paddison, E. Spohr, and M. Schuster, Transport in proton conductors for fuel-cell applications: Simulations, elementary reactions, and phenomenology, *Chem. Rev.*, **104**, No. 10, 4637–4678 (2004).
20. S. J. Peighambaroust, S. Rowshanzamir, and M. Amjadi, Review of the proton exchange membranes for fuel cell applications, *Int. J. Hydrogen Energy*, **35**, No. 17, 9349–9384 (2010).
21. F. Ublekov, H. Penchev, V. Georgiev, I. Radev, and V. Sinigersky, Protonated montmorillonite as a highly effective proton-conductivity enhancer in p-PBI membranes for PEM fuel cells, *Mater. Lett.*, **135**, 5–7 (2014).
22. Z. Siroma, J. Hagiwara, K. Yasuda, M. Inaba, and A. Tasaka, Simultaneous measurement of the effective ionic conductivity and effective electronic conductivity in a porous electrode film impregnated with electrolyte, *J. Electroanal. Chem.*, **648**, No. 2, 92–97 (2010).
23. D. Shou, Y. Tang, L. Ye, J. Fan, and F. Ding, Effective permeability of gas diffusion layer in proton exchange membrane fuel cells, *Int. J. Hydrogen Energy*, **38**, No. 25, 10519–10526 (2013).
24. T. Schaffer, T. Tschinder, V. Hacker, and J. O. Besenhard, Determination of methanol diffusion and electroosmotic drag coefficients in proton-exchange-membranes for DMFC, *J. Power Sources*, **153**, No. 2, 210–216 (2006).
25. J. Tan, Y. J. Chao, M. Yang, W.-K. Lee, and J. W. Van Zee, Chemical and mechanical stability of a silicone gasket material exposed to PEM fuel cell environment, *Int. J. Hydrogen Energy*, **36**, No. 2, 1846–1852 (2011).
26. R. K. Ahluwalia, X. Wang, J. Kwon, A. Rousseau, J. Kalinoski, B. James, and J. Marcinkoski, Performance and cost of automotive fuel cell systems with ultra-low platinum loadings, *J. Power Sources*, **196**, No. 10, 4619–4630 (2011).
27. Y. Zhang and R. Pitchumani, Numerical studies on an air-breathing proton exchange membrane (PEM) fuel cell, *Int. J. Heat Mass Transf.*, **50**, Nos. 23–24, 4698–4712 (2007).
28. A. Beicha, Modeling and simulation of proton exchange membrane fuel cell systems, *J. Power Sources*, **205**, 335–339 (2012).
29. J.-J. Hwang, Y.-J. Chen, and J.-K. Kuo, The study on the power management system in a fuel cell hybrid vehicle, *Int. J. Hydrogen Energy*, **37**, No. 5, 4476–4489 (2012).

30. J.-Y. Park, Y. Seo, S. Kang, D. You, H. Cho, and H. Na, Operational characteristics of the direct methanol fuel cell stack on fuel and energy efficiency with performance and stability, *Int. J. Hydrogen Energy*, **37**, No. 7, 5946–5957 (2012).
31. T. S. Zhao, C. Xu, R. Chen, and W. W. Wang, Mass transport phenomena in direct methanol fuel cells, *Prog. Energy Combust. Sci.*, **35**, No. 3, 275–292 (2009).
32. R. K. Ahluwalia and X. Wang, Direct hydrogen fuel cell systems for hybrid vehicles, *J. Power Sources*, **139**, Nos. 1–2, 152–164 (2005).
33. A. Veziroglu and R. Macario, Fuel cell vehicles: State of the art with economic and environmental concerns, *Int. J. Hydrogen Energy*, **36**, No. 1, 25–43 (2011).
34. R. A. Silva, T. Hashimoto, G. E. Thompson, and C. M. Rangel, Characterization of MEA degradation for an open air cathode PEM fuel cell, *Int. J. Hydrogen Energy*, **37**, No. 8, 7299–7308 (2012).
35. E. Cetinkaya, I. Dincer, and G. F. Naterer, Life cycle assessment of various hydrogen production methods, *Int. J. Hydrogen Energy*, **37**, No. 3, 2071–2080 (2012).
