 © 2012 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2012v081n03ABEH004290

Nanostructured materials for low-temperature fuel cells †

A B Yaroslavtsev, Yu A Dobrovolsky, N S Shaglaeva, L A Frolova, E V Gerasimova, E A Sanginov

Contents

I.	Introduction	191
II.	Proton-conducting membranes	192
III.	Nanostructured electrocatalysts	203
IV.	Conclusion	213

Abstract. The data on nanostructured materials used in the design of low-temperature fuel cells is generalized. The factors responsible for the increase in conductivity of hybrid membranes containing inorganic nanoparticles are analyzed. The approaches to enhancing the efficiency of platinum catalysts that provide transition from conventional systems to nanosized catalysts including 'core – shell' polymetallic systems are discussed. The hypotheses that explain the reasons for the enhanced stability of these catalysts with respect to carbon monoxide impurity are considered. The bibliography includes 497 references.

I. Introduction

The energy demands of modern civilization increase every year. Thus, according to the International Energy Agency, world's primary power production has more than doubled in the period from 1973 to 2008. The role of one or another energy source also gradually changes. Thus, in the beginning of the 19th century, the main energy source was wood; in the beginning of the 20th, 70% of power was produced by coal combustion but coal was displaced by petroleum as soon as in the middle of this century.[1] According to prognoses,[2–4] the maximum level of oil production reached to date will soon drop down. As a consequence, as soon as in the late 21st century oil will be mainly used in chemical synthesis. Natural gas will be used for power generation a little longer. The redistribution of energy sources can also be observed today. Thus, from 1973 to 2008, the share of oil in the world production of primary energy decreased from 46.1% to 33.2% (Fig. 1).

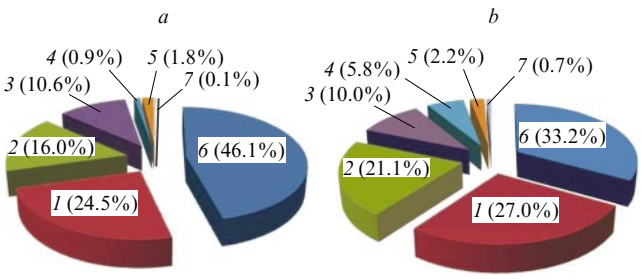


Figure 1. Diagrams of world production of primary energy in the period from 1973 (*a*) to 2008 (*b*) (according to http://www.energy-land.info/analitic-show-63720).
Source: (*1*) coal, (*2*) natural gas, (*3*) biomass, (*4*) nuclear power stations, (*5*) water-power engineering, (*6*) petroleum, (*7*) miscellaneous sources.

In the recent past, the trends in variation of production volumes of different kinds of goods (including power) were determined first of all by the demands of economy, whereas in the last decades, these trends were largely determined by other factors, for example, those associated with the stricter environmental requirements to the production safety. Combustion of oil, coal and gas (to a lesser extent) is accom-

A B Yaroslavtsev N S Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russian Federation. Fax (7-495) 954 12 79,
A V Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prosp. 29, 119991 Moscow, Russian Federation. Fax (7-495) 633 85 20, tel. (7-495) 952 24 87,
e-mail: yaroslav@igic.ras.ru
Yu A Dobrovolsky, L A Frolova, E V Gerasimova, E A Sanginov Institute of Problems of Chemical Physics, Russian Academy of Sciences, prosp. Akad. Semenova 1, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-496) 522 35 07, tel. (7-496) 522 16 57,
e-mail: dobr@icp.ac.ru (Yu A Dobrovolsky), laf@icp.ac.ru (L A Frolova), krizhi@gmail.com (E V Gerasimova), san_e@mail.ru (E A Sanginov)
N S Shaglaeva National Research Irkutsk State Technical University, ul. Lermontova 83, 664074 Irkutsk, Russian Federation. Fax (7-395) 240 50 09, tel. (7-395) 240 54 26,
e-mail: ShaglaevaNS@yandex.ru

Received 17 November 2011
Uspekhi Khimii **81** (3) 191 – 220 (2012); translated by T Ya Safonova

† Dedicated to Academician O M Nefedov on the occasion of his 80th birthday.

panied by atmospheric discharge of vast amounts of carbon, sulfur and nitrogen oxides and also products of incomplete combustion of fuels. Figure 1 shows that in the same period of 1973–2008, the power produced by nuclear power stations substantially increased (from 0.9% to 5.8%) as well as the power from alternative sources such as sun, wind and water.

At the same time, the accumulation of energy in portable devices to be used in sites remote from power lines is also a burning problem. It is assumed that the universal decision of this problem is to develop fuel cells that convert the energy of hydrogen (or hydrogen-containing compounds) oxidation by air oxygen.[5] In view of high importance of this subject, the sharp increase in the fuel cell production is predicted, first of all, for transport needs.[6] It is also assumed that fuel cells are a good choice for the reserve power sources to be used in kindergartens, schools, hospitals, banks and other organizations where the sudden cut-off of energy can lead to serious humanitarian and economic problems.

Initially, the fuel cells were developed for needs of space industry.[7] Attention was focused on the design of high-technology devices for the direct conversion of chemical energy to electricity bypassing the low-efficient combustion process. The prerequisites for the wider development of hydrogen energy appeared in the late 20th century. During the energy crisis, the International Association for Hydrogen Energy was founded (1974). Almost three decades later, the prospects for the development in this field were declared by the EC Committee.[6]

Due to their high efficiency (up to 90%) and the low levels of environmental pollution (the use of hydrogen entails no hazardous emission) and noise, the fuel cells are considered as the most promising devices for the conversion and storage of energy necessary for operation of cellular, stationary and portable devices. In connection with this, the future development of 'hydrogen economy' is widely discussed in mass media issues and scientific journals.[8,9] The modern studies of fuel cells are aimed at increasing their efficiency, reliability, service life, decreasing their cost and starting temperature and also at developing the means for the control and optimization of electrochemical processes occurring in fuel cells.[10]

Depending on the electrolyte nature, five main types of fuel cells are distinguished: alkaline, solid polymer, phosphoric acid, molten carbonate and solid oxide fuel cells. They vary in the nature of mobile ions, the working temperature range, the type of fuel and the electrode and electrocatalyst materials.

In recent years, considerable attention has been paid to the design of low-temperature (working temperature of up to 130 °C) fuel cells based on proton-exchange membranes, which include both hydrogen–air cells and cells utilizing alcohols (methanol, ethanol, *etc*.) as the fuel.[11,12] The largest number of publications in this field are devoted to the development of methanol–air cells. However, to date, the specific characteristics of these fuel cells are far inferior than those of the hydrogen–air cells, which is associated with the low activity of anodic catalysts used and high permeability of membranes for alcohols.

Figure 2 illustrates the design of a hydrogen–air fuel cell.[13,14] Its key unit is a proton-conducting membrane.

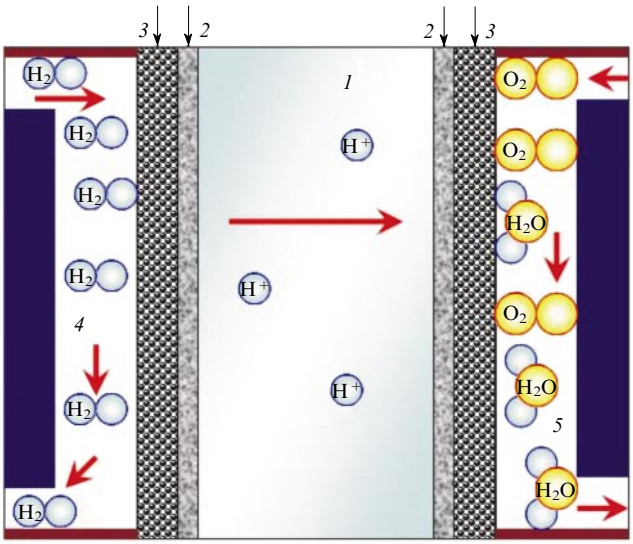


Figure 2. Fuel cell scheme.
(*1*) Proton-conducting membrane; (*2*) catalytic layers; (*3*) gas-diffusion layers; (*4*, *5*) anodic and cathodic bipolar plates with gas channels, respectively.

Oxygen and hydrogen (hydrogen-containing gases) are sorbed on catalyst layers; the chemical reactions also occur there. Protons are transferred to the anode under the action of the chemical potential gradient.

It should be noted that in the design of fuel cells, nanostructured materials are used most often. This concerns, first of all, the proton-conducting membranes the porous structure of which (the characteristic pore size is several nanometres) provides active proton transport[15] and also the catalysts (the efficiency of their operation is maximum for nanosized particles). It also deserves mention that the gas-diffusion layers on which the catalyst is supported operate with the maximum efficiency when contain nanosized elements; in some cases, bipolar plates are also prepared from nanocomposites.

The ion-conducting inorganic composites used in the design of medium-temperature fuel cells and the hybrid membranes (membranes for low-temperature fuel cells) have already been described.[16] This is why the former are left beyond the scope of the present review, while the latter are considered exclusively in their proton-conducting form for which the latest achievements are demonstrated. The goal of this publication is to generalize information on the properties of nanomaterials used in the design of low-temperature fuel cells.

II. Proton-conducting membranes

1. Perfluorinated membranes

Several reviews were devoted to the properties of ion-exchange membranes (*e.g*., see Refs 17–23). The most well-known and promising polymer membranes are perfluorinated sulfonated cation-exchange membranes Nafion and their analogues (Table 1).[19,24–29] A Nafion-type membrane represents a copolymer of tetrafluoroethylene and a perfluorinated sulfo-group-containing monomer

$$-\left(-(CF_2CF_2)_x-CFCF_2-\right)_n$$
$$O(CF_2CF)_y-O(CF_2)_zSO_3H$$
$$CF_3$$

The lengths of repeating units in the polymer chains (x, y and z) vary from company to company. For instance, these parameters are similar for Nafion membranes and their Russian analogue MF-4SK (see Table 1).[27,29]

Table 1. Parameters x, y, z of some perfluorinated proton-exchange membranes.

Membrane	Manufacturer (country)	x	y	z
Nafion	E.I. Du Pont de Nemours and Co. Inc. (USA)	5–13.5	1	2
MF-4SK	Plastpolymer (Russia)	4–15	1	2
Flemion	Asahi Glass Company (Japan)	3–10	0–1	1–5
Aciplex-S	Asahi Chemical Industry (Japan)	1.5–14	0	2–5
Dow	Dow Chemical Company (USA)	3.6–10	0	2

The staring monomers for the polymeric base of perfluorinated membranes include tetrafluoroethylene and perfluorinated sulfo-group-containing monomers prepared by a multistep synthesis with the target product yield of $<30\%$. A new practically feasible synthesis of a perfluoronated polymer electrolyte for proton-conducting membranes was reported.[30] It is based on aqueous emulsion copolymerization of tetrafluoroethylene with perfluoro(3,6-dioxa-4-methyloct-7-ene)sulfonyl fluoride. According to the authors, this process is characterized by high productivity, the efficient use of the expensive sulfo-monomer and the possibility of control of the equivalent mass of the copolymer.

The sulfo-group concentration is estimated by a number of parameters such as the cation-exchange capacity expressed in moles of H^+ per gramme of the polymer and the equivalent weight, which is reciprocal to the cation-exchange capacity. During copolymerization, it is possible to control the cation-exchange membrane capacity by varying the comonomer ratio. Commercial membranes have the equivalent weights from 900 to 1300; however, membranes with equivalent weights of 1000 or 1100 g of the polymer per mole of H^+ are used most often.[28] This content of sulfo groups both ensures high proton conductivity and satisfactory mechanical properties of membranes.

Furthermore, methods for the synthesis of perfluorinated ionomers with carboxyl and phosphonic groups and manufacture of membranes from these ionomers have also been developed, but they have not found wide use.[28] As the example, Table 2 lists the main characteristics of Nafion-117 membranes.

Now we consider the cluster model of the membrane structure in order to understand the cause for the high proton conductivity. The hydrocarbon or perfluorinated chains are mainly hydrophobic, whereas the functional groups are hydrophilic. This is why self-assembling processes occur in the membranes to form clusters of functional groups.[31] The totality of hydrocarbon or perfluorinated chains form the main matrix of the membrane.

Table 2. Selected characteristics of Nafion-117 membranes.

Parameter	Units of measurement	Average value
Exchange capacity	mg equiv.	~ 0.91 (to 1.0)
Surface resistance	$\Omega\ cm^{-2}$	$\sim 0.09-0.12$
Service life	h	to 50 000
Proton conductivity	$S\ cm^{-1}$	
at 30 °C		$\sim 10^{-2}$
at 80 °C		~ 0.1
Current density for voltage of 0.45 V	$mA\ cm^{-2}$	$\sim 250-640$
Methanol diffusion coefficient	$cm^2\ s^{-1}$	2×10^{-6}
Water absorption	(%)	~ 15
Cost	US dollars for 1 m^2	~ 700

The functional groups of sulfonic-acid membranes are prone to hydration. The clusters of SO_3H groups capture water from the environment. Thus, for hydrogen-form Nafion membranes in dilute aqueous solutions, the number of water molecules per sulfo group can reach 16–18.[32,33] According to NMR studies, even in the air-dry state, the sulfonic-acid membranes retain two water molecules, which bind a proton to form an $H_5O_2^+$ ion.[34]

Based on X-ray and small-angle neutron scattering studies of sulfonic-acid membranes, Gierke *et al.*[35,36] arrived at the conclusion that ordered clusters should be present in the structure of such membranes. They put forward a model for the structure of perfluorinated sulfonic-acid membranes (Nafion), which is now most widely acknowledged and is often considered as the generalized model of the structure of homogeneous ion-exchange membranes. According to this model, the clusters closely resemble spheres and represent reverse micelles formed by water molecules (Fig. 3) with extra protons produced upon dissociation of the ion-exchange SO_3H groups. Along the outer micelle boundary, SO_3^- anions are attached. This structure provides the minimum surface energy and limits (or eliminates) the contact of the hydrophobic matrix with water.[31]

For ions to be transferred through a membrane, the membrane pores should be connected with one another by channels (see Fig. 3). The formation of clusters is associated

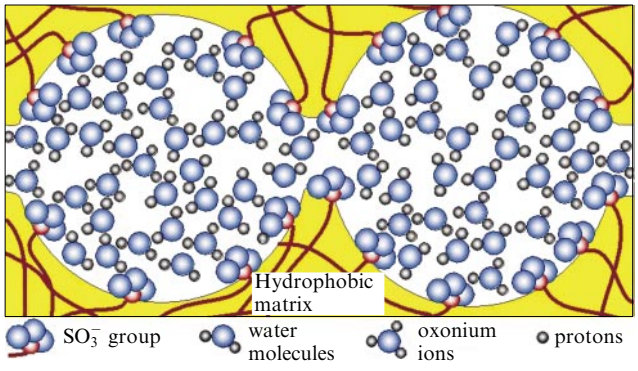


Figure 3. Pore structure of a cation-exchange polymer membrane in its hydrogen form.

only with transformations of the configuration of polymer chains. The change in the Gibbs energy upon this transformation is rather small, so that the systems of pores and channels with similar energies can be formed in various ways. The ease of the pore and channel transformations in the membrane is due to the mobility of polymer chain fragments.

According to calculations by Gierke and Hsu (cited based on Refs 3 and 15), the average pore volume in Nafion membranes with the equivalent mass of 1200 varies from 2.5 to 4.7 nm^3 for their moisture content varying from 5% – 6% to 33.6%. In addition, the moisture content of membranes, the pore size and the number of water molecules in the pores decrease with the increase in the cation atomic mass in the series from H^+ to Cs^+, while the number of sulfo groups, on the contrary, almost doubles (Table 3). The conversion of a membrane into the swollen state also entails a substantial increase in the distances between the pore centres, namely, from 2 – 3 nm in the dry state to 4 – 5 nm for water content of ~20 mass.%.[35, 36]

Table 3. The moisture content of membranes {[H_2O] (%)}, average numbers of water molecules (n_{H_2O}) and sulfo groups (n_{SO_3}) per cluster (pore) and pore size (d) for different cationic forms of Nafion membranes.[31]

Cation	[H_2O] (%)	n_{H_2O}	n_{SO_3}	d/nm
H^+	33.6	1690	76	4.74
Li^+	29.7	1430	72	4.49
Na^+	21.0	1120	80	4.21
K^+	8.7	520	89	3.45
Rb^+	8.1	560	103	3.56
Cs^+	5.9	470	120	3.50

Note. The equivalent mass of membranes is 1200; membranes were exposed to boiling water for 1 h for their saturation with water.

A different model of the membrane structure was proposed.[37] The authors arrived at the conclusion that the system of pores and channels has a comb-like shape (Fig. 4). The complete separation of polymer chains and water never occurs, so-called gel regions composed of a mixture of these 'phases' being located between them. According to this model, the matrix is formed by hydrophobic chains with the functional groups being oriented into the interlayer space.[37, 38]

In essence, in the comb-like model, the wider segments of the transport channels are analogues of pores and the narrower segments are equivalent to the Gierke channels. The main difference between the two models is that according to the comb-like model, the pores need not be shaped like spheres with similar size. However, Gierke, too, accepted these conditions as an assumption convenient for building his model; hence, the difference between these models is minor. Based on the data obtained for saturation with D_2O, it was concluded [39] that coarse pores form a large portion of the MF-4SK membrane (Russia) and not all of these pores are connected by channels.

The dependence of the specific resistivity of the MF-4SK membranes on the sulfo-group content (Fig. 5*a*) is non-monotonic. The increase in their concentration to ~8% leads to a sharp decrease in the membrane resistivity; for larger sulfo-group contents, the resistivity changes much more slowly. At the same time, an increase in the degree of sulfonation gives rise to a virtually linear increase in the

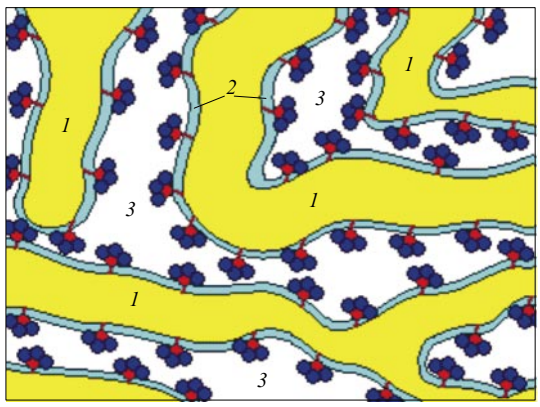


Figure 4. Model of the comb-like structure of perfluorinated MF-4SK membranes.
(*1*) Polymer chains; (*2*) gel regions; (*3*) transport channels containing attached ions, counter-ions and water molecules.

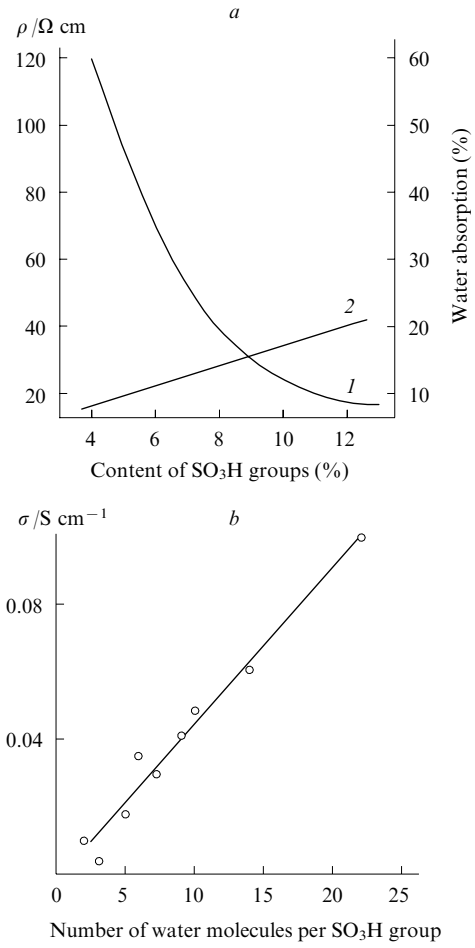


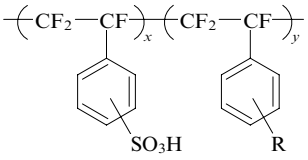
Figure 5. Specific bulk resistance (*1*) and water absorption (*2*) of MF-4SK membranes *vs*. the sulfo-group content (*a*)[27] and proton conductivity of Nafion-115 membranes *vs*. the water content (*b*).[40]

moisture content and conductivity of the membranes (Fig. 5 *b*),[40] which implies a linear dependence between the conductivity and the degree of sulfonation. As the temperature increases, the membrane conductivity increases according to the Arrhenius law up to ~90 °C.

According to the data of differential scanning calorimetry (DSC), the perfluorinated membranes are stable in inert media up to 300 °C; at higher temperatures, the processes of desulfonation and destruction of the ether side chains occurs. The destruction of the polymer backbone takes place at temperatures of > 450 °C.[41]

The main advantages of Nafion membranes are their chemical and thermal stability, the high proton conductivity and strength. However, there are several drawbacks such as the sharp drop of conductivity at low humidity, the relatively high permeability of the membranes for hydrogen (10^{-11}–10^{-10} mol cm^{-1} s^{-1} atm^{-1}, current loss 1–10 mA cm^{-2}) and methanol (10^{-6} mol cm^{-2} s^{-1}, current loss 50–100 mA cm^{-2}) and their high cost, which limit their practical applications.[19] Moreover, at ~90°C perfluorinated membranes lose their water even under high humidity conditions, which results in a decrease in conductivity. This factor is of particular importance because at temperatures below 120 °C, poisining of platinum present in the catalyst by carbon monoxide traces present in hydrogen poses a serious problem,[11] which substantially limits their use.

Of considerable interest are the membranes based on poly(α,β,β -trifluorostyrene) (BAM3G), which were developed by the Ballard Power System Company (Canada).



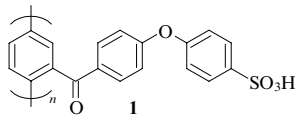
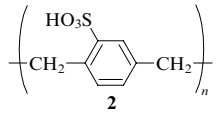
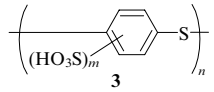
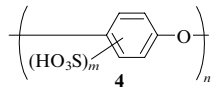
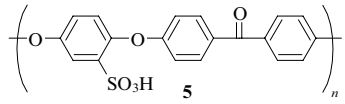
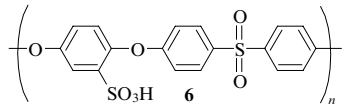
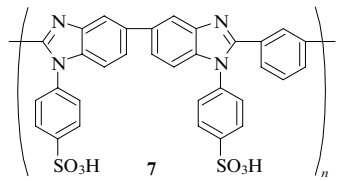
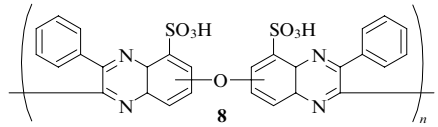
These membranes are cheaper than Nafion but they are characterized by a higher exchange capacity, which determines their far higher degrees of swelling as compared with Nafion and Dow membranes (see Table 1). Fuel cells based on BAM3G membranes demonstrate characteristics similar to those observed for Nafion and Dow membranes at low current densities and superior characteristics at current densities > 0.6 A cm^{-2} (Ref. 23).

Proton-conducting membranes based on polyvinyl alcohol esterified by phenolsulfonic acids were prepared.[42] An increase in the phenolsulfonic acid content enhances the conductivity of these membranes. Their drawbacks are the relatively low mechanical strength and the high degradation rate when operated in a fuel cell.

2. Polycondensation membranes

At present, considerable attention is drawn to new proton-conducting membranes, particularly, those based on sulfonated aromatic condensation polymers. Polycondensation membranes are characterized by high thermal stability and good mechanical properties. Moreover, they are cheaper than perfluorinated membranes and the materials for their production are commercially available. The conventional method for their synthesis consists of sulfonation of aromatic condensation polymers (Table 4).[43–45]

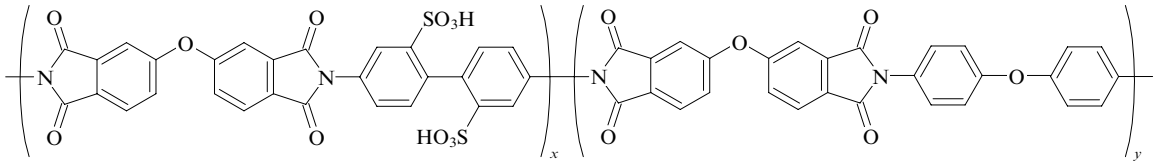
Table 4. Sulfonation products of certain organic polymers.

