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Materials for Bipolar Plates for Proton-conducting Membrane Fuel Cells

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Abstract—The review is devoted to the present state of research and development in the field of construction materials for bipolar plates for hydrogen–air fuel cells with polymeric proton-conducting membranes. Principal requirements for such materials are considered and criteria for their selection are formulated.

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Over the past years there has been a well-defined tendency for replacement of classical liquid electrolyte fuel cells (FCs) by completely solid state devices. Important components of a solid state FC are bipolar (BPs) and end plates [1, 2]. Bipolar plates link together separate cells in a FC stack to form membrane electrode assemblies (MEAs) that control heat, gas, and electric flows.

Bipolar plates work in fairly rigid conditions: temperatures of about 100°C or higher, aggressive medium (ion-exchange membranes are commonly made of acidic materials), presence of oxidants, such as hydrogen peroxide, formed as by-products of FC processes). Therefore, of practical importance are such characteristics of BPs as specific electrical conductivity and heat conductivity, corrosion and heat resistance at operating temperatures, stability in moisture-rich conditions, chemical stability in the presence of reagents, lack of components poisonous for MEAs, and low gas permeability.

CONSTRUCTION OF FUEL CELL

To understand requirements for BPs, one should first consider the overall construction of a FC and functions BP fulfill in FC. A FC is an electrochemical device that directly converts fuel's chemical energy into electrical. The most important advantage of FCs over energy-producing systems comprising heat engines and generators is the lack of intermediate energy conversion into heat and mechanical energy; as a result, the performance of electrochemical devices is not restricted by the Carnot cycle and can be very high. Low operating temperatures of FCs (unlike heat engines that are operated at maximum temperatures for higher performances) prevent formation of ecologically hazardous products, such as nitrogen oxides. Fuel cells are categorized into powerful high-temperature, medium-temperature, and portable low-temperature.

Let us first consider a single FC (Fig. 1). It contains a thin polymeric membrane coated on both sides with catalytic electrode layers. Such assembly is called a membrane electrode assembly. The membrane is capable of transmitting protons and does not transmit gases, viz. fuel and oxidant. Outside the electrodes there are layers of a porous or fibrous material with high electronic conductivity, that are called gas diffusion layers (GDLs). These layers serve to supply gaseous reactants, normally hydrogen or air, to remove electrochemical reaction products, i.e. water, and to collect generated electricity (Fig. 1). In such FC gaseous hydrogen in oxidized on the anode, giving up two electrons to the gas diffusion layer and two protons to the proton-exchange membrane. The protons pass through the membrane under the electrochemical potential and combine with adsorbed air oxygen to form a water molecule. For the reaction to occur requires uniform distribution of reactants over the whole surface of gas diffusion layers, reliable electrical contact with these layers and between all

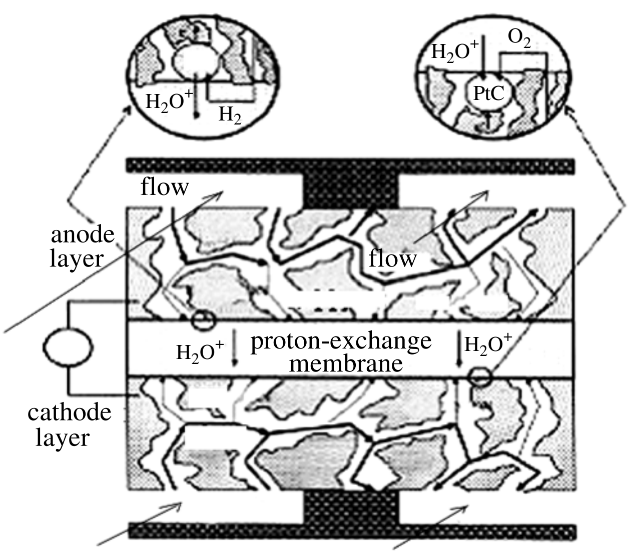


Fig. 1. Structure of a membrane electrode assembly (MEA). Arrangement of principal units between gas flow along BP channels and flows in MEA.

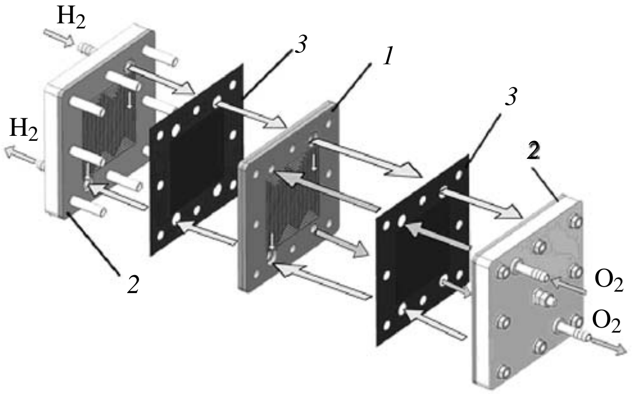


Fig. 2. Scheme of the simplest FC stack: (*1*) bipolar plate, (*2*) end plates (1/2 of bipolar), and (*3*) MEA with seals.

layers for transmitting fairly large current flows (up to 1 A cm^{-2}), as well as operative management of outgoing water for it not to block ("flood") pores of the gas diffusion layer. Furthermore, the thin film MEA should be mechanically fixed. The above-listed functions all are fulfilled by an element of an up-to-date FC, viz. a bipolar plate. In a single FC these are two end plates that embrace the whole system. Thus, their main function is to supply fuel and oxidant to MEA, to remove reaction products, and to collect electricity generated by the fuel cell.

A FC stack (Fig. 2) consists of a package of sequential MEAs and bipolar plates, pressed, through sealing elements, between current-collecting plates. At the ends of the stack there are end, rather than bipolar, plates with a system of gas channels one side only (the other side contacts with current-collecting plates). The whole package is fixed with pins or other construction elements. The MEA–BP construction is furnished with longitudinal axle channels and radial collectors for reagent in- and outflow.

GENERAL REQUIREMENTS FOR BIPOLAR PLATES

Let us first consider general requirements for bipolar and end plate materials. The main function bipolar plates fulfill in a FC stack is to supply and evenly distribute working gases over the active surface. Bipolar plates provide supply of fuel and oxidant individually to each MEA and prevent their mixing. With air, rather than pure oxygen, as oxidant, one should provide its continuous flow and mixing so that the oxygen concentration on the working membrane surface is maintained constant. To this end, the working surface of BP is covered with a network of gas channels of a computed, not infrequently quite an intricate profile. Since the plate separates the oxygen and hydrogen spaces, the air and hydrogen permeability of its material should be as low as possible. Moreover, the gas spaces should be sealed over the plate edge, most commonly with special seals.