36. P. A. Pilavachi, A. I. Chatzipanagi, and A. I. Spyropoulou, Evaluation of hydrogen production methods using the analytic hierarchy process, *Int. J. Hydrogen Energy*, **34**, No. 13, 5294–5303 (2009).
37. M. P. De Wit and A. P. C. Faaij, Impact of hydrogen onboard storage technologies on the performance of hydrogen fuelled vehicles: A technoeconomic well-to-wheel assessment, *Int. J. Hydrogen Energy*, **32**, No. 18, 4859–4870 (2007).
38. X.-Z. Yuan, H. Li, S. Zhang, J. Martin, and H. Wang, A review of polymer electrolyte membrane fuel cell durability test protocols, *J. Power Sources*, **196**, No. 22, 9107–9116 (2011).
39. N. Zamel and X. Li, Effect of contaminants on polymer electrolyte membrane fuel cells, *Prog. Energy Combust. Sci.*, **37**, No. 3, 292–329 (2011).
40. K.-S. Choi, H.-M. Kim, H. C. Yoon, M. E. Forrest, and P. A. Erickson, Effects of ambient temperature and relative humidity on the performance of Nexa fuel cell, *Energy Convers. Manag.*, **49**, No. 12, 3505–3511 (2008).
41. D. Liu and S. Case, Durability study of proton exchange membrane fuel cells under dynamic testing conditions with cyclic current profile, *J. Power Sources*, **162**, No. 1, 521–531 (2006).
42. Q. Shen, M. Hou, D. Liang, Z. Zhou, X. Li, Z. Shao, and B. Yi, Study on the processes of start-up and shutdown in proton exchange membrane fuel cells, *J. Power Sources*, **189**, No. 2, 1114–1119 (2009).
43. I. Jang, I. Hwang, and Y. Tak, Attenuated degradation of a PEMFC cathode during fuel starvation by using carbon-supported IrO<sub>2</sub>, *Electrochim. Acta*, **90**, 148–156 (2013).
44. R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, et al., Scientific aspects of polymer electrolyte fuel cell durability and degradation, *Chem. Rev.*, **107**, No. 10, 3904–3951 (2007).
45. F. Markert, S. K. Nielsen, J. L. Paulsen, and V. Andersen, Safety aspects of future infrastructure scenarios with hydrogen refuelling stations, *Int. J. Hydrogen Energy*, **32**, No. 13, 2227–2234 (2007).
46. N. Z. Muradov and T. N. Veziroglu, From hydrocarbon to hydrogen-carbon to hydrogen economy, *Int. J. Hydrogen Energy*, **30**, No. 3, 225–237 (2005).
47. V. Ananthachar and J. J. Duffy, Efficiencies of hydrogen storage systems onboard fuel cell vehicles, *Solar Energy*, **78**, No. 5, 687–694 (2005).
48. C. Li, P. Peng, D. W. Zhou, and L. Wan, Research progress in LiBH<sub>4</sub> for hydrogen storage: a review, *Int. J. Hydrogen Energy*, **36**, No. 22, 14512–14526 (2011).
49. R. Oriňakova and A. Oriňak, Recent applications of carbon nanotubes in hydrogen production and storage, *Fuel*, **90**, No. 11, 3123–3140 (2011).
50. M. C. Galassi, B. Acosta-Iborra, D. Baraldi, C. Bonato, F. Harskamp, N. Frischauf, and P. Moretto, Onboard compressed hydrogen storage: Fast filling experiments and simulations, *Energy Procedia*, **29**, 192–200 (2012).
51. R. K. Ahluwalia, T. Q. Hua, and J. K. Peng, On-board and off-board performance of hydrogen storage options for light-duty vehicles, *Int. J. Hydrogen Energy*, **37**, No. 3, 2891–2910 (2012).
52. M. D. Paster, R. K. Ahluwalia, G. Berry, A. Elgowainy, S. Lasher, K. McKenney, and M. Gardiner, Hydrogen storage technology options for fuel cell vehicles: well-to-wheel costs, energy efficiencies, and greenhouse gas emissions, *Int. J. Hydrogen Energy*, **36**, No. 22, 14534–14551 (2011).
