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ENERGY CONSERVATION, NEW, AND RENEWABLE ENERGY SOURCES

Low-Temperature Fuel Cells: Outlook for Application in Energy Storage Systems and Materials for Their Development

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Abstract—Low-temperature fuel cells (FCs) are perspective alternative energy sources. They cannot, however, be considered as a primary energy source, because no hydrogen in pure form, used in their operation, exists in nature. The development of devices to autonomously supply and store energy can be considered as one of the most promising applications of low-temperature FCs. In the latter case, the primary purpose is to compensate differences in peaks of producing and consuming energy both in the seasons and time of day. The first part of the review describes this problem. The second part involves analyzing nanomaterials used in FCs, so that hybrid membranes, including inorganic nanoparticles, are high priority in this regard. Their incorporation into the pores of the membranes leads to an improvement in transport properties in many cases, including an increase in ionic conductivity and selectivity of transport processes. These properties of the hybrid membranes are discussed by using a model of limited elasticity of walls of the pores. Catalysts, being platinum nano-size particles, play an important role in the FC. To reduce their costs and increase activity, some approaches, implying decrease in particle sizes or using two-component particles, for example, alloys and 'core-shell' particles, are used. In the latter case, platinum, localized on the surface, determines activity of the catalyst, whereas the second metal increases surface area and catalyst activity. The main reasons for changes in properties of the materials and effect of the catalyst support on electrochemical processes in FCs are also considered.

Keywords: energy storage, independent power supply, fuel cell, proton conducting membrane, catalyst

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Most of the technologies used by humankind are energy intensive, and their progress is inevitably accompanied by an increase in energy demand. The world production of primary energy grows by approximately half for every 35 years according to the International Energy Agency data. In addition, some redistribution of variety types of energy sources in this production is constantly observed. More than 90% of the energy was produced from wood at the beginning of the 19th century, whereas in the beginning of the 20th century, 70% of the energy was derived from coal, and since the mid 20th century, oil was on the first place as an energy source [1]. Oil will, however, be used primarily in chemical synthesis toward the end of the 21st century according to forecasts [2]. At the same time, the role of oil is not uniquely dominant in the modern energy sector. At the beginning of the 21st century, for example, the proportion of oil in primary energy production was only 40% and, moreover, it is gradually decreasing. The change from one energy source to another was previously determined by economic factors. At present, however, it is substantially due to the struggle for the improvement in the ecological situation on the Earth. A significant amount of carbon, sulfur, and nitrogen oxides, as well as products of incomplete combustion of fuel, penetrates into the atmosphere upon combusting oil, coal, and gas, so that it has led to a significant deterioration of the ecological situation. The environmental requirements for existing and newly created productions, vehicles and other energy consumers, including autonomous and redundant power supplies, are constantly toughened for the recent decades in this regard.

The problem of independent power supply in Russia is also very important despite a well-developed and centralized power supply system. Approximately 70% of Russia's vast territory with a total population of 10–20 million people is not covered by a centralized power supply. Conditions of communications in these areas do not allow supplying fuel regularly and cost-effectively. Solving this problem can be achieved by using renewable energy sources, namely sun and wind, which are universally accessible and attract attention

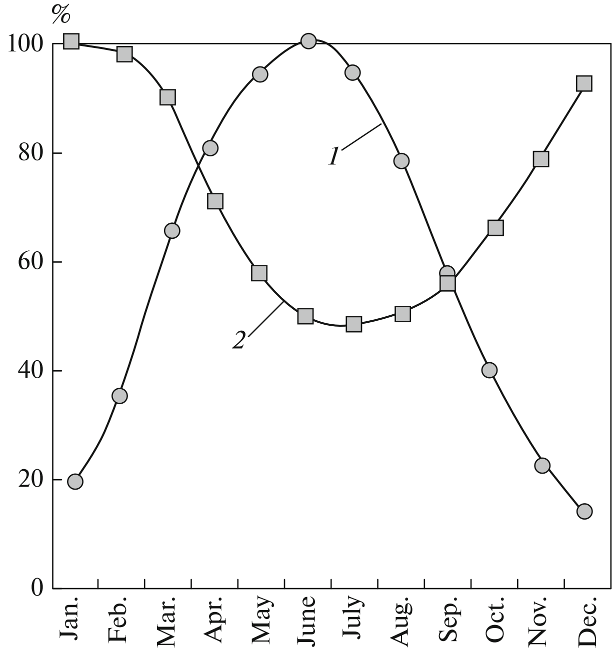

Fig. 1. Graphs of (*1*) power generation with the use of photovoltaic cells and (*2*) power consumption in the climatic conditions of Khakassia Republic [9], expressed in percent of the maximum value.

because of its relative cheapness, ecological purity, and safety.