The second function of BP is to collect current from MEA, i.e. reliable electric contact with gas diffusion layers and low intrinsic electric resistance in the transverse direction (current direction in the stack) are required. To this end, the BP material should exhibit good conducting properties, and BP surfaces should be flat and clear to ensure sealing contact. This entails stringent requirements to geometric accuracy of BP fabrication. Furthermore, of importance is also resistance to corrosion under FC operation conditions, since corrosion impairs the surface and, as a consequence, electric contact.

The third function of bipolar plates is to provide water management, i.e. to remove water generated by the electrochemical reaction from the cathode and, at the same time, to supply water for maintaining required membrane hydration level. Of particular importance is the hydration function from the anodic side where no water is generated. The plate surface from the cathodic side should be hydrophobic to avoid "flooding" of channels. Therefore, in designing gas distribution channels one must make proper allowance that the BP material combines hydrophobic and hydrophilic properties.

To maintain the required working temperature of MEA, i.e. provide fast heating on the start and effective removal of heat released, the plate material should possess a high electrical conductivity. Furthermore, plates are not infrequently additionally supplied with channels for refrigerant for cases where air flow is insufficient for cooling or another oxidant is used. In this case the plate material should be impenetrable for refrigerant, too.

For mechanical strength and rigidity of the stack the BP material should be sufficiently strong and rigid to ensure required electric contact with MEA and withstand pressure, preserve mechanical characteristics at FC operating temperatures and possess a sufficiently low thermal expansion coefficient to prevent damage of stack on thermocycling (initiation, heating, shutdown, and cooling). At the same time, the material should be elastic: Excessive rigidity constitutes danger, since MEA materials can appreciably change in volume during operation or due to humidity variations.

It is important to note that bipolar plates are, along with membrane electrode assemblies, typical elements of FC stacks. According to estimates of the US Department of Energy (DOE), on transfer to hydrogen technologies the demand for stacks may attain a million per year, i.e. 100000 per month. Provided a stack comprises 120 cells, the monthly production of BPs can be estimated at 12 millions, i.e. 400000 per day!

The DOE formalized in part the requirements for bipolar plates [3]. Of them requirements to physicochemical and mechanical properties, as well as economic parameters deserve special mention.

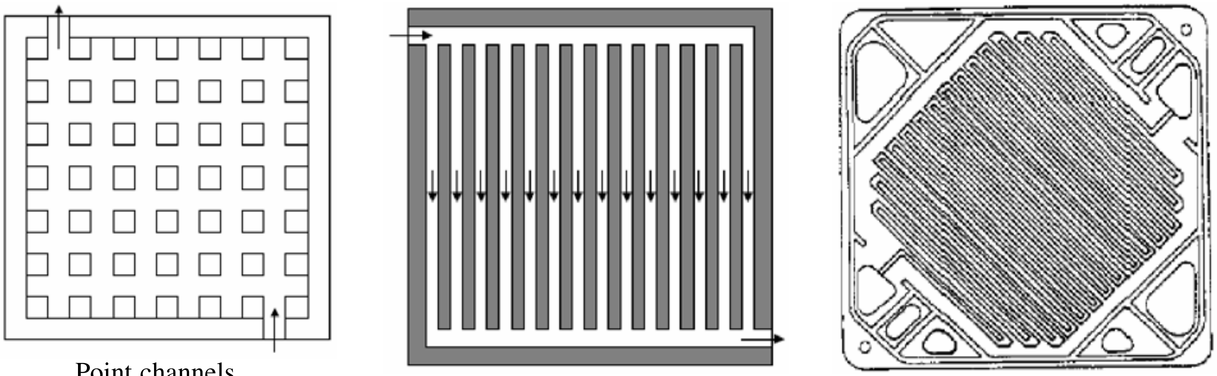
Physicochemical properties. The most important properties of BP are high specific electro- and thermoconductivities. According to the DOE requirements, in 2010 the electroconductivity should be no less than 100 $\mathrm{S\,cm^{-1}}$, i.e. the specific resistance should be no more than 100 $\mu\Omega\,\mathrm{m}$. At present typical values of 600 $\mathrm{S\,cm^{-1}}$ and 17 $\mu\Omega\,\mathrm{m}$ are attained.

The total plate resistance, including contact, should be no more than 0.01 $\Omega\,\mathrm{cm^{-2}}$. This value is determined by the requirement that the voltage drop on BP be no more than 5% of the voltage generated on MEA over the entire range of currents characteristic of FC, i.e. up to 1–2 $\mathrm{A\,cm^{-2}}$.

Furthermore, BP should be electrochemically and chemically stable in the presence of reagents typical of FC processes, i.e. hydrogen, CO, CO_2, air, strong acids, hydrogen peroxide, and other peroxides. The plate should be thermally stable at operating temperatures (80–200°C, depending on the type of the membrane) and increased (up to 100%) humidity, and should have low thermal expansion and gas permeability rates. The DOE hydrogen permeability limit is 2×10^{-6} $\mathrm{cm^3\,s^{-1}\,cm^{-2}}$ at 80°C and 0.3 μPa, which is equivalent to a leakage current of less than 0.1 $\mathrm{mA\,cm^{-2}}$. The focus on hydrogen permeability is explained by the fact that this gas has a high diffusion capacity.

Furthermore, BP should not release sulfur-containing compounds, iron and copper ions, and other substances that can poison catalysts and destroy other MEA materials. The plate should be less than 1 $\mathrm{kg\,kW^{-1}}$ rated capacity in weight and as thin as possible. Over the entire operating period, the plate surface should not be subject to corrosion. According to DOE requirements, the corrosion current in the FC environment should be no higher than 1 $\mu\mathrm{A\,cm^{-2}}$.

Mechanic properties. Of particular importance among mechanic properties are strength characteristics; BP should ensure stability of the construction on FC assembly and operation. The DOE target for the flexural strength is no less than 4 MPa. Proper surface


Point channels

Linear channels

Spiral and serpentine channels

Fig. 3. Geometries of BP gas channels.

treatment is also of importance: The BP surface roughness near contacts and seals should be low so that the stack is hermetic, and the BP thickness should be uniform within 0.02 mm.

The fraction of BP in the total weight of FC is up to 80% [4], and, therefore, the plate material should be as light as possible. According to [5], the weight of 1 cm^2 of BP should be no more than 5 g.

Economic requirements. The cost of both materials and fabrication should be minimal. According to DOE estimates, the present cost of a FC stack [6] is about 75$/kW, and that of its bipolar plates is no more than 10$/kW, which comprises 13–14%. The DOE target is 6$/kW, i.e. no more 1$ for a plate with a surface area of 500 cm^2.