53. H. Huo, Y. Wu, and M. Wang, Total versus urban: Well-to-wheels assessment of criteria pollutant emissions from various vehicle/fuel systems, *Atmos. Environ.*, **43**, No. 10, 1796–1804 (2009).
54. P. Jaramillo, C. Samaras, H. Wakeley, and K. Meisterling, Greenhouse gas implications of using coal for transportation: Life cycle assessment of coal-to-liquids, plug-in hybrids, and hydrogen pathways, *Energy Policy*, **37**, No. 7, 2689–2695 (2009).

55. C.-J. Zhong, J. Luo, B. Fang, B. N. Wanjala, P. N. Njoki, R. Loukrakpam, and J. Yin, Nanostructured catalysts in fuel cells, *Nanotechnology*, **21**, No. 062001 (2010).
56. D. Mott, J. Luo, P. N. Njoki, Y. Lin, L. Wang, and C.-J. Zhong, Synergistic activity of gold-platinum alloy nanoparticle catalysts, *Catal. Today*, **122**, Nos. 3–4, 378–385 (2007).
57. S. Yao, L. Feng, X. Zhao, C. Liu, and W. Xing, Pt/C catalysts with narrow size distribution prepared by colloidal-precipitation method for methanol electrooxidation, *J. Power Sources*, **217**, 280–286 (2012).
58. L. Chen, M. Guo, H.-F. Zhang, and X.-D. Wang, Characterization and electrocatalytic properties of PtRu/C catalysts prepared by impregnation reduction method using  $\text{Nd}_2\text{O}_3$  as dispersing reagent, *Electrochim. Acta*, **52**, No. 3, 1191–1198 (2006).
59. H. Kim and S. H. Moon, Chemical vapor deposition of highly dispersed Pt nanoparticles on multi-walled carbon nanotubes for use as fuel cell electrodes, *Carbon*, **49**, No. 4, 1491–1501 (2011).
60. B. A. Cheney, J. A. Lauterbach, and J. G. Chen, Reverse micelle synthesis and characterization of supported Pt/Ni bimetallic catalysts on  $\gamma\text{-Al}_2\text{O}_3$ , *Appl. Catal. Gen.*, **394**, Nos. 1–2, 41–47 (2011).
61. C. Paoletti, A. Cemmi, L. Giorgi, R. Giorgi, L. Pilloni, E. Serra, and M. Pasquali, Electrodeposition on carbon black and carbon nanotubes of Pt nanostructured catalysts for methanol oxidation, *J. Power Sources*, **183**, No. 1, 84–91 (2008).
62. Y. Ra, J. Lee, I. Kim, S. Bong, and H. Kim, Preparation of Pt–Ru catalysts on Nafion( $\text{Na}^+$ )-bonded carbon layer using galvanostatic pulse electrodeposition for proton-exchange membrane fuel cell, *J. Power Sources*, **187**, No. 2, 363–370 (2009).
63. S. Karimi and F. R. Foulkes, Pulse electrodeposition of platinum catalyst using different pulse current waveforms, *Electrochem. Comm.*, **19**, 17–20 (2012).
64. S. Woo, I. Kim, J. K. Lee, S. Bong, J. Lee, and H. Kim, Preparation of cost-effective Pt–Co electrodes by pulse electrodeposition for PEMFC electrocatalysts, *Electrochim. Acta*, **56**, No. 8, 3036–3041 (2011).
65. C.-T. Hsieh, J.-M. Wei, J.-S. Lin, and W.-Y. Chen, Pulse electrodeposition of Pt nanocatalysts on graphene-based electrodes for proton exchange membrane fuel cells, *Catal. Comm.*, **16**, No. 1, 220–224 (2011).
66. Y. Zhao, L. Fan, J. Ren, and B. Hong, Electrodeposition of Pt–Ru and Pt–Ru–Ni nanoclusters on multiwalled carbon nanotubes for direct methanol fuel cell, *Int. J. Hydrogen Energy*, **39**, No. 9, 4544–4557 (2014).