Initial polymer	Sulfonation product formula
Poly(phenoxybenzoyl-*p*-phenylene)	 **1**
Poly(*p*-xylylene)	 **2**
Poly(phenylene sulfide)	 **3**
Poly(phenylene oxide)	 **4**
Poly(ether ether ketone)	 **5**
Poly(ether ether sulfone)	 **6**
Poly(N-phenylbenzimidazole)	 **7**
Poly(2-phenylquinoxaline)	 **8**

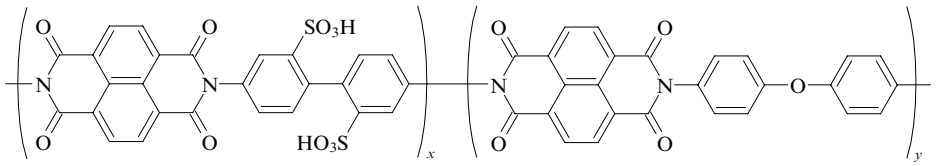
The sulfonation agents used include concentrated sulfuric or chlorosulfonic acids, methanesulfonic acid mixed with concentrated sulfuric acid and acetyl sulfate. The sulfonation rate of the mentioned polymers can be controlled by varying the reaction time and the acid concentration. The sulfonation gave samples without traces of polymer chemical destruction or cross-linking and with the degree of sulfonation varying from 30% to 100%. Membranes based on sulfonated polymers **1**–**8** exhibit fairly high proton conductivity.

Sulfonated polyimides **9**, **10** were synthesized by polycondensation of aromatic diamines with anhydrides of phthalic and naphthalic acids. When operating within a fuel cell, sulfonated naphthalic polyimides **10** demonstrated parameters comparable with those of Nafion membranes[46] but after 70 h of operation, their characteristics considerably deteriorated.

The Ballard Advanced Materials Company (Canada) has developed membranes based on sulfonated poly(phenylquinoxalines) **11**.[47]

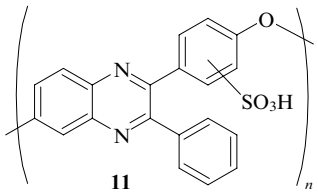


9



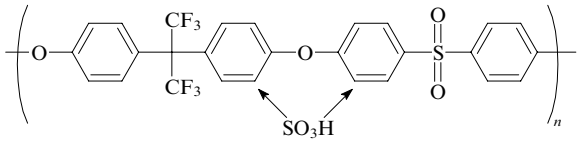
10

These membranes are characterized by good mechanical properties but cannot compete with perfluorinated membranes.



11

Sulfonation of poly(aryl ether sulfones) by chlorosulfonic acid results in different positions of sulfo groups.[33]



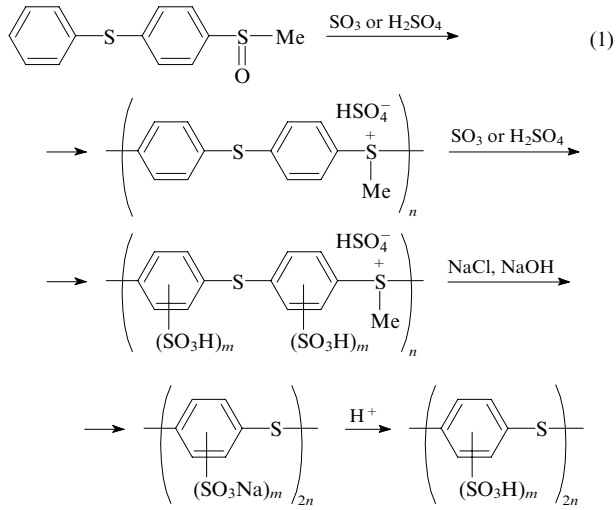
Sulfonated poly(aryl ether sufones) are insoluble in water and for the degree of sulfonation of $\sim 90\%$ their ptoton conductivity reaches that of Nafion membranes. However, these membranes are characterized by a high degree of swelling, which considerably impairs their mechanical properties. To reduce the degree of swelling, sulfonated poly(aryl ether sulfones) are cross-linked with diamines; however, this entails a substantial decrease in their proton conductivity.

Sulfonation of poly(ether ether ketones) with sulfuric acid was reported.[48] The proton conductivity of membranes based on sulfonated poly(ether ether ketones) **5** is relatively low: $\sim 10^{-5}$ S cm^{-1} for the degree of sulfonation of 65%.

The polymerization of 4-methylsulfenyldiphenyl sulfide (initiated by sulfuric acid or in the presence of sulfur trioxide) produced first of all a sulfonated polysulfonium cation, which is then transformed to sulfonated poly(phenylenesulfide) **3**.[49]

The proton conductivity of the membranes prepared from sulfonated poly(phenyl sulfide) at 25 °C is $\sim 10^{-2}$ S cm^{-1}.

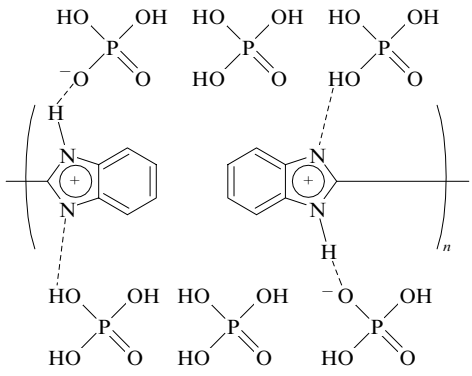
New proton-conducting membranes based on phenyl-substituted polyphenylenes with phosphonate groups PO_3H_2 in the side chain were obtained.[50] Phenyl-substituted polyphenylenes are chemically and thermally stable polymers with good mechanical and barrier properties; they can be easily functionalized. The presence of six bulky phenyl substituents and isomerically different chain units makes it possible to form films by casting from solution, introduce from one to four phosphonate groups per repeating chain unit (which are responsible for the high ionic conductivity and hydrophilicity) and also control the degree of phosphonation in order to obtain sufficient proton conductivity.



(1)

Lately, the interest of scientists in proton-conducting membranes based on the acid–basic polymer complexes quickened.[51] The main merit of such membranes is that they can be used in a wide temperature range in both wet and dry atmospheres.

Of most practical interest are the membranes based on poly(benzimidazole) complexes with phosphoric acid.[52] The structure of H_3PO_4-doped commercially available poly[2,2′-(*m*-phenylene)-5,5′-dibenzimidazole] can be represented as



Doping with acids gives rise to proton conductivity strongly dependent on the degree of doping. The proton conductivity, as a parameter slightly sensitive to humidity, reaches 0.13 $S\,cm^{-1}$ for a high level of doping (up to 1600 mol.%) and 160 °C. The membranes exhibit high thermal stability (up to 160–200 °C) and low methanol permeability. They proved to be highly efficient as parts of high-temperature fuel cells (up to 200 °C). These membranes are manufactured by PEMEAS (Germany) and Celanese (USA). Their main drawbacks are the low mechanical strength and the fact that in contact with water, phosphoric acid is washed out from the regions of catalytic and gas-diffusion layers of the membrane. This blocks the gas pores and causes degradation of bipolar plates. The removal of phosphoric acid results in a decrease in the membrane proton conductivity. Modifying polybenzimidazole with silicon dioxide can somewhat increase the ionic conductivity. Moreover, in the presence of silicon dioxide, the extent of washing out of phosphoric acid from the hybrid membranes substantially decreases.[53]

The introduction of heterocycles (imidazole and pyrazole) into sulfo-group-containing poly(ether ketones) and oxy acids extended the range of materials with proton-transport activity. For example, the proton-conducting properties of hybrid materials based on polyvinylphosphinic acid and nitrogen-containing heterocycles (imidazole, pyrazole and 1-methylimidazole) were studied.[19] The obtained materials displayed high proton conductivity ($\sim 10^{-3}$ S cm^{-1} at 150 °C) in dry atmosphere. The current density of a fuel cell based on tungstophosphoric acid and imidazole was 10 mA cm^{-2} at 80 °C.[44]

3. Polycondensation of alkoxysilanes with polymer matrices

Rapid progress is being made in the studies of hydrolytic polycondensation of alkoxysilane derivatives in the presence of various polymer matrices or inorganic and organic compounds with acid fragments. The first and the most thorough study of the sol–gel process was carried out for the hydrolytic polycondensation of tetraethoxysilane to afford polysilicic acids of low molecular mass or hydrated silica gel. This process is based on hydrolysis and polycondensation to form siloxane bonds. Ultimately, this produces a three-dimensional cross-linked polysiloxane network of silica gel with high molecular mass.

Hydrolytic polycondensation of tetraethoxysilane in the presence of orthophosphoric acid and alkylaromatic polyionenes (oligomeric quaternary ammonium salts) afforded silicophosphate proton-conducting membranes with the conductivity of 10^{-2} S cm^{-1} at 130 °C.[54] A drawback of these membranes is their brittleness. An attempt was made[55] to improve their mechanical properties by introducing 3-glycidoxypropyltri(methoxy)silane into silicate–H_3PO_4 gels. However, the polymer chains based on 3-glycidoxypropyltri(methoxy)silane are short and tend to form a three-dimensional network; hence, such membranes lack sufficient flexibility.

A new class of membranes with a matrix made of organic–inorganic network and H_3PO_4 were synthesized.[54] The imidazole rings were grafted on alkoxysilane by means of nucleophilic substitution. The following organosilicon compounds were used as substituted imidazoles and alkoxysilanes: 2-tri(ethoxy)silylpropylthioethyl-1*H*-benzimidazole synthesized from 3-mercaptopropyltri(methoxy)silane and 2-(chloromethyl)benzimidazole; 2-[(4-tri(ethoxy)silylethylphenylmethyl)thio]-1*H*-imidazole synthesized from 2-mercaptoimidazole and (chloromethyl)phenylethyltri(ethoxy)silane; 2-[(3-tri(ethoxy)silylpropyl)thio]-1*H*-imidazole obtained by the reaction between 2-mercaptoimidazole and 3-iodopropyltri(methyl)ethoxysilane. Such membranes doped with phosphoric acid demonstrated high proton conductivities at low humidity, high thermal stability and good mechanical properties. Their proton conductivity increases with an increase in the H_3PO_4 content and at elevated temperatures to reach 3.2×10^{-3} S cm^{-1} at 110 °C.

The sol–gel process used in the synthesis of organic-inorganic systems provides simultaneously a polymer matrix and an inorganic silica network; this method rules out phase separation of the components, thus giving highly homogeneous materials.[56] The formation of composites as interpenetrating networks of organic and inorganic polymers opens up wide possibilities for functionalizing hybrid structures with various groups and substituents. In certain cases, most often, in the formation of copolymers from alkoxysilanes and organic monomers, covalent binding of the system components can be achieved. This was used to prepare composites involving polyimide and polyamide,[57] polyacrylic,[58] polyvinylidene fluoride[59] and other materials.[60]

Composites of this type can also be formed by mixing a pre-synthesized polymer with tetraethoxysilane. This is a simpler method, because the stage of organic monomer polymerization is excluded. This process may ultimately produce copolymers and form interpenetrating networks.

Several publications were devoted to the formation of organic–inorganic copolymers by the sol–gel method using tetraethoxysilane and polymer derivatives of nitrogen-containing heterocyclic compounds.[61–63] According to electron microscopic data, the structure of composites is formed by aggregated regular-shaped globules largely measuring 300 nm.[63]

New organic–inorganic copolymers were synthesized by the sol–gel method with the participation of tetraethoxysilane and vinyl chloride copolymers with vinyl derivatives of nitrogen-containing heterocyclic compounds. The conditions of synthesis of polymers and copolymers based on vinylpyridines and vinyl chloride were discussed.[64–66] It was shown that copolymerization of vinyl chloride with *N*-

Table 5. Proton conductivity (σ) of polymer films based on vinylpyridines and composites based on them (doped with 9 M H_3PO_4).

Film composition	Mass fractions of components	σ /S cm^{-1}
Poly(4-vinylpyridine)	—	2.8×10^{-5}
Poly(5-vinyl-2-methylpyridine)	—	6.7×10^{-5}
Copolymer of 2-methyl-5-vinylpyridine with vinyl chloride	—	9.1×10^{-3}
Copolymer of 5-vinyl-2-methylpyridine with vinyl acetate	—	5.5×10^{-5}
SiO_2–poly(4-vinylpyridine)	1.3 : 1	5.6×10^{-3}
SiO_2–poly(5-vinyl-2-methyl pyridine)	0.8 : 1	2.0×10^{-2}
SiO_2–copolymer of 5-vinyl-2-methylpyridine with vinyl chloride	1 : 1	4.0×10^{-2}
SiO_2–copolymer of 5-vinyl-2-methylpyridine with vinyl acetate	1.4 : 1	1.0×10^{-2}

and *C*-vinyl-substituted nitrogen-containing heterocyclic compounds is accompanied by dehydrochlorination of vinyl chloride units.

Films that acquired proton conductivity upon orthophosphoric acid doping were synthesized. The proton conductivity of the membranes synthesized from solutions of vinylpyridine homopolymers was $\sim 2.8 \times 10^{-5}$ S cm^{-1} at 25 °C; for membranes prepared from solutions of 5-vinyl-2-methylpyridine–vinyl chloride and 5-vinyl-2-methylpyridine–vinyl acetate copolymers, the proton conductivities were 9.1×10^{-3} and 5.5×10^{-5} S cm^{-1}, respectively (Table 5).[67]

A new class of organic-inorganic membranes synthesized by the sol–gel method from polysiloxanes and tungstophosphoric acid, which have high conductivity at elevated temperatures, was considered.[68]

4. Hybrid membranes containing nanoparticles

Despite their wide diversity, the number of ion-exchange membranes suitable for the efficient use in fuel cells is not too large; moreover, none of them meets all the requirements of manufacturers. Thus the widely used perfluorinated sulfonated cation-exchange materials such as Nafion are characterized by relatively low thermal stability, which gives no way for preventing the irreversible adsorption of carbon monoxide on platinum catalysts and, hence, for the direct use of cheap hydrogen synthesized by conversion of hydrocarbons, alcohols and coal.[69] Furthermore, their high proton conductivity is possible only at very high humidity close to 100%, which substantially complicates the fuel cell design. The comparatively high cost of these membranes also deserves mention.[70] At the same time, in contrast, the membranes based on polybenzimidazole doped with phosphoric acid can work at elevated temperatures and low humidity; however, serious problems are caused by washing out of phosphoric acid, which is responsible for their high proton conductivity. Hence, since the late 1980s, the studies on the targeted modification of membrane materials to obtain hybrid membranes containing inorganic and high-molecular-mass components have been actively conducted. This approach is considered as the most promising for upgrading fuel cells with ion-exchange membranes.[16, 34, 71, 72]

The keen interest in hybrid membranes is explained by their unique transport (higher ionic conductivity, lower gas permeability) and mechanical properties and also by the high thermal stability. These features are due to synergism of the properties of individual components.[71, 73, 74] Most often, these membranes are synthesized by the simplest, practically feasible method which involves the introduction of nanoparticles into the solution from which membranes are cast. However, fine particles tend to form aggregates which are not always destroyed in solution. This reduces the efficiency of modification.

Yet another promising method for the synthesis of hybrid materials consists of preparing nanoparticles directly in the membrane pores.[70, 71] The starting reactants may be efficiently adsorbed in nanopores, which limits the reaction volume. The pore walls may isolate the formed particles from one another and decrease the surface tension forces, thus providing the thermodynamic stability of the nanoparticles formed. In this case, pores act as a sort of nanoreactors.[70]

Nanosized inorganic additives used for modifying membranes can be divided into two large groups, namely, the compounds containing no mobile protons (silicon, titanium, zirconium, aluminium oxides, zeolites, *etc.*) and substances that introduce additional protons into the transport process (zirconium hydrogen phosphates, heteropolyacids and their salts, oxides with sulfonated surfaces).

Silicon dioxide is used most often for the modification of membranes. It is usually obtained by hydrolysis of tetraethoxysilane or other organosilicon compounds. The majority of studies in this field were devoted to modification of perfluorinated sulfonic acid membranes such as Nafion.[75–83] In the majority of cases, a considerable gain in conductivity was achieved. As the main advantages of hybrid membranes, one can mention their lower gas and methanol permeabilities[80–84] and higher mechanical strength.[85]

Figure 6 shows the temperature dependences of the proton conductivity for certain MF-4SK membranes modified with hydrated silicon dioxide.[86] The conductivity of these membranes exceeds that of the reference sample throughout the whole temperature range. For doped membranes, the activation energy of conductivity decreases to 10–12 kJ mol^{-1}, while for the reference sample it is 13.7 ± 0.6 kJ mol^{-1}. The dependence of the conductivity on the silicon dioxide content in a membrane passes through a maximum at 2.5 vol.% SiO_2 (Fig. 7). The activation energy of conductivity reaches its minimum for the SiO_2 content of 2.5 vol.%.

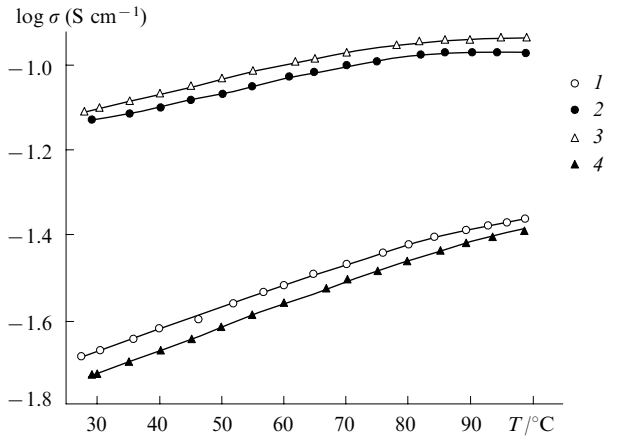


Figure 6. Temperature dependences of the conductivity of MF-4SK membranes doped with hydrated silicon dioxide.[86] Content of silicon dioxide in the samples (vol.%): (*1*) 4.4, (*2*) 2.6, (*3*) 1.7; (*4*) reference sample.

It is important that membranes of this type exhibit high proton conductivity at a low humidity and elevated temperatures.[83] Hybrid membranes can also retain moisture due to the reverse diffusion of water formed in the cathodic region.[87] Watanabe *et al.*[88, 89] put forward a concept of 'self-humidifying' membranes, which is not quite an appropriate name.

The use of hybrid SiO_2–Nafion membranes allows the working temperature of fuel cell to be substantially increased. Thus fuel cells with a membrane containing up

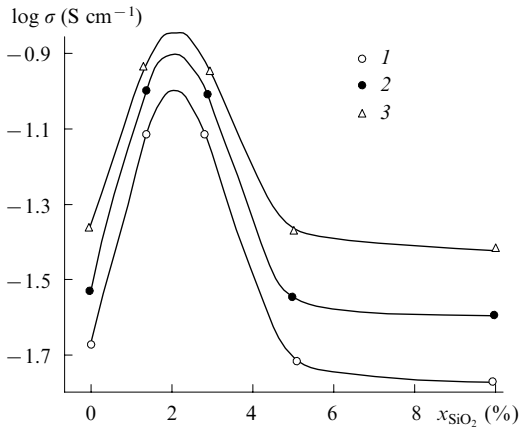


Figure 7. Conductivity of the MF-4SK membranes doped with silicon dioxide on its content at 30 (*1*), 60 (*2*) and 99 °C (*3*).[86]

to 10 mass % SiO_2 are four times superior as regards the current characteristics over analogous cells with Nafion-115 membranes at 130 °C. The low methanol permeability and the high working temperature of hybrid membranes prevent them from being efficiently used in direct methanol fuel cells. Thus at 145 °C and the voltage of 0.5 V, the power density of a cell based on these membranes reaches 350 mW cm^{-2} (Refs 90 and 91).

Such composite materials were also synthesized on the basis of other polymers.[92–100] Among the most popular types are the hybrid membranes based on sulfonated poly(ether ether ketone). After modification of this polymer with mesoporous silicon dioxide, the conductivity can increase 4-fold.[94, 95]

Good results were obtained in the sulfonation of the silica surface. The SiO_2-SO_3H/Nafion membranes exhibit higher selectivity in fuel cells due to their high proton conductivity and low methanol permeability.[101–103] Similar results were obtained for silicon dioxide particles modified with fragments of various sulfonic acids[102, 104] and even with fragments of silicon alkoxides (as the precursors), which retain the organic fragments after hydrolysis.[105] The introduction of silicon dioxide into sulfonated poly(ether ether ketone) provided the conductivity of 3×10^{-2} S cm^{-1} at 100 °C.[92] Direct methanol fuel cells with such membranes exhibit the maximum power density of >50 mW cm^{-2}, which is much higher than analogous characteristics of fuel cells with non-doped Nafion-115 membranes or membranes based on sulfonated poly(ether ether ketone). The effect of the origin of SiO_2 on the transport characteristics of membranes based on sulfonated poly(aryl ether sulfone) was also studied.[96]

By adding heteropolyacids that are adsorbed on silica surface, the surfacer acidity can be increased.[106–109] At 100% relative humidity, the proton conductivity of hybrid membranes is close to the conductivity of original Nafion membranes, but the former is much higher at low humidity.[107] Similar results were obtained for membrane modification with silicon dioxide and caesium tungstophosphate.[110] Hybrid membranes with heteropolyacids on particles of several metal dioxides were studied.[111] Their conductivity reached 1.6×10^{-2} S cm^{-1} at 120 °C and 35% relative humidity.

Nafion membranes with additives of tungstosilicic, tungstophosphoric or molybdophosphoric heteropolyacids synthesized by Ramani *et al.*[112] had a high moisture content and ionic conductivity of 1.5×10^{-2}, 2.5×10^{-2} and 9.5×10^{-2} S cm^{-1}, respectively. This is higher than the conductivity of original Nafion-117 membranes under the same conditions (1.3×10^{-2} S cm^{-1}). At 120 °C and 35% relative humidity, the conductivity of these membranes is $\sim 1.5\times10^{-2}$ S cm^{-1} (Ref. 113).

However, heteropolyacids are washed out almost completely when the membrane is kept in water.[114] An increase in the hydrolytic stability of the membranes was achieved when heteropolyacids were added together with hydrated silicon dioxide[107, 110, 115–117] or as insoluble caesium salts.[109, 114, 118–120] Using IR spectroscopy, it was shown[110] that stabilization was achieved due to interaction between a heteropolyacid and SiO_2.

The introduction of heteropolyacids is accompanied by a decrease in the thermal stability of the perfluorinated polymer matrix. For various acids, the degradation temperature was observed to decrease by 20–50 °C.[112, 121] At the same time, when heteropolyacids were introduced in combination with SiO_2 (Refs 107 and 115), the thermal stability remained virtually unchanged. In several publications,[122, 123] tungstophosphoric heteropolyacid and its caesium salt were used for modifying Teflon-containing Nafion membranes.