Reducing the environmental load must be ensured by increasing the energy efficiency in production, improvements in technological processes, and using new energy sources. The alternative, environmentally friendly, and renewable energy sources, therefore, attract great attention. These could be energy of wind, rivers, tides, and biomass processing. The greatest efforts are mostly associated with the developing solar cells that have two major disadvantages. Although the first of them—low efficiency—is not quite so critical, the second, frequency of incoming solar energy, is far more important. This determines need to jointly use solar cells with energy storage systems. The lithium-ion batteries and combinations of water steam electrolysers and fuel cells (FCs), where the energy from hydrogen oxidation is used, are, therefore, commonly considered [3].

The prerequisites for the broad developing hydrogen energy appeared in the late 20th century. Using FCs is assumed to be one of the most promising way to generate energy for mobile, portable, and many other stationary devices, including energy storage systems, because of their high energy efficiency (up to 90%), low level of sound, and environmental pollution, because only water forms when using hydrogen [4, 5]. Special attention is paid to developing low-temperature FCs on the basis of proton exchange membranes. The main purpose of this review is, therefore, to summarize the literature data discussing primarily current state of low temperature FCs and of materials used in them, as well as to provide some prospects to use systems where hydrogen cycle is utilized for energy storage and autonomous power supply.

RESERVE ELECTRIC POWER SUPPLY SYSTEMS ON THE BASIS OF FCS

To accumulate electrical energy obtained from primary renewable sources, namely sun and wind, is an important step towards the widespread introduction of solar and wind power points to supply independent customers in remote areas. This is an actual problem, especially in Russia, where there are large areas not covered with electrical grids [6], and some of them have significant potential for renewable energy sources [7]. The traditional technical solution for the power supplying to consumers in remote areas consists in diesel electrical power stations. Using renewable energy sources can significantly reduce the consumption of expensive organic fuel primarily owing to transport cots [8].

A significant difference in production and consumption of energy with photovoltaic modules in the summer and winter periods (Fig. 1) indicates a high relevance of excess energy accumulation in the summer season with its issuance upon low activity of solar radiation. The significant imbalance between power flux of solar energy and energy consumption during the day is also important. If the maximum sun activity is in midday, the maximum power consumption is approximately at 8:00 p.m.

Russia has considerable solar and wind energy resources [9]. This is seen, for example, from the distribution maps of solar radiation and mean wind speed throughout Russian territory that were made with NASA long-term satellite observations [10, 11]. The annual solar radiation in the remote northern regions is approximately 800 kW h/m^2, whereas it exceeds 1500 kW h/m^2 in the southern regions. There were also revealed large seasonal variations in solar activity. In Moscow, for example, the daily amount of solar radiation in December is 0.33 kW h/m^2, whereas it is 5.6 kW h/m^2 in June. The potential of solar energy is largest in the North Caucasus, Black and Caspian seas, south of Siberia, in the Russian Far East, and some other regions [9].

There are many areas where the annual average wind speed exceeds 6.0 m/s according to the Russia wind atlas. The highest mean wind speed values were revealed along the Barents, Kara, Bering, and Okhotsk seas coasts. The other areas with relatively high wind speeds, 5–6 m/s, are the East Siberian, Chukchi, Japan, and Laptev seacoasts [9].

A comparative analysis of the costs of electricity generated with diesel generators and combined power equipment, consisting of wind power plants (WPPs), FCs, and/or diesel power plants shows that the prices of obtained electrical power can be decreased twice in realizing a combined system [12].

Electrochemical batteries are widely used in power plants with renewable energy sources [13]. For the objects with a moderate total capacity of energy consumption (1–15 kW), only flow redox batteries and systems, using hydrogen cycle, can significantly compete with the traditional electrochemical storage devices by weight and size, cost, resource performance, and self-discharge rate characteristics [14]. Flow redox batteries are described in detail in [15, 16]. Their disadvantage is low specific characteristics. The weight and size characteristics are simply inessential for the stationary sources, but electrolytes in redox batteries, working in Russian winter conditions, must be placed in a heated container, so that it significantly increases the energy consumption for its own needs. This fact, as well as high efficiency (50–55%) and no harmful emissions, are advantages of FCs, so that low-temperature hydrogen-air FC systems are considered to be promising [15]. It should also be noted that it is possible to significantly improve the parameters in FC systems upon reaching high pressures in hydrogen storage systems [16].

