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# Composite materials with ionic conductivity: from inorganic composites to hybrid membranes

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**Abstract. Information on composite materials with ionic conductivity including inorganic composites and hybrid polymeric ion exchange membranes containing inorganic or polymeric nanoparticles is generalized. The nature of the effect of increase in the ionic conductivity in this type of materials and the key approaches used for theoretical estimation of the conductivity are considered. Data on the ionic conductivity and some other important properties of composites and membrane materials are presented. Prospects for utilization of composite materials and hybrid membranes in hydrogen power engineering are briefly outlined. The bibliography includes 314 references.**

## I. Introduction

Modern chemical research is increasingly oriented to solving environmental safety problems. Human activity leads to rapid environmental pollution.[1] As a consequence, environmental safety of production facilities and waste processing including sewage sanitation go to the forefront. Yet another crucially important problem is the search for and design of novel energy sources.[2, 3] Solution to these problems is to a great extent related to utilization of membrane materials and solid electrolytes, which are traditionally used for sewage cleaning, manufacturing of gas and liquid sensors and various electrochemical devices.[4]

A common feature of solid electrolytes and ion-exchange membrane materials is high ionic conductivity. This allows such materials to be widely used in electrochemistry. At the same time, in most cases the materials should not only exhibit high ionic conductivity, but also meet some other requirements related to specific features of a certain process or apparatus. In this connection the properties of the starting materials are far from being optimum. For some reasons, the available solid electrolytes and membranes are of limited use. In the case of solid electrolytes, this first of all is a relatively low strength, which is especially characteristic of thin plates used in fabrication of fuel cells. Often, such plates exhibit not only low ionic conductivity, but also high gas permeability. Polymeric ion-exchange membranes are free from these drawbacks.

When using ion-exchange membranes in hydrogen power engineering, additional difficulties may appear. Namely, most often there is a need for moistening and temperature control; chemical degradation of membrane occurs, as well as rapid poisoning of the catalyst with small admixtures of carbon monoxide, which is unavoidably present in hydrogen produced by conversion of coal, hydrocarbons, alcohols, *etc*.[5] This gives an impetus to search for novel types of solid electrolytes and membranes. But the range of suitable materials is not wide. Recently, only a few novel solid proton-conducting electrolytes or membranes have been designed, all of them having the same drawbacks and being noncompetitive in properties with the Nafion perfluorinated membranes, which were initially developed for elctrochemical production of chlorine.[4, 5] That is why researchers pay increasing attention to the synthesis of composite materials offering some advantages over single-phase samples.[6, 7]

It should be noted that in a vast majority of cases the case in point is fabrication of nanocomposites. Changes in the properties of composites are first of all due to interfacial phenomena. A decrease in the average particle size leads to an increase in the surface area of the interface and therefore to changes in the properties of materials. Thus, it is most appropriate to fabricate composites from nanoparticles. In this case the particle size is comparable with the thickness of the surface Debye layer (main changes in the properties are

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observed within this layer). That is why studies on composite materials with ionic conductivity are closely related to research on nanomaterials and nanotechnologies, the most dynamic fields of modern natural science.[8,9]

The history of the studies of ionic conductivity in nanocomposites is relatively short. In 1973, Liang[10] reported enhancement of ionic conductivity by several orders of magnitude in the system comprised of lithium iodide characterized by relatively low cation mobility, and finely dispersed alumina (dielectric). The mixture of two chemically noninteracting compounds unexpectedly acquired a qualitatively new property. Rapid recognition of this discovery and numerous studies carried out in this field were due to prospects for utilization of such systems in the design of high-capacity capacitors and lithium cells.[11] Shortly after this discovery (in the late 1970s – early 1980s), investigations aimed at enhancing the ionic conductivity of silver, mercury, lithium and copper(I) halides by doping with finely dispersed powder of an inert phase (mainly comprised of alumina, silica and titania) were carried out.[12–20] At nearly the same time, Shahi and Wagner,[21,22] as well as Hartwig *et al.*[23] reported the enhancement of ionic conductivity in two-phase mixtures of solid electrolytes ($AgI-AgBr$, $LiI-NH_4I$). More recently, the number of studies on the subject increased.