A slight improvement of voltammetric characteristics of hydrogen – air fuel cells based on hybrid Nafion membranes was observed after the addition of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.[119] The maximum decrease in the methanol permeability (down to 2.2×10^{-7} cm^2 s^{-1}) was observed after doping of these membranes with both tungstophosphoric acid and SiO_2.[115]

The modification with heteropolyacids was also used for improving the properties of membranes based on sulfonated poly(ether ether ketone),[124] polyethers[125] and several other polymers.[126–129] The conductivity of synthesized membranes was $(1-9)\times10^{-2}$ S cm^{-1}. The maximum conductivity (0.17 S cm^{-1}) for such materials is reached at 80 °C and at 100% relative humidity.[128] It deserves mention that for membranes based on heteropolyacid-doped sulfonated poly(ether ether ketone), the methanol permeability was more than 20 times lower than that of Nafion-117.[128]

Zirconium hydrogen phosphate is also often used to modify the Nafion membranes. First of all, its addition increases the moisture content in the membranes and allows membrane operation above 100 °C.[84, 86, 130–137] The proton conductivity of modified membranes is often somewhat lower as compared with original membranes[130, 133, 137, 138] and decreases with the increase in the zirconium phosphate content. Thus at 100 °C and 90% relative humidity, the conductivity of Nafion membranes containing 25 mass % of zirconium phosphate decreases from 0.07 to 0.03 S cm^{-1} (Ref. 135). At the same time, the introduction of a small amount of zirconium phosphate (1 mass % – 5 mass %) led to an increase in the conductivity of the MF-4SK membranes.[90] A quasi-elastic neutron scattering study has shown that the mobility of water molecules in Nafion membranes is virtually independent of the presence of zirconium phosphate nanoparticles.[139] The most valuable observation is that in the presence of zirconium phosphate, the high-temperature conductivity of membranes increases

and their mechanical properties are substantially improved.[134, 135]

The use of hybrid membranes containing 23 mass % of zirconium phosphate induces a 4-fold increase in the power of hydrogen–oxygen fuel cells (for a cell with Nafion-115 membranes, the power was ~ 0.44 W cm^{-2} at 130 °C).[131] The power of fuel cells with analogous membranes increased 1.5-fold under conditions of low humidity for the content of mesoporous zirconium phosphate of 5 mass %.[140]

Nafion membranes containing Teflon and zirconium phosphate were also used.[141, 142] Zirconium hydrogen phosphate improved the conductivity of sulfonated poly(ether ether ketone) [143–145] and polyvinyl alcohol.[146]

Among other dopants, several oxides of polyvalent elements should be mentioned. Thus, various modifications of titanium dioxide (including those shaped as nanotubes) were used for improving the properties of Nafion membranes [147–157] and membranes based on poly(ether ether ketone).[158, 159] Zirconium oxide was employed for this purpose more rarely.[150, 154, 160–163] The following oxides were used yet more rarely: Al_2O_3,[150] HfO_2, Ta_2O_5,[154] ZnO (Ref. 155) and WO_3 (Refs 54, 164) and also sulfonated titanium [165, 166] and zirconium oxides,[167–169] binary oxides (ZrO_2-SiO_2) [170] and gels based on silicon and phosphorus oxides.[171] An increase in the proton conductivity at high temperatures (> 100 °C) was achieved by modifying Nafion membranes with the $SiO_2-ZrO_2-P_2O_5$ (Ref. 172) or zirconium sulfophenyl phosphate [173] gels.

A hydrogen–air fuel cell with a Nafion–3 mass % TiO_2 membrane reached a power density of 514 mW cm^{-2} at 110 °C.[174] The modification of Nafion membranes with titanium dioxide containing sulfo groups was shown [164] to enhance their mechanical and thermal stability, decrease their methanol permeability and increase the power of fuel cells.

Considerable attention is paid to hybrid membranes with added nanoparticles of natural or synthetic materials (zeolites, alumina, silicates) [151, 175–189] or surface-modified particles of zeolites and silicates.[190–192] For instance, the modification with Laponite [187] sharply enhanced the physicochemical properties of sulfonated poly(aryl ether sulfone) and decreased its methanol permeability (the permeability was 1.55×10^{-7} cm^2 s^{-1} for the composite and 3.47×10^{-6} cm^2 s^{-1} for the initial membrane). The maximum power density of a fuel cell with such hybrid membrane reached 190 W cm^{-2} at 70 °C.

The use of nanosized zeolites modified with sulfo groups favours the retention of proton conductivity and a decrease in the methanol permeability.[193] Perhaps, the greatest success was achieved for the synthesis of functionalized nanoparticles in the Nafion membrane matrix.[181] The synthesized hybrid membranes containing 5 mass % of a filler retained their proton conductivity, while their methanol permeability decreased by 40%; as a result, the power of direct methanol fuel cells increased by 93% for the use of 5 M methanol solution.

Lately, modification of proton-conducting membranes also involved the use of nanostructured carbon materials. Thus, modification with C_{60} fullerene and fullerenol improved the transport properties of Nafion membranes in wide temperature and humidity ranges.[194] The introduction of single-walled carbon nanotubes into membranes did not affect the power characteristics of hydrogen – air fuel cells but substantially increased the mechanical properties for a low content of nanotubes.[195, 196] The proton conductivity of Nafion membranes was increased by almost an order of magnitude for 100% relative humidity as a result of introduction of single-walled carbon nanotubes (0.05 mass %) functionalized with sulfo groups.[197] This improved the mechanical properties and enhanced the power of a hydrogen–oxygen fuel cell the power density of which increased from 210 to 260 mW cm^{-2}.

To increase the proton conductivity, membrane materials can be doped with acids, similarly to the introduction of phosphoric acid into polybenzimidazole.[45, 198] Membranes with the high proton conductivity synthesized based on polyvinyl alcohol doped with phenolsulfonic acid were considered.[42, 199]

5. Causes of accelerated ion transport in hybrid membranes

The increase in ionic conductivity upon the formation of composite solid electrolytes is, as a rule, due to the increase in the defect concentration at the electrolyte/dopant interface by several orders of magnitude, which is caused by adsorption of some labile ions on the dopant surface.[200, 201] Therefore, such a characteristic as the affinity of the dopant particle surface for the protons of functional sulfo groups appears to be important. From this viewpoint, the optimal result should be reached by the introduction of a weak base, *e.g.*, polyaniline, into perfluorinated sulfonic acid membranes. The addition of small amounts of polyaniline (~ 2 vol.%) approximately doubles the membrane conductivity.[202] However, a further increase in its content leads to a rapid decay of conductivity because protons are excluded from the transport process (their abstraction from nitrogen atoms of polyaniline requires a large amount of energy).

This result can be considered as evidence for the fact that the MF-4SK conductivity is determined first of all by the proton transfer according to the vacancy mechanism. However, membranes containing silicon dioxide deposited in an acid medium are characterized by higher conductivity as compared with membranes containing silicon dioxide deposited in an alkaline medium,[117] although the latter is much more prone to proton adsorption. It should also be borne in mind that the dissociation constant of SO_3H groups in perfluorinated membranes such as MF-4SK is 10^6 (Ref. 14) and in a membrane containing considerable amounts of water molecules, the mentioned groups are completely dissociated. Hence, protons travel by the Grotthuss mechanism, *i.e.*, from one water molecule to another.[15] In this system, the electric charge can be carried by oxonium ions the concentration of which correlates with the content of functional groups. This is why the possibility that the majority of dopants (oxides, metal or polyaniline particles) may somehow be responsible for the increase in the defect concentration in perfluorinated membranes such as Nafion or MF-4SK is ruled out.

The increase in the moisture content upon the introduction of particles with hydrophilic surfaces is often considered as a possible reason for the higher conductivity.[71, 203] Indeed, in membranes modified with silicon or zirconium oxides, a certain increase in the moisture content was observed.[117, 204] However, for membranes doped by polyaniline [202] or silver particles with hydrophobic surfaces, the moisture content was found to decrease, whereas their conductivity could increase.[205]

To understand the reason for the higher conductivity of membranes containing dopants, one can compare their conductivities with the data obtained in NMR studies. The diffusion coefficients of protons found from ^{1}H NMR spectra are mainly determined by the migration of protons and water molecules in wide channels. These coefficients are much higher than the diffusion coefficients of protons calculated from the data on conductivity (Fig. 8),[206] the latter being limited by the proton migration through narrow channels. In this case, the ^{1}H NMR relaxation rate in composite membranes may be either higher or lower than that in initial systems, whereas the composite conductivity is higher.[206] Hence it can be concluded that the higher ionic conductivity of hybrid membranes is first of all associated with the dopant effect on the ion transport in channels.

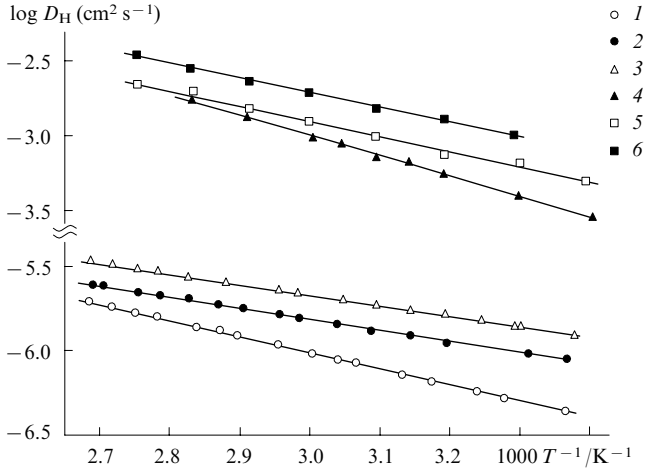


Figure 8. Temperature dependences of the proton diffusion coefficients calculated from proton conductivity values (*1–3*) and NMR spectroscopy data (*4–6*) for MF-4SK membrane.[206] (*1*, *5*) Unmodified membrane; (*3*, *6*) silicon dioxide-modified membrane; (*2*, *4*) zirconium hydrogen phosphate-modified membrane.

The dopant nanoparticles are formed in membrane pores to which the precursor and the reagent have penetrated. It would seem obvious that occupying a certain volume of pores, nanoparticles should displace water from them. However, the moisture content is determined by water binding to the protons of functional groups and the number of these groups does not change with modification. Hence, the number of water molecules in the matrix should remain unchanged (or somewhat increase due to additional adsorption of hydrophilic particles on the surface). Indeed, according to calculations carried out based on the thermogravimetric data, the overall volume of pores increased ~1.5-fold after the introduction of 2.6 vol.% SiO_2.[207] Upon the addition of hydrophobic particles, the moisture content of membranes somewhat decreases; however, in this case, too, the pore volume increases.

An increase in the number of pores naturally results in the increase in the volume of channels that connect the pores (Fig. 9 *a*,*b*),[205] which in turn accelerates the transport of protons through narrow channels (the process that determines the conductivity of membrane as a whole). This should obviously be accompanied by a decrease in the activation energy of conductivity which gradually

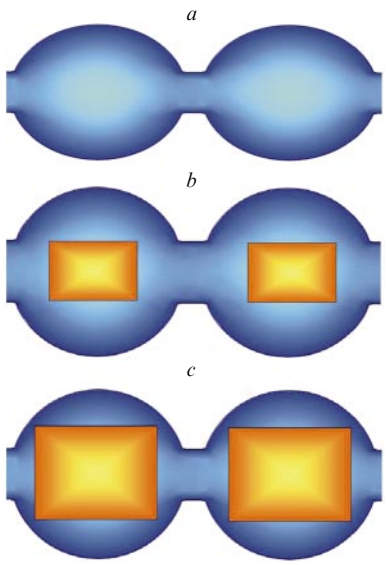


Figure 9. Pore structure for the original (*a*) and nanoparticle-modified membranes (*b*, *c*) in terms of the model of the limited elasticity of pore walls.[205]

approaches the activation energy for the transport in the pores. In the ideal case, this value can approach the activation energy of conductivity of aqueous acid solutions equal to ~5 kJ mol^{-1}.

At the same time, as the volume fraction of nanoparticles exceeds 3 vol.%–4 vol.%, the conductivity decreases (see Fig. 7) and the activation energy increases. This is accompanied by a decrease in the moisture content of membranes and a slight increase in the pore size. Taking into account the aforesaid, it can be assumed that the elasticity of pore walls is limited. Naturally, as the pore volume increases, the efforts needed for their widening should increase. In accordance with Hook's law, each part of the pore surface experiences the impact of an elastic force (pressure) which is in direct proportion to the strain.[207]

Obviously, the driving force of pore widening is a decrease in the chemical potential of water inside the pores due to the interaction of water with protons and fixed SO_3^- ions, which have formed through dissociation of functional groups. This force is determined by the osmotic pressure. Under equilibrium conditions, the elastic forces and the osmotic pressure level off. Another possible reason could be the electrostatic and van der Waals forces, which favour the self-assembling processes in membranes. Thus, the widening of pores increases the distance between SO_3^- groups. This should be accompanied by the appearance of energetically less favourable contacts between the hydrophobic matrix sites containing polar water molecules in pores and the oxonium ions in solution. This would increase the system energy and, as a consequence, give rise to counteracting compressive forces.

According to qualitative estimates,[207] an increase in the content (size) of hydrophobic dopant particles should lead to a decrease in the moisture content of membranes, the same as for the metal and polyaniline particles.[202, 205] For hydrophilic particles, the moisture content passes through a maximum at a low dopant concentration, as in the case of silicon and zirconium oxides.[207] Thus, at a high dopant

content, the increased elastic forces prevent further widening of pores and favour a decrease in the moisture content.

Based on this model, the decrease in the conductivity at high concentration of nanoparticles can be related to a decrease in the solution mobility inside the membrane pores where the dopant occupies a part of pore volume and blocks the conduction channels. Moreover, new narrow channels between pore walls and dopant particles are formed, which limits the conductivity (Fig. 9 *c*).

The proposed model has its physicochemical substantiation in which an allowance for the nature of dopant particles can be made by considering their susceptibility to hydration. For instance, doping a membrane with silicon and zirconium oxides is very efficient due to the sorption of additional water molecules on their hydrophilic surface. At the same time, the nature of dopant particles can substantially affect the membrane conductivity. As mentioned above, silicon dioxide nanoparticles deposited from an acidic medium enhance the conductivity more efficiently than analogous particles deposited from an alkaline medium.[117] Dissociation of OH surface groups of silicon hydroxide deposited in an acidic medium affords additional protons which simultaneously act as charge carriers and capture additional water molecules. This is why to make doping more efficient, strong acids should be added. Then the concentration of charge carriers increases due to dopant protons. This can be achieved by simultaneous modification of the membrane with both silicon dioxide and heteropolyacids.[117]

One of the chief merits of hybrid membranes is the possibility of fuel cell operation at low environmental humidity; under these conditions, the conductivity of conventional membranes decreases by several orders of magnitude.[16, 71] Lowering down the humidity leads to gradual degradation of membranes and a dramatic decrease in the pore and channel volume as a result of which the conductivity decays. In hybrid membranes, a part of pore volume is occupied by dopant particles, which prevents sharp narrowing of the pores. For 10% relative humidity, the pore volume in a membrane containing 4 vol.% of silicon dioxide is doubled as compared with the original MF-4SK membrane; as a consequence, the size of channels connecting the pores is also greater.

At the same time, inside the pores, narrow segments appear which limit the proton transfer by the Grotthuss mechanism.[208] This effect also cannot be considered as the only one. For high humidity, a proton is transferred between closely spaced water molecules with equal proton affinity (Fig. 10 *a*). In this process, the functional groups localized on the membrane pore walls are barely involved. A decrease in humidity leads to membrane dehydration. However, according to NMR data,[209] protons in dehydrated MF-4SK membranes are present in the form of $H_5O_2^+$ ions bound exclusively by hydrogen bonds to SO_3^- groups, which have much lower proton-acceptor ability than water molecules. In this case, the direct proton transfer between $H_5O_2^+$ cations is complicated due to the high enthalpy of proton transfer reaction

$$H_5O_2^+ + H_5O_2^+ \longrightarrow 2\,H_2O + 2\,H_3O^+. \qquad (2)$$

Of no less importance is the fact that these groups are remote from one another (Fig. 10 *b*). Even for a low humidity, the transport between them by means of the remaining water molecules is hampered. Under these conditions, the proton conductivity is limited by proton hopping. As the distance between oxygen atoms of proton-containing groups involved in the transfer increases, the activation energy for these hops also increases and their frequency drops down.[210] The role of pore walls in the transfer inevitably increases.

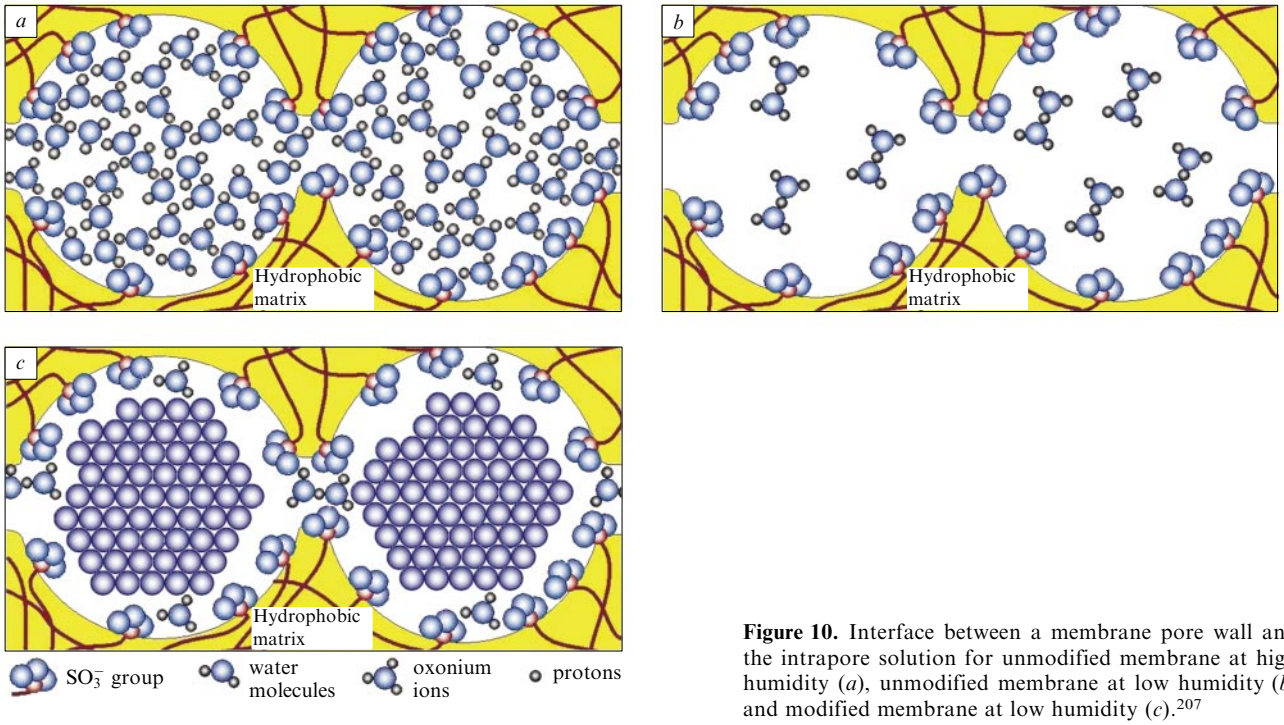


Figure 10. Interface between a membrane pore wall and the intrapore solution for unmodified membrane at high humidity (*a*), unmodified membrane at low humidity (*b*) and modified membrane at low humidity (*c*).[207]

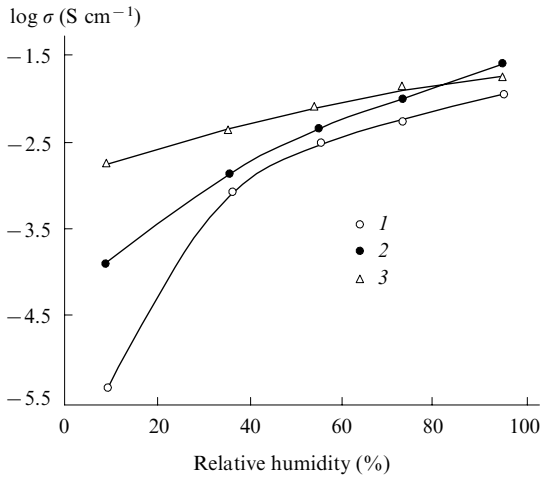


Figure 11. Conductivity *vs.* the relative humidity at 25 °C for different membranes.[117]
(*1*) MF-4SK, (*2*) MF-4SK + SiO_2, (*3*) MF-4SK + SiO_2 + $H_3PW_{12}O_{40}$.

The pores of hybrid membranes contain a considerable number of oxygen-bearing groups which also can take part in the proton transfer process (Fig. 10 *c*). This substantially shortens the hop length. Most probably, this factor makes the main contribution to the gain in the conductivity of hybrid membranes at low humidity. This is why under these conditions their conductivity turns out to be substantially higher than the conductivity of non-doped membranes.[207]

Note that the nature of the doping agent surface has a considerable effect on the conductivity.[117] Thus co-doping of a membrane with silicon dioxide and a heteropolyacid induced a more than an order of magnitude increase in its conductivity for 10% humidity as compared with the membrane doped only with SiO_2 (Fig. 11). This is associated with the introduction of an additional number of acidic charge carriers (protons) and weakening of the proton-acceptor ability of the dopant particles.

III. Nanostructured electrocatalysts

1. The main electrochemical processes in hydrogen and direct methanol fuel cells

In fuel cells, air oxygen serves in most cases as the oxidant. The choice of fuel is determined by its cost, chemical activity and energy density. Hydrogen is still the most promising fuel, being the only fuel oxidized at a reasonable rate which influences the fuel cell efficiency. However, the hydrogen storage and its delivery to the anode present additional complications. This is why, liquid fuels such as, *e.g.*, alcohols, seem to be the more rational choice for future applications.

Oxygen electroreduction at the cathode is a slow process as compared with anodic reactions. For instance, the effective current density of hydrogen oxidation (i_a^0) equal to 0.1 A cm^{-2} substantially exceeds that of oxygen reduction (i_k^0 = 6 A cm^{-2}).[211] Moreover, intermediate products capable of activating the corrosion processes on electrode material are formed on the cathode. Hence, the service life and the work characteristics of fuel cells are largely determined by electrochemical properties of the cathode. In hydrogen–air fuel cells, the oxygen reduction [Table 6, reaction (4)] is the main cathodic process.

Table 6. Oxidation reactions in fuel cells (cathodic and anodic half-reactions and the overall process) and the corresponding standard potentials.

Electrochemical reaction			E^0/V
Hydrogen as the reactant			
Anode	$H_2 \rightarrow 2H^+ + 2e$	(3)	0.000
Cathode	$2H^+ + 2e + \frac{1}{2}O_2 \rightarrow H_2O$(liquid)	(4)	1.229
Overall reaction	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$(liquid)	(5)	1.229
Methanol as the reactant			
Anode	MeOH(liquid) + $H_2O \rightarrow$ $\rightarrow CO_2 + 6H^+ + 6e$	(6)	0.016
Cathode	$6H^+ + 6e + \frac{3}{2}O_2 \rightarrow 3H_2O$(liquid)	(7)	1.229
Overall reaction	MeOH + $\frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$(liquid)	(8)	1.213

The efficiency of energy conversion is mainly limited by kinetic factors. According to Wang,[212] the following mechanisms can be distinguished for oxygen reduction on platinum:

— oxygen can be reduced directly to H_2O with the uptake of four electrons (direct electroreduction of oxygen);

— oxygen reduction may include the intermediate formation of H_2O_2 without the O–O bond cleavage, which is followed by transformations of hydrogen peroxide.

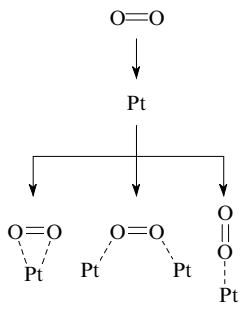
The most attractive process is the oxygen reduction to water molecules by the four-electron mechanism. The incomplete reduction of oxygen to H_2O_2 is characterized by not only lower efficiency of energy conversion but also the appearance of free radicals, which activate the corrosion processes on electrode materials and in the membrane.

The first stage of the cathodic process is the interaction of O_2 molecules or oxygen-containing species with the adsorption sites on the catalyst surface. There are three models of oxygen adsorption (Scheme 1) on the Pt electrode surface:

— the Griffiths model (the oxygen π-orbital interacts partly with unoccupied orbitals of an electrode metal atom);

— the 'bridge model' (oxygen adsorption involving two adsorption sites);

Scheme 1



— the Pauling model (only one oxygen atom in a molecule is involved in the reaction with a metal atom).

The majority of scientists assume that on the platinum electrode, the first two adsorption types are realized, *i.e.*, those favouring the oxygen molecule dissociation and the four-electron reaction mechanism.[213]

The hydroxyl and oxide groups (intermediates in oxygen reduction) adsorbed on the surface are also catalytic poisons. This is why the oxygen reduction on the oxidized platinum surface proceeds more slowly than on 'clean' platinum.[213–215]

By using platinum alloys, one can achieve acceleration of the oxygen reduction reaction, because on the surface of such alloys the $(OH)_{ads}$ formation on platinum atoms may be inhibited (due to the joint effect of the surface geometry and the electronic structure).[216] According to certain data,[217] the adsorption of hydroxyl groups on alloys can start at more positive potentials (for Pt/C, this value is, as a rule, >0.8 V).[218]

The quest for methods that would enhance the activity of cathodic catalysts should be directed to the development of new materials capable of activating the oxygen reduction *via* the four-electron mechanism and also resistant to poisoning with oxygen-containing adsorbates.