A system with an intermediate hydrogen energy carrier can be considered as the most effective in the majority of parameters for reserve power supply systems, using hydrogen technologies. These systems differ from most batteries in principle of action. A substance, being energy source, accumulates outside the device, where it is produced and used. Hydrogen cycle systems include a hydrogen source that receives energy from a primary renewable source, hydrogen or, sometimes, oxygen storage system, and return conversion system of hydrogen into energy. Hydrogen cylinders, a fossil fuel converter, or a electrochemical hydrogen generator (electrolyzer) can be used as hydrogen source. Fuel hydrogen systems are lighter than the diesel generators and batteries producing the same amount of power, and, as a result, they can be mounted in those areas where to set heavy batteries is far difficult.

The electrolysers work according to the same principles as FCs; however, instead of the current generation, they decompose water into hydrogen and oxygen when potential difference above 1.23 V is applied to the electrodes. The electrolysers with solid polymer electrolyte permit high pressures in gas lines (4–12 MPa), which allows pumping hydrogen and oxygen into storage systems without additional compression. At the same time, the costs of alkali electrolysers are lower because of no platinum catalysts and solid polymer membrane, as well as pipes and containers designed for high pressures.

Figure 2 shows a schematic diagram of hydrogen cycle with FCs. When generation of base source is excess or consumption is low, the generated hydrogen and oxygen are stored in gas holders. If supporting base source of power is necessary, the gases are supplied into FCs [17]. Using hydrogen cycle, one can accumulate excess energy produced by the primary source; whereas to compensate short peaks and decays of energy generation (up to daily) is possible with standard accumulate batteries [18]. Mutual compensation of failures in generating solar panels and wind plants is also possible [18, 19].

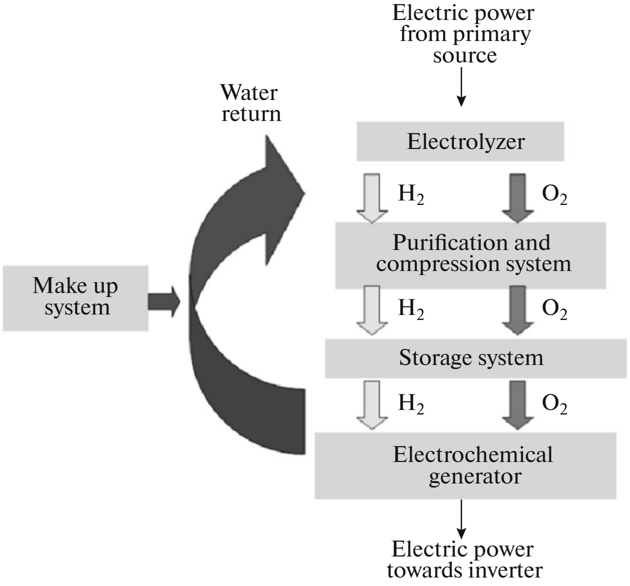

Fig. 2. Schematic diagram of the hydrogen cycle of electricity storage by using electrolyzer and fuel cell.

Another modification of the hydrogen cycle is also possible, when the stored hydrogen is directed towards catalytic boiler, where its combustion energy is converted into steam used then in a steam turbine [20, 21]. The disadvantages of such a scheme are relatively long starting turbine and, more importantly, its low efficiency [21].

To combine production of heat and energy in hybrid solar-hydrogen plant is advisable [22]. Using combined production (cogeneration) of heat and electricity with FCs can significantly increase the overall system efficiency. The dependence of amount of heat, released from FCs, on current, flowing through them, has been calculated [16, 22]. Some part of heat can be then used, for example, for heating water through the heat-exchange system.

The simulation results show that the cogeneration of heat is able to increase average efficiency per year of using energy up to 80% if FCs are considered to be part of a hybrid solar-hydrogen plant [22]. Optimizing the system can lead to decrease in unit costs for electric power up to 15%, as well as to cover almost half the annual energy needs to heat water with recovering heat from the FCs and disposal of unused hydrogen.