The aim of this review is to generalize the data on the properties of composites based on solid electrolytes or ion-exchange membranes with high ionic conductivity and on some practical applications of these composites.

## II. Point defects at interfaces

In spite of considerable interest in the enhancement of ionic conductivity in nanocomposites, the nature of this phenomenon was not reliably established for long. For instance, Stoneham *et al.*[24] believed that formation of the high-conducting phase is due to trace water adsorbed at interfaces. However, no water was detected in most related systems. The nature of changes in the composite electrolytes was understood when considering defect formation at interfaces. It was Wagner[13] who assumed that enhancement of conductivity in binary systems $MI-Al_2O_3$ (M is metal) is related to an increase in the concentration of defects in salts containing mobile cations $M^+$. It is this hypothesis that serves a basis for modern theories of transport phenomena in composite materials.

The surface of a crystal is imperfect because it includes atoms or ions with noncompensated and unsaturated system of bonds. As a consequence, the surface is often highly reactive, which can manifest itself in, *e.g.*, the interaction with other solid, liquid or gaseous chemicals. This feature of surfaces was reported by Aleskovsky[25] who noted that the surface of a crystal can readily be completed through the interaction with atoms or molecules of other compounds. For instance, calcined particles of water-free silica gel show high adhesion to walls of a vessel or coagulate to complete a system of bonds.

Thus, a distinctive feature of finely dispersed alumina or silica used by Liang[10,11] and other researchers is high sorption activity of their surface.

However, the conditions for sorption of lithium or aluminium cations and iodide or oxygen anions on the surface of the alien phase are different. This is the reason for preferred sorption of a particular kind of ions, which most often occurs at the interface. For instance, only lithium cations exhibit high mobility in the system $LiI-Al_2O_3$; they cannot penetrate into the interior of alumina particles, but can be adsorbed on their surface. The system remains electrically neutral due to the appearance of cationic vacancies in lithium iodide; as a consequence, LiI becomes negatively charged (Fig. 1). However, owing to Coulomb interaction with the positively charged interface these vacancies are concentrated within a very thin Debye layer ($\sim 1-2$ nm thick) near the interface. Thus, at the $LiI/Al_2O_3$ interface one deals with the formation of an electrical double layer similar to that known for metal/electrolyte solution interfaces (see, *e.g.*, a monograph[26]).

Unfortunately, direct experimental proofs of this interaction in composites are scarce. Nevertheless, they were obtained in some cases. For instance, sorption processes in composite solid electrolytes based on acid iron sulfate and silica were detected.[27] The IR spectrum of this system showed no characteristic stretching band of OH groups on the surface of silica gel; these groups are only slightly involved in the formation of hydrogen bonds. More reactive protons of the acid sulfate were sorbed at the surface of silica gel, which led to formation of a highly defective interfacial layer.

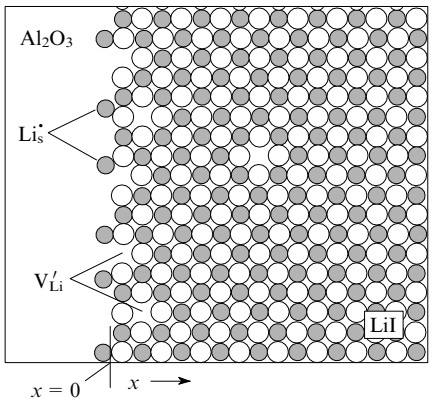



**Figure 1.** Formation of an electrical double layer at $LiI/Al_2O_3$ interface.
For notations $Li^{\bullet}_s$ and $V'_{Li}$, see text.