In the mechanism of electrochemical oxidation of hydrogen on platinum (M), the following two stages can be singled out: the slow dissociation of hydrogen molecules and their subsequent fast electrochemical oxidation.[219]

$$H_2 + 2M \rightleftharpoons 2MH \text{ (Tafel reaction)}, \quad (9)$$

$$2MH \rightleftharpoons 2M + 2H^+ + 2\bar{e} \text{ (Volmer reaction)}. \quad (10)$$

As a rule, hydrogen fuel contains trace amounts (ppm units) of a catalytic poison, carbon monoxide (CO). Despite the preferential CO adsorption on platinum, the hydrogen oxidation even on the remaining small areas of free platinum surface proceeds so quickly that induces a potential of the anode. Unfortunately, this potential is lower than that required for CO oxidation so that the surface coverage with carbon monoxide is determined by the CO adsorption isotherm. Thus, the current density or the rate of hydrogen oxidation in the presence of CO can be described as follows:

$$i_{H_2/CO} = i_{H_2}(1-\Theta_{CO})^2, \quad (11)$$

where Θ_{CO} is the catalyst surface coverage with CO molecules.

The effective activation energy of hydrogen oxidation increases with the increase in the concentration of CO whose molecules are preferentially adsorbed on the sites most suitable for hydrogen oxidation.[220] As a result, the current density dramatically decreases (Fig. 12). To enhance the activity of catalysts and improve their CO tolerance, different approaches are used which are discussed below.

The methanol oxidation on the anode is described by Eqn (6) (see Table 6). The methanol chemisorption on Pt catalysts proceeds through the stage of formation of irreversibly adsorbed CO groups (reaction intermediate) bound to the surface.[221] In the process, the surface coverage of the Pt electrode with carbon monoxide can reach 90% so that the majority of active sites are occupied.

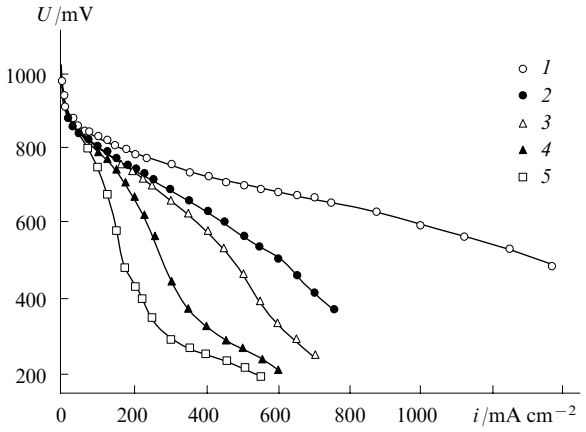


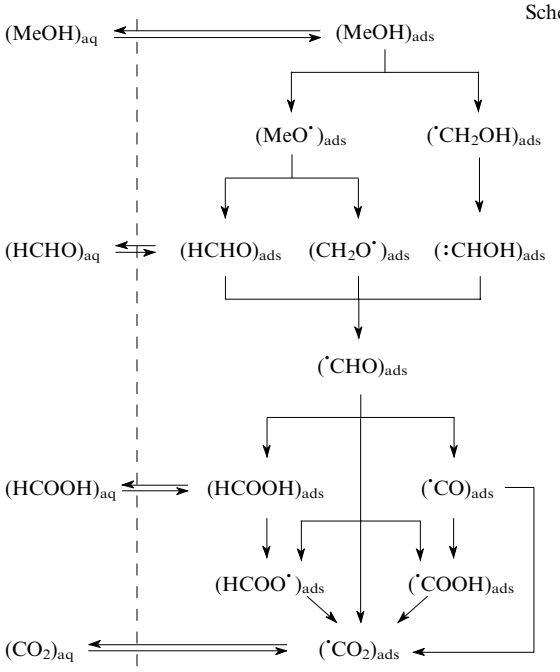
Figure 12. Effect of CO impurity in hydrogen on current voltage characteristics of a fuel cell (Nafion membrane 80 °C, $p_{H_2} = 0.22$ MPa, $p_{O_2} = 0.24$ MPa).[220]
CO content/ppm: (*1*) 0, (*2*) 25, (*3*) 50, (*4*) 100, (*5*) 250.

Scheme 2 illustrates the mechanism of methanol oxidation on the Pt electrode. The reaction can proceed simultaneously by several parallel routes. It was shown that methanol may be oxidized relatively fast to afford weakly bound active intermediates formed from MeOH and OH group, which are quickly oxidized to CO_2.[222,223]

The processes of CO adsorption and desorption depend strongly on the potential and specific features of the metal surface.[224] For CO to be oxidized to CO_2, the adsorbed an OH groups should be available.[225]

The development of efficient electrocatalysts should address systems capable of inhibiting the CO formation on the surface or favourable for the CO oxidation at lower potentials than on clean platinum and also for the formation of adsorbed OH and CHO groups.[221] This is achieved by using platinum alloys with other metals or by platinum deposition on oxide supports.

Scheme 2



2. Platinum catalysts for fuel cells. The size effect

The first studies in the field of low-temperature fuel cell technology employed relatively large amounts of platinum black (up to 30 mg Pt per cm^2 of the electrode surface), which determined the high cost of the resulting catalyst. The transition from platinum black to supported catalysts (*e.g.*, on carbon black) allowed the platinum consumption to be reduced to 0.3–0.4 mg Pt per cm^2 of the catalyst surface [226] with the retention of fuel cell power characteristics.[227, 228]

Many electrocatalytic processes are characterized by the so-called structural effects associated with the influence of the platinum particle surface orientation and size. For instance, the activity of crystal faces in the oxygen electroreduction (in sulfuric acid solution) increases in the following order:[229, 230]

Pt(111) < Pt(100) < Pt(110).

The size effect on the activity of platinum catalysts is demonstrated by cyclic voltammograms (Fig. 13). The decrease in the grain size is accompanied by an increase in currents of both processes that occur in the fuel cell. The optimal particle sizes reported by different authors somewhat differ (which is caused by different catalyst pretreatment procedures and different reaction conditions). Thus it was shown [231] that the optimal specific activity for platinum in the reaction of methanol electrooxidation was reached for the particle diameter of 3 nm; the specific activity was observed [232, 233] to weaken for the particle size < 4.5 nm; for the reaction of oxygen electroreduction (in 0.1 M $HClO_4$ solution), the optimal size of platinum particles was found to be ~2.8 nm. [234]

For stabilization of platinum in its highly dispersed nanocrystalline state, highly dispersed supports are used, which makes it possible to increase the catalytically active platinum surface to the maximum extent with reducing the platinum consumption. Moreover, in some cases, the support can take part in the catalytic process at three-phase boundaries, increasing the electronic conductivity of the catalytic layer, its CO tolerance and the stability of metal clusters.

Today, the majority of commercial catalysts used in low-temperature fuel cells represent platinum (or a platinum-based alloy) dispersed on a support (carbon black). The use of carbon black increases the degree of dispersion of platinum due to the high porosity and the metal interaction with the support.[229] The size of metal nanograins in commercial catalysts is in the 2.5–5 nm range for the metal content varying from 5 mass % to 80 mass %.[235, 236]

Among the companies manufacturing carbon black-supported platinum catalysts, best known are E-TEK and Johnson Matthey (the Hispec brand) (Table 7) and also BASF (the Selectra Catalysts brand). Catalysts supported on carbon nanotubes are commercially available (manufactured by the German company HIAT). The US Company 3M produces platinum catalysts deposited on nanowhiskers (Fig. 14).

Table 7. Average size of platinum particles (d) and specific surface area (s) of catalysts manufactured by Johnson Matthey and E-TEK.[235, 236]

Catalyst	d/nm	s/m^2 (g Pt)$^{-1}$
Product of Johnson Matthey (UK)		
37 mass % Pt/AC 01	2.3	130
57 mass % Pt/AC 01	2.8	85
Product of E-TEK (Germany)		
67 mass % Pt/AC 01	3.5	60
10 mass % Pt/Vulcan XC72R	2.0	140
20 mass % Pt/Vulcan XC72R	2.5	112
40 mass % Pt/Vulcan XC72R	3.9	72
Pt (black)	100	28

Note. AC 01 and Vulcan XC72R are carbon black brands.

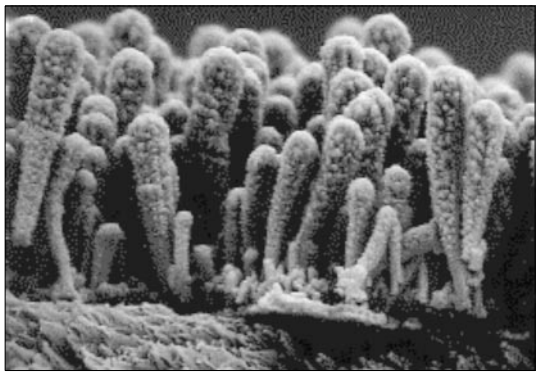


Figure 14. Photomicrograph of a catalyst manufactured by 3M Company (according to http://www.jmfuelcells.com). Nanowhiskers, frame size 750 × 750 nm.

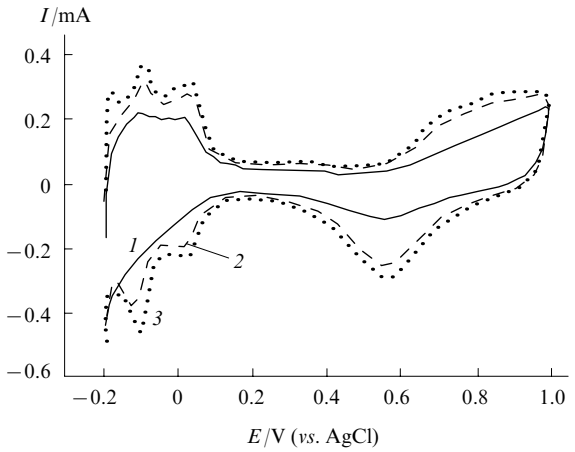


Figure 13. Voltammograms of processes proceeding in the presence of a Pt/carbon black catalyst (0.5 M H_2SO_4, 298 K) with grain size of 4.2 (*1*), 3.5 (*2*) and 2.9 nm (*3*).[228]

The main drawbacks of platinum catalysts may include their degradation during long-term service within a fuel cell, which occurs by the following mechanisms: dissolution, aggregation of particles and poisoning by carbon monoxide for catalysis deposited on the anode or by oxygen-containing groups for the cathodic reduction of oxygen, *etc.*[237] Moreover, the use of platinum catalysts is complicated by their contamination with oxidation products of methanol or ethanol.

For carbon-supported catalysts, the most serious problem is the corrosion of carbon. Its oxidation in the presence of moisture is described by the following equations:

$$C + 2H_2O \longrightarrow CO_2 + 4H^+ + 4e, \quad (12)$$

$$C + H_2O \longrightarrow CO + 2H^+ + 2e. \quad (13)$$

The standard potentials of these reactions are 0.207 and 0.518 V, respectively.[238] At these potentials, carbon is oxidized very slowly; however, at long-term fuel-cell operation, the carbon content in catalytic layers is depleted.[239] A carbon support can be oxidized by air oxygen and also by hydrogen peroxide formed as a by-product of oxygen electroreduction on platinum catalysts.[238]

$$C + H_2O_2 \longrightarrow (CO)_{ads} + H_2O, \quad (14)$$

$$(CO)_{ads} + H_2O_2 \longrightarrow CO_2 + H_2O. \quad (15)$$

In both cases, platinum can accelerate the degradation of catalytic layers.[239] The corrosion of carbon supports leads to detachment of platinum particles, their aggregation and isolation, which seriously affects the fuel cell performance (Fig. 15).

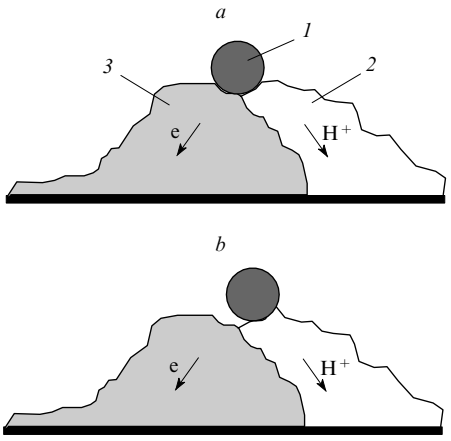


Figure 15. Illustration of the original (*a*) and coordinated (*b*) states of the platinum – carbon – ionomer three-phase contact.
(*1*) Metal particle (active site), (*2*) ionomer, (*3*) carbon support.

Two most promising ways of improvement of catalyst properties may be as follows:

— elaboration of catalytic systems based on transition metal alloys with platinum;

— development of highly efficient corrosion-resistant methanol and ethanol tolerant catalysts by using nanostructured oxide materials as the supports.

A support for catalysts in a fuel cell should exhibit the high electronic conductivity and have a large specific surface area and also be resistant to corrosion and oxidation. These requirements severly narrow the range of materials suitable as supports. Conducting metal oxides and polymers and also certain metal carbides, nitrides and phosphides are used most often as alternatives to carbon.

3. Bimetallic catalysts used in low-temperature fuel cells

The chief drawback of platinum catalysts is their degradation on long-term work within a fuel cell, which may occur by different mechanisms (see above). Due to diffusion of alcohols through membranes, the use of platinum catalysts (even as cathodes) is complicated by their poisoning with oxidation products of alcohols. Moreover, the natural resources of platinum are limited and this metal is quite expensive. To solve the concomitant problems, multicomponent catalytic systems based on platinum with the introduction of other cheaper metals that impart the desired properties to the catalysts are being developed. For example, the use of platinum alloys can enhance the catalyst stability and increase its service life. According to several studies,[240–244] alloy particles exhibit a weaker trend for agglomeration as compared with platinum clusters. This is associated with the decrease in mobility of alloy particles on a support; furthermore, the alloying metals suppress the support dissolution. However, the majority of alloys are insufficiently stable when used in a fuel cell.

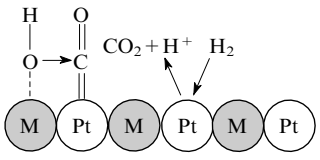
Several main trends can be distinguished in the development of CO-tolerant anodic catalysts. As compared with pure platinum, the bimetallic Pt-containing catalysts can be much more tolerant to CO present in the fuel. As the second element, Ru, Sn, Ge, Co, Cr, Fe, Ni, Pd, Os, Mo, Mn, *etc.* may be chosen. Such catalysts are used in the form of metal alloys or clusters deposited on platinum.[245–250] The most efficient binary Pt-based catalytic systems to be used with the $H_2 + CO$ mixture and methanol as fuels are the Pt–Ru/C catalysts [251–254] which were studied by several authors.[243, 254–258]

In several cases, three-component catalysts based on Pt–Ru alloys were shown to exhibit electrocatalytic activity comparable with that of Pt/C or Pt–Ru/C catalysts.[259–266] Attention is focused on Pt and Ru alloys with Ni, Pd, Co, Rh, Ir, Mn, Cr, W, Zr and Nb. Platinum alloys with Fe, Ni, Co, Mo and Ru proved to be highly CO-tolerant demonstrating adequate stability in the H_2 oxidation in the presence of 100 ppm CO.[266]

To remove $(CO)_{ads}$ from the surface, it is necessary that oxygen-containing groups be present in the neighbouring surface sites and be capable of oxidizing the adsorbed carbon monoxide to CO_2, thus freeing the platinum surface sites required for hydrogen oxidation. The bifunctional mechanism according to which ruthenium activates the processes of water chemisorption and CO electrooxidation on the neighbouring platinum atom was proposed [245] (Scheme 3) and confirmed later by many research groups.[245, 267–271] Perhaps this mechanism also predominates for catalysts based on Pt–M alloys (M = Sn, Mo, *etc.*) [245, 246, 248, 272, 273] and also on platinum with the surface modified with ruthenium,[274–276] molybdenum [255, 256, 277–279] or tin.[280–283]

Scheme 3

$$Pt-(CO)_{ads} + M-OH = Pt + CO_2 + H^+ + M + e$$



However, the bifunctional mechanism ignores the possible variations of the CO binding energy on platinum associated with the presence of ruthenium and fails to describe the effect of competitive adsorption of CO and OH groups on the ruthenium surface. The origin of this

effect is still unclear. On the one hand, according to the model discussed by Camara *et al.*,[283] the Fermi level shifts. As a result, the interaction energy between platinum and $(CO)_{ads}$ changes. This 'ligand effect'[284–286] weakens the Pt–CO bond and facilitates the electrooxidation of carbon monoxide by OH groups on the platinum surface or, alternatively, by means of activation of water chemisorption on the platinum surface.

Lately, the cathodic catalytic schemes based on transition metal alloys with platinum that are tolerant to simple organic fuels and have electrocatalytic characteristics comparable with those of platinum catalysts have been actively elaborated.[287–289] The higher electrochemical activity of alloys in the oxygen reduction is mainly associated with structural and electronic effects as well as with inhibition of formation of $(OH)_{ads}$ groups.

According to certain data,[287–301] the higher activity of platinum-based alloys is associated with a decrease in catalyst lattice parameters and, hence, in the distance between the neighbouring platinum atoms. Presumably, the decrease in the Pt–Pt bond length favours the formation of active sites more advantageous for oxygen adsorption. Thus, the formation of platinum alloys with certain metals of smaller atomic radii enhances the catalytic activity. On the other hand, an increase in the lattice parameters (as a result of introduction of metals with larger atomic radii) impairs the catalytic properties (Fig. 16).[290]

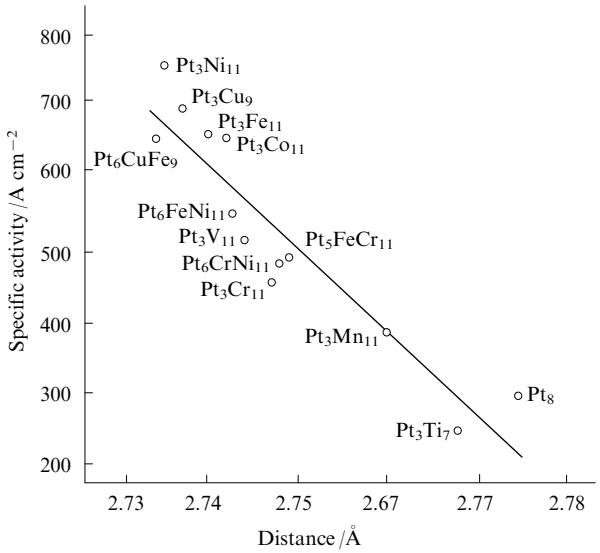


Figure 16. Catalytic activity *vs.* the distance between the closest platinum atoms in alloys.[290]

The relationship between the electronic structure of the surface of intermetallic compounds Pt_3M (M = Ni, Co, Fe, Ti, V) and their catalytic activity in the oxygen reduction reaction was studied.[291] In the researchers' opinion, to exhibit higher catalytic activity, a platinum alloy should meet two opposite requirements:

— provide considerably high energy for adsorption of O_2 and intermediates (O^{2-}, O_2^{2-}, H_2O_2, *etc.*);

— favour relatively low surface coverage with oxygen-containing groups and specifically adsorbed anions.

When oxygen is strongly bound to the catalyst surface, the rate of oxygen reduction is limited by the rate of oxide removal from the surface. Conversely, if the catalyst binds oxygen too weakly, its reduction is limited by the rate of electron and proton transfer to adsorbed oxygen. These effects usually correlate with one another. For instance, the $Pt_3Ni(111)$ catalyst with an atomic platinum layer on the surface exhibits high activity in the oxygen reduction, which is 90 times higher than the characteristics of commercial Pt/C catalysts. This is attributed to the joint effect of the surface geometry, electronic structure and adsorption properties of this catalyst.[292]

According to experimental data,[216,217,293–297] the optimal ratio of elements in Pt–M alloys (M = Fe, Co, Ni, Mn, Cr) is ~7:3. Tafel plots of oxygen reduction (Fig. 17) suggest that in the presence of these alloys, the electrode potential is 20–30 mV higher than in the presence of platinum, which corresponds to a 2–5-fold increase in the catalyst specific activity. A Pt–Cr alloy demonstrated the best catalytic characteristics.[294]

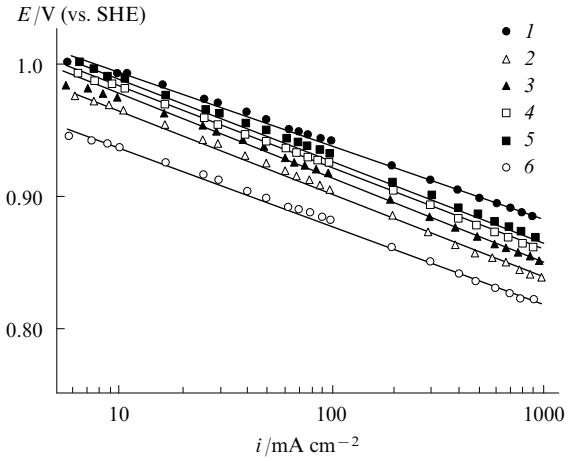


Figure 17. Tafel plots of oxygen reduction on various binary platinum alloys (90 °C, 5 atm).[294] (*1*) Pt–Cr/C, (*2*) Pt–Ni/C, (*3*) Pt–Co/C, (*4*) Pt–Mn/C, (*5*) Pt–Fe; for a comparison, the values for a Pt/C catalyst are shown (*6*). Metal load: 0.3 mg cm^{-2}.

When Pt–M alloys are used, the electrode potential increases by 20–40 mV for M = Ti, Mn, Fe.[297] For these alloys, the effective Tafel slopes were found to be similar, which points to related mechanisms of oxygen reduction on the catalysts made of these alloys and pure platinum. The electrocatalytic activity of thin Pt–Ni, Pt–Co and Pt–Fe films synthesized by magnetron sputtering was studied.[294,297–299] The highest current density at $E = 0.76$ V was demonstrated by binary platinum alloys containing ~30 mass % of Ni, 40 mass % of Co and 50 mass % of Fe. The current densities on these alloys exceeded the corresponding value for pure platinum by factors of 10, 15 and 20, respectively. Thus, under the conditions of fuel cell operation, Pt alloys can exhibit specific catalytic activity higher than pure platinum.

The mechanisms of oxygen adsorption and reduction on Pt_3M (M = Co, Ir) catalysts with the core–shell structure were studied by quantum chemical calculations based on the density functional theory.[300] The challenge was to find the

way for designing a nanostructured catalyst for fuel cells that would reproduce the highest electronic and morphological properties of the best catalysts and provide durable operation of fuel cells. Such experiments were carried out by several Russian scientists. Thus highly efficient catalysts containing platinum, cobalt and chromium or platinum, cobalt and palladium were synthesized by Tarasevich and co-workers.[301–304] Acid treatment of the catalysts resulted in the removal of cobalt and chromium from the surface to form a typical core–shell structure. The shell should be relatively loose and have a large surface area. Catalyst samples successfully passed lifetime trials:[303] despite their substantially lower platinum content (approximately half), they surpassed their commercial analogues in the activity. Samples of nanostructured catalysts based on platinum-coated transition metals were synthesized (Fig. 18).[305] The electron diffraction patterns of such materials demonstrated reflections from both the transition metal and platinum coating crystal lattices.

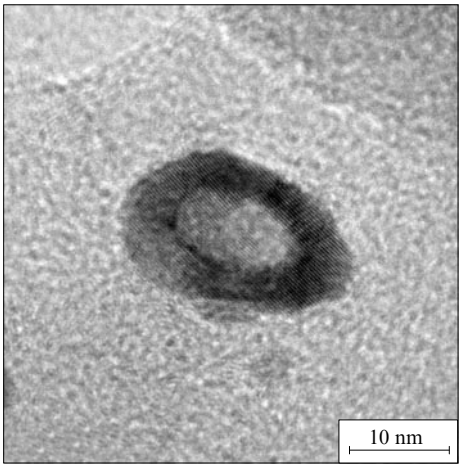


Figure 18. Electron microscopic image of a copper particle in a platinum shell.

When comparing the data obtained to date, one can draw a more substantiated conclusion on the origin of the higher activity of bimetallic catalysts in the oxygen reduction and their tolerance to CO traces. Insofar as the active surface of such catalysts is formed by platinum, the possibility that the effect of bifunctional catalysis manifests itself is virtually zero. Hence, it seems more justified that the main contribution to the improvement of properties of these catalysts is made by the shift of the Fermi level of outer d-electrons as a result of the 'ligand effect' from the more active metal.

4. Nanostructured carbon supports

The activity and stability of a catalyst strongly depends on its support. At present, a variety of nanostructured carbon materials were proposed as the supports for electrocatalysts, namely, single- and multi-walled nanotubes, fibres, fullerene soot, *etc*. The length of fibres can reach several micrometres and their diameter is 10–200 nm; the diameter of carbon nanotubes can amount to 0.3–10 nm and their length reaches several hundreds of micrometres.