67. F. Yang, K. Cheng, X. Xiao, J. Yin, G. Wang, and D. Cao, Nickel and cobalt electrodeposited on carbon fiber cloth as the anode of direct hydrogen peroxide fuel cell, *J. Power Sources*, **245**, No. 1, 89–94 (2014).
68. D. Gruber, N. Ponath, J. Muller, and F. Lindstaedt, Sputter-deposited ultra-low catalyst loading for PEM fuel cells, *J. Power Sources*, **150**, 67–72 (2005).
69. M. Alvisi, G. Galtieri, L. Giorgi, R. Giorgi, E. Serra, and M. A. Signore, Sputter deposition of Pt nanoclusters and thin films on PEM fuel cell electrodes, *Surf. Coat. Technol.*, **200**, Nos. 5–6, 1325–1329 (2005).
70. M. Laurent-Brocq, N. Job, D. Eskenazi, and J.-J. Pireaux, Pt/C catalyst for PEM fuel cells: Control of Pt nanoparticles characteristics through a novel plasma deposition method, *Appl. Catal.*, **B147**, 453–463 (2014).
71. G. Dorcioman, D. Ebrasu, I. Enculescu, N. Serban, E. Axente, F. Sima, C. Ristoscu, and I. N. Mihailescu, Metal oxide nanoparticles synthesized by pulsed laser ablation for proton exchange membrane fuel cells, *J. Power Sources*, **195**, No. 23, 7776–7780 (2010).
72. J. Chen, D. Li, H. Koshikawa, M. Asano, and Y. Makaewa, Crosslinking and grafting of polyetheretherketone film by radiation techniques for application in fuel cells, *J. Membr. Sci.*, **362**, Nos. 1–2, 488–494 (2010).
73. G. Ya. Gerasimov, Radiation methods in the nanotechnology, *J. Eng. Phys. Thermophys.*, **84**, No. 4, 947–963 (2011).
74. D. S. Yang, K. S. Sim, H. D. Kwen, and S. H. Choi, One-step preparation of Pt–M and FP–MWNT catalysts (M = Ru, Ni, Co, Sn, and Au) by  $\gamma$ -ray irradiation and their catalytic efficiency for CO and MeOH, *J. Ind. Eng. Chem.*, **18**, No. 1, 538–545 (2012).
75. G. A. Tritsarlis, J. K. Norskov, and J. Rossmeisl, Trends in oxygen reduction and methanol activation on transition metal chalcogenides, *Electrochim Acta*, **56**, No. 27, 9783–9788 (2011).
76. A. L. Stottlemeyer, T. G. Kelly, Q. Meng, and J. G. Chen, Reactions of oxygen-containing molecules on transition metal carbides: surface science insight into potential applications in catalysis and electrocatalysis, *Surf. Sci. Rep.*, **67**, Nos. 9–10, 201–232 (2012).

77. V. Di Noto, E. Negro, S. Polizzi, P. Riello, and P. Atanassov, Preparation, characterization and single-cell performance of a new class of Pd-carbon nitride electrocatalysts for oxygen reduction reaction in PEMFCs, *Appl. Catal.*, **B 111–112**, 185–199 (2012).
78. J. H. Zagal, S. Griveau, J. F. Silva, T. Nyokong, and F. Bedioui, Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions, *Coord. Chem. Rev.*, **254**, Nos. 23–24, 2755–2791 (2010).
79. R. Othman, A. L. Dicks, and Z. Zhu, Non precious metal catalysts for the PEM fuel cell cathode, *Int. J. Hydrogen Energy*, **37**, No. 1, 357–372 (2012).
80. L. Qu, Y. Liu, J.-B. Baek, and L. Dai, Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells, *ACS Nano*, **4**, No. 3, 1321–1326 (2010).
81. Z. Yang, H. Nie, X. Chen, X. Chen, and S. Huang, Recent progress in doped carbon nanomaterials as effective cathode catalysts for fuel cell oxygen reduction reaction, *J. Power Sources*, **236**, 238–249 (2013).
82. S. Wang, D. Yu, and L. Dai, Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction, *J. Am. Chem. Soc.*, **133**, No. 14, 5182–5185 (2011).
83. N. Jung, D. Y. Chung, J. Ryu, S. J. Yoo, and Y.-E. Sung, Pt-based nanoarchitecture and catalyst design for fuel cell applications, *Nano Today*, **9**, No. 4, 433–456 (2014).