Various energy sources (sun, wind, and their combination) can be used to power an electrolyser. Combining solar and wind power plants was shown to be optimum [23, 24]. In this case, the reliability of the system increases, whereas cost of the solar cell and a wind turbine decreases because of reduction of their peak power. A concept of home hydrogen fueling stations with generating high-pressure hydrogen (up to 70 MPa) for FCs, as well as with photovoltaic generator and water electrolyser, is described [25]. Such a station consists of an array of solar cells, electrolysis system, and hydrogen storage and dosing. The average amount of obtained hydrogen was approximately 0.67 kg per day upon output hydrogen pressure from the electrolyser of 13.8 MPa [25].

Using hydrogen technologies is provided not only in stand-alone systems but also in systems connected with the central network. Applying hydrogen as an accumulator of wind and sun energy during periods of excess generation and failure consumption is considered [26]. An analysis of the joint using solid polymer [27] and alkali electrolysers [28] with solar panels has been performed. The tests of alkali electrolyser H2 IGen 300/1/25 (Hydrogenics) showed a high integral energy conversion coefficient, determined as a ratio between energy for producing hydrogen and its calorific value, namely 77.7%, when it operates in conjunction with the wind turbine under a peak power of 6 kW, and 78.5%, when it works with solar power plant. No controlling primary power source was carried out in both cases.

The units having power up to 30 kW can be based on direct current tire with charge controllers to transfer energy from the solar cells to electrolyzers and batteries. Having powers over 30 kW, a circuit on alternating current is preferable, where each power supply has own voltage converter [29].

TYPES OF FCS AND MATERIALS USED THEREIN

Working scheme of FCs. FC is an electrochemical device in which chemical energy of fuel and oxidant converts into electrical and thermal energy. Using FCs is one of the most environmentally friendly ways to generate electricity. The hydrogen and oxygen contained in air react to form water vapor. The FCs operate almost silently because of no moving parts. In addition, the total electric and thermal efficiency of FC systems can reach 90%.

There are five main types of FCs depending on the electrolyte used: a solid polymer (SPFC), alkaline (AFC), phosphate (PFC), those with molten carbonate electrolyte (MCFC), and solid oxide (SOFC). The SPFCs and AFCs have 80–100°C, the PFCs possess 200°C, MCFCs have 650°C, and SOFCs possess 800–1000°C operating temperatures. The FCs are divided into low-temperature (SPFCs and AFCs), medium temperature (PFCs), and high temperature (MCFCs and SOFCs) depending on operating temperature.

The most promising for use in stationary power industry are high-temperature SOFCs [30] and also MCFCs and SPFCs. All these devices, in some manner, can be considered as primary energy sources. The advantages of SOFCs are presence of nonplatinum catalysts, less sensitive to catalyst poisons in comparison with SPFCs, electrooxidation of CO, a relatively low electrode polarization, and, as a result, high current densities and no liquid components. Along with electrical power, the high-potential heat forms in SOFCs that can be used in thermal machines. The start time of SOFCs, however, is long enough (up to few hours) because of high operating temperature, and they damage easily under frequent on/off switching. They should, therefore, be used only for the constant generation of electricity and heat.

Low-temperature FCs, unlike SOFCs, gain quickly stationary power values, do not require preheating up to operating temperature, and can withstand a significant amount of on/off cycles [30, 31]. Considering these parameters, to use low-temperature FCs is advisable in various independent and reserve power supply systems, including combination with wind power and solar panels. At present, the prototypes of stationary power plants with SPFCs, having a capacity from one to hundreds of kilowatts, are being developed for small power objects by both foreign and Russian companies [32]. With these advantages, the SPFCs become most popular and dynamically developed. It should be noted that their market occupies almost 90% of the total sales of FCs.

Figure 3 shows a schematic diagram of a hydrogen–air FC. A proton conducting membrane is its main element. Oxygen sorption, hydrogen (hydrogen-containing gases), and reaction between them occur on catalyst layers. Proton transfer toward anode takes place under chemical potential gradient [33–36].

The main features of proton-conducting membranes and catalysts, being the most important elements in FCs, will be discussed later. Using a polymer membrane as an electrolyte results in relatively low operating temperatures of FCs, so that it provides a quick start. A promising fuel is hydrogen, because it oxidizes rapidly enough in FCs and with high efficiency. This parameter is significantly lower in oxidazing alcohols, which appear to be more attractive because of their greater compactness (they are liquid). Pure oxygen or that derived from the air can also be as oxidant. The latter option is definitely more attractive, despite a fact that a potential difference in FCs becomes somewhat low in this case [36].