DESIGN OF CHANNELS

For high performance of a polymer proton-exchange membrane fuel cell (PEMFC) it is necessary to minimize resistance to all transport flows, which is strongly dependent on the architecture of BP gas channels. The principal functions of BP, specifically fuel and oxidant supply and water and heat management, are directly related to the geometry of channels. Several shapes of BP surface channels have been proposed (Fig. 3).

Along with distribution of gaseous reagents and transportation of water, the structure of channels should provide sufficient electric contact between BP and gas diffusion layers, i.e. baffles between channels should be sufficiently wide, have a plane surface, etc. Channels should not create high resistance to transport flows and, at the same time, provide gas and water exchange with GDL. Removal of water into channels over the entire thickness of GDL should also be provided (Fig. 1). At the same time, channels should not be too wide, since the GDL surface over a channel has no electric and thermal contact with BP. To meet these contradictory requirements, the size of channels and walls between them should be thoroughly optimized. To this end, a complex structure is fabricated, with high accuracy and smoothness, on the plate surface (Fig. 3). The use of milling makes BP much more expensive. Therefore, the plate material is desirable to allow cheaper techniques, such as punching or extrusion, to be used for channel fabrication.

Different requirements for the anode and cathode sides of BPs, following from different properties of working gases, should also be noted. Here we can formulate three principal differences.

Shape of gas channels. As gases pass through the working area of FC, the partial pressure of hydrogen remains invariable, whereas the partial pressure of air oxygen falls. For FC to operate effectively, the oxygen partial pressure should fall by no more than 15%. For this reason, the air flow can be higher than the hydrogen flow by more than an order of magnitude. And, as a result, gas channels on the anodic side may be spiral- and serpentine-shaped, whereas those on the cathodic side are normally linear and as short as possible.

Corrosion resistance. During FC operation, no products are released on the anodic side, whereas on the cathodic side hydrogen peroxide and highly active oxygen radicals are formed as byproducts, which requires BP materials resistant to such species to be used on the oxygen side.

Hydrophilicity/hydrophobicity. During FC operation water is generated on the oxygen side of MEA and should be effectively removed from the working area to avoid flooding of GDLs, which is especially important at high current densities. In this connection the cathode side of BP should be hydrophobic. At the same time, for the anode side this property is not critical.

Produced and developed bipolar plates can be divided into two large groups: carbon- and metal-based. Each type has its intrinsic advantages and disadvantages. Stamping from metallic foil is more attractive in terms of cost and feasibility of large-scale production. However, some intricate problems therewith arise, associated with metal corrosion in the aggressive FC environment. Let us consider each type of BP separately.

METAL BIPOLAR PLATES

In view of the better corrosion resistance of carbon, most emphasis is put on the development of carbon materials and coatings. At the same time, the search for materials and coatings for metalbased BP is still being continued. This is first of all explained by better mechanic properties and lower cost of metal BP compared to carbon. Metal BP is most frequently made of special alloyed steels [7], such as 316L special steel for medical implants. This stainless steel features an excellent resistance to aggressive media, being resistant to usual, grain-boundary, point, and contact corrosion. The principal advantage of metallic BP is the manufacturability of steel and the use of the low-cost stamping technique for thin steel sheets. Stamping makes readily feasible innovative metal architectures, such as serpentine gas channels and integrated liquid cooling system. Steel sheets are thin, and, therefore, lighter than carbon. In the report of the French Atomic Energy Agency [8], multilayer stamped stainless-steel plates were proposed. Such system was tested on 316L stainless steel, but corrosion caused gradual degradation of FC (near 0.2% per day); therewith, steel plates contributed one third of MEA degradation.

The danger of corrosion consists in that it destroys BP surface, thereby sharply increasing resistance and ohmic loss. Importantly, corrosion results in that metal cations pass into MEA, poison catalyst, and favor degradation of the polymeric proton-conducting membrane. Such metals include iron, nickel, and copper, which are common steel constituents.

In terms of minimal cost, weight, and thickness, of interest are bipolar plates made of aluminum foil or aluminum–magnesium alloys. Aluminum and magnesium ions are not catalyst poisons, but the high chemical activity of light alloys makes them hardly suitable for BP applications. In this case, some special corrosion protection technology should be developed. Had this problem been solved, stamped aluminum foil plates would have been 2–3 times lighter than carbon, half as thin, and much cheaper. Thus, Gladczuk et al. [9] reported on a tantalum-coated aluminum BP. One more serious disadvantage of aluminum and light alloys is their high thermal expansion coefficient (24 μm m^{-1} deg^{-1}), which entails mechanic degradation of the BP/MEA contact on thermocycling, i.e. FC startupσhuidown.

Completely titanium or nickel plates may prove promising. Regretfully, high corrosion resistance is only characteristic of high-purity titanium by the iodide process, but it is fairly expensive. However, pure titanium still corrodes too fast, within 300–500 h [10]. Moreover, machining of titanium, like power metallurgy, is much more expensive than steel sheet stamping [11]. Titanium is heavier than aluminum and its alloys. However, titanium is a fairly promising material for BP applications, since it is highly corrosion-resistant, possesses good mechanic properties (strength and hardness), and titanium ions are not too poisonous for catalysts and ionexchange membranes.

Titanium bipolar plates are presently produced on an industrial scale [12], but they should be protected from corrosion in the aggressive FC environment. Davies et al. [10] compared the contact resistances of plates of commercial graphite, titanium, and AISI 310 and AISI 316 stainless steels (Table 1). Oxide layer formed on all the metal plates, and its thickness grew during FC operation. The metal resistance order was as follows: AISI 310 SS > Ti > AISI 316 SS. Corrosion resistance of plates of high-purity titanium and AISI 316L steel with lower carbon contents was also studied. These materials already compare in corrosion resistance with commercial graphite, but titanium ranks below graphite.

Metals offer some undeniable advantages over carbon as BP materials. They possess higher thermo- and electroconductivities, lack of porosity, gas impermeability (as a result, metal plates can be very thin), and high strength, including flexural strength, which, too, allows production of thinner plates. Metal plates are also quite attractive from the economic viewpoint: Materials are fairly inexpensive and amenable to facile and cheap working, such as stamping.