84. L. Li and Y. Xing, Pt–Ru nanoparticles supported on carbon nanotubes as methanol fuel cell catalysts, *J. Phys. Chem.*, **C111**, No. 6, 2803–2808 (2007).
85. S. M. Andersen, M. Borghei, P. Lund, Y.-R. Elina, A. Pasanen, E. Kauppinen, V. Ruiz, P. Kauranen, and E. M. Skou, Durability of carbon nanofiber (CNF) and carbon nanotube (CNT) as catalyst support for proton exchange membrane fuel cells, *Solid State Ion*, **231**, 94–101 (2013).
86. N. Karousis, N. Tagmatarchis, and D. Tasis, Current progress on the chemical modification of carbon nanotubes, *Chem. Rev.*, **110**, No. 9, 5366–5397 (2010).
87. Y.-C. Chiang, M.-K. Hsieh, and H.-H. Hsu, The effect of carbon supports on the performance of platinum/carbon nanotubes for proton exchange membrane fuel cells, *Thin Solid Films*, **570**, Pt. B, 221–229 (2014).
88. K. Shimizu, J. S. Wang, and C. M. Wai, Application of green chemistry techniques to prepare electrocatalysts for direct methanol fuel cells, *J. Phys. Chem.*, **A114**, No. 11, 3956–3961 (2010).
89. J. Qian, W. Wei, H. Huang, Y. Tao, K. Chen, and X. Tang, A study of different polyphosphazene-coated carbon nanotubes as a Pt–Co catalyst support for methanol oxidation fuel cell, *J. Power Sources*, **210**, 345–349 (2012).
90. Z. Liu, Q. Shi, R. Zhang, Q. Wang, G. Kang, and F. Peng, Phosphorus-doped carbon nanotubes supported low Pt loading catalyst for the oxygen reduction reaction in acidic fuel cells, *J. Power Sources*, **268**, 171–175 (2014).
91. S. Jing, L. Luo, S. Yin, F. Huang, Y. Jia, Y. Wei, Z. Sun, and Y. Zhao, Tungsten nitride decorated carbon nanotubes hybrid as efficient catalyst supports for oxygen reduction reaction, *Appl. Catal.*, **B147**, 897–903 (2014).
92. W.-L. Qu, D.-M. Gu, Z.-B. Wang, and J.-J. Zhang, High stability and high activity Pd/ITO-CNTs electrocatalyst for direct formic acid fuel cell, *Electrochim. Acta*, **137**, 676–684 (2014).
93. J. Zhang, S. Tang, L. Liao, W. Yu, J. Li, F. Seland, and G. M. Haarberg, Improved catalytic activity of mixed platinum catalysts supported on various carbon nanomaterials, *J. Power Sources*, **267**, 706–713 (2014).
94. E. Antolini, Graphene as a new carbon support for low-temperature fuel cell catalysts, *Appl. Catal.*, **B 123–124**, 52–68 (2012).
95. Y. Hu, P. Wu, Y. Yin, H. Zhang, and C. Cai, Effects of structure, composition, and carbon support properties on the electrocatalytic activity of Pt–Ni-graphene nanocatalysts for the methanol oxidation, *Appl. Catal.*, **B 111–112**, 208–217 (2012).
96. L. Zeng, T. S. Zhao, L. An, G. Zhao, X. H. Yan, and C. Y. Jung, Graphene-supported platinum catalyst prepared with ionomer as surfactant for anion exchange membrane fuel cells, *J. Power Sources*, **275**, 506–515 (2015).
97. D. He, Y. Jiang, H. Lv, M. Pan, and S. Mu, Nitrogen-doped reduced graphene oxide supports for noble metal catalysts with greatly enhanced activity and stability, *Appl. Catal.*, **B 132–133**, 379–388 (2013).
98. R. K. Ahluwalia, X. Wang, J. Kwon, A. Rousseau, J. Kalinoski, B. James, and J. Marcinkoski, Performance and cost of automotive fuel cell systems with ultra-low platinum loadings, *J. Power Sources*, **196**, No. 10, 4619–4630 (2011).