Proton-conducting membranes for FCs. The ion exchange membrane in an FC is to provide transport of protons from an anode to a cathode along with the separation of gases on the cathode and anode. Polymer membranes in low and medium-temperature FCs must possess the following characteristics [5, 37]: high proton conductivity to prevent internal losses, low electronic conductivity to prevent inadvertent discharge, low gas permeability by hydrogen and oxygen to prevent losses of fuel and oxidant, good mechanical properties to allow thin membranes to be strong and flexible [38], and stability at higher temperatures.

To produce low and medium-temperature FCs, the perfluorinated sulfo cation-exchange membranes Nafion, having the desired characteristics, are predominantly used. These membranes are stable up to 300°C, as well as to acids, oxidants, and reducing agents because of high strength of the C–F bond [39]. Today, the perfluorinated sulfo cation-exchange membranes are manufactured by several companies under different trademarks (see the table).

The self-organization of perfluorinated polymer chains occurs to form the basis of a membrane, whereas functional groups are combined into clusters, whose size depends on the flexibility of the chains. These clusters, containing hydrophilic functional groups, can be involved in a hydration process that causes swelling of the ion exchanger and leads to a substantial restructuring of its structure [40]. The fixed SO_3^- ions situate along the periphery of a hydrated cluster with a spherical shape according to the Gierke model (Fig. 4) [41]. The internal volume of the cluster (or pores in hydrated state) is filled with an aqueous solution containing counterions formed in dissociation of the functional groups. The counterions and fixed ions form a double electric layer near the walls of membranes pores. The pore size is typically 2–5 nm depending on degree of hydration.

The fact that rapid transfer of ions occurs through the membranes allowed us to assume that there are channels connecting adjacent pores (see Fig. 4). With increasing water uptake of the membrane, the diameter of pores and channels connecting them rises, so that it causes increase in conductivity.

The main advantages of perfluorinated membranes Nafion are chemical and thermal stability, high proton conductivity, and strength [42–44]. Some disadvantages, such as sharp decrease in conductivity at low humidity, insufficiently low permeability of membranes by hydrogen [10^{-16}–10^{-15} mol/(cm s Pa)] and methanol (10^{-6} cm^{-2} s^{-1}), as well as the high cost, which also must be considered, however, limit their practical application [45]. The perfluorinated membranes lose water at temperatures above 90°C and even under high humidity, causing them to fall in conductivity.

Thus, on the one hand, low operating temperatures of Nafion membranes are their advantage because the FCs based on them do not require long and energy intensive start procedure; on the other hand, there is a problem concerning poisoning of platinum catalysts by carbon monoxide impurities present in hydrogen [46, 47]. Its sorption is irreversible at temperatures up to 120°C. Even small amount of CO impurities leads to a significant decrease in FCs capacity below this temperature. This does not allow directly using relatively cheap hydrogen produced in conversion of hydrocarbons, alcohols, and carbon [48], so that it significantly limits utilizing low-temperature FCs.

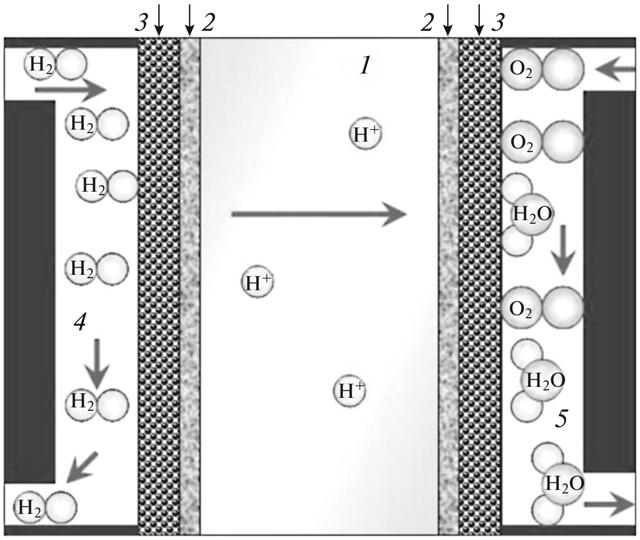

Fig. 3. Schematic diagram of a fuel cell: (*1*) proton conducting membrane, (*2*) catalytic layers, (*3*) gas diffusion layers, and (*4*, *5*) anode and cathode bipolar plates with gas channels [36].