The most complete version of the theory of sorption processes in composite electrolytes was reported by Maier[28–37] who considered these processes as sorption of cationic vacancies (V) or interstitials (i) at the interface. Owing to Coulomb attraction, the oppositely charged defects present in excess form the so-called 'surface charge', which rapidly decreases when moving into the interior of the crystal.[6,28,38] To obtain a quantitative description of the phenomenon, the formation of defects at the interface is usually treated as a process involving the formation of cationic vacancies and interstices in the bulk of the crystal

$$M_M + V_s = M^{\bullet}_s + V'_M, \quad (1)$$

$$M^{\bullet}_s + V_i = M^{\bullet}_i + V_s, \quad (2)$$

which is accompanied by the appearance and annihilation of metal cations at the surface. Following Kroger and Vink,[39] here the subscripts indicate that a given particle occupies an atomic site, an interstice or is at the surface of the crystal (s). The superscripts indicate a positive (a dot)

and negative (prime) charge of the particle relative to the stoichiometrically specified charge for a given lattice.[40]

Quasi-chemical reactions (1) and (2) can be characterized by the Gibbs energies $\Delta G_v$ and $\Delta G_i$. If $\Delta G_v < \Delta G_i$, the interface is enriched with cations and the concentration of vacancies near the interface increases relative to their concentration in the bulk. At $\Delta G_v > \Delta G_i$, the reverse process occurs. The maximum content of defects is attained within the Debye layer, namely, their concentration changes from $C_0$ to $1.7C_\infty$ ($C_0$ is the concentration of defects at the surface of the particle, $x = 0$; $C_\infty$ is the bulk concentration of defects at the longest distance from the interface). For most practically important cases, the thickness of the Debye layer ($\lambda$) is much smaller than the size of the crystal along the $x$ axis (see Fig. 1) and can be determined from the relation

$$\lambda = \left(\frac{\varepsilon\varepsilon_0 kT}{2e^2 C_\infty}\right)^{1/2}, \quad (3)$$

where $\varepsilon$ and $\varepsilon_0$ are the relative and absolute dielectric permittivities of the material, respectively, and e is the electron charge. The concentration profile of defects can be described as follows[28]

$$N_v = N_{v\infty}\exp[Z], \quad (4)$$

$$N_i = N_{i\infty}\exp[-Z], \quad (5)$$

where

$$Z = 4\tanh^{-1}\left[\exp\left(-\frac{x}{\lambda}\right)\tanh\frac{Z_0}{4}\right], \quad (6)$$

$$Z_0 = Z(x=0) = -\frac{\Delta G_v - \Delta G_i}{CRT}. \quad (7)$$

The difference between the electric potentials in the bulk ($\phi$) and at the surface ($\phi_0$) is given by

$$\phi - \phi_0 = \frac{\Delta G_v - \Delta G_i}{2e}. \quad (8)$$

If the particle size is much larger than the thickness of the Debye layer, the potential difference (8) takes a constant value. Wonnell and Slifkin[41,42] determined the surface potential of silver chloride and bromide crystals in air. When heated from 298 to 550 K the surface potential changes from $-0.1$ to $-0.25$ eV. The room-temperature concentration of cationic interstices at the surface of these compounds is three orders of magnitude higher than the corresponding bulk value.[41]

Various types of interaction at interfaces between solids (Fig. 2) have been reported.[43] In systems comprised of alumina and lithium iodide, silver chloride or a divalent metal fluoride, monovalent ions ($Li^+$, $Ag^+$, $F^-$) with the highest mobility are adsorbed at the interface, while the concentration of vacancies increases in the Debye layer near the interface (see Fig. 2 *a*,*b*).[32,42] Sorption of ammonia on the AgCl surface with the formation of rather strong complexes with silver ions causes the concentration of cationic vacancies to increase (see Fig. 2 *c*).[29] At the same time, the interaction of silver chloride or calcium fluoride with Lewis bases ($BF_3$ or $AsF_5$) results in the formation of strong anionic complexes on the surface. This is accompanied by an increase in the concentration of silver cations in interstices or the concentration of vacancies occupying fluoride ion sites in the Debye layer (see Fig. 2 *d*).[29,31,42]