However, all advantages of metals as BP material are much depreciated by their principal disadvantage, viz. low corrosion resistance. Titanium plates that hold the greatest promise are rather expensive and require expensive working technologies. Thus, in view of the fact that the FC medium is quite aggressive, metal plates should be protected with corrosion-

Table 1. Transition resistance between two bipolar plates pressed to each other, upon exposure to a mixture of air and water vapor

Plate material	Exposition, h	*R*, Ohm
AISI 304 steel	240	0.9
AISI 316L steel	24	0.11
AISI 316Ti steel (doped with titanium)	24	0.1
Titanium	72	0.2
	240	0.4
Molybdenum	72	0.2
	240	1
Nickel	72	0.2
	240	1
Iridium	72	0.1
	240	200

resistant coatings. Development of such coating forms a separate problem, since ordinary corrosion protection means serve to depreciate principal advantages of metal bipolar plates: increase their cost and complicate technology or deteriorate electro- and thermoconductivity, or, not in frequently, both.

METHODS FOR CORROSION PROTECTION OF METAL PLATES

The tendency of even best stainless-steel bipolar plates for corrosion necessitates search for corrosion-resistant coatings. This search is complicated by the requirement that the coating not impair the electrical and thermal parameters of BPs. Therefore, two types of corrosion-resistant coatings are proposed: coatings from more resistant metals, from gold to titanium, and semiconductor film coatings. The latter are made of tin dioxide or oxides, nitrides, or carbides of metals incorporated into plates, such as nickel or chromium for steel. Table 2 shows that MEA with steel plates with a tin dioxide corrosion-resistant coating are much less contaminated with metal anions.

Gold is one of the best materials for corrosion-resistant coatings. However, electrochemical gilding is an expensive process, which much raises the cost of plates. Even more expensive techniques were patented, for example, cladding of titanium plated with niobium [12]. Corrosion-resistant coatings on steel and aluminum, formed by magnetron sputtering were also proposed [13].

Progress was made in chemical treatment to form protective conducting films on metal surface [14–18]. Thus, for example, protective coatings of a chromium nitride conducting film formed by nitriding of stainless-steel or chromium–nickel alloy surfaces were patented [16]. Good results were also obtained by nitriding of AISI446 stainless-steel and model Ni–Cr alloy surfaces [19]. This technique allows a chromium nitride (CrN/Cr_2N) corrosion-resistant conducting film to be formed on the alloy surface. Carbide [17] or semiconductor tin dioxide films were also suggested [18]. A problem is to obtain zero-defects coatings.

Specific technologies are required for corrosion protection of aluminum and light alloy plates. Direct coating, say with gold, is unstable due to formation of intermetallic compounds and much different thermal expansion coefficients of these metals (Table 3). More or less satisfactory results could be attained by multilayer electrochemical coating [20]: An aluminum alloy plate is first covered with copper, then with nickel, and, finally, with gold.

Table 2. Concentrations of Fe, Cr, and Ni ions after polarization of PEMFC

BP material	Ion concentrations after 7.5-h operation, ppm					
	near anode			near cathode		
	Fe	Cr	Ni	Fe	Cr	Ni
316L steel	21.18	4.60	2.49	9.02	1.94	1.41
SnO_2/AISI 316L	10.83	1.97	1.38	1.12	0.10	0.11
AISI 317L steel	3.98	0.65	0.39	1.29	–	–
SnO_2/AISI 317L	4.03	0.69	0.56	0.87	–	–
AISI 441 steel	622.9	135.7	1.07	462.8	101.2	0.95
SnO_2/AISI 441	24.15	4.51	–	330.3	68.72	0.60
AISI 444 steel	141.5	37.86	0.30	328.3	67.97	0.94
SnO_2/AISI 444	12.70	2.09	–	64.42	13.73	0.22

Table 3. Comparison of corrosion currents of different BPs with metal protective coatings

Plate and coating materials	Corrosion curent, μA cm^2
Aluminum	122
Pd–Ni coating on aluminum	9.8
Al coating on aluminum	1.38
Pd–Ni coating on polymer	7.9

Regretfully, the currently known coatings are unable to fully protect from corrosion. According to [21], even protected steel plates suffer corrosion; therewith FC degrades by about 10% within 1000 h (as a result of catalyst poisoning and degradation of polymeric membrane under the action of heavy metal ions, including gold). Provided the degradation degree is linear in time, the FC power with be halved within 5000 h, which is absolutely unsatisfactory for practical applications.

POLYMER–METAL SANDWICH STRUCTURES

Bipolar plates comprising two porous thin metal plates applied on both sides of a gasimpermeable support of conducting plastic were developed [22]; however, such construction obviously combines all drawbacks of its constituents. A nonconducting polymer support is also possible. In the latter case, BP sides are connected by outer conductors according to a selected scheme [23]. The disadvantage of this construction is the need for fairly thick coatings that allow transverse currents. In this case, however, corrosion is weaker than with metallic coatings on aluminum, and the plate is lighter than an aluminum one (Table 4). A sandwich structure of a polymer–graphite composite on both sides of a metal support is developed.

Polymer–metal BPs are applied for special purposes. For instance, the German Aerospace Center [24] produces segmented bipolar plates for research on current distribution in experimental fuel cells of gold foil on glass fiber plastic with built-in current sensor grid.

INTEGRATED BIPOLAR PLATES

At present the use of advanced and mass microelectronic technologies resulted in the development of miniaturized devices with a very complex microstructure, and their high-volume production cost is extremely low.

These technologies hold much promise for manufacturing small-size fuel cells. Therewith, ordinary proton-conducting polymeric membranes can be used, and microelectronic technologies allow production of bipolar plates integrated with gas diffusion layers (on the basis of microporous silicon, Fig. 4) [25].

One more approach makes use of a hyperfine silicon layer as proton-exchange membrane. In this case, a fully integrated cell can be designed [25]. However, in spite of the extensive technological search, no adequate substitutes for polymer proton-exchange membranes have been found.

Integrated technologies are suitable for manufacturing bipolar plates for traditional FCs. Thus, Hsieh et al. [26] reported the use of excimer laser lithography for machining classical gas channels in sheet poly(methyl methacrylate). Bipolar plates were fabricated by magnetron sputtering of a copper or silver layer 0.2–1 μm thick on a plastic billet. However, the referees did not perform resource tests of the BP. These plates are similar to any plates with polymer-supported metal sandwich structures.