To increase the range of operating temperatures, as well as to reduce the cost of membranes (the price of perfluorinated membranes is too high), considerable attention is paid to create new proton-conducting membranes. The polycondensed membranes, based on sulfonated aromatic condensation polymers, for example, are known to possess thermal stability and good mechanical properties [49]. Moreover, they are cheaper than the perfluorinated polymers. These membranes are typically prepared with sulfonation of aromatic condensation polymers [50, 51]. The membranes based on complexes of polybenzimidazole with phosphoric acid, which have high thermal stability up to 200°C, conductivity up to 0.13 S/cm at 160°C, and low permeability by methanol, also attract attention [52]. The proton conductivity in such systems varies

Table

Trademark	Manufacturing Company	Country
Nafion®	DuPont	United States
Dow®	Dow Chemical	United States
Flemion®	Asahi glass company	Japan
Aquivion®	Solway	Belgium
MF-4SC	Plastpolymer	Russia

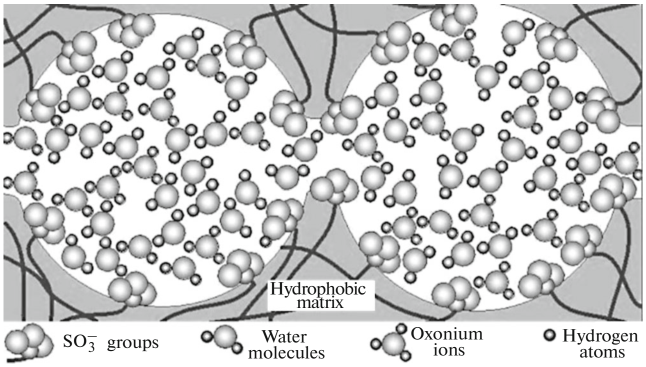

Fig. 4. Structure scheme of pores of polymer cation exchange membrane in proton form [42].

considerably in their doping with phosphoric acid and slightly depends on the humidity. The main disadvantages of these membranes are low mechanical strength and washing away phosphoric acid from them upon contact with water. Water entering into the regions of catalytic and gas diffusion layers results in blockage of gas pores and degradation of bipolar plates. Furthermore, removing phosphoric acid causes a decrease in proton conductivity of the membrane. Thus, the membranes based on complexes of polybenzimidazole with phosphoric acid do not provide long-term operation of FCs.

To reduce the cost of the ion-exchange membrane, the other sulfonated poly(ether ether ketone)s were tested as electrolytes in FCs. Such membranes, however, degrade rapidly in harsh operating conditions of FCs [49] and are rarely used in FCs despite low cost.

The sulfo-containing membranes on the basis of poly-α,β,β-trifluorostyrene and substituted α,β,β-trifluorostyrene (BAM3G) can also be considered. These materials possess significantly higher degree of swelling than those of Nafion-type membranes. The FCs on the basis of these polymers show characteristics similar to those obtained with Dow and Nafion membranes under low current densities and higher characteristics obtained upon current densities above 0.6 A/cm^2 [53].

As already mentioned, even Nafion perfluorinated sulfo cation-exchange materials, used widely, have several disadvantages, including that their high proton conductivity is achieved at relatively low temperatures and high humidity, close to 100%, so that it significantly complicates the design of FCs. Intensive works on modifying these materials are performed to produce hybrid membranes containing inorganic and high molecular components since the late 1980s in this regard [54–57]. This approach is considered as the most promising to improve FCs containing ion exchange membranes.

The interest in hybrid membranes is determined by their transport properties (the ability to increase ionic conductivity and to reduce permeability) and increased thermal stability that is often associated with the synergistic properties of the individual components [58–60]. A direction devoted to studying gas permeability of such membranes should be noted [60–64]. There are also a significant number of studies devoted to investigation their mechanical properties [65–67].

To modify sulfo cation-exchange membranes, a wide range of different additives (dopants) that can be divided into several groups according to various criteria, namely hydrophobic (carbon nanotubes, oxides with hydrophobized surfaces, etc.) and hydrophilic (oxides, salts, etc.) are used [2, 55, 57]. The most common additive used for modifying ion-exchange membranes is a silica. The advantages of the hybrid membranes having SiO_2 nanoparticles are increase in conductivity, decrease in permeability relatively to gases and methanol [4, 34, 68–71], and increase in mechanical strength [72, 73]. The silica particles used to improve the properties of membranes, however, often underwent chemical modification, particularly by adding hydrophobic [74–76] and proton-acceptor [75, 77] or proton-donor groups [76, 78, 79]. The hybrid membranes with silica possess high proton conductivity even at low humidity and high temperatures [80]. Using hybrid membranes containing SiO_2 nanoparticles with sulfonated surface leads to an increase in FCs power because of their high proton conductivity and low permeability relatively to gases and methanol [81, 82].