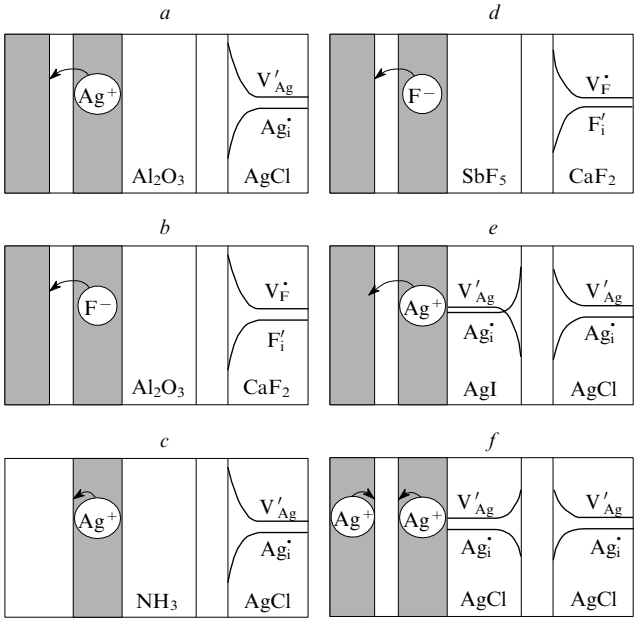



**Figure 2.** Defect formation at different interfaces. $AgCl/Al_2O_3$ (*a*), $CaF_2/Al_2O_3$ (*b*), $AgCl/NH_3$ (*c*), $CaF_2/SbF_5$ (*d*), AgI/AgCl (*e*), and AgCl/AgCl (*f*). The right side of each plot shows changes in the concentration of main types of defects in the electrolyte layer.

These phenomena were observed not only in the interaction of ionic salts with oxides. For instance, contact between β-AgI and AgBr or AgCl also leads to significant enhancement of conductivity.[44,45] The reason is the difference between the chemical potentials of silver in AgI and AgCl (see Fig. 2 *e*,*f*).

Concluding this Section, it should be noted that the effect described here is manifested not only in the systems comprising two solid phases. Even if one phase is a noble gas or vacuum, one type of crystal-forming ions is mainly adsorbed at the interface. That is why researchers pay increased attention to studies of ion mobility in the systems formed by nanoparticles.

## III. The influence of the size effects on ionic conductivity

Among proton-conducting solid electrolytes, zirconium hydrogen phosphate occupies a particular position. This compound has been intensively studied in the USA[46] and Italy[47] by researchers working in the field of solid state ionics. Proton conductivity is due to intense proton exchange between the anion and water and is characterized by significant anisotropy ($\sigma_{x,y} \gg \sigma_z$).[48] An important feature is that the conductivity of a sample depends on the degree of its dispersion, *i.e.*, on the preparation procedure. Depending on the degree of crystallinity, the conductivity of a sample can change by at least five orders of magnitude, the proton mobility at the surface being four orders of magnitude higher than in the bulk.[49] We have shown[50] that the dependence of the conductivity of acid zirconium, iron and indium sulfates on the particle size in logarithmic coordinates represents two linear portions. The conductivity of samples containing rather large particles is nearly

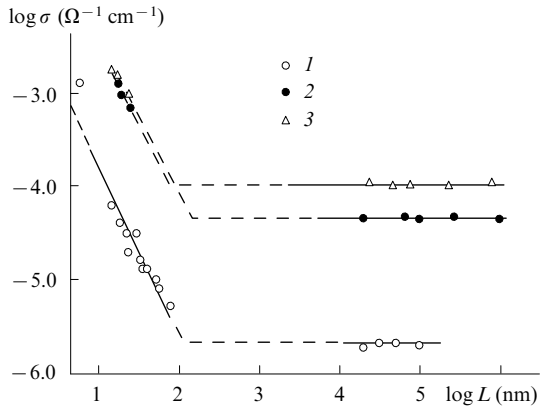



**Figure 3.** Conductivity along the normal to the crystallographic axis *z* plotted *vs.* particle size: $Zr(HPO_4)_2 \cdot H_2O$ (*1*), $FeH(SO_4)_2 \cdot 4H_2O$ (*2*) and $InH(SO_4)_2 \cdot 4H_2O$ (*3*).[50]

constant; if the particle size is less than 100 nm, the conductivity dramatically increases (Fig. 3).