It is assumed that conducting carbon nanotubes or nanofibres with large specific surface areas could replace the conventionally used graphite and specially treated carbon black. The use of nanostructured carbon materials can increase the efficiency of catalysts, reduce the consumption of platinum group metals, extend the service life of catalysts[305] and decrease their sensitivity to carbon monoxide.[306–309] The maximum efficiency was demonstrated by catalysts based on 'stack'-type carbon nanofibres.[310] In addition, success was achieved in the development of carbon supports with the graphite structure[311] and also of amorphous supports.[312]

Optimal properties are obtained when the catalyst is formed directly on a carbon support. To strengthen the bond between the catalyst and the support material, the surface of the latter is pre-modified. The most widely used modification method is treatment of the carbon material surface with acids.[309–313] The best characteristics were demonstrated by samples prepared with the use of carbon nanotubes or nanofibres treated with a mixture of nitric and sulfuric acids. Such pretreatment gives rise to the maximum number of oxygen-containing groups on the support surface. The treatment with potassium persulfate proved to be an efficient oxidation method giving a good yield of carboxyl groups.[314] The electrochemical modification of carbon nanostructures aimed at their covalent binding to diazonium salts or phenol derivatives was also used.[315, 316] Another version of surface modification by creating surface defects is plasma treatment of the surface.[317–321]

The procedure of catalyst preparation on such materials involves the deposition of platinum complexes on the modified support surface followed by their reduction (Fig. 19). Metal clusters measuring ~2 nm are uniformly distributed over the surface of carbon nanotubes (Fig. 20).[322, 323]

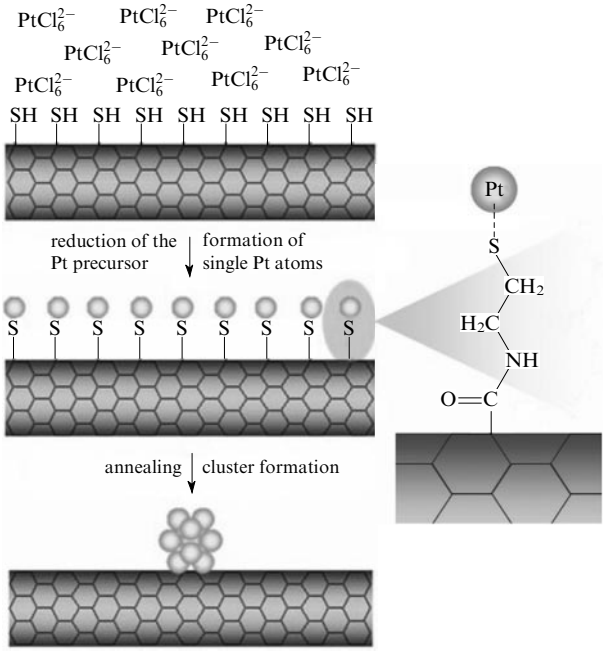


Figure 19. Scheme of the synthesis of platinum clusters.[322]

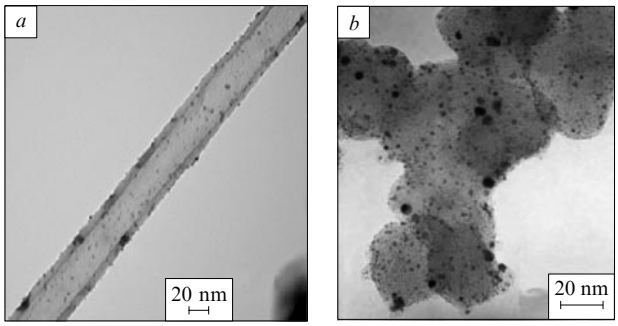


Figure 20. Photomicrographs of platinum on multi-walled carbon nanotubes (*a*)[322] and carbon black (*b*).[323]

Lately, the attention of scientists was focused on the development of the colloidal method of preparation of platinum catalysts.[323–326] The reduction of platinum is carried out in solutions of highly viscous substances (*e.g.*, ethylene glycol) or in the presence of surfactants. Due to the more uniform distribution of particles in solution, this provides an additional possibility of controlling the size distribution of catalyst clusters.[327–329] Platinum can also be deposited on carbon supports by electrochemical methods. For example, platinum catalysts were synthesized[330, 331] by an electrochemical procedure according to which platinum was deposited on a porous carbon paper impregnated with dispersed carbon particles, Teflon and Nafion.

5. Oxide-based supports

Unfortunately, carbon materials are insufficiently stable in the oxidative medium of fuel cells. In connection with this, the search is carried out for non-carbon support materials. The growing number of recent studies have been devoted to metal oxides (MO_x), which are not only more corrosion-resistant in oxidative media than carbon materials but also may act as promoters in the oxygen electroreduction (for example, MnO_x, SiO_2, WO_x, NbO_2, TiO_2)[332–343] or methanol and CO oxidation (for example, RuO_2, SnO_2, TiO_2, Nb_2O_5).[344–350] Nanoparticles of MO_x can be either dispersed on the support surface together with platinum particles[343, 351–354] or used as the supports for catalysts.[355, 356]

The oxides used as the supports are most often semiconductors. To enhance their electronic conductivity, it is the practice to use non-stoichiometric compositions (*e.g.*, Ti_4O_7), doped tin and titanium dioxides, nanostructured oxides (*e.g.*, TiO_2 nanotubes, WO_3 nanorods), *etc*. Sometimes, the support represents a non-conducting oxide with the addition of a conducting phase (*e.g.*, soot, tungsten carbides and nitrides, *etc*.).

Platinum catalysts deposited on nanostructured titanium dioxide (nanorods, nanoribbons, nanowires, *etc*.) were shown[357–366] to exhibit high catalytic activity in oxygen reduction and methanol oxidation and also high electrochemical stability. The authors[363–366] attributed this to the high stability, large specific surface area and adequate conductivity of nanostructured TiO_2. Moreover, the support nanostructure may provide a better distribution of the catalyst and formation of a catalytic layer having a porous structure, which makes easier the access of reactants to the electrochemical reaction zone and enhances the catalytic activity.[367]

Titanium dioxide is a wide band gap semiconductor with a band gap of 3.23 eV.[368] The electronic conductivity of TiO_2 is low ($\sim 10^{-13}$ S cm^{-1}) but it increases as it is partially reduced. The reduction products with the general composition Ti_nO_{2n-1} are known as the Magnelli phases. The electronic conductivity of a commercial electrode material based on Ti_4O_7 (Ebonex, manufactored by Atraverda Ltd, UK) is close to 10^3 S cm^{-1}, which is comparable with the conductivity of graphite. This material proved to be electrochemically stable in sulfuric acid solutions in the potential range from 0 to 2 V *vs*. SHE in 1 M sulfuric acid at room temperature.[369, 370]

The oxide Ti_4O_7 was used as the support for a platinum catalyst.[370] The characteristics of the synthesized catalyst within a hydrogen–air fuel cell proved to be comparable with the characteristics of a commercial catalyst manufactured by E-TEK Company (Fig. 21). Insofar as Ti_4O_7 is formed upon the high-temperature (~ 1000 °C) reduction of titanium dioxide, its nanoparticles are difficult to prepare; this is responsible for additional complications in the improvement of the corersponding catalysts.[370, 371]

When low-conducting titanium dioxide is usded as the support, a high-conducting phase, *e.g.*, carbon black or titanium nitride, is added after the deposition of platinum.[372, 373] The corrosion resistance of the materials prepared in this way was shown to be higher.[343, 372, 373] As

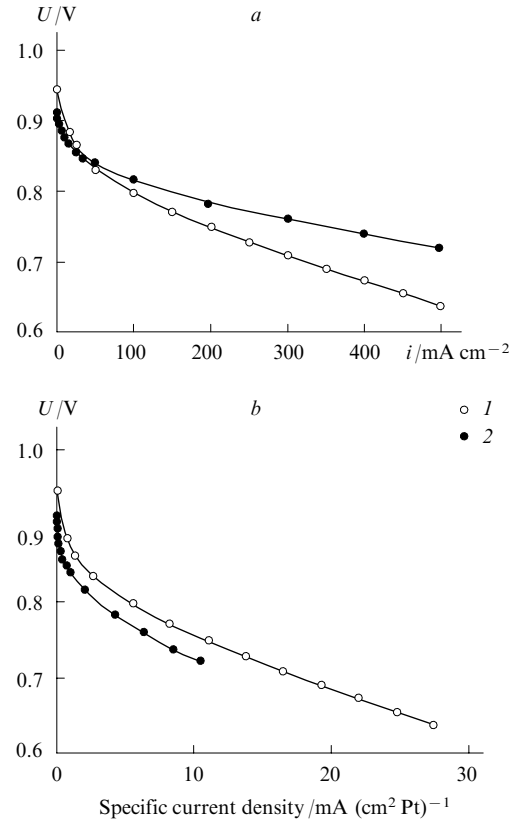


Figure 21. Voltammograms of membrane-electrode blocks based on 20% Pt/C E-TEK catalyst (*1*) and 5% Pt/Ti_4O_7 catalyst (*2*) (*a*) and analogous data *vs*. specific surface area of platinum (*b*).[370]

carbon black is being added, the oxygen reduction current on such catalysts increases to become comparable with the currents observed on platinum/carbon catalysts.[343]

Yet another method for improving the conductivity characteristics of titanium dioxide is its doping with an electron-donating substance, for example, niobium, vanadium or tantalum. The high-temperature synthesis ($\sim$1000 °C) of solid solutions $Nb_xTi_{1-x}O_2$ was reported to produce a material with electronic conduction and a moderate specific surface area.[374] At $\sim$700 °C, the mixed oxide undergoes a phase transition from anatase to less catalytically active rutile,[375] which may diminish the promoting effect of the support.

It was shown[376] that $Ti_{0.9}Nb_{0.1}O_2$ is more resistant to oxidation than Ti_4O_7. The thermal oxidation of Ti_4O_7 already begins at 400 °C; moreover, this material turned out to be electrochemically unstable at potentials of oxygen evolution. The presence of a defect-free oxygen lattice in $Ti_{0.9}Nb_{0.1}O_2$ accounts for its thermal and electrochemical stability.

The activity of catalysts based on niobium-doped titanium dioxide in the reactions of oxygen electroreduction and methanol oxidation was studied.[377–379] Nanocrystalline niobium-doped titanium dioxide with the average grain size of 10–20 nm was prepared.[376, 378, 379] Platinum particles with the average size of 3 nm were deposited on its surface. Presumably, the high degree of dispersion of platinum and the metal–support interactions are responsible for the higher catalytic activity of this material as compared with platinum on carbon black. A platinum–ruthenium catalyst supported by nanocrystalline $Ti_{0.9}Nb_{0.1}O_2$ is also more active than the commercial Pt–Ru/C catalyst manufactured by E-TEK.[377] When used in a fuel cell, $Pt-Ru/Ti_{0.9}Nb_{0.1}O_2$ catalysts generated a current 46% higher as compared with the Pt–Ru/C E-TEK catalyst.

A one-step synthesis of a nanocomposite consisting of TiO_2 (in the anatase form) nanoparticles coated with carbon and then with platinum deposited on the carbon surface was proposed.[380] The carbon layer thickness was 2–4 nm. The electronic conductivity and the specific surface area of this composite material were higher as compared with Vulcan XC72 carbon black. The activity and stability of the catalyst based on TiO_2 nanoparticles in methanol electrooxidation were higher that the activity of a carbon-supported platinum catalyst; this was attributed not only to proper support characteristics but also to the high-degree dispersion of platinum on this material. The increase in the degree of dispersion and the activity of platinum catalysts in the presence of titanium dioxide was also noted by other scientists.[340, 381] The size of catalyst grains was 1–2 nm,[381] which is smaller than the size of Pt–Ru alloy particles on carbon black (3–4 nm). Moreover, the catalytic activity of the new material in methanol oxidation was found to be higher as compared with the commercial Pt–Ru/C catalyst (E-TEK).

Sulfur-doped platinum catalysts based on carbon nanotubes coated with titanium dioxide ($Pt/S-TiO_2/C$) were proposed.[382, 383] It was shown that the activity of such systems in methanol oxidation and their tolerance to poisoning with carbon monoxide surpass the corresponding characteristics of $Pt-TiO_2-C$ composites.

Platinum catalysts deposited on ruthenium-doped titanium dioxide were proposed.[384, 385] It was shown that mixed oxides $Ru_xTi_{1-x}O_2$ exist as solid solutions up to $x = 0.5$. Depending on their composition, the conductivity of $Ru_xTi_{1-x}O_2$ varied from 0.1 to 100 S cm^{-1}. The $Ru_{0.71}Ti_{0.29}O_2$ support proved to be most efficient, providing twice higher specific activity of catalysts than the commercial Pt/C catalyst (E-TEK).

Of high interest are supports based on tin dioxide. It is well known that on the surface of this oxide, the chemisorption of water molecules to form surface OH groups occurs at lower potentials than on the platinum surface. This is why the electrooxidation of CO[386] and low-molecular-weight alcohols such as methanol[387, 388] and ethanol[387] proceeds more readily on the neighbouring platinum atoms. Doping with antimony can increase the SnO_2 conductivity up to 10–0.1 S cm^{-1} as compared with 10^{-3}–10^{-6} S cm^{-1} for undoped SnO_2.[389, 390]

Based on the results of studies by cyclic voltammetry, it was shown[390] that hydrogen adsorption–desorption processes for Pt and Pt/SnO_2 catalysts (1 M H_2SO_4 solution as the electrolyte) proceed in the same manner, whereas the anodic current for the platinum oxide film formation (at potentials >0.8 V) and the cathodic current for its reduction are lower for Pt/SnO_2.

A comparative study of the electrochemical properties of $Pt/Sn_{0.98}Sb_{0.02}O_x$ (platinum deposited on an antimony-doped tin dioxide film with the average grain size of $\sim$ 10 nm)[387] and platinum electrodes demonstrated higher steady-state currents of methanol electrooxidation for the platinum oxide electrode. The effect of the platinum load in the $Pt/Sn_{1-x}Sb_xO_y$ electrode on its catalytic activity and stability in methanol and ethanol electrooxidation processes was studied.[391–393] A decrease in the platinum load was shown to favour the optimization of the size of platinum particles on the oxide support. The best compositions contained $\sim$5 mass %–10 mass % Pt. The stability and activity of $Pt/Sn_{1-x}Sb_xO_y$ catalysts proved to be higher than the analogous characteristics of Pt/C catalysts. It is interesting that metal oxide catalysts with the optimal content of platinum were more active as compared with Pt/C, despite the much lower conductivity of $Sn_{1-x}Sb_xO_y$ ($\sim$0.1–4 S cm^{-1}) as compared with carbon ($\sim$100 S cm^{-1}). This also points to the activating effect of the oxide support on the electrochemical process. The data confirming the high activity of catalytic systems based on antimony-doped tin dioxide was also reported elsewhere.[394–397]

The properties of catalysts supported on ruthenium-doped SnO_2 were studied.[385, 398–401] The introduction of ruthenium into tin dioxide was shown to enhance the activity and stability of platinum catalysts on these supports. Presumably, the interaction between RuO_x and SnO_2 favours the formation of hydroxyl groups that activate the oxidation of catalytic poisons strongly adsorbed on platinum (for instance, CO) and also provide easier methanol electrooxidation.

An interesting consequence of the metal–support interactions was reported[402] for the $Au-SnO_x$ system. Gold nanoparticles deposited on SnO_x catalyze the four-electron reaction of oxygen electroreduction, whereas gold deposited of carbon black preferentially catalyzes the two-electron process to form hydrogen peroxide.

Indium–tin oxide may serve as yet another example of non-carbon supports based on nanocrystalline doped oxides.[403, 404] Thus, it was shown[403] that the electrochemical and thermal stability of the synthesized oxide material

is much higher as compared with commercial catalysts Hispec-4000 (Johnson Matthey) and platinum on carbon black. Platinum supported on nanocrystalline tin dioxide doped with indium was reported to exhibit a higher catalytic activity in methanol electrooxidation.[404–409]

Promising materials to be used as catalyst supports include ruthenium,[343] iridium,[374] silicon[410] and cerium[411] oxides, hydrated ruthenium oxide $RuO_x \cdot n H_2O$, which exhibits proton conduction, and anhydrous RuO_x, which is an electronic conductor.[412] The activity of a RuO_x-supported platinum–ruthenium catalyst in methanol electrooxidation was shown to be comparable with the activity of a Pt–Ru catalyst on Vulcan XC72 carbon black, whereas the former catalyst supported on $RuO_x \cdot n H_2O$ was inactive.[410,412–415]

The use of iridium oxide as an individual support and as an additive to tin or ruthenium dioxide made it possible to substantially increase the catalytically active surface of platinum and made it more CO-tolerant.[416–420]

The Pt/SiO_2 catalysts are ~4 times more active in ethanol electrooxidation than platinum black. The support prepared by etching silicon dioxide was shown to be corrosion resistant in acidic media and only weakly susceptible to poisoning with ethanol oxidation products.[421–425]

According to experimental data,[411,426–429] the catalysts supported on cerium oxide and mixed cerium–zirconium oxides ($Pt-Ce_xZr_{1-x}O_2/C$) and also on sulfonated zirconium oxide ($Pt/S-ZrO_2$) are sufficiently stable and exhibit higher activity in methanol and CO electrooxidation as compared with Pt/C.

Considerable attention of scientists is attracted to platinum catalysts supported on tungsten and molybdenum oxides. A substantial increase in the stability of Pt/WO_3 catalysts as compared with the commercial Hispec-4000 catalyst was noted.[430–432] The catalytic activity of the oxide material in the oxygen reduction exceeded the activity of the carbon-containing catalyst Hispec-4000 both before and after the oxidation cycles. The oxides WO_x and MoO_x are not only corrosion resistant but can also increase CO tolerance. Thus, Pt/MO_x (M = Mo, W) catalysts supported on carbon were shown[263,349,433–439] to be more stable in fuel cells than the Pt–Ru/C catalysts. This was explained by the bifunctional mechanism and(or) the spillover effect.[436,438]

The Pt/MoO_x catalyst proved to be more CO tolerant (for the CO content in hydrogen of 80 ppm) than Pt–Ru catalysts.[440,441] However, the resistance to poisoning in the presence of CO was substantially lower for the former catalyst than for the latter. According to voltammetric studies, the surface coverage with adsorbates formed in the CO oxidation on Pt/MoO_x is more complete than on Pt–Ru; this is why the electrooxidation of hydrogen on Pt/MoO_x is partly inhibited.

The Pt/WO_x systems are also catalytically active in the oxidation of the $H_2 + CO$ mixture, although this effect is not so high as for the use of the Pt–Ru catalyst.[439–442] Tungsten oxides actively catalyze the reactions occurring in fuel cells. The catalytic activity of WO_x is attributable to the fast change in the tungsten oxidation state and the involvement of the redox pairs W^{6+}/W^{4+} (Ref. 443) or W^{6+}/W^{5+} (Ref. 438) in the process.

The efficient operation of electrodes requires not only the adequate catalysis of the electrode process but also favourable conditions for the electron and proton transport. In the majority of cases, this is achieved by introducing a proton-conducting polymer into the electrode composition. However, in this case, a part of platinum becomes inaccessible for the gas. This problem can be solved by replacing the three-phase boundary by a two-phase boundary. For this to happen, the oxide should exhibit both electronic and proton conduction, for example, like non-stoichiometric tungsten compounds H_xWO_3.[239,443,444]

The use of tungsten oxide nanofibres as the supports for platinum catalysts proved to be sufficiently efficient.[445] Platinized fibres synthesized on alumina supports are characterized by the high stability and catalytic activity in the methanol electrooxidation reaction. Tungsten oxide is also known to promote the action of other catalysts in the reaction of oxygen electroreduction.[333,432,443] A catalytic mechanism was proposed according to which tungsten oxide accelerates the decomposition of the hydrogen peroxide intermediate.[443]

An interesting trend in the development of catalysts for oxidation of CO and organic fuels is the synthesis of platinum catalysts deposited on composite supports based on ion-conducting heteropoly compounds, for example, heteropolyacid salts $M'_{3-x}H_xPM_{12}O_{40}$ (where M′ = K, Cs, Rb, NH_4; M = W, Mo), *i.e.*, inorganic solid electrolytes with high proton conductivity.[446–453] These catalytic systems exhibit high activity in many chemical and electrochemical reactions. The possibility of using platinized heteropoly compounds as the catalysts of anodic processes in low-temperature hydrogen–air fuel cells was demonstrated.[453–456]

6. Carbide-based supports

Back in the early 1960s, it was observed that carbides of certain transition metals such as tungsten, tantalum and titanium exhibit the catalytic activity in oxygen electroreduction in acidic media.[446,457,458] Moreover, carbides exhibit high electronic conductivity and corrosion resistance; hence, they can be used as platinum-free catalysts[459] and also as supports for platinum.[460]

Tungsten carbide holds the greatest promise for the use in fuel cells, as it has the highest catalytic activity among metal carbides and high corrosion resistance.[459,460] It was noted[461] that the catalytic activity of platinum on WC after 30 electrochemical oxidation cycles in the range of 0.6–1.8 V decreased by 20%, whereas the Pt/Vulcan XC72 catalyst almost completely lost its activity as soon as after ten cycles. It was assumed that after oxidation cycles, the tungsten surface is partly covered by conducting WO_x film. Meanwhile, the oxidation of carbon leads to liberation of gaseous CO and CO_2, destruction of the support and the loss of catalytic activity of the platinum surface. The stability and activity of WC-supported catalysts in the oxygen reduction can be considerably enhanced by doping tungsten carbide with tantalum.[462,463]

The use of tungsten carbides as supports for platinum catalysts is efficient due to their high corrosion resistance and intrinsic catalytic activity and also because of the synergistic effect that enhances the activity of platinum in contact with carbide.[464] The enhanced efficiency of catalysts supported on tungsten carbides as compared with activity of Pt/C catalysts was reported.[465,466] The current density of oxygen reduction on the Pt/W_2C-C catalyst is two orders of magnitude higher than on Pt/C.

Tungsten carbide-supported catalysts are highly active not only in oxygen reduction but also in the processes of methanol and hydrogen electrooxidation in the presence of CO.[467–469] The higher activity of the Pt/WC catalyst in the methanol electrooxidation as compared with pure platinum and also its higher resistance to CO poisoning were noted, which can be associated with weaker adsorption of CO on Pt/WC.[467] The increase in the carbon monoxide tolerance in the reaction of hydrogen electrooxidation carried out in hydrogen mixed with CO was also observed for Pt–Ru/W_2C and Pt–Ru/WC systems.[470,471]

The catalytic activity of composite structures based on palladium nanoparticles supported on tungsten carbide modified with multiwalled carbon nanotubes in the reaction of ethanol electrooxidation exceeded the activity of the Pt/C catalyst by a factor of five, which was interpreted[472,473] as being due to the structure of carbon nanotubes and the appearance of synergism between the noble metal and the carbide. The synthesized composites also exhibited high catalytic activity in methanol and ethylene glycol electrooxidation.

Fairly efficient platinum catalysts on the supports based on tungsten carbide microspheres were proposed.[474] The activity of this material in methanol electrooxidation exceeded several times the activity of a standard catalyst manufactured by E-TEK. One of the factors determining the efficient operation of this catalyst was the ability of platinum to form finer dispersions on the microspheres as compared with carbon supports.

7. Supports based on conducting polymers

Conducting polymers such as polyacetylene, polypyrrole, polyaniline and their derivatives attract attention as a new class of synthetic materials which can be used as supports. The properties of polyaniline were studied most thoroughly. It is characterized by high electronic conductivity in its protonated form and the chemical and electrochemical stability. The conditions of synthesis of polyaniline are sufficiently simple and reproducible. Due to the listed qualities, this polymer is promising for electrocatalysis as a component of membrane-electrode blocks.[475] Polyaniline is used as a coating of bipolar plates,[476] for modifying polymer membranes[477] and as a catalyst support.[478] In several studies, it was shown that polyaniline exhibits intrinsic electrocatalytic activity in electroreduction of oxygen and electrooxidation of methanol and hydrogen.[479,480] A polyaniline catalyst served for the design of a fuel-cell prototype that contained no platinum-group metals and had a power density of ~ 5 mW cm^{-2} (Ref. 481).