Microelectronics makes use of print technologies involving construction of planar systems. As applied to FC stacks, a planar construction means either use of a single cell of large area and conversion the generated voltage (usually 0.6 V) to a required value by means of electronic converters or use of planar chains with individual units linked by a system of jumpers (Fig. 5). O'Hayre et al. [27] suggested the print-circuit board technology for manufacturing planar plates

Table 4. Effect of material on BP weight

Material	Density, g cm^{-3}	Thickness, mm	Specific weight per active area, g cm^{-2}	BP weight per 0.5 W cm^{-2}, kg kW^{-1}
Graphite	2.25	1.5	0.35	0.7
Stainless steel	8	0.1	0.08	0.16
Aluminum	2.7	0.5	0.14	0.27
Titanium	4.5	0.5	0.23	0.45

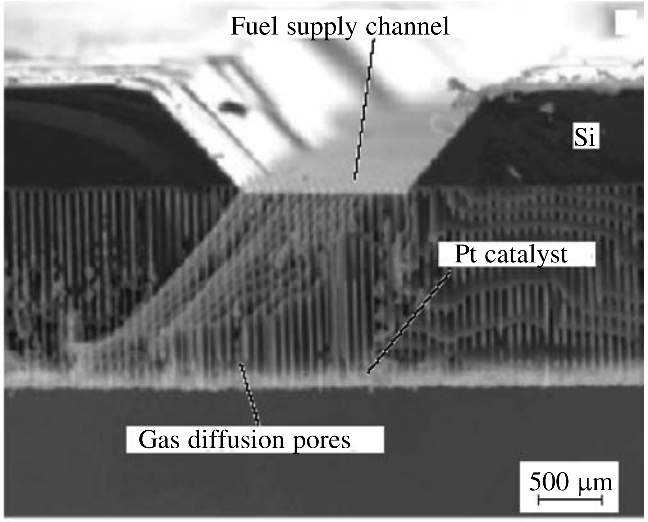


Fig. 4. Section of the anode part of an integral nanoporous silicon FC.

for portable FC arrays. Membrane electrode assemblies (formed on a single membrane) directly contacted with a foiled glass fiber plastic plate (this material is common in electronic industry and comprises a glass fiber plastic–epoxide resin composite with glued copper foil). The foil layer contained etched parallel channels, the glass fiber plastic contained drilled gas inlet holes, and the copper foil was gilded. The back sides of there plates were covered with glass fiber plastic boards with a sea serpent-shaped cut flow channel and plate seals. The three layers were clamped with a sealant. The authors also suggested a more intricate "microstack" channel architecture. As a result, planar stacks of 12 and 16 cells exhibited good characteristics: 380 W cm^{-2} at a stack thickness of 1.3 cm. One unexpected advantage of this type stacks is the possibility of on-line changing the unit connection scheme using built-in electronic switches instead of passive jumpers.

Real microelectronic technologies on silicon crystal plates are based on more radical solutions. Meyers and Maynard [28] suggested use of dependence of the rate of silicon etching in etching acid on the concentration of holes in the single crystal for forming a complex system of etched gas channels. The latter are coated with porous silicon membranes formed in holes of conducting platinum or insulating silicon nitride masks. Such a complex structure was obtained exclusively by electrochemical etching through mask holes: First a thin nonconducting porous silicon layer was made and then gas channels were etched through its pores by electropolishing. Thus obtained end plates were covered with catalyst and then by a proton-

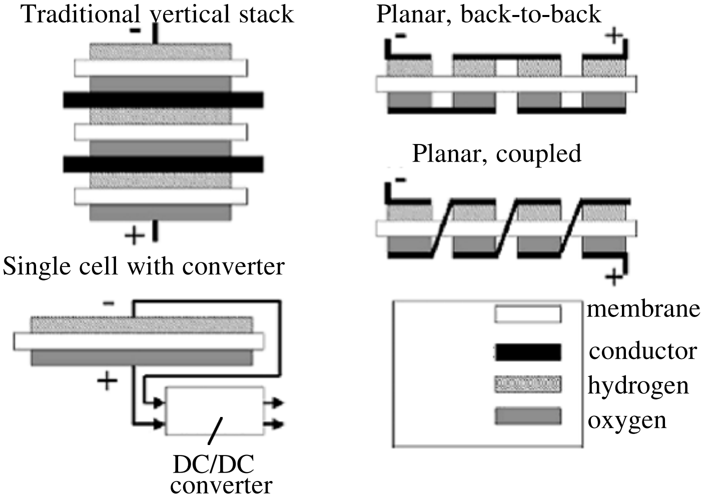


Fig. 5. Variants of assembling bipolar plates into stacks.

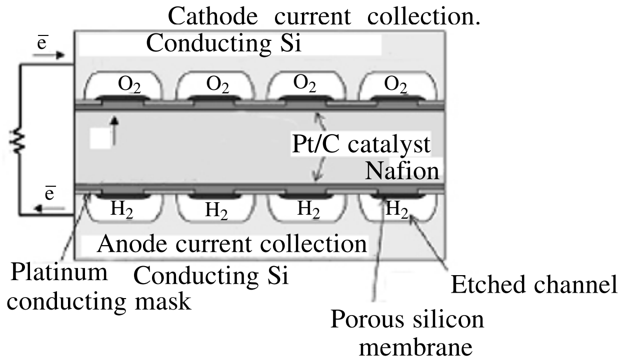


Fig. 6. Structure of channels in a two-layer stack comprising silicon plates with etched channels.

conducting polymer film (Nafion), after which two such half cells were glued together to form a planar microscopic FC stack (Fig. 6). The referees also suggested a completely monolithic structure with fuel and oxidant channels alternating within a single silicon support bulk and the proton-exchange membrane pressed on one side. Unfortunately, these microstacks were not tested experimentally, even though they were found promising by mathematical simulation.

Wainright et al. [29] developed an integrated FC combined in a single hybrid integrated circuit with sensor, microcontroller, and wireless data transfer scheme. Therewith, the hydrogen source (sodium borohydride or metal hydride solution) is embedded in the same aluminum "tablet" (Fig. 7). The planar cell architecture necessitated anode and cathode plates, but plates, as such, were in contradiction with the "print scheme" ideology. As a result, the anode and cathode plates combined with a gas diffusion layer were fabricated by printing high-porosity gold layers on a microporous nylon support. The authors provided evidence showing that their developed device is efficient and its technical characteristics fir those of an alternative energy source, viz. disposable serial lithium battery, and FC had a fivefold benefit in power on pulse load (characteristic of radiocommunication schemes). Regretfully, no real ways to recharging the built-in hydrogen source were suggested in the cited work.

BIPOLAR PLATES ON THE BASIS OF CARBON AND GRAPHITE POLYMER COMPOSITES

Carbon bipolar plates feature the highest corrosion resistance and lack of catalyst poisoning with plate material. Single crystal graphite has scarcely been used as BP material because it easily exfoliates along the cleavage plane and is expensive. Turbostrate graphite and glass carbon possessing good mechanic and electric properties and gas impermeability are quite expensive materials. Moreover, glass carbon billets are quite hardly workable to obtain complex-shaped channels and, therefore, such cost-is-no-object technologies as laser or electron-beam are required. Therefore, glass carbon is an unsuitable material for commercial fuel cells for economic reasons. However, glass carbon is applied as construction units for bench, research, and experimental fuel cells. Figure 8 shows end plates for the metering cell with gas supply and temperature control reinforcement for MEA research, developed by the Institute of Problems of Chemical Physics of the Russian Academy of Sciences and Tensor and Elins Companies. The MEA comprises glass carbon bipolar plates with laser-machined gas-distribution channels [30].