One of the most promising areas is introducing SiO_2 nanoparticles containing heteropoly acids or their insoluble acid salts on the surface into the Nafion membrane [83–87]. This increases proton conductivity of the hybrid membranes at low humidity. The improvement in current-voltage characteristics of the hydrogen-air FCs based on Nafion hybrid membrane with salt of phosphotungstic acid has been revealed [88]. The maximum decrease in permeability by methanol (up to 2.2×10^{-7} cm^2/s) has been reached by codoping with phosphotungstic acid and SiO_2 [89]. The cesium salt of phosphotungstic heteropoly acid provides additional promotion of catalytic reactions on FC electrodes [90].

The acidic zirconium phosphate additives allow using Nafion membrane at temperatures above 100°C and improve their mechanical properties [91–93]. The proton conductivity of these membranes often appears to be slightly less than those of the original Nafion membrane [94]. Using such membranes containing mesoporous zirconium phosphate of approximately 5% wt. has increased FC capacity by 1.5 times under low humidity [95].

To modify membranes of FCs, some oxides of polyvalent elements are also used as additives. Titanium dioxide, for example, is utilized in modifying Nafion membranes [96–100]. Such a modification of Nafion membranes with sulfonic groups imparts them high mechanical and thermal stability, and it also reduces permeability by methanol and increases capacity of the methanol FCs [100, 101]. To modify the Nafion membranes, a zirconia, including that with sulfonated surface, was used [102–104]. The other oxides were utilized less commonly for such a purpose [73]. The improvements in proton conductivity under high temperatures (above 100°C) have been achieved in modifying Nafion membranes with SiO_2–ZrO_2–P_2O_5 gels [105] or zirconium sulphophenyl phosphate [106].

To modify proton-conducting membranes, nanoscale carbon materials were also widely used in recent years. The introduction of carbon nanotubes into membranes did not change the capacity of the hydrogen-air FCs, although their low amount significantly improved the mechanical properties [107–109]. To increase the proton conductivity of the membranes by one order was possible in modifying Nafion membranes with carbon nanotubes functionalized with sulfonic groups [110]. This has allowed improving mechanical properties and has enhanced the power of hydrogen-oxygen FCs from 210 to 260 mW/cm^2 under 60°C.

To explain an effect mechanism of embedded nanoparticles on conductive properties, a model of limited elasticity of the pore walls of the membrane materials has been proposed [111]. Covering a certain pore volume, nanoparticles increase their own size, which leads to an increase in the size of the connecting channels that limit membrane conductivity. The force required to expand the pores, however, increases with raising their volume. The water uptake of the membranes, therefore, reduces with increasing dopant content and, accordingly, the size of its particles [112]. The dopant fills some part of pore volume within the membrane and overlaps the conduction channels when nanoparticle concentration is above 3–4% in volume. When acidity of the dopant increases because of binding strong acids with its surface, the concentration of the carriers can increase due to the protons of the dopant, for example, in simultaneous doping membranes with silica and heteropoly acids [113]. An important factor is also hydrophilicity of the surface of the nanoparticles that enhances conductivity of the membranes.

In hybrid membranes, the particles of the dopant occupy some volume of the pores, so that it prevents a sharp narrowing of the pores in dehydration process. In addition, the nanoparticles incorporated into the pores of the membranes contain a lot of additional oxygen-containing groups that can participate in proton transfer process. This leads to decrease in proton jump length, and it has a significant contribution into increasing conductivity of the hybrid membranes upon low humidity [114]. In this case, the nature of the surface of the doping agent is even more important. The simultaneous doping of the membrane with SiO_2 and heteropoly acid deposited on its surface increases conductivity of MF-4SC by more than an order under 10% humidity as compared with that doped with only SiO_2 [85]. This is primarily due to incorporating an additional number of acidic protons that are carriers of current.

Catalysts for low temperature FCs. Oxygen reduction on a cathode occurs more slowly than the anode reaction [115]. In most cases, kinetics of the processes occurring in FCs is, therefore, limited by the oxygen reduction. At the same time, even trace CO amounts in hydrogen have a significant effect on kinetics. Carbon monoxide adsorbs irreversibly on platinum upon low temperatures and blocks a hydrogen oxidation process. The current density in the FCs, therefore, decreases dramatically with increasing CO concentration in hydrogen [116].