99. V. Lee, V. Berejnov, M. West, S. Kundu, D. Susac, J. Stumper, R. T. Atanasoski, M. Debe, and A. P. Hitchcock, Scanning transmission X-ray microscopy of nanostructured thin film catalysts for proton-exchange-membrane fuel cells, *J. Power Sources*, **263**, 163–174 (2014).

100. M. K. Debe and R. J. Poirier, Postdeposition growth of a uniquely nanostructured organic film by vacuum annealing, *J. Vac. Sci. Technol.*, **A12**, No. 4, 2017–2022 (1994).
101. L. Gancs, T. Kobayashi, M. K. Debe, R. Atanasoski, and A. Wieckowski, Crystallographic characteristics of nanostructured thin film fuel cell electrocatalysts — a HRTEM study, *Chem. Mater.*, **20**, No. 7, 2444–2454 (2008).
102. K. A. Mauritz and R. B. Moore, State of understanding of Nafion, *Chem. Rev.*, **104**, No. 10, 4535–4586 (2004).
103. H. S. Thiam, W. R. W. Daud, S. K. Kamarudin, A. B. Mohammad, A. A. H. Kadhum, K. S. Loh, and E. H. Majlan, Overview on nanostructured membrane in fuel cell applications, *Int. J. Hydrogen Energy*, **36**, No. 4, 3187–3205 (2011).
104. S. Licoccia and E. Traversa, Increasing the operation temperature of polymer electrolyte membranes for fuel cells: from nanocomposites to hybrids, *J. Power Sources*, **159**, No. 1, 12–20 (2006).
105. J.-H. Seol, J.-H. Won, K.-S. Yoon, Y. T. Hong, and S.-Y. Lee, SiO<sub>2</sub> ceramic nanoporous substrate-reinforced sulfonated poly(arylene ether sulfone) composite membranes for proton exchange membrane fuel cells, *Int. J. Hydrogen Energy*, **37**, No. 7, 6189–6198 (2012).
106. H. Zarrin, D. Higgins, Y. Jun, Z. Chen, and M. Fowler, Functionalized graphene oxide nanocomposite membrane for low humidity and high temperature proton exchange membrane fuel cells, *J. Phys. Chem.*, **C 115**, No. 42, 20774–20781 (2011).
107. B. P. Tripathi, M. Schieda, V. K. Shahi, and S. P. Nunes, Nanostructured membranes and electrodes with sulfonic acid functionalized carbon nanotubes, *J. Power Sources*, **196**, No. 3, 911–919 (2011).
108. H. Hanot and E. Ferain, Industrial applications of ion track technology, *Nucl. Instrum. Meth. Phys. Res.*, **B267**, No. 6, 1019–1022 (2009).
109. A. Waheed, D. Forsyth, A. Watts, A. F. Saad, G. R. Mitchell, M. Farmer, and P. J. F. Harris, The track nanotechnology, *Radiat. Meas.*, **44**, Nos. 9–10, 1109–1113 (2009).
110. A. G. Chmielewski, D. K. Chmielewska, J. Michalik, and M. H. Sampa, Prospects and challenges in application of gamma, electron and ion beams in processing of nanomaterials, *Nucl. Instrum. Methods Phys. Res.*, **B265**, No. 1, 339–346 (2007).
111. S. K. Chakarvarti, Track-etch membranes enabled nanomicrotechnology: a review, *Radiat. Meas.*, **44**, Nos. 9–10, 1085–1092 (2009).
112. M. Yoshida, Y. Kimura, J. Chen, M. Asano, and Y. Maekawa, Preparation of PTFE-based fuel cell membranes by combining latent track formation technology with graft polymerization, *Radiat. Phys. Chem.*, **78**, No. 12, 1060–1066 (2009).
113. S. McWhorter, C. Read, G. Ordaz, and N. Stetson, Materials-based hydrogen storage: attributes for near-term, early market PEM fuel cells, *Curr. Opin. Solid State Mater. Sci.*, **15**, No. 2, 29–38 (2011).
114. S. S. Mao, S. Shen, and L. Guo, Nanomaterials for renewable hydrogen production, storage and utilization, *Prog. Nat. Sci. Mater. Int.*, **22**, No. 6, 522–534 (2012).