Unlike glass carbon, ordinary molded natural graphite is fairly cheap, but it is a porous material and inapplicable as such because of gas permeability, insufficient mechanic strength, and considerable anisotropy in properties. In this case, composite materials are the best technical solution. Various graphite–polymer composites and those on the basis of inorganic binding agents are widely used. The most promising candidates for BP applications are polymer composites prepared in two different ways. The first involves impregnation of graphite plates with a monomer or an oligomer followed by polymerization,

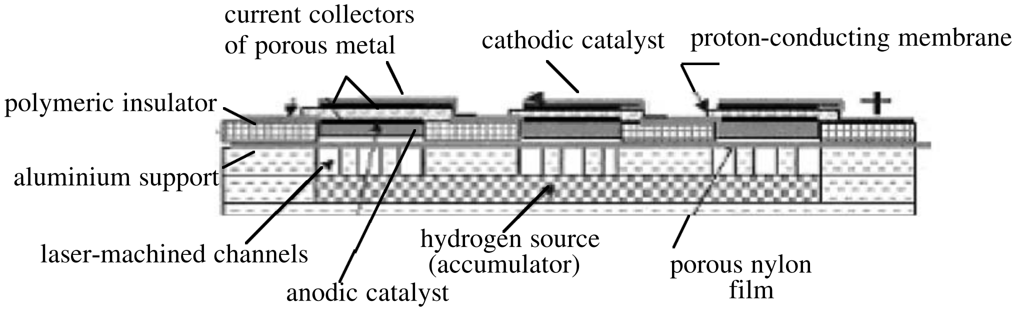


Fig. 7. Stack of fuel cells, integrated with a hydrogen accumulator.

or impregnation with polymer solution. Therewith, low-cost commercial graphite plates are treated to make them gas-impermeable and improve (slightly) their mechanic properties.

The second technology involves mixing a polymeric matrix and conducting graphite particle. At particle contents higher than the percolation threshold, a conducting composite is formed.

The history of technics shows that composites prove to be the best solution in cases where material should meet quite contradictory requirements. Graphite-based composites, such as polymer carbon and thermally expanded graphite systems, seem to hold nowadays the greatest promise.

MOLDED GRAPHITE COMPOSITES

Composites are a matrix of thermoreactive or thermoplastic polymers with conducting corrosion-resistant fillers, such graphite flakes, carbon fibers, or soot. When the fraction of conducting fillers is large, the electro- and thermoconductivities of the resulting material are close to those of graphite.

The polymer fraction in such composites is fairly low, normally no larger than 30 wt% and, having the percolation structure with continuous chain of conducting particles in the polymeric matrix, the composite possesses high conductivity and mechanic properties of the polymer. Composite produce can be obtained using conventional technologies: extrusion, molding, rolling, injection molding, etc. The most important advantage of composites is the possibility of controlling the hydrophilicity/hydrophobicity of plates by selecting binding polymer.

Clearly, requirements to binding polymer are quite high, since the same polymer is BP material [31]. The polymer should ensure low gas permeability of the composite, be thermally stable at FC operating temperatures, possess low thermal expansion coefficient, and be resistant to enhanced humidity and to acids (up to pH ~4) and oxidants, and liberate catalytic poisons and compounds sensitive to electrooxidation (Table 5). Corrosion of graphite–polymer composites was studied by various research techniques (tests in climate chambers, recording polarization curves) and in real fuel cells. At least commercial plates showed no dependence of pure BP resistance on time, and corrosion currents on polarization experiments were no higher than 16×10^{-9} A cm^{-2}, i.e. they fit the DOE target values.

Table 5. Polymers used in graphite–polymer composite bipolar plates

Polymer	Advantages	Disadvantages
Fluoropolymers, polyvinylidene fluoride	Chemical resistance, hydrophobicity	High cost, high viscosity
Liquid crystalline polymer	High heat resistance, low viscosity	High cost
Polyphenylene sulfide	High heat resistance (up to 230°C), low viscosity	High cost
Polypropylene	Low cost, readily manufacturable	Long extrusion cycle
Poltphenylene	High heat resistance; softening point 200°C	Additional hardening is required;
Phenol resins	Low cost	medium heat resistance; hydrolysis at $T > 100$°C
Vinyl ether	Readily manufacturable	

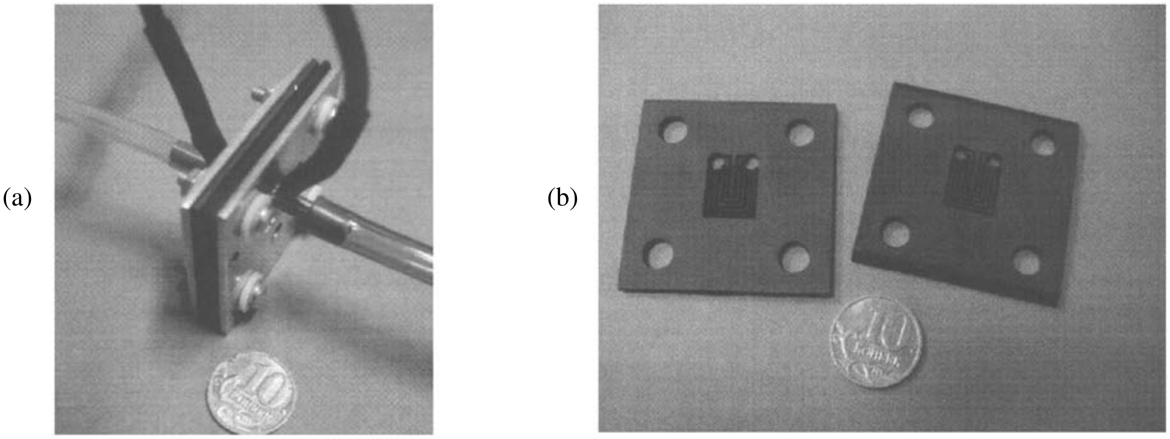


Fig. 8. Measuremnt cell with gas-conducting and temperature-controlling armature for MEA studies: (a) assembled cell and (b) glassy carbon bipolar plates.