Generally, if the mobility of charge carriers at the surface and in the bulk is $\mu_s$ and $\mu_v$, respectively, the total conductivity is given by

$$\sigma = v\sigma_v + (1-v)\sigma_s = n[v\mu_v + (1-v)\mu_s], \tag{9}$$

where $v$ is the volume fraction of surface, $n$ is the total number of charge carriers; and $\sigma_s$, $\sigma_v$ are the specific conductivities at the surface and in the bulk, respectively.[50] The contributions of the surface and bulk components become equal when

$$\frac{v}{1-v} = \frac{\mu_v}{\mu_s} = \frac{\sigma_v}{\sigma_s} \tag{10}$$

or

$$v \approx \frac{\mu_v}{\mu_s} = \frac{\sigma_v}{\sigma_s}, \tag{11}$$

because $\mu_s \gg \mu_v$.

If the number of charge carriers on the surface is higher than in the bulk, their contribution determines the total conductivity of the compound. Therefore, a typical plot of the proton conductivity of a compound *vs.* degree of dispersion has two portions (see Fig. 3). Namely, for large particles the conductivity is determined by the bulk component and is independent of the degree of dispersion (straight line parallel to the abscissa axis), whereas for small particles the conductivity increases as the particle size decreases. Almost linear character of this dependence is due to the fact that all three compounds studied [50] had layered structures and were characterized by two-dimensional (2D) conductivity. Therefore, the surface fraction for them is nearly inversely proportional to the particle size.

Unfortunately, for these compounds, preparation of samples containing particles smaller than 10 nm in average size faces severe difficulties. A good model for such a system is provided by high-water heteropolyacids, *e.g.*, $H_3PW_{12}O_{40} \cdot 29H_2O$ whose anions have an almost spherical shape and a diameter of about 1 nm. This acid has a very high room-temperature conductivity of nearly 0.17 $\Omega^{-1}$ cm$^{-1}$ (Ref. 51), which approaches the value that can be obtained by extrapolating the dependences shown in Fig. 3 to a particle size of 1 nm. In fact, the sublattice containing protons and water molecules moving within channels with low proton affinity is in the 'molten' state typical of superionic conductors. Therefore, this compound provides almost ideal conditions for proton transfer;[43] here the proton mobility is $\sim 6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and approaches that of aqueous solutions of acids.

Thus, it is transfer across the surface that is responsible for high ionic conductivity of some systems whose conductivity at high degrees of crystallinity is negligible. Mention may be made of high 'surface' proton conductivity of finely dispersed particles of hydrated oxides of polyvalent elements $EO_x \cdot n H_2O$,[52] whose cores have rather small radii (usually, a few nanometres) and a chemical composition similar to that of corresponding oxide (or hydroxide). The developed surface of such particles contains a large number of hydroxyl groups and water molecules depending on the acidity of core-forming compound, the E−O−H bonds can dissociate with elimination of a proton or hydroxyl group. The proton conductivity is due to the presence of aqueous solution containing $OH^-$ or $H_3O^+$ ions on the surface of particles.[43]

Ionic conductivity of nanosystems attracts the attention of many researchers and has been a subject of some reviews.[6, 7, 53, 54] Initially, the emphasis was placed on the increased concentration of defects due to curvature of the crystallite surface. However, calculations using the Thomson–Kelvin equation showed that the energy of defect formation for particles of size 10 and 1 nm decreases by only 0.3 and 3 kJ mol$^{-1}$, respectively.[7] This means that the concentration of defects cannot significantly increase owing to surface curvature. Much larger contributions to the ionic conductivity come from the high specific fraction of surface in nanomaterials [55] and from the increase in the concentration of defects at grain boundaries (see above).[6, 56, 57] In the case of solid electrolytes the size effect has a simple explanation. For large particles, the contribution of the surface component to the total conductivity is negligible compared to that of the bulk component. For small particles, the conductivity can almost completely be governed by the properties of the surface, moreover, reduction of the particle size to the nano scale may cause the boundaries of the Debye layer with high concentration of defects to overlap and the entire nanoparticle to become high-conducting (Fig. 4).[43, 57]