The majority of publications are devoted to polyaniline used as the support for catalysts in direct methanol fuel cells. The merits of these supports include not only their intrinsic electrocatalytic activity in the reactions involved but also the enhanced stability against the poisoning effect of methanol oxidation products[482] and the advantageous use of platinum crystallites dispersed throughout the polymer matrix.[483] For instance, catalysts prepared by electrodeposition of platinum on polyaniline with relatively low metal loads (0.1 mg cm^{-2}) exhibited the activity in methanol electrooxidation comparable with the platinum activity; moreover, they were more CO tolerant.[484–486] The higher activity of platinum and palladium particles on polyaniline films as compared with Pt/Pt or Pd/Pt catalysts in electrooxidation of methanol, CO and formic acid was attributed[487] to the interaction between metal and polymer particles. Thus, the activity of palladium on a polyaniline film in the electrooxidation of formic acid exceeds more than 20-fold the activity of Pd/Pt catalysts prepared by electroplating of palladium on smooth platinum.

The stability and catalytic activity of polyaniline-supported catalysts can be enhanced by using platinum alloys in place of pure platinum.[488–492] Polyaniline-supported catalysts based on Pt–M (M = Cr, Ni, In, Co, Sb, Bi, Pb, Mn) were studied.[489] The anodic current of methanol electrooxidation, which characterizes the activity of these catalysts, strongly depends on the morphology and electronic conductivity of polyaniline synthesized by electropolymerization of aniline from acid solutions (H_2SO_4, HNO_3, $HClO_4$, HBF_4 and HCl). The strongest activity was exhibited by catalysts on polyaniline films deposited from solutions in sulfuric acid. The activity of all polyaniline-supported metal catalysts studied was higher as compared with catalysts applied directly on glassy carbon electrodes (Fig. 22). The highest current density of methanol electrooxidation was reached for the Pt–Sn/polyaniline catalyst.

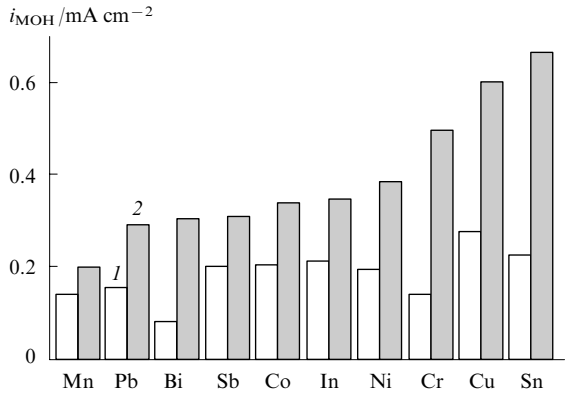


Figure 22. Diagram of activity of polyaniline-supported catalysts. (*1*) Pt/M, (*2*) Pt–M/polyaniline.

Platinum–ruthenium catalysts pertain to the most efficient catalysts. They exhibit high catalytic activity in methanol electrooxidation on carbon supports and, being supported on polyaniline, demonstrate resistance to contamination with CO. The optimal ruthenium content in the alloy for the methanol electrooxidation was shown to be 32 at.%.[491]

Platinum catalysts deposited on polyaniline nanofibres hold promise for direct methanol fuel cells.[483,492] Platinum nanoparticles supported on polyaniline nanofibres have a smaller average diameter and a narrower size distribution as compared with carbon black supports. Hence, as opposed to Pt/C catalysts, a Pt/polyaniline catalyst has larger electrochemically active platinum surface area and demonstrates higher activity in methanol electrooxidation.

An efficient platinum catalyst based on composite structures involving polyaniline and multiwalled carbon nanotubes was prepared.[493] As a result of mofidication with nanotubes, the electronic conductivity of polyaniline increased by more than an order of magnitude. Moreover, the catalytic activity of this composite material in methanol

electrooxidation also increased. Based on IR spectroscopic studies, it was assumed that in the prepared composite, the charge transfer interaction between nanotubes and polyaniline takes place, which results in stabilization of quinoid units.

Among conducting polymers which proved to be suitable as the fuel-cell catalysts, attention should also be drawn to poly(3,4-ethylenedioxythiophene). Platinum catalysts supported on this polymer exhibit high stability and catalytic activity in both oxygen reduction and methanol electrooxidation reactions.[494, 495] After 1500-h trials in an air electrode, this catalyst showed no signs of degradation and retained the activity with respect to oxygen reduction.[337] It is interesting that the activity of these catalysts in the methanol electrooxidation increases after their long-term storage in air.[496, 497] This is associated with the increase in the material porosity, which makes platinum active sites more accessible to methanol.

IV. Conclusion

Hydrogen power engineering is a modern knowledge-intensive branch which actively uses the achievement of different scientific fields including materials science, polymer chemistry, membrane transport, electrochemistry, catalysis, nanotechnology. The fast ionic transport in proton-conducting membranes becomes possible due to self-assembling processes to form pores and channels with characteristic sizes of 2 – 5 nm in the membrane matrix. The acceleration of ion transport, especially at low humidity, was achieved due to incorporation of various nanoparticles, first of all, of the inorganic origin. The best results are obtained upon the modification of nanoparticles aimed at imparting acidic properties to them.

High performance operation of a fuel cell requires that the size of platinum catalyst particles be about several nanometres. This favours its maximum activity and reduces the consumption of expensive platinum. Yet another way to increase the efficiency of operation of fuel cells and reduce their cost is gradual changeover to polymetallic systems aimed at the enhancement of the carbon monoxide tolerance of the catalyst. According to modern views, this can be achieved *via* the redistribution of electron density of the metal and also by the formation of two closely located catalytic sites that provide acceleration of CO oxidation. Often, it proves to be most advantageous to use nanosized bimetallic particles with the core – shell structure.

An important role belongs to the gas-diffusion layer, *i.e.*, the support for the platinum catalyst, which provides the efficient current drainage and the delivery of reacting gases to the catalyst. Lately, the role of the gas-diffusion layer was mainly played by various forms of fine-grain carbon for which the introduction of nanosized materials, particularly, nanotubes, proved to be efficient. A modern trend is the transition to non-carbon supports, first of all, conducting oxides of transition metals. Supports can be made of other compounds, *e.g.*, carbides or conducting polymers, particularly, polyaniline.

Note in conclusion that the rapid development of nanotechnologies made it possible to substantially enhance the efficiency of fuel cell operation and decrease their cost. These two factors were the obstacles to the development of hydrogen power engineering, which is very attractive due to the low hydrogen density and high environmental safely of fuel cell operation. Bearing in mind the aforementioned, one can expect acceleration of the development of this important field in the nearest decades and the use of its achievements in the national economy, first of all, in the energy supply of vehicles (cars, airplanes, *etc.*) and portable devices.

References

1. J E Girard *Principles of Environmental Chemistry* (Sudbury, MA: Jones and Bartlett, 2005)
2. D Root, E Attanasi *Am. Assoc. Petrol. Geol. Bull.* 3 (1978)
3. J D Parent *A Survey of the United States and Total World Production, Proves Reserves, and Remaining Recoverable Resources of Fossil Fuels and Uranium as of December 31, 1977* (Chicago: Institute of Gas Technology, 1979)
4. J O M Bockris, T N Veziroglu *Int. J. Hydrogen Energy* **8** 323 (1983)
5. D S Scott, W Hafele *Int. J. Hydrogen Energy* **15** 1539 (1990)
6. *Hydrogen Energy and Fuel Cells — A Vision of Our Future. Final Report of the High Level Group. Eur20719 EN* (Luxemburg: European Commission. Office for Official Publications of the European Committees, 2003)
7. US P. 3282875 (1966)
8. J O M Bockris, T N Veziroglu, S Debbi *Solar Hydrogen Energy: The Power to Save the Earth* (London: Optima, 1991)
9. T N Veziroglu, F Barbir *Hydrogen Energy Technologies* (Vienna: UNIDO, 1998)
10. C-Y Wang *Chem. Rev.* **104** 4727 (2004)
11. L Carrette, K A Friedrich, U Stimming *Fuel Cells* **1** 5 (2001)
12. A S Aricò, S Srinivasan, V Antonucci *Fuel Cells* **1** 133 (2001)
13. *Handbook of Fuel Cells — Fundamentals, Technology and Applications. Fuel Cell Technology and Applications* Vol. 3 (Eds W Vielstich, A Lamm, H A Gasteiger) (Chichester: Wiley, 2003)
14. K-D Kreuer, S J Paddison, E Spohr, M Schuster *Chem. Rev.* **104** 4637 (2004)
15. A B Yaroslavtsev, V V Nikonenko, V I Zabolotskii *Russ. Chem. Rev.* **72** 393 (2003) [*Usp. Khim.* **72** 438 (2003)]
16. A B Yaroslavtsev *Russ. Chem. Rev.* **78** 1013 (2009) [*Usp. Khim.* **78** 1094 (2009)]
17. M Rikukawa, K Sanui *Prog. Polym. Sci.* **25** 1463 (2000)
18. J Rozi'ere, D J Jones *Annu. Rev. Mater. Res.* **33** 503 (2003)
19. Q F Li, R H He, J O Jensen, N J Bjerrum *Chem. Mater.* **15** 4896 (2003)
20. M A Hickner, H Ghassemi, Y S Kim, B R Einsla, J E McGrath *Chem. Rev.* **104** 4587 (2004)
21. Yu A Dobrovolsky, E V Volkov, A V Pisareva, Yu A Fedotov, D Yu Likhachev, A L Rusanov *Ros. Khim. Zh.* **50** (6) 95 (2006) [a]
22. V Neburchilov, J Martin, H Wang, J Zhang *J. Power Sources* **169** 221 (2007)
23. Yu A Dobrovolsky, E A Sanginov, A L Rusanov *Al'tern. Energet. Ekol.* (8) 112 (2009) [b]
24. S J Peighambardoust, S Rowshanzamir, M Amjadi *Int. J. Hydrogen Energy* **35** 9349 (2010)
25. H S Thiam, W R W Daud, S K Kamarudin, A B Mohammad, A A H Kadhum, K S Loh, E H Majlan *Int. J. Hydrogen Energy* **36** 3187 (2011)
26. US P. 3041317 (1962)
27. Yu A Panshin, S G Malkevich, Ts S Dunaevskaya *Ftoroplasty* (Fluoroplastics) (Leningrad: Khimiya, 1978)
28. R Souzy, B Ameduri *Prog. Polym. Sci.* **30** 644 (2005)
29. S S Ivanchev, S V Myakin *Russ. Chem. Rev.* **79** 101 (2010) [*Usp. Khim.* **79** 117 (2010)]

30. S S Ivanchev, V S Likhomanov, O N Primachenko, S Ya Khaikin, V G Barabanov, V V Kornilov, A S Odinokov, Yu V Kul'velis, V T Lebedev, V A Trunov *Membrany Membr. Tekhnol.* **2** (1) (2012) [c] (in the press)
31. *Perfluorinated Ionomer Membranes* (Eds A Eisenberg, H L Yager) (Washington, DC: American Chemical Society, 1982)
32. K A Mauritz, R B Moore *Chem. Rev.* **104** 4535 (2004)
33. G Gebel *Polymer* **41** 5829 (2000)
34. V I Volkov, A N Ponomarev, E A Sanginov, A A Pavlov, A B Yaroslavtsev *Al'ternat. Energet. Ekol.* (2) 67 (2008) [b]
35. T D Gierke, G E Munn, F C Wilson *J. Polym. Sci. B, Polym. Phys.* **19** 1687 (1981)
36. W Y Hsu, T D Gierke *J. Membr. Sci.* **13** 307 (1983)
37. A N Ozerin, A V Rebrov, A N Yakunin, L P Bogovtseva, S F Timashev, N F Bakeev *Vysokomol. Soedin., Ser. A* **28** 254 (1986) [d]
38. A V Rebrov, A N Ozerin, D I Svergun, L P Bobrova, N F Bakeev *Vysokomol. Soedin., Ser. A* **32** 1593 (1990) [d]
39. V A Trunov, V T Lebedev, Yu S Grushko, A E Sokolov, I I Ivanova, V B Rybakov, T M Yur'eva, S S Ivanchev, D Torok *Kristallografiya* **52** 536 (2007) [e]
40. T A Zawodzinski, J M Neeman, L O Sillerud, S Cottesfeld *J. Phys. Chem.* **95** 6040 (1991)
41. S H Almeida, Y Kawano *J. Therm. Anal. Calor.* **58** 569 (1999)
42. Yu A Dobrovolsky, A V Pisareva, L S Leonova, A I Karelin *Al'tern. Energet. Ekol.* (12) 36 (2004) [b]
43. M Yamada, I Honma *Polymer* **46** 2986 (2005)
44. K D Kreuer *Chem. Mater.* **8** 610 (1996)
45. A L Rusanov, D Yu Likhatchev, K Müllen *Russ. Chem. Rev.* **71** 761 (2002) [*Usp. Khim.* **71** 862 (2002)]
46. G Gebel, P Aldebert, M Pineri *Polymer* **42** 359 (2001)
47. A E Steck, C Stone, in *Proceedings of the 2nd International Symposium on New Materials for Fuel Cell and Modern Battery Systems, Montreal, 1997* p. 792
48. G Robertson, S D Mikhailenko, K P Wang *J. Membr. Sci.* **219** 113 (2003)
49. E Tsuchida, K Yamamoto, E Shouji, J Katoh, M Matsuo, H Kamiya *Macromolecules* **27** 7504 (1994)
50. M L Keshtov, A R Khokhlov *Vysokomol. Soedin., Ser. B* **50** 732 (2008) [d]
51. S Li, Z Zhen, M Liu, M Nakanishi *Electrochim. Acta* **8** 1351 (2006)
52. J Mader, L Xiao, T J Schmidt, B C Benicewicz *Adv. Polym. Sci.* **216** 63 (2008)
53. A A Lysova, I I Ponomarev, A B Yaroslavtsev *Zh. Neorg. Khim.* **57** (2012) [f] (in the press)
54. A Matsuda, T Kanzaki, Y Kotani, M Tatsumisago, T Minami *Solid State Ionics* **139** 113 (2001)
55. T Tezuka, K Tadanada, A Matsuda, A Hayasi, M Tatsumisado *Electrochem. Commun.* **7** 245 (2005)
56. J-P He, H-M Li, X-Y Wang, Y Gao *Eur. Polym. J.* **42** 1128 (2006)
57. F Qiu, Z Da, D Yang, G Cao, P Li *Dyes Pigm.* **77** 564 (2008)
58. R Sengupta, A Bandyopadhyay, S Sabharwal, T K Chaki, A K Bhowmick *Polymer* **46** 3343 (2005)
59. T Ogoshi, Y Chujo *J. Polym. Sci. A: Polym. Chem.* **43** 3543 (2005)
60. K Yoshikai, T Ohsaki, M Furukawa *J. Appl. Polym. Sci.* **85** 2053 (2002)
61. N S Shaglaeva, O V Lebedeva, Yu N Pozhidaev, R G Sultangareev, S S Bochkareva, L A Es'kova *Zh. Fiz. Khim.* **81** 406 (2007) [g]
62. Yu N Pozhidaev, O V Lebedeva, S S Bochkareva, N S Shaglaeva, M G Voronkov *Persp. Mater.* 268 (2008)
63. O V Lebedeva, Yu N Pozhidaev, R G Sultangareev, A S Pozdnyakov, S S Bochkareva, E A Orkhokova, N S Shaglaeva *Zh. Prikl. Khim.* **82** 1869 (2009) [h]
64. N S Shaglaeva, O V Lebedeva, L V Kanitskaya, G A Pirogova, R G Sultangareev, L A Es'kova *Vysokomol. Soedin., Ser. B* **45** 827 (2003) [d]
65. N S Shaglaeva, O V Lebedeva, Yu N Pozhidaev, R G Sultangareev, M V Markova, V N Salaurov *Vysokomol. Soedin., Ser. B* **50** 2035 (2008) [d]
66. O V Lebedeva, Yu N Pozhidaev, N S Shaglaeva, S S Bochkareva, L A Es'kova *Zh. Prikl. Khim.* **84** 128 (2011) [h]
67. O V Lebedeva, Yu N Pozhidaev, N S Shaglaeva, A S Pozdnyakov, S S Bochkareva *Khim. Tekhnol.* (1) 20 (2010)
68. H Nakajima, O Nishikawa, T Sugimoto, S Nomura *Solid State Ionics* **162 – 162** 237 (2003)
69. G Pourcelly *Membrany Membr. Tekhnol.* **1** 11 (2011) [c]
70. A B Yaroslavtsev, V V Nikonenko *Ros. Nanotekhnol.* **4** 33 (2009) [i]
71. D J Jones, J Roziere, in *Handbook of Fuel Cells — Fundamentals, Technology and Applications. Fuel Cell Technology and Applications* Vol. 3 (Eds W Vielstich, A Lamm, H A Gasteiger) (Chichester: Wiley, 2003) p. 447
72. A B Yaroslavtsev *Solid State Ionics* **176** 2935 (2005)
73. T Xu *J. Membr. Sci.* **263** 1 (2005)
74. B Bonnet, D J Jones, J Roziere, L Tchicaya, G Alberti, M Casciola, L Massinelli, B Bauer, A Peraio, E Ramunni *J. New Mater. Electrochem. Syst.* **3** 87 (2000)
75. S K Young, W L Jarrett, K A Mauritz *Polym. Eng. Sci.* **41** 1529 (2001)
76. S-O Kim, J S Kim *Macromol. Res.* **10** 174 (2002)
77. Y J Kim, W C Choi, S I Woo, W H Hong *J. Membr. Sci.* **238** 213 (2004)
78. S Ren, G Sun, C Li, Z Liang, Z Wu, W Jin, X Qin, X Yang *Fuel Cells Bull.* **12** 12 (2006)
79. S Ren, G Sun, C Li, Z Liang, Z Wu, W Jin, X Qin, X Yang *J. Membr. Sci.* **282** 450 (2006)
80. R Jiang, H R Kunz, J M Fenton *J. Membr. Sci.* **272** 116 (2006)
81. A D'Epifanio, B Mecher, E Fabbri, A Rainer, E Traversa, S Licoccia *J. Electrochem. Soc.* **154** B1148 (2007)
82. Y Tominaga, I-C Hong, S Asai, M Sumita *J. Power Sources* **171** 530 (2007)
83. E Yu Voropaeva, I A Stenina, A B Yaroslavtsev *Zh. Neorg. Khim.* **53** 1797 (2008) [f]
84. H Tang, Z Wan, M Pan, S P Jiang *Electrochem. Commun.* **9** 2003 (2007)
85. J-C Tsai, J-F Kuo, C-Y Chen *J. Power Sources* **174** 103 (2007)
86. E Yu Voropaeva, I A Stenina, A B Yaroslavtsev *Zh. Neorg. Khim.* **53** 1637 (2008) [f]
87. H T Wang, B A Holmberg, L M Huang, Z B Wang, A Mitra, J M Norbeck, Y S Yan *J. Mater. Chem.* **12** 834 (2002)
88. M Watanabe, H Uchida, Y Seki, M Emori *J. Electrochem. Soc.* **143** 3847 (1996)
89. H Hagihara, H Uchida, M Watanabe *Electrochim. Acta* **51** 3979 (2006)
90. K T Adjemian, S Srinivasan, J Benziger, A B Bocarsly *J. Power Sources* **109** 356 (2002)
91. K T Adjemian, S J Lee, S Srinivasan, J Benziger, A B Bocarsly *J. Electrochem. Soc.* **149** A256 (2002)
92. F Lufrano, V Baglio, P Staiti, A Arico, V Antonucci *Desalination* **199** 283 (2006)
93. Y-F Lin, C-C M Ma, Y-Y Lin, C-Y Yen, C-H Hung *Key Eng. Mater.* **334 – 335** 945 (2007)
94. V K Shahi *Solid State Ionics* **177** 3395 (2007)
95. C-Y Yen, C-H Lee, Y-F Lin, H-L Lin, Y-H Hsiao, S-H Liao, C-Y Chuang, C-C M Ma *J. Power Sources* **173** 36 (2007)
96. L M de Carvalho, A R Tan, G A de Souza *J. Appl. Polym. Sci.* **110** 1690 (2008)
97. M Baias, D E Demco, I Colicchio, B Blumich, M Moller *Chem. Phys. Lett.* **456** 227 (2008)