A serious disadvantage of ordinary graphite–polymer composites is their low mechanic strength, which is associated with the requirement to preserve high electroconductivity characteristic of graphite. To resolve this contradiction, more complex composites are suggested. Carbon and/or metal fibers, metal-coated carbon nanofibers, and even carbon textile gauzes were suggested as composite fillers [32], which allowed the fraction of conducting filler to be reduced without sacrifice of composite conductivity.

For instance, a composite comprising epoxide resin or polyvinyl alcohol and fiber filler (for instance, glass fiber) with a minor (less than 35%) fraction of large (no less than 1/10 produce thickness) particles of thermally expanded graphite was patented [33]. Large particles ensure good conductivity even at their low content. On the other hand, large particles do not adversely affect accuracy in fabrication of complex-shaped gas and/or liquid flow channels, since thermally expanded graphite is molded no worse than polymer.

Apart from molding, other conventional plastic working technologies are applied, for example, extrusion of thermoplastic polymer composites [34] or injection molding of a graphite–polyvinyl ether composite [35]. Bipolar plates on the basis of composites are commercially produced by DuPont, H_2Economy, ICM Plastics, and Ned Stack.

THERMALLY EXPANDED GRAPHITE MATERIALS

A fairly novel material, thermally expanded graphite (TEG) or foamed graphite (FG), most commonly produced by heat treatment of acceptor-type graphite intercalation compounds (GICs) hold great promise for BP applications. Analysis of published data shows that TEG is largely manufactures by the acid procedure. In particular, the first stage involves chemical treatment in the graphite–sulfuric acid–oxidant system, the second, hydrolysis of the resulting IGC, and the third, thermal shock (foaming). Foamed graphite possesses a number of unique properties, specifically low bulk density, large specific surface area, moldability without binders, resistance to aggressive media, and high electroconductivity, and can be applied in various industries: aviation and space engineering, metallurgy, and oil, gas, chemical, petrochemical, and pulp and paper industries.

The manufacture of TEG induced invention of a series of low-density carbon materials (for instance, graphite foil) that have preserve all properties of graphite and acquired new consumer characteristics: elasticity and plasticity. Graphite foil is normally applied for production of sealants (seals, glands, etc.), bursting disks, resistance heaters, as well as heat and radiation protection means.

Thermally expanded graphite foil are appreciably gas-, especially hydrogen-permeable and feature considerable specific electro- and thermoconductivity anisotropies, i.e. the perpendicular plate conductance is much lower than parallel. Compared to composites, this orientation effect is considered as the principal drawback of BP materials. However, the higher transversal resistance of planar graphite foil layers is compensated for by the possibility of producing thinner plates, since graphite foil is sufficiently soft, and the contact resistance turns out to be lower than with rigid materials.

Graphite foils make it possible to devise multilayer structures with gas-impermeable inner carbon layers. Additional advantages of graphite foil are its low specific weight even compared to massive graphite and good machinability. However, for this material to be actually applied in fuel cells, it should be made mechanically stronger and gas tighter. These problems both can be solved by impregnation with polymeric binders. The most suitable of them are phenol–aldehyde, furan, acrylate, and epoxide resins. There are several techniques for making channels in such foil plates. One involves laminating a clean graphite spacer layer with layers of other graphite sheets with stencil masks of required structure patterns; therewith, the cabonizing adhesive is applied so that layers are clamped together. Another technique is mechanic deformation, specifically stamping, molding, or cutting.

The TEG flakes are 0.3–5 mm is size, i.e. they are 5–10 times larger than synthetic graphite particles in the above-described composites. Since, the limiting size of channels is set depending on particle size, one can form finer structures in composites. In an alternative technology, flow channels are in the electrode support rather in plate surface; thus, bipolar plates can be fabricated from a thin graphite foil thus decreasing stack weight.

Bipolar plates of TEG, both straight and incorporated in graphite–polymer composites, are produced by SGL Carbon GmbH (SIGRAFLEX®). Parameters of these plates are given in Table 6.

Several variants of bipolar plates on the basis of TEG, including metal-graphite sandwiches, are being collaboratively developed by Unikhimtek, Institute of New Carbon Materials and Technologies of Russian Academy of Sciences, and IPCP RAS (Fig. 9).

Table 6. Properties of commercial bipolar plates

Parameter	BP material and producer		
	Carbon composite (Schunk)	Thermally expanded graphite (SGL)	Impregnated graphite (Porvair)
Density, g cm^{-3}	1.9	2.1	1.25
Water uptake, %	0.15		
Flexural strength, MPa	40	40	41
Young's modulus, n mm^{-2}		12 000	
Compression strength, MPa	50	60	
Specific electrical resistance at plate surface, μΩ m	90	100	14
Specific electrical resistance at right angle to plate surface, μΩ m	120	500	14
Maximum temperature, °C	190	120	210
Thermal expansion coefficient, 1/K	11×10^{-6} 28×10^{-6}	14×10^{-6}	
Specific thermoconductivity, W m^{-1} K^{-1}	55	20	
Gas permeability (in air), cm^2 Pa^{-1} s^{-1}		10^{-5}	

GRAPHITE AND CARBON COMPOSITE COATINGS

Additional corrosion protection for metal bipolar plates with better mechanic properties and lower cost than graphite ones can be provided by carbon coatings. To endow composite plates with chemical resistance and gas impermeability and to increase their surface conductance, graphite coatings can be applied. For example, bipolar plates can be made of a light and low-cost material, namely aluminum or aluminum–magnesium alloys and then to coat them on both sides with a thin (since mechanic strength is not critical) layer of graphite-based conducting polymer [36]. Such layer imparts chemical resistance to BP and, moreover, can exhibit catalytic activity, provided a catalyst is deposited on graphite. However, such manufacturing strategy is fairly difficult to realize.

Besmann et al. [37] described the vapor deposition technology of surface coating with graphite nanofibers; such coating simultaneously improves gas-distribution properties of FC in assembly due to better surface diffusion.

Intermediate technical solutions are based on the invention of a gas-tight core, polymeric or metallic, perhaps porous with pores filled with a hydrophilic material to create a gas seal to prevent water exchange between cells. Electroconducting fibers, commonly carbon, are embedded in the core which is then coated with a carbon composite [38]. However, such structures are fairly complicated and poorly manufacturable to serve for solving one of the principal tasks: to reduce the cost of fuel cells.