The catalyst activity increases with decreasing particle size. This minimizes the amount of active catalyst, but it leads to its rapid degradation. According to the data [117, 118], the optimal activity of platinum is achieved when particle size is 3 nm, although decrease in specific activity of platinum was revealed when particle size was less than 4.5 nm [119]. The size of platinum nanoparticles of commercial catalysts is 2.5–5.0 nm [120].

The high cost and low stability of the catalyst are main barriers to commercialize FCs [121]. Developing alternative catalysts when inexpensive materials are used is an important part in constructing low cost FCs [122–126]. A Pt/Ni catalyst possesses high activity in oxygen electroreduction [127–132]. The composition of alloys involves some noble metals, iron triad elements, etc. [133–136]. Moreover, the Pt/Ru is the most effective electrocatalyst of anode among the binary alloys [133, 137–139]. The alloys of platinum with Fe, Co, Ni, Mo, and Ru possess high tolerance to CO [140]. It should also be noted that the alloying metals suppress dissolution of Pt, although they degrade rapidly.

Watanabe suggested a bifunctional oxidation mechanism of CO, adsorbed on Pt, with water, chemisorbed on the other metal, which is often used to explain tolerance of platinum alloys to CO [141–143]. According to Camara's et al. theory [144], the alloy formation results in a shift of the Fermi level of platinum and, as a consequence, to change in interaction between Pt and CO molecules. This helps to alleviate electrochemical oxidation of CO with adsorbed OH groups or water molecules [145].

To improve the activity of FC catalysts, 'core-shell' alloys are developed [146]. Thus, the platinum and cobalt nanoparticles show a significantly improved catalytic activity and reduce the catalyst cost by five times [147]. The researchers obtained high performance catalysts containing platinum, cobalt, and chromium or palladium [148]. The acid treatment results in removing cobalt and chromium from a surface. When consumption of platinum is low, these catalysts are superior to analogues by stability and activity. This eliminates the possibility of an effect of the bifunctional catalysis because of active platinum surface of such catalysts.

Thus, an assumption that increasing Fermi level is the dominant contribution to improvement of their catalytic properties because of introducing more active metal seems to be more reasonable.

A carrier plays an important role. Nanostructured carbon materials (carbon nanotubes, fibers, and fullerenes) are most commonly used as carriers of catalysts [149–151]. One can increase the efficiency of the catalysts, increase their service life, and reduce sensitivity to carbon monoxide in using carbon nanotubes or nanofibers [152]. The metal oxide carriers show greater stability in oxidative environment and can have promoting effect in oxygen electroreduction reactions [153–156] or in oxidizing methanol and CO [157]. The oxide nanoparticles can be dispersed on a carrier surface together with the platinum particles [158, 159] or can be used as a substrate in catalyst [160].

The activity of platinum catalysts, applied on different forms of nanoscale titanium dioxide, has been shown [161–163]. The power of FCs based on Pt/Ru catalyst, having titanium oxide as a carrier, is approximately 1.5 times higher than that applied with carbon [164]. Electrooxidation of CO on neighbor platinum atoms is facilitated by chemisorption of water on the surface of tin dioxide [165]. The data on high activity of catalytic systems based on tin dioxide and doped with antimony or ruthenium are given in [166–168]. The catalysts having tungsten cesium oxide as a carrier have shown high activity in CO and methanol electrooxidation reactions [169].

CONCLUSIONS

(1) The systems of independent power supply and energy storage on the basis of renewable energy sources and fuel cells are very promising and attract great attention of a wide range of researchers. Russia has also significant prospects in using such systems. The imperfection and high cost of membranes and electrocatalysts used to construct fuel cells impose significant restrictions to develop them in modern conditions.

(2) Considering the requirements for electrolyte of hydrogen-air fuel cells, to use perfluorinated sulfocontaining Nafion membranes, including hybrid membranes, whose composition involves inorganic nanoparticles, is advisable. The composition and structure of the catalyst nanoparticles and choice of a carrier are important.

(3) Promising carriers for electrocatalysts are materials on the basis of metal oxides, such as those of titanium and tin, which reveal high stability in an oxidizing environment and can have a promoting effect in oxygen electroreduction reactions.

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