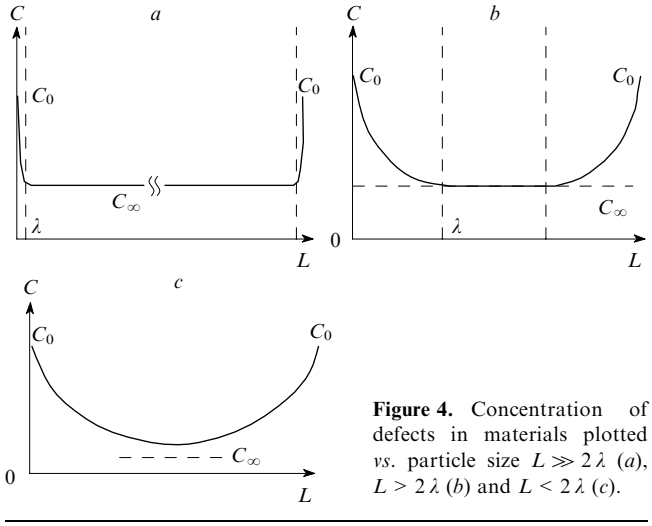



**Figure 4.** Concentration of defects in materials plotted *vs.* particle size $L \gg 2\lambda$ (*a*), $L > 2\lambda$ (*b*) and $L < 2\lambda$ (*c*).

Similar dependences are also characteristic of ionic conductivity of composite materials, namely, it increases just because of the increase in the concentration of defects at interfaces, and therefore the larger the surface area of interfaces the higher the conductivity of the system.

Studies on the ionic conductivity and thermodynamics of nanocomposites revealed that the physical properties of ionic salts in such systems are significantly different from those of individual compounds.[58–63] At high concentration and degree of dispersion of the oxide phase, the formation of a composite leads to dispersion of the salt MX through solid-phase 'spillover' across the oxide surface. In the limiting case, almost the entire volume of the salt may undergo transition to the so-called 'surface' state. The formation of a 'surface phase' in composite materials with high mobility was detected by NMR spectroscopy,[64] from a decrease in the endothermic effect corresponding to the superionic phase transition and from reduction of the superionic transition temperature for some ionic salts ($Li_2SO_4$, AgBr, AgI, $CsHSO_4$, $RbHSO_4$) participating in the formation of composites. At high content of the oxide component, the phase transition disappears.[58,65–70] Based on these data, one can suggest the formation of a new superionic phase with high degree of cation disorder at interfaces between particles in the composite.

## IV. Theoretical calculations of ionic conductivity of composites

Generally, electrical conductivity calculations of heterogeneous systems are far from being a new problem. Usually, they are carried out in the framework of model approximations using a series and parallel connection of elements of these systems with different resistance. Here, to solve the problem is to determine the total conductivity ($\sigma_{sum}$) of a system comprised of two individual phases with the conductivities and volume fractions $\sigma_1$, $(1-\eta_2)$ and $\sigma_2$, $\eta_2$, respectively. The conductivities of the simplest models with conducting fragments connected in series and in parallel are given by

$$\sigma_{sum}^{-1} = (1-\eta_2)\sigma_1^{-1} + \eta_2\sigma_2^{-1}, \tag{12}$$

$$\sigma_{sum} = (1-\eta_2)\sigma_1 + \eta_2\sigma_2 . \tag{13}$$

Real systems are usually much more complicated. Relations (12) and (13) only define the lower and upper limiting values of the conductivity of composite materials. Actually, alternation of particles connected in series and in parallel in real composites leads to intermediate cases. In this connection mention may be made of conductivity calculations for composite materials, proposed by Landau and Lifshitz[71] and by other authors.[72,73]

However, none of the currently available models can provide an explanation for dramatic enhancement of conductivity of composite materials. Transport phenomena in solids occur through migration of defects.[41] As shown above, the concentration of defects at the interface can increase by several orders of magnitude. In addition, noncompensated valences and smaller steric hindrances to transfer in the near-surface layer usually lead to much higher ion mobility at the interface compared to the bulk of the sample.[43] This causes an increase in the ionic conductivity of the near-surface layers of composites.