COMPARISON OF DIFFERENT MATERIALS FOR BIPOLAR PLATES

At present there no unambiguous choice between BP materials of different types. As usual in engineer-

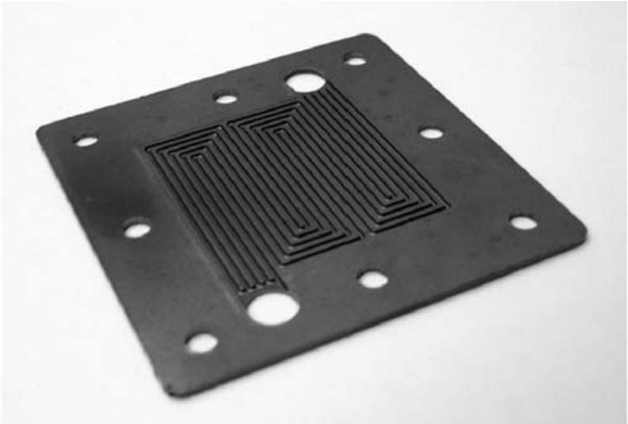


Fig. 9. Bipolar plate of thermally expanded graphite, designed by Unikhimtek, INUMIT, and IPCP RAS.

ing, several materials will find application. In cases where cost is of importance, the choice is metal plates, while durability is the cornerstone, graphite or even glass carbon. When lightweight is required, plates of TEG or even aluminum–magnesium alloys or sputtered plastic can be applied. Estimated weights of plates of different materials are given in Table 4, and estimated transient resistances are listed in Table 1.

The cost of plates of different materials can be estimated in the following way. Graphite composites are expensive but readily mechanically manufacturable, and a convenient technologies of their manufac ture (extrusion, rolling, etc.) are available. Titanium is expensive and hardly manufacturable. Stainless steel is low-cost and fairly machinable.

Table 6 compares different commercial graphite plates. Search for coatings for metal plates and development of graphite–polymer composites can be considered the most actual lines of further research and development in the field of BP materials.

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REFERENCES

1. *http://www.porvairfuelcells.com/bipolar.htm.*
2. *http://sgroup.cms.schunkgroup.com/sixcms/media.php/33/SchunkBipolarPlates14042003.pdf.*
3. *http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf.*
4. Tsuchiya, H. and Kobayashi, O., *Int. J. Hydrogen Energy,* 2004, vol. 29, p. 985.
5. Hermann, A., Chaudhuri, T., and Spagnol, P., *Ibid.,* 2005, vol. 30, p. 1297.
6. *http://www.hydrogen.energy.gov/pdfs/review05/fc1_lightner.pdf.*
7. Jousse, F. and Granier, J., *Towards a New Conception of the Bipolar Plate,* Clefs CEA, Grenoble, winter 2000–2001, no. 44, p. 52.
8. Grainer, J., *http://www.cea.fr/gb/publications/Clefs50/pdf/076a083baurens-gb.pdf.*
9. Gladczuk, L., *MRS Bulletin,* paper no. FF7.2.
10. Davies, D.P., Adcock, P.L., Turpin, M., and Rowen, S.J., *J. Appl. Electrochem.,* 2000, vol. 30, part 1, p. 101.
11. US Patent 776624; RU Patent 2182387.
12. *http://www.tech-etch.com/photoetch/fuelcell.html.*
13. US Patent 2004/007751.
14. Wind, J., Span, R., Kaiser, W., and Bohm, G., *J. Power Sources,* 2002, vol. 105, p. 256.
15. Lee, S.-J., Huang, C.-H., Lai, J.-J., and Chen, Yu.-P., *Ibid.,* 2004, vol. 131, p. 162.
16. US Provisional Patent Application 60/563.923, filled Apr. 21, 2004.
17. US Patent 5798188.
18. Wang, H., Brady, M.P., Teeter, G., and Turner, J.A., *J. Power Sources,* 2004, vol. 138, p. 79.
19. Wang, H., Teeter, G., and Turner, J., *J. Electrochem. Soc.,* 2005, vol. 152, p. B99.
20. Woodman, A.S., Taylor, E.J., Anderson, E.B., Weil, R. et al., *Proc. 2nd Int. Symp. on Electrochemical Technology Applications in Electronics,* Pennington, NJ: The Electrochemical Soc., 1993.
21. Mallant, R.K.A.M., Koene, F.G.H., Verhoeve, C.W.G., and Ruiter, A., *Solid Polymer Fuel Cell Research at ECN, presented at the Fuel Cell Seminar,* San Diego, CA, 1994, p. 503.
22. US Patent 6103413.
23. Soo-Gil Park, Mee-Hye Oh, Yeo-Seong Yoon, Takahiro Shimizu, *Tetsuya Osaka. Meet. Abstr. Electrochem. Soc.,* 2006, vol. 501, p. 149.
24. Schonbuer St., Kaz T., Sander H., and Gulov E., Abstracts of Papers, *2nd Eur. PEFC Forum,* Lucerne, Switzerland, 2003.
25. Zabrodskii, A.G., *Usp. Fiz. Nauk,* 2006, vol. 176, p. 444.
26. Hsieh, S.-S., Kuo, J.-K., Hwang, C.-F., and Tsai, H.-H., *Microsystem Technologies,* 2004, vol. 10, p. 121.
27. O'Hayre, R., Braithwaite, D., Hermann, W. et al., *J. Power Sources,* 2003, vol. 124, p. 459.
28. Meyers, J.P. and Maynard, H.L., *Ibid.,* 2002, vol. 109, p. 76.
29. Wainright, J.S., Savinell, R.F., Liu, C.C., and Litt, M., *Electrochim. Acta,* 2003, vol. 48, p. 2869.
30. Aldoshin, S.M., Dobrovol'skii, Yu.A., and Tarasov, B.P., *Materialy konferentsii "Vysokie tehnologii XXI veka"* (Proc. Conf. "High Technologies of XXI Century"), Moscow, 2006, p. 309.
31. Rosberg, K. and Trapp, V., *Handbook of Fuel Cell Fundamentals,* Vielstich, W., Gasteiger, H.A., and Lamm, A., New York: Wiley, 2003, vol. 3, part 26.
32. US Patent 2005167873-A1; US Provisional Patent Application 11/096.632.
33. US Patent 2004/0062974A1; US Provisional Patent Application 10/603.684.
34. Heinzel, A., Mahlendorf, F., Neimzig, O., and Kreuz, C., *J. Power Sources,* 2004, vol. 125, p. 35.
35. Kuan, H.-C., Ma, C. M., Chen, K.H., and Chen, S.-M., *Ibid.,* 2004, vol. 134, p. 7.
36. CA Patent 2486049-A1.
37. Besmann, T.M., Klett, J.W., and Burchell, T.D., *Materials for Electrochemical Energy Storage,* Ginley, D.S., Doughty, D.H., Takamura, T., Zhang, Z., and Scrosati, B., Eds., Warrendale, PA: Mater. Res. Soc., vol. 496.
38. US Patent 2003232234-A1.

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