98. C Hartmann-Thompson, A Merrington, P I Carver, D L Keeley, J L Rousseau, D Hucul, K J Bruza, L S Thomas, S E Keinath, R M Nowak, D M Katona, P R Santurri *J. Appl. Polym. Sci.* **110** 958 (2008)
99. I Colicchio, D E Demco, M Baias, H Keul, M Moeller *J. Membr. Sci.* **337** 125 (2009)
100. Suryani, Y L Liu *J. Membr. Sci.* **332** 121 (2009)
101. Y-F Lin, C-Y Yen, C-C M Ma, S-H Liao, C-H Lee, Y-H Hsiao, H-P Lin *J. Power Sources* **171** 388 (2007)
102. B P Ladewig, R B Knott, A J Hill, J D Riches, J W White, D J Martin, J C D da Costa, G Q Lu *Chem. Mater.* **19** 2372 (2007)
103. F Pereira, K Vallé, P Belleville, A Morin, S Lambert, C Sanchez *Chem. Mater.* **20** 1710 (2008)
104. C Li, G Sun, S Ren, J Liu, Q Wang, Z Wu, H Sun, W Jin *J. Membr. Sci.* **272** 50 (2006)
105. P Staiti, A S Aricò, V Baglio, F Lufrano, E Passalacqua, V Antonucci *Solid State Ionics* **145** 101 (2001)
106. Z-G Shao, P Joghee, I-M Hsing *J. Membr. Sci.* **229** 43 (2004)
107. H-J Kim, Y-G Shul, H Han *J. Power Sources* **158** 137 (2006)
108. G Ye, C A Hayden, G R Goward *Macromolecules* **40** 1529 (2007)
109. L Wang, B L Yi, H M Zhang, D M Xing *Electrochim. Acta* **52** 5479 (2007)
110. V Ramani, H R Kunz, J M Fenton *J. Membr. Sci.* **279** 506 (2006)
111. M Helen, B Viswanathan, S S Murthy *J. Membr. Sci.* **292** 98 (2007)
112. V Ramani, H R Kunz, J M Fenton *J. Membr. Sci.* **232** 31 (2004)
113. H Xu, M Wu, Y Liu, V Mittal, F Kassim, B Vieth, L Bonville, H R Kunz, J M Fenton *Electrochem. Soc. Trans.* **3** 561 (2006)
114. V Ramani, H R Kunz, J M Fenton *Electrochim. Acta* **50** 1181 (2005)
115. W Xu, T Lu, C Liu, W Xing *Electrochim. Acta* **50** 3280 (2005)
116. A Mahreni, A B Mohamad, A A H Kadhum, W R W Daud, S E Iyuke *J. Membr. Sci.* **327** 32 (2009)
117. E Yu Safronova, I A Stenina, A B Yaroslavtsev *Zh. Neorg. Khim.* **55** 16 (2010) [f]
118. V Ramani, H R Kunz, J M Fenton *J. Power Sources* **152** 182 (2005)
119. M Amirinejad, S S Madaeni, M A Navarra, E Rafiee, B Scrosati *J. Power Sources* **196** 988 (2011)
120. Y Xiang, M Yang, J Zhang, F Lan, S Lu *J. Membr. Sci.* **368** 241 (2011)
121. V Ramani, H R Kunz, J M Fenton *J. Membr. Sci.* **266** 110 (2005)
122. M Li, Z-G Shao, H Zhang, Y Zhang, X Zhu, B Yi *Electrochem. Solid State Lett. A* **9** 92 (2006)
123. S Xue, G Yin *Acta Polym. Sinica* 1083 (2006)
124. L Li, Y Wang *J. Power Sources* **162** 541 (2006)
125. M Yamada, I Honmia *J. Phys. Chem. B* **110** 20486 (2006)
126. J T Hinatsu, M Mizuhata, H Takenaka *J. Electrochem. Soc.* **141** 1493 (1994)
127. P Genova-Dimitrova, B Baradie, D Foscallo, C Poinsignon, J Y Sanchez *J. Membr. Sci.* **185** 59 (2001)
128. J Shan, G Vaivars, H Luo, R Mohamed, V Linkov *Pure Appl. Chem.* **78** 1781 (2006)
129. Z Wang, N H i, C Zhao, X Li, T Fu, H Na *J. Polym. Sci. B: Polym. Phys.* **44** 1967 (2006)
130. C Yang, S Srinivasan, A S Arico, P Creti, V Baglio, V Antonucci *Electrochem. Solid State Lett.* **4** A31 (2001)
131. P Costamagna, C Yang, A B Bocarsly, S Srinivasan *Electrochim. Acta* **47** 1023 (2002)
132. C Yang, S Srinivasan, A B Bocarsly, S Tulyani, J B Benziger *J. Membr. Sci.* **237** 145 (2004)
133. F Bauer, M Willert-Porada *Fuel Cells* **6** 261 (2006)
134. G Alberti, M Casciola, D Capitani, A Donnadio, R Narducci, M Pica, M Sganappa *Electrochim. Acta* **52** 8125 (2007)
135. S Sang, Q Wu, K Huang *J. Membr. Sci.* **305** 118 (2007)
136. A I Fomenkov, I Yu Pinus, A S Peregudov, Ya V Zubavichus, A B Yaroslavtsev, A R Khokhlov *Vysokomol. Soedin., Ser. A* **49** 1299 (2007) [d]
137. Y Zhang, H Zhang, C Bi, X Zhu *Elecrochim. Acta* **53** 4096 (2008)
138. A Paciaroni, M Casciola, E Cornicchi, M Marconi, G Onori, M Pica, R Narducci, A Orecchini *J. Phys.: Condens. Matter* **18** S2029 (2006)
139. R Jiang, H R Kunz, J M Fenton *Electrochim. Acta* **51** 5596 (2006)
140. A K Sahu, S Pitchumani, P Sridhar, A K Shukla *Fuel Cells* **9** 139 (2009)
141. L-C Chen, T L Yu, H-L Lin, S-H Yeh *J. Membr. Sci.* **307** 10 (2008)
142. H Luo, S Ji, G Vaivars, B Bladergroen, V Linkov *South African J. Chem.* **60** 85 (2007)
143. B P Tripathi, V K Shahi *J. Colloid Interface Sci.* **316** 612 (2007)
144. M Huang, Y Wang, Y Cai, L Xu *Acta Polym. Sinica* (4) 337 (2007)
145. M Helen, B Viswanathan, S S Murthy *Appl. Catal., A* **321** 71 (2007)
146. V Baglio, A S Aricò, A Di Blasi, V Antonucci, P L Antonucci, S Licoccia, E Traversa, F S Fiory *Electrochim. Acta* **50** 1241 (2005)
147. S N Lvov, E Chalkova, G M Rybka, M V Fedkin, D J Wesolowski, M G Roelofs *Elecrtochem. Soc. Trans.* **3** 73 (2006)
148. M B Satterfield, P W Majsztrik, H Ota, J B Benziger, A B Bocarsly *J. Polym. Sci., B* **44** 2327 (2006)
149. K T Adjemian, R Dominey, L Krishnan, H Ota, P Majsztrik, T Zhang, J Mann, A B Bocarsly *Chem. Mater.* **18** 2238 (2006)
150. F Mura, R F Silva, A Pozio *Electrochim. Acta* **52** 5824 (2007)
151. S Y Chen, C C Han, C H Tsai, J Huang, Y W Chen-Yang *J. Power Sources* **171** 363 (2007)
152. I Nicotera, T Zhang, A Bocarsly, S Greenbaum *J. Electrochem. Soc.* **154** B466 (2007)
153. V Di Noto, R Gliubizzi, E Negro, M Vittadello, G Pace *Electrochim. Acta* **53** 1618 (2007)
154. W-B Yang, H Zhu, M Wang, S-C Zhang *J. Funct. Mater.* **38** 2077 (2007)
155. P Kalappa, J-H Lee *Polym. Int.* **56** 371 (2007)
156. Y Patil, K A Mauritz *J. Appl. Polym. Sci.* **113**. 3269 (2009)
157. E I Santiago, R A Isidoro, M A Dresch, B R Matos, M Linardi, F C Fonseca *Electrochim. Acta* **54** 4111 (2009)
158. B R Matos, E I Santiago, F C Fonseca, M Linardi, V Lavayen, R G Lacerda, L O Ladeira, A S Ferlauto *J. Electrochem. Soc.* **154** B1358 (2007)
159. M A Navarra, F Croce, B Scrosati *J. Mater. Chem.* **17** 3210 (2007)
160. N H Jalani, K Dunn, R Datta *Electrochim. Acta* **51** 553 (2005)
161. A Saccà, I Gatto, A Carbone, R Pedicini, E Passalacqua *J. Power Sources* **163** 47 (2006)
162. V S Silva, B Ruffmann, H Silva, V B Silva, A Mendes, L M Madeira, S Nunes *J. Membr. Sci.* **284** 137 (2006)
163. Z-G Shao, H Xu, I-M Hsing, H Zhang *Chem. Eng. Commun.* **194** 667 (2007)
164. C H Rhee, Y Kim, J S Lee, H K Kim, H Chang *J. Power Sources* **159** 1015 (2006)
165. Z Wu, G Sun, W Jin, H Hou, S Wang, Q Xin *J. Membr. Sci.* **313** 336 (2008)
166. Y Zhai, H Zhang, J Hu, B Yi *J. Membr. Sci.* **280** 148 (2006)
167. S Ren, G Sun, C Li, S Song, Q Xin, X Yang *J. Power Sources* **157** 724 (2006)
168. Y Zhang, H Zhang, X Zhu, C Bi *J. Phys. Chem. B* **111** 6391 (2007)

169. K T Park, U H Jung, D W Choi, K Chun, H M Lee, S H Kim *J. Power Sources* **177** 247 (2008)
170. V Tricoli, F Nannetti *Electrochim. Acta* **48** 2625 (2003)
171. M Aparicio, L C Klein, K T Adjemian, A B Bocarsly *Ceram. Trans.* **127** 167 (2002)
172. Y-T Kim, K-H Kim, M-K Song, H-W Rhee *Curr. Appl. Phys.* **6** 612 (2006)
173. J Liu, T Xu, C Wu, G Shao *Rec. Pat. Eng.* **1** 214 (2007)
174. A Sacca, A Carbone, E Passalacqua, A D'Epifanio, S Licoccia, E Traversa, E Sala, F Traini, R Ornelas *J. Power Sources* **152** 16 (2005)
175. M-K Song, S-B Park, Y-T Kim, H-W Rhee, J Kim *Mol. Cryst. Liquid Cryst.* **407** 411 (2003)
176. B A Holmberg, H Wang, J M Norbeck, Y Yan *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **45** 24 (2004)
177. V Baglio, A S Arico, A Di Blasi, P L Antonucci, F Nannetti, V Tricoli, V Antonucci *J. Appl. Electrochem.* **35** 207 (2005)
178. V Baglio, A Di Blasi, A S Aricò, V Antonucci, P L Antonucci, F Nannetti, V Tricoli *Electrochim. Acta* **50** 5181 (2005)
179. Z X Liang, T S Zhao, J Prabhuram *J. Membr. Sci.* **283** 219 (2006)
180. S C Byun, Y J Jeong, J W Park, S D Kim, H Y Ha, W J Kim *Solid State Ionics* **177** 3233 (2006)
181. Z Chen, B Holmberg, W Li, X Wang, W Deng, R Munoz, Y Yan *Chem. Mater.* **18** 5669 (2006)
182. M I Ahmad, S M J Zaidi, S U Rahman *Desalination* **193** 387 (2006)
183. F J Fernández-Carretero, V Compañ, E Riande *J. Power Sources* **173** 68 (2007)
184. X Li, E P L Roberts, S M Holmes, V Zholobenko *Solid State Ionics* **178** 1248 (2007)
185. E N Gribov, E V Parkhomchuk, I M Krivobokov, J A Darr, A G Okunev *J. Membr. Sci.* **297** 1 (2007)
186. W Lee, H Kim, T K Kim, H Chang *J. Membr. Sci.* **292** 29 (2007)
187. Y S Choi, T K Kim, E A Kim, S H Joo, C Pak, Y H Lee, H Chang, D Seung *Adv. Mater.* **20** 2341 (2008)
188. X He, H Tang, M Pan *J. Appl. Polym. Sci.* **108** 529 (2008)
189. M H-S Mohammad, H E Shahriar, G Reza, M Homayoun *Energy Fuels* **22** 2539 (2008)
190. C H Rhee, H K Kim, H Chang, J S Lee *Chem. Mater.* **17** 1691 (2005)
191. W Lu, D Lu, J Liu, C Li, R Guan *Polym. Adv. Technol.* **18** 200 (2007)
192. B A Holmberg, X Wang, Y S Yan *J. Membr. Sci.* **320** 86 (2008)
193. B A Holmberg, X Wang, Y S Yan *Microporous Mesoporous Mater.* **74** 189 (2004)
194. K Tasaki, R DeSousa, H B Wang, J Gasa, A Venkatesan, P Pugazhendhi, R O Loutfy *J. Membr. Sci.* **281** 570 (2006)
195. Y H Liu, B L Yi, Z G Shao, D M Xing, H M Zhang *Electrochem. Solid. State* **9** A356 (2006)
196. A I Perepelkina, E Yu Safronova, V G Sevast'yanov, A S Shalimov, A B Yaroslavtsev *Membrany Membr. Tekhnol.* **2** (2012) [c] (in the press)
197. R Kannan, B A Kakade, V K Pillai *Angew. Chem., Int. Ed.* **47** 2653 (2008)
198. Yu A Dobrovolsky, P Dzhannash, B Laffit, N M Belomoina, A L Rusanov, D Yu Likhachev *Elektrokhimiya* **43** 515 (2007) [j]
199. V V Starkov, Yu A Dobrovolsky, N V Lyskov, G L Klimenko *Al'tern. Energet. Ekol.* (6) 24 (2007) [b]
200. J Maier *J. Phys. Chem. Solids* **46** 309 (1985)
201. J Maier *Solid State Chem.* **23** 171 (1995)
202. A A Lysova, I A Stenina, S V Dolgopolov, Yu G Gorbunova, N A Kononenko, A B Yaroslavtsev *Dokl. Akad. Nauk* **427** 508 (2009) [k]
203. A B Yaroslavtsev *Russ. Chem. Rev.* **66** 579 (1997) [*Usp. Khim.* **66** 641 (1997)]
204. I A Stenina, E Yu Voropaeva, A A Ilyina, A B Yaroslatsev *Polym. Adv. Technol.* **20** 566 (2009)
205. S A Novikova, G Yu Yurkov, A B Yaroslavtsev *Mendeleev Commun.* **20** 89 (2010)
206. E Yu Voropaeva, E A Sanginov, V I Volkov, A S Pavlov, A S Shalimov, I A Stenina, A B Yaroslavtsev *Zh. Neorg. Khim.* **53** 1643 (2008) [f]
207. A B Yaroslavtsev, Yu A Karavanova, E Yu Safronova *Membrany Membr. Tekhnol.* **1** 3 (2011) [c]
208. A B Yaroslavtsev *Khimiya Tverdogo Tela* (The Chemistry of Solids) (Moscow: Nauchnyi Mir, 2009) p. 328
209. V I Volkov, E V Volkov, S V Timofeev, E A Sanginov, A A Pavlov, E Yu Safronova, I A Stenina, A B Yaroslavtsev *Zh. Neorg. Khim.* **55** 355 (2010) [f]
210. A B Yaroslavtsev, D L Gorbatchev *J. Mol. Struct.* **416** 63 (1997)
211. N Wagner, W Schnurnberger, B Mueller, M Lang *Electrochim. Acta* **43** 3785 (1998)
212. B Wang *J. Power Sources* **152** 1 (2005)
213. Y Xu, M Mavrikakis *J. Phys. Chem. B* **107** 9298 (2003)
214. N Wakabayashi, M Takeichi, H Uchida, M Watanabe *J. Phys. Chem. B* **109** 5836 (2005)
215. T Yuichi, T Kento, U Mikito, O Toshiaki *Corros. Sci.* **51** 1560 (2009)
216. K C Neyerlin, R Srivastava, C Yu, P Strasser *J. Power Sources* **186** 261 (2009)
217. S Mukerjee, S Srinivasan, M P Soriaga *J. Electrochem. Soc.* **142** 1409 (1995)
218. R C Koffi, C Coutanceau, E Garnier, J-M Léger, C Lamy *Electrochim. Acta* **50** 4117 (2005)
219. Z B Wang, G P Yin, J Zhang, Y C Sun, P F Shi *J. Power Sources* **160** 37 (2006)
220. K Ota, Y Nakagawa, M Takahashi *J. Electroanal. Chem.* **179** 179 (1984)
221. C Lamy, A Lima, V LeRhun, F Delime, C Coutanceau, J M Liger *J. Power Sources* **105** 283 (2002)
222. T V Parsons *J. Electroanal. Chem.* **257** 45 (1988)
223. X Li, I Sabir, J Park *J. Power Sources* **163** 933 (2007)
224. U H Jung, S U Jeong, K T Park, H M Lee, C Kook, D W Choi, S H Kim *Int. J. Hydrogen Energy* **32** 4459 (2007)
225. T R Ralph, G A Hards, J E Keating, S A Campbell, D P Wilkinson, M Davis, J St-Pierre, M C Johnson *J. Electrochem. Soc.* **144** 3845 (1997)
226. M Weber, J T Wang, S Wasmus, R F Savinell *J. Electrochem. Soc.* **143** 158 (1996)
227. F Barbir *Fuel Cell Technology: Reaching Towards Commercialization* (London: Springer, 2006)
228. M S Wilson, S Gottesfeld *J. Appl. Electrochem.* **1** 1 (1992)
229. N M Markovic, T J Schmidt, V Stamenkovic, P N Ross *Fuell Cells* **1** 105 (2001)
230. N M Markovic, H A Gasteiger, P N Ross *J. Phys. Chem.* **100** 6715 (1996)
231. K Kinoshita *J. Electrochem. Soc.* **137** 845 (1990)
232. P A Attwood, B D McNicol, R T Short *J. Appl. Electrochem.* **10** 213 (1980)
233. S Mukerjee, J McBreen *J. Electroanal. Chem.* **448** 163 (1998)
234. S D Knights, K M Colbow, J St-Pierre, D P Wilkinson *J. Power Sources* **127** 127 (2002)
235. K-Y Chan, J Ding, J Ren, S Cheng, K Y Tsang *J. Mater. Chem.* **14** 505 (2004)
236. W Xing, in *PEM Fuel Cell Electrocatalysts and Catalyst Layers Fundamentals and Applications* (Ed. J Zhang) (London: Springer, 2008) p. 1003
237. M R Tarasevich, V A Bogdanovskaya, E P Lubnin, L A Reznikova *Korroziya: Mater. Zashch.* **10** 22 (2006)
238. P J Kulesza, K Miecznikowski, B Baranowska, M Skunik, S Fiechter, P Bogdanoff, I Dorbandt *Electrochem. Commun.* **8** 904 (2006)

239. S Maass, F Finsterwalder, G Frank, R Hartmann, C Merten *J. Power Sources* **176** 444 (2008)
240. S Kotaro, S Minhua, R Adzic *Polymer Electrolyte Fuel Cell Durability* (New York: Springer, 2009)
241. L M Roen, C H Paik, T D Jarvi *Electrochem. Solid State Lett. A* **7** 19 (2004)
242. H A Gasteiger, S S Kocha, B Sompalli, F T Wagner *Appl Catal. B* **56** 9 (2005)
243. H R Colon-Mercado, H Kim, B N Popov *Electrochem. Commun.* **6** 795 (2004)
244. Z Wei, H Guo, Z Tang *J. Power Sources* **62** 233 (1996)
245. H A Gasteiger, N Markovic, P N Ross, E J Cairns *J. Phys. Chem.* **98** 617 (1994)
246. M R Tarasevich, V A Bogdanovskaya, B M Grafov, N M Zagudaeva, K V Rybalka, A V Kapustin, Yu A Kolbanovskii *Elektrokhimiya* **41** 840 (2005)[j]
247. K Wang, H A Gasteiger, N M Markovi, P N Ross *Electrochim. Acta* **41** 2587 (1996)
248. H A Gasteiger, N M Markovi, P N Ross *J. Phys. Chem.* **99** 8945 (1995)
249. A Kabbabi, R Faure, R Durand, B Beden, F Hahn, J-M Léger, C Lamy *J. Electroanal. Chem.* **444** 41 (1998)
250. M Watanabe, S Motoo *J. Electroanal. Chem.* **60** 275 (1975)
251. M Watanabe, M Uchida, S Motoo *J. Electroanal. Chem.* **229** 349 (1987)
252. D C Papageorgopoulos, M Keijzer, F A de Bruijn *Electrochim. Acta* **48** 197 (2002)
253. T R Ralph, M P Hogarth *Platinum Met. Rev.* **46** 117 (2002)
254. M P Hogarth, T R Ralph *Platinum Met. Rev.* **46** 146 (2002)
255. R C Urian, A F Gulla, S Mukerjee *J. Electroanal. Chem.* **554–555** 307 (2003)
256. W Gang, S Raja, L Deyu, L Ning *Electrochim. Acta* **53** 7622 (2008)
257. C Zhiming, L Changpeng, L Jianhui, X Wei *Electrochim. Acta* **53** 7807 (2008)
258. D-J Guo, L Zhao, X-P Qiu *J. Power Sources* **177** 334 (2008)
259. M Goetz, H Wendt *J. Appl. Electrochem.* **31** 811 (2001)
260. G L Holleck, D M Pasquariello, S L Clauson, in *Proceedings of the 2nd International Symposium on Proton Conducting Membrane Fuel Cells, Boston, 1998* Vol. 2, p. 150.
261. A Lima, C Coutanceau, J M Liger, C Lamy *J. Appl. Electrochem.* **31** 379 (2001)
262. M Gotz, H Wendt *Electrochim. Acta* **43** 3637 (1998)
263. A S Arico, P Creti, N Giordano, V Antonucci *J. Appl. Electrochem.* **26** 959 (1996)
264. R Liu, H Iddir, Q Fan, G Hou, A Bo, K L Ley, E S Smotkin, Y E Sung, H Kim, S Thomas, A Wieckowski *J. Phys. Chem. B* **104** 3518 (2000)
265. M Watanabe, H Igarashi, T Fujino *Electrochemistry* **67** 1194 (1999)
266. W Vogel, J Lundquist, P Ross, P Stonehart *Electrochim. Acta* **20** 79 (1975)
267. M Iwase, S Kawatsu, in *Proceedings of the 1st International on Proton Conducting Membrane Fuel Cells, Pennington, 1995* Vol. 1, p. 12
268. H-F Oetjen, V M Schmidt, U Stimming, F Trila *J. Electrochem. Soc.* **143** 3838 (1996)
269. S R Brankovic, J X Wang, R R Adži *Electrochem. Solid State Lett. A* **4** 217 (2001)
270. H A Gasteiger, N M Markovic, P N Ross *J. Phys. Chem.* **99** 16757 (1995)
271. J Kua, W A Goddard III *J. Am. Chem. Soc.* **121** 10928 (1999)
272. M Arenz, V Stamenkovic, P N Ross, N M Markovic *Electrochem. Commun.* **5** 809 (2003)
273. C Lu, R I Masel *J. Phys. Chem. B* **105** 9793 (2001)
274. C Lu, C Rice, R I Masel, P K Babu, P Waszczuk, H S Kim, E Oldfield, A Wieckowski *J. Phys. Chem. B.* **106** 9581 (2002)
275. T M Koper *Surf. Sci.* **548** 1 (2004)
276. B Hammer, J K Norsko *Surf. Sci.* **343** 211 (1995)
277. D C Skelton, R G Tobin, D K Lambert, C L DiMaggio, G B Fisher *J. Phys. Chem. B* **103** 964 (1999)
278. H Massong, H Wang, G Samjeske, H Baltruschat *Electrochim. Acta* **46** 701 (2000)
279. J McBreen, S Mukerjee *J. Electrochem. Soc.* **142** 3399 (1995)
280. S J Lee, S Mukerjee, E A Ticianelli, L McBreen *Electrochim. Acta* **44** 3283 (1999)
281. S Mukerjee, R C Urian *Electrochim. Acta* **47** 3219 (2002)
282. W-Z Hung,W-H Chung, D-S Tsai, D P Wilkinson, Y-S Huong *Electrochim. Acta* **55** 2116 (2010)
283. G A Camara, E A Ticianelli, S Mukerjee, S J Lee, J McBreen *J. Electrochem. Soc.* **149** A748 (2002)
284. G A Camara, M J Giz, V A Paganin, E A Ticianelli *J. Electroanal. Chem.* **537** 21 (2002)
285. P Liu, A Logadottir, J K Norskov *Electrochim. Acta* **48** 3731 (2003)
286. S-J Liao, H-Y Liu, H Meng *J. Power Sources* **171** 471 (2007)
287. E Antolini, T Lopes, E R Gonzalez *J. Alloys Compd.* **461** 253 (2008)
288. V Jalan, E J Taylor *J. Electrochem. Soc.* **130** 2299 (1983)
289. M Min, J Cho, K Cho, H Kim *Electrochim. Acta* **45** 4211 (2000)
290. M Watanabe, Y Zhu, H Uchida *J. Phys. Chem. B* **104** 1762 (2000)
291. V R Stamenkovic, B Fowler, B S Mun, G Wang, P N Ross, C A Lucas, N M Marković *Science* **315** 495 (2007)
292. S Mukerjee, S Srinivasan *J. Electroanal. Chem.* **357** 201 (1993)
293. T Toda, H Igarashi, M Watanabe *J. Electrochem. Soc.* **145** 4185 (1998).
294. S Mukerjee, S Srinivasan, in *Handbook of Fuel Cells — Fundamentals, Technology and Applications. Fuel Cell Technology and Applications* Vol. 3 (Eds W Vielstich, A Lamm, H A Gasteiger) (Chichester: Wiley, 2003) p. 467
295. A V Guterman, E B Pakhomova, V E Guterman, Yu V Kabirov, V P Grigor'ev *Neorg. Mater.* **45** 829 (2009)[l]
296. V E Guterman, L E Pustovaya, A V Guterman, L L Vysochina *Elektrokhimiya* **43** 1147 (2007)[j]
297. T R Ralph, M P Hogarth *Platinum Met. Rev.* **46** 3 (2002)
298. T Toda, H Igarashi, M Watanabe *J. Electroanal. Chem.* **460** 258 (1999)
299. T Toda, H Igarashi, H Uchida, M Watanabe *J. Electrochem. Soc.* **146** 3750 (1999)
300. C-T Rafael, B B Perla *Surf. Sci.* **602** 3531 (2008)
301. RF P. 2331144 (2008)
302. M R Tarasevich, V A Bogdanovskaya *Al'tern. Energet. Ekol.* (12) 24 (2009)[b]
303. V M Andoralov, M R Tarasevich, S V Kuznetsov, V A Bogdanovskaya *Elektrokhimiya* **46** 1002 (2010)[j]
304. V A Bogdanovskaya, M R Tarasevich, O V Lozovaya *Elektrokhimiya* **47** 902 (2011)[j]
305. V E Guterman, S V Belenov, T A Lastovina, E P Fokina, N V Prutsakova, Ya B Konstantinova *Elektrokhimiya* **47** 997 (2011)[j]
306. X Wang, W Li, Z Chen, M Waje, Y Ya *J. Power Sources* **158** 154 (2006)
307. A Halder, S Sharma, M S Hegde, N Ravishankar *J. Phys. Chem. C* **113** 1466 (2009)
308. Y Tang, H Cong, R Zhong, H-M Chen *Lett. Ed. Carbon* **42** 3251 (2004)
309. L Li, G Wu, B O Xu *Carbon* **44** 2973 (2006)
310. J-S Zheng, X-S Zhang, P Li, J Zhu, X-G Zhou, W-K Yuan *Electrochem. Commun.* **9** 895 (2007)
311. F Su, J Zeng, Y Yu, L Lv, J Lee, X Zhao *Carbon* **43** 2366 (2005)
312. Z R Ismagilov, M A Kerzhentsev, N V Shikina, A S Lisitsyn, L B Okhlopkova, Ch N Barnakov, M Sakashita, T Iijima, K Tadokoro *Catal. Today* **102–103** 58 (2005)
313. J S Guo, G Q Sun, Q Wang, G X Wang, Z H Zhou, S H Tang, L Jiang, B Zhou, Q Xin *Carbon* **44** 152 (2006)