115. J. Zheng, X. Liu, P. Xu, P. Liu, Y. Zhao, and J. Yang, Development of high pressure gaseous hydrogen storage technologies, *Int. J. Hydrogen Energy*, **37**, No. 1, 1048–1057 (2012).
116. S. H. Ho and M. M. Rahman, Forced convective mixing in a zero boil-off cryogenic storage tank, *Int. J. Hydrogen Energy*, **37**, No. 13, 10196–10209 (2012).
117. M. Conte, P. P. Prossini, and S. Passerini, Overview of energy/hydrogen storage: state-of-the-art of the technologies and prospects for nanomaterials, *Mater. Sci. Eng.*, **B108**, Nos. 1–2, 2–8 (2004).
118. D. Pukazhselvan, V. Kumar, and S. K. Singh, High capacity hydrogen storage: Basic aspects, new developments and milestones, *Nano Energy*, **1**, No. 4, 566–589 (2012).
119. B. Sakintuna, F. Lamari-Darkrim, and M. Hirscher, Metal hydride materials for solid hydrogen storage: a review, *Int. J. Hydrogen Energy*, **32**, No. 9, 1121–1140 (2007).
120. H. Shao, W. Ma, M. Kohno, Y. Takata, G. Xin, S. Fujikawa, S. Fujino, S. Bishop, and X. Li, Hydrogen storage and thermal conductivity properties of Mg-based materials with different structures, *Int. J. Hydrogen Energy*, **39**, No. 18, 9893–9898 (2014).
121. S. Barcelo, M. Rogers, C. P. Grigoropoulos, and S. S. Mao, Hydrogen storage property of sandwiched magnesium hydride nanoparticle thin film, *Int. J. Hydrogen Energy*, **35**, No. 13, 7232–7235 (2010).
122. H. Shao, M. Felderhoff, and F. Schuth, Hydrogen storage properties of nanostructured MgH<sub>2</sub>/TiH<sub>2</sub> composite prepared by ball milling under high hydrogen pressure, *Int. J. Hydrogen Energy*, **36**, No. 17, 10828–10833 (2011).

123. C. Li, P. Peng, D. W. Zhou, and L. Wan, Research progress in  $\text{LiBH}_4$  for hydrogen storage: a review, *Int. J. Hydrogen Energy*, **36**, No. 22, 14512–14526 (2011).
124. M. Armandi, B. Bonelli, K. Cho, R. Ryoo, and E. Garrone, Study of hydrogen physisorption on nanoporous carbon materials of different origin, *Int. J. Hydrogen Energy*, **36**, No. 13, 7937–7943 (2011).
125. Y. Yürüm, A. Taralp, and T. N. Veziroglu, Storage of hydrogen in nanostructured carbon materials, *Int. J. Hydrogen Energy*, **34**, No. 9, 3784–3798 (2009).
126. M. Hirscher, B. Panella, and B. Schmitz, Metal-organic frameworks for hydrogen storage, *Micropor. Mesopor. Mater.*, **129**, No. 3, 335–339 (2010).
127. A. Azzouz, Achievement in hydrogen storage on adsorbents with high surface-to-bulk ratio — Prospects for Si-containing matrices, *Int. J. Hydrogen Energy*, **37**, No. 6, 5032–5049 (2012).
128. C. Tian, Z. Wang, M. Jin, W. Zhao, and Y. Meng, Transformation mechanism of a  $\text{H}_2$  molecule from physisorption to chemisorption in pristine and B-doped  $\text{C}_{20}$  fullerenes, *Chem. Phys. Lett.*, **511**, Nos. 4–6, 393–398 (2011).
129. H. Lee, M. C. Nguyen, and J. Ihm, Titanium-functional group complexes for high-capacity hydrogen storage materials, *Solid State Comm.*, **146**, Nos. 9–10, 431–434 (2008).
130. Y. Gao, N. Zhao, J. Li, E. Liu, C. He, and C. Shi, Hydrogen spillover storage on Ca-decorated graphene, *Int. J. Hydrogen Energy*, **37**, No. 16, 11835–11841 (2012).