314. L A Langley, D H Fairbrother *Carbon* **45** 47 (2007)
315. D-J Guo, H-L Li *Electroanalysis* **17** 869 (2005)
316. J L Bahr, J Yang, D V Kosynkin, M J Bronikowski, R E Smalley, J M Tour *J. Am. Chem. Soc.* **123** 6536 (2001)
317. N Massoni, A Beaumont-Martinent, J-Y Laurent *J. Power Sources* **166** 68 (2007)
318. M Carmo, T Roepke, F Scheiba, C Roth, S Moeller, H Fuess, J G R Poco, M Linardi *Mater. Res. Bull.* **44** 51 (2009)
319. Z Tang, Q Li, G Lu *Carbon* **45** 41 (2007)
320. A Felten, C Bittencourt, J-F Colomer, G Van Tendeloo, J-J Pireaux *Carbon* **45** 110 (2007)
321. J L Hueso, J P Espinds, A Caballero, J Cotrino, A R Gonzvlez-Elipe *Carbon* **45** 89 (2007)
322. Y-T Kim, K Ohshima, K Higashimine, T Uruga, M Takata, H Suematsu, T Mitani *Angew. Chem., Int. Ed.* **45** 407 (2006)
323. F Vigier, C Coutanceau, A Perrard, E M Belgsir, C Lamy *J. Appl. Electrochem.* **34** 439 (2004)
324. W Li, C Liang, J Qiu, W Zhou, H Han, Z Wei, G Su, Q Xi *Carbon* **40** 787 (2002)
325. X Guo, D-J Guo, X-P Qiu, L-Q Chen, W-T Zhu *Electrochem. Commun.* **10** 1748 (2008)
326. A O Neto, A Y Watanabe, S R M de Rodrigues, M Linardi, C A Forbicini, E V Spinacg *Ionics* **14** 577 (2008)
327. X Li, W-X Chen, J Zhao, W Xing, Z-D Xu *Carbon* **43** 2168 (2005)
328. J Zhao, W Chen, Y Zheng, X Li, Z Xu *J. Mater. Sci.* **41** 5514 (2006)
329. M Gangeri, S Perathoner, G Centi *Inorg. Chim. Acta* **359** 4828 (2006)
330. Y Zhao, Y E, L Fan, Y Qiu, S Yang *Electrochim. Acta* **52** 5873 (2007)
331. Y Liu, J Chen, W Zhang, Z Ma, G F Swiegers, C O Too, G G Wallace *Chem. Mater.* **20** 2603 (2008)
332. N R Elezovic, B M Babic, V R Radmilovic, L M Vracar, N V Krstajic *Electrochim. Acta* **54** 2404 (2009)
333. P J Kulesza, K Miecznikowski, B Baranowska, M Skunik, A Kolary-Zurowska, A Lewera, K Karnicka, M Chojak, I Rutkowska, S Fiechter, P Bogdanoff, I Dorbandt, G Zehl, R Hiesgen, E Dirk, K S Nagabhushana, H Boennemann *J. Appl. Electrochem.* **37** 1439 (2007)
334. P J Kulesza, B Grzybowska, M A Malik, M T Galkowski *J. Electrochem. Soc.* **144** 1911 (1997)
335. H China, S Campbell, O Kesler *J. Electrochem. Soc. B* **156** 1232 (2009)
336. M S Saha, M N Banis, Y Zhang, R Li, X Sun, M Cai, F T Wagner *J. Power Sources* **192** 330 (2009)
337. K Sasaki, L Zhang, R R Adzic *Phys. Chem. Chem. Phys.* **10** 159 (2008)
338. J Shim, C-R Lee, H-K Lee, J-S Lee, E J Cairns *J. Power Sources* **102** 172 (2001)
339. L Xiong, A Manthiram *Electrochim. Acta* **49** 4163 (2004)
340. M Gustavsson, H Ekström, P Hanarp, L Eurenius, G Lindbergh, E Olsson, B Kasemo *J. Power Sources* **163** 671 (2007)
341. X-Y Xie, Z-F Ma, X Wu, Q-Z Ren, X Yuan, Q-Z Jiang, L Hu *Electrochim. Acta* **52** 2091 (2007)
342. N R de Tacconi, C R Chenthamarakshan, K Rajeshwar, W-Y Lin, T F Carlson, L Nikiel, W A Wampler, S Sambandam, V Ramani *J. Electrochem. Soc. B* **155** 1102 (2008)
343. S von Kraemer, K Wikander, G Lindbergh, A Lundblad, A E C Palmqvist *J. Power Sources* **180** 185 (2008)
344. P Justin, G Ranga Rao *Int. J. Hydrogen Energy* **36** 5875 (2011)
345. J W Long, R M Stroud, K E Swider-Lyons, D R Rolison *J. Phys. Chem. B* **104** 9772 (2000)
346. Q Lu, B Yang, L Zhuang, J Lu *J. Phys. Chem. B* **109** 1715 (2005)
347. L Jang, G Sun, S Sun, J Liu, S Tang, H Li, B Zhou, Q Xin *Electrochim. Acta* **50** 5384 (2005)
348. L Jang, L Colmenares, Z Jusys, G Q Sun, R J Behm *Electrochim. Acta* **53** 377 (2007)
349. K-W Park, K-S Ahn, Y-C Nah, J-H Choi, Y-E Sung *J. Phys. Chem. B* **107** 4352 (2003)
350. A V Grigorieva, E A Goodilin, L E Derlyukova, T A Anufrieva, A B Tarasov, Yu A Dobrovolsky, Yu D Tretyakov *Appl. Catal.: General* **362** 20 (2009)
351. H Song, X Qiu, F Li *Electrochim. Acta* **53** 3708 (2008)
352. X Liu, J Chen, G Liu, L Zhang, H Zhang, B Yi *J. Power Sources* **195** 4098 (2010)
353. D He, L Yang, S Kuang, Q Cai *Electrochem. Commun.* **9** 2467 (2007)
354. A Bauer, C Song, A Ignaszak, R Hui, J Zhang, L Chevallier, D Jones, J Roziere *Electrochim. Acta* **55** 8365 (2010)
355. N Rajalakshmi, N Lakshmi, K S Dhathathreyan *Int. J. Hydrogen Energy* **33** 7521 (2008)
356. S-Y Huang, P Ganesan, B N Popov *Appl. Catal., B* **102** 71 (2011)
357. M Hepel, I Dela, T Hepel, J Luo, C J Zhong *Electrochim. Acta* **52** 5529 (2007)
358. C-S Chen, F-M Pan *Appl. Catal., B* **91** 663 (2009)
359. D-S Kim, E F A Zeid, Y-T Kim *Electrochim. Acta* **55** 3628 (2010)
360. L Xing, J Jia, Y Wang, B Zhang, S Dong *Int. J. Hydrogen Energy* **35** 12169 (2010)
361. P Xiao, H Song, X Qiu, W Zhua, L Chen, U Stimming, P Bele *Appl. Catal., B* **97** 204 (2010)
362. X He, C Hu *J. Power Sources* **196** 3119 (2011)
363. M Wang, D Guo, H Li *J. Solid State Chem.* **178** 1996 (2005)
364. J M Macak, P J Barczuk, H Tsuchiya, M Z Nowakowska, A Ghicov, M Chojak, S Bauer, S Virtanen, P J Kulesza, P Schmuki *Electrochem. Commun.* **7** 1417 (2005)
365. S H Kang, T-Y Jeon, H-S Kim, Y-E Sung, W H Smyrl *J. Electrochem. Soc.* **155** B1058 (2008)
366. S H Kang, Y-E Sung, W H Smyrl *J. Electrochem. Soc.* **155** B1128 (2008)
367. D V Bavykin, J M Friedrich, F C Walsh *Adv. Mater.* **18** 2807 (2006)
368. O Madelung, U Rössler, M Schulz, in *Non-Tetrahedrally Bonded Binary Compounds II* (Eds S Kück, H Werheit, O Madelung) (London: Springer, 2006) Vol. 1D, p. 535
369. L He, H F Franzen, D C Johnson *J. Appl. Electrochem.* **26** 785 (1996)
370. T Ioroi, Z Siroma, N Fujiwara, S Yamazaki, K Yasuda *Electrochem. Commun.* **7** 183 (2005)
371. N V Krstajic, L M Vracar, V R Radmilovic, S G Neophytides, M Labou, J M Jaksic, R Tunold, P Falarase, M Milan *Surf. Sci.* **601** 1949 (2007)
372. WO 119407 (2006)
373. WO 124248 (2006)
374. D Morris, Y Dou, J Rebane, C E J Mitchell, R G Egdell *Phys. Rev. B* **61** 13445 (2000)
375. J Arbiol, J Cerda, G Dezanneau, A Cirera, F Peiro, A Cornet, J R Morante *J. Appl. Phys.* **92** 853 (2002)
376. G Y Chen, S R Bare, T E Mallouk *J. Electrochem. Soc.* **149** A1092 (2002)
377. B L García, R Fuentes, J W Weidner *Electrochem. Solid State Lett.* **10** B108 (2007)
378. K Park, K Seol *Electrochem. Commun.* **9** 2256 (2007)
379. S L Gojkovic, B M Babic, V R Radmilovic, N V Krstajic *J. Electroanal. Chem.* **639** 161 (2010)
380. S Shanmugam, A Gedanken *Small* **3** 1189 (2007)
381. J-M Chen, L S Sarma, C-H Chen, M-Y Cheng, S-C Shih, G-R Wang, D-G Liu, J-F Lee, M-T Tang, B-J Hwang *J. Power Sources* **159** 29 (2006)
382. H Song, P Xiao, X Qiu, W Zhu *J. Power Sources* **195** 1610 (2010)

383. D-J Guo, X-P Qiu, L-Q Chen, W-T Zhu *Carbon* **47** 1680 (2009)
384. O E Haas, S T Briskeby, O E Kongstein, M Tsypkin, R Tunold, B T Borresen *J. New Mater. Electrochem. Syst.* **11** 9 (2008)
385. L A Frolova, Yu A Dobrovolsky *Izv. Akad. Nauk, Ser. Khim.* 1076 (2011) [m]
386. T Okanishi, T Matsui, T Takeguchi, R Kikuchi, K Eguchi *Appl. Catal., A* **298** 181 (2006)
387. Z Liu, B Guo, L Hong, T H Lim *Electrochem. Commun.* **8** 83 (2006)
388. A L Santos, D Profeti, P Olivi *Electrochim. Acta* **50** 2615 (2005)
389. E E Kohnke *J. Phys. Chem. Solids* **23** 1557 (1962)
390. I Saadeddin, B Pecquenard, J P Manaud, R Decourt, C Labrugere, T Buffeteau, G Campet *Appl. Surf. Sci.* **253** 5240 (2007)
391. W J Zhou, B Zhou, W Z Li, Z H Zhou, S Q Song, G Q Sun, Q Xin, S Douvartzides, M Goula, P Tsiakaras *J. Power Sources* **126** 16 (2004)
392. K-S Lee, I-S Park, Y-H Cho, D-S Jung, N Jung, H-Y Park, Y-E Sung *J. Catal.* **258** 143 (2008)
393. L A Frolova, Yu A Dobrovolsky, N G Bukun *Elektrokhimiya* **47** 745 (2011) [j]
394. A T Marshall, R G Haverkamp *Electrochim. Acta* **55** 1978 (2010)
395. D J You, K Kwon, C Pak, H Chang *Catal. Today* **146** 15 (2009)
396. C Pan, Y Li, Y Ma, X Zhao, Q Zhang *J. Power Sources* **196** 6228 (2011)
397. D-J Guo *J. Power Sources* **196** 679 (2011)
398. H L Pang, X H Zhang, X X Zhong, B Liu, X G Wei, Y F Kuang, J H Chen *J. Colloid Interface Sci.* **319** 193 (2008)
399. A B Bhise, D J Late, N S Ramgir, M A More, I S Mulla, V K Pillai, D S Joag *Thin Solid Films* **516** 6388 (2008)
400. R Berenguer, C Quijada, E Morallon *Electrochim. Acta* **54** 5230 (2009)
401. J-M Lee, S-B Han, Y-W Lee, Y-J Song, J-Y Kim, K-W Park *J. Alloys Compd.* **506** 57 (2010)
402. W S Baker, J J Pietron, M E Teliska, P J Bouwman, D E Ramaker, K E Swider-Lyons *J. Electrochem. Soc.* **153** A1702 (2006)
403. H China, S Campbell, O Kesler *J. Power Sources* **161** 893 (2006)
404. G Chang, M Oyama, G Hirao *J. Phys. Chem. B* **110** 1860 (2006)
405. A Kulprathipanja, J L Falconer *Appl. Catal., A* **261** 77 (2004)
406. V Ganesh, D L Maheswari, S Berchmans *Electrochim. Acta* **56** 1197 (2011)
407. B-K Kim, D Seo, J Y Lee, H Song, J Kwak *Electrochem. Commun.* **12** 1442 (2010)
408. P Diao, J Wang, D Zhang, M Xiang, Q Zhang *J. Electroanal. Chem.* **630** 81 (2009)
409. Y Song, Y Ma, Y Wang, J Di, Y Tu *Electrochim. Acta* **55** 4909 (2010)
410. K Lasch, G Hayn, L Jörissen, J Garche, O Besenhardt *J. Power Sources* **105** 305 (2002)
411. Y Bai, J Wu, X Qui, J Xi, J Wang, J Li, W Zhu, J Chen *Appl. Catal., B* **73** 144 (2007)
412. L P R Profeti, D Profeti, P Olivi *Int. J. Hydrogen Energy* **34** 2747 (2009)
413. É C G Rufino, P Olivi *Int. J. Hydrogen Energy* **35** 13298 (2010)
414. Y Takasu, K Oohori, N Yoshinaga, W Sugimoto *Catal. Today* **146** 248 (2009)
415. E Tsuji, A Imanishi, K-I Fukui, Y Nakato *Electrochim. Acta* **56** 2009 (2011)
416. A Chen, J Daniel, L Russa, B Miller *Langmuir* **20** 9695 (2004)
417. Y Zhang, C Wang, N Wan, Z Mao *Int. J. Hydrogen Energy* **32** 400 (2007)
418. A T Marshall, S Sunde, M Tsypkin, R Tunold *Int. J. Hydrogen Energy* **32** 2320 (2007)
419. J A Sawicki, K Marcinkowska, F E Wagner *Nucl. Instrum. Meth. Phys. Res. Sect., B* **268** 2544 (2010)
420. F Ye, J Li, X Wang, T Wang, S Li, H Wei, Q Li, E Christensen *Int. J. Hydrogen Energy* **35** 8049 (2010)
421. H-B Zhu, H-M Zhang, Y-M Liang, Y Zhang, B Yia *Electrochem. Solid State Lett.* **9** A49 (2006)
422. L Wang, D M Xing, Y H Liu, Y H Cai, Z-G Shao, Y F Zhai, H X Zhonga, B L Yi, H M Zhang *J. Power Sources* **161** 61 (2006)
423. J H Liu, X X Chen, K Z Zhong, H H Cui, Y F Zhou *J. Colloid Interface Sci.* **307** 139 (2007)
424. B Seger, A Kongkanand, K Vinodgopal, P V Kamat *J. Electroanal. Chem.* **621** 198 (2008)
425. M S Hino, S Kobayashi, K Arata *J. Am. Chem. Soc.* **101** 6439 (1979)
426. G D Yadav, J J Nair *Microporous Mesoporous Mater.* **33** 1 (1999)
427. M Waqif, J Bachelier, O Saur, J-C Lavalley *J. Mol. Catal.* **72** 127 (1992)
428. S Hara, M Miyayama *Solid State Ionics* **168** 111 (2004)
429. Y Suzuki, A Ishihara, S Mitsushima, N Kamiya, K Ota *Electrochem. Solid State Lett. B* **10** 105 (2007)
430. H Chhina, S Campbell, O Kesler *J. Electrochem. Soc. B* **154** 533 (2007)
431. Z Zhang, X Wang, Z Cui, C Liu, T Lu, W Xing *J. Power Sources* **185** 941 (2008)
432. Z Cui, L Feng, C Liu, W Xing *J. Power Sources* **196** 2621 (2011)
433. J Mann, N Yao *Langmuir* **22** 10432 (2006)
434. S Mukerjee, R C Urian, S J Lee, E A Ticianelli *J. Electrochem. Soc. A* **151** 1094 (2004)
435. T Ioroi, K Yasuda, Z Siroma, N Fujiwara, Y Miyazaki *J. Electrochem. Soc.* **150** A1225 (2003)
436. T Matsui, K Fujiwara, T Okanishi, R Kikuchi, T Takeguchi, K Eguchi *J. Power Sources* **155** 152 (2006)
437. A C C Tseung, K Y Chen *Catal. Today* **38** 439 (1997)
438. T Ioroi, T Akita, S Yamazaki, Z Siroma, N Fujiwara, K Yasuda *Electrochim. Acta* **52** 491 (2006)
439. Z H Zhou, W S Li, Z Fu, X D Xiang *Int. J. Hydrogen Energy* **35** 936 (2010)
440. K Machida, M Enyo, G Adachi, J Shiokawa *J. Electrochem. Soc.* **135** 1955 (1988)
441. P K Shen, A C Tseung *J. Electrochem. Soc.* **141** 3082 (1994)
442. K Y Chen, P K Shen, A C Tseung *J. Electrochem. Soc.* **142** 185 (1995)
443. A K Shukla, M K Ravikumar, A S Arico, G Candiano, V Antonucci, N Giordano, A Hamnett *J. Appl. Electrochem.* **25** 528 (1995)
444. Jin Zhao, A M Baranov, A E Ukshe, A V Knotko, L A Frolova, Yu A Dobrovolsky *Al'ternat. Energet. Ekol.* (8) 175 (2009) [b]
445. O Nakamura, O Kodama, I Ogino, Y Miyake *Chem. Lett.* **8** (1) 17 (1979)
446. T Maiyalagan, B Viswanathan *J. Power Sources* **175** 789 (2008)
447. O Nakamura, I Ogino *Mater. Res. Bull.* **17** 231 (1982)
448. A Hardwick, P G Dickens, R C T Slade *Solid State Ionics* **13** 345 (1984)
449. R C T Slade, J Barker, H A Pressman, J H Strange *Solid State Ionics* **28–30** 594 (1988)
450. K D Kreuer, M Hampele, K Dolde, A Rabenau *Solid State Ionics* **28–30** 589 (1988)
451. R C T Slade, H A Pressman, E Skou *Solid State Ionics* **38** 207 (1990)

452. U Mioc, M Davidovic, N Tjapkin, P Colomban, A Novak *Solid State Ionics* **46** 103 (1991)
453. R C T Slade, M J Omana *Solid State Ionics* **58** 195 (1992)
454. JP P. 76106694 (1976)
455. O Nakamura, I Ogino, T Kodama *Solid State Ionics* **3–4** 347 (1981)
456. Jin Zhao, A E Ukshe, L S Leonova, A V Chub, L A Frolova, Yu A Dobrovolsky *Al'ternat. Energet. Ekol.* (12) 39 (2010) [b]
457. F Mazza, S Trassatti *J. Electrochem. Soc.* **110** 847 (1963)
458. J Y Kim, T-K Oh, Y Shin, J Bonnett, K S Weil *Int. J. Hydrogen Energy* **36** 4557 (2011)
459. H Zhong, H Zhang, G Liu, Y Liang, J Hu, B Yi *Electrochem. Commun.* **8** 707 (2006)
460. K Lee, L Zhang, J Zhang, in *PEM Fuel Cell Electrocatalysts and Catalyst Layers: Fundamentals and Applications* (Ed. J Zhang) (London: Springer, 2008) p. 715
461. S S Zhang, H Zhu, H M Yu, J B Hou, B L Yi, P W Ming *Chin. J. Catal.* **28** 109 (2007)
462. H Chhina, S Campbell, O Kesler *J. Power Sources* **164** 431 (2007)
463. L Kunchan, I Akimitsu, M Shigenori, K Nobuyuki, O Ken-ichiro *Electrochim. Acta* **49** 3479 (2004)
464. Y Hara, N Minami, H Matsumoto, H Itagak *Appl. Catal.: General* **332** 289 (2007)
465. M B Zellner, G Jingguang *J. Electrochem. Soc.* **152** A1483 (2005)
466. H Meng, P K Shen *J. Phys. Chem. B* **109** 22705 (2005)
467. L G Santos, K S Freitas, E A Ticianelli *J. Solid State Electrochem.* **11** 1541 (2007)
468. E C Weigert, A L Stottlemyer, M B Zellner, J G Chen *J. Phys. Chem. C* **111** 14617 (2007)
469. X G Yang, C Y Wang *Appl. Phys. Lett.* **86** 224104 (2005)
470. M K Jeon, H Daimon, K R Lee, A Nakahara, S I Woo *Electrochem. Commun.* **9** 2692 (2007)
471. R Venkataraman, H R Kunz, J M Fenton *J. Electrochem. Soc., A* **150** 278 (2003)
472. L Guojin, J S Cooper, P J McGinn *J. Power Sources* **161** 106 (2006)
473. H Fengping, G F Cui, Z D Wei, P K Shen *Electrochem. Commun.* **10** 1303 (2008)
474. X Hu, Z F Zeng, F P Hu, J G Wang, P K Shen *Chin. J. Catal.* **29** 1027 (2008)
475. R Ganesan, J S Lee *Angew. Chem., Int. Ed.* **44** 6557 (2005)
476. G A Rimbu, I Stamatin, C L Jackson, K Scott *J. Optoelectron. Adv. Mater.* **8** 670 (2006)
477. J Shine, J C McClurea, R Chianellia, P Picha, P J Sebastian *Int. J. Hydrogen Energy* **30** 1339 (2005)
478. C-H Wanga, C-C Chen, H-C Hsu, H-Y Du, C-P Chen, J-Y Hwang, L C Chen, H-C Shih, J Stejskale, K H Chen *J. Power Sources* **190** 279 (2009)
479. L Niu, Q Lia, F Wei, X Chen, H Wang *Synt. Met.* **139** 271 (2003)
480. V G Khomenko, V Z Barsukov, A S Katashinskii *Electrochim. Acta* **50** 1675 (2005)
481. G A Rimbu, M Iordoc, R Vasilescu-Mirea, I Stamatin, I Iordache, T Zaharescu *J. Optoelectron. Adv. Mater.* **2** 876 (2008)
482. A G Zabrodski, M E Kompan, V G Malyshkin, I Yu Sapurina *Tech. Phys. Lett.* **32** 758 (2006)
483. P K Rajenda, N Munichandrainah *J. Power Sources* **103** 300 (2002)
484. H H Zhou, S Q Jiao, J H Chen, W Z Wei, Y F Kuang *J. Appl. Electrochem.* **34** 455 (2004)
485. M R Tarasevich, V A Bogdanovskaya, B M Grafov, N M Zagudaeva, K V Rybalka, A V Kapustin, Yu A Kolbanovskii *Elektrokhimiya* **41** 840 (2005) [j]
486. K V Rybalka, M R Tarasevich, B M Grafov, V A Bogdanovskaya, L A Beketaeva *J. New Mater. Electrochem. Syst.* **10** 81 (2007)
487. F Kadirgan, F Ficicioglu, I Becerik *Turk. J. Chem.* **22** 91 (1998)
488. B I Podlovchenko, Yu M Maksimov, T D Gladysheva, E A Kolyadko *Elektrokhimiya* **36** 825 (2000) [j]
489. A Lima, F Hahn, J-M Léger *Elektrokhimiya* **40** 369 (2004) [j]
490. J Yano, T Shiraga, A Kitani *J. Solid State Electrochem.* **12** 1179 (2008)
491. C T Hable, M S Wrighton *Langmuir* **9** 3284 (1993)
492. T Kessler, L A Castro *J. Appl. Electrochem.* **32** 825 (2002)
493. Z Chen, L Xu, W Li, M Waje, Y Yan *Nanotechnology* **17** 5254 (2006)
494. J Shi, Z Wang, H-L Li *J. Mater. Sci.* **42** 539 (2007)
495. B Winther-Jensen, O Winther-Jensen, M Forsyth, D R MacFarlane *Science* **321** 671 (2008)
496. S Patra, N Munichandraiah *Langmuir* **25** 1732 (2009)
497. J F Drillet, R Dittmeyer, K Juttner *J. Appl. Electrochem.* **37** 1219 (2007)

[a] — *Mendeleev Chem. J. (Engl. Transl.)*
[b] — *Int. Sci. J. Altern. Energy Ecol. (Engl. Transl.)*
[c] — *Memb. Memb. Technol. (Engl. Transl.)*
[d] — *Polym. Sci. (Engl. Transl.)*
[e] — *Crystallogr. Rep. (Engl. Transl.)*
[f] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[g] — *Russ. J. Phys. Chem. Ser. A (Engl. Transl.)*
[h] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[i] — *Nanotechnol. Russ. (Engl. Transl.)*
[j] — *Russ. J. Electrochem. (Engl. Transl.)*
[k] — *Dokl. Phys. Chem. (Engl. Transl.)*
[l] — *Inorg. Mater. (Engl. Transl.)*
[m] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*