A model for the description of conductivity of composites with inclusion of the contribution of interfaces was proposed by Maier.[28,74] We will consider it taking the interaction between a MX ionic crystal and an inert (nonconducting) phase B as an example assuming that the interface is parallel to the vector of potential difference (Fig. 5 *a*).

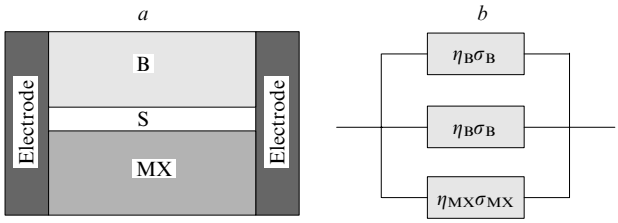



**Figure 5.** A 'bicrystal' (*a*) comprised of an ionic crystal (MX), inert phase (B) and interfacial layer with high concentration of defects (S) and its equivalent electrical circuit (*b*).

The conductivity of this system can be calculated as that of the system including three resistances connected in parallel (Fig. 5 *b*):

$$\sigma_{sum} = \eta_B\sigma_B + \eta_{MX}\sigma_{MX} + \eta_s\sigma_s , \tag{14}$$

where $\eta$ and $\sigma$ are the volume fractions and conductivities of each component, respectively. The products $\eta_B\sigma_B$ and $\eta_{MX}\sigma_{MX}$ denote the contributions of the inert phase and ionic crystals MX, respectively; and $\eta_s\sigma_s$ is the contribution of the conductivity of the Debye 'charged' layer. Usually, the contribution of the inert phase ($\eta_B\sigma_B$) can be neglected. The predominant contributions are $\eta_{MX}\sigma_{MX}$ for large crystals and $\eta_s\sigma_s$ for small ones. Maier proposed a relation for the contribution of the surface component, which has a relatively simple form:

$$\eta_s\sigma_s \approx q\mu_v(2\lambda)(C_{v0}C_{vn})^{1/2}, \tag{15}$$

where $q$ and $\mu_v$ are the charge and mobility of a vacancy, respectively, and $C_{v0}$ and $C_{vn}$ are the vacancy concentrations at the surface and in the bulk of the crystal, respectively. According to this relation, the contribution of the Debye layer to the conductivity of the system can be represented as the contribution of a resistance of thickness $2\lambda$ with some averaged concentration of charge carriers, connected in parallel.

Real composites are complex polycrystalline systems comprising a large number of conducting and non-conducting crystals and having numerous interfaces. The conductivity of a polycrystalline sample composed of small cubic tiny crystals with the edge length $L$ can be described using the model of cubic blocks (Fig. 6). Assuming that the particle size $L \gg 2\lambda$, a small contribution to the conductivity from the layers arranged normal to the direction of the vector of potential difference can be neglected. The ratio of the interface and bulk components of the conductivity to the total conductivity of the system can be determined from the relation

$$\frac{\eta_{MX}\sigma_{MX}}{\eta_s\sigma_s} = \frac{(L-2\lambda)\sigma_{MX}}{2\lambda\sigma_s} . \tag{16}$$

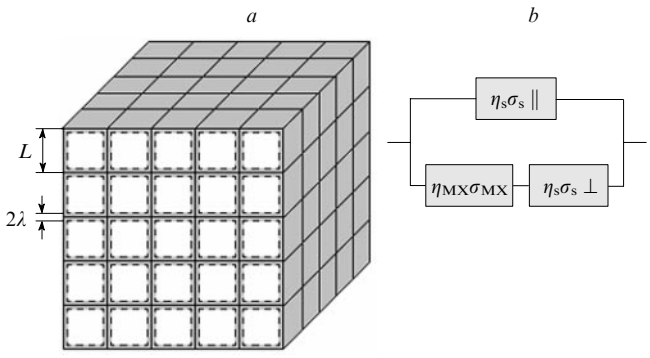



**Figure 6.** Model of cubic blocks (*a*) and its equivalent electrical circuit (*b*).
The high conducting Debye layer is shown in gray.

Conductivity calculations of real heterogeneous systems are even more complicated. The main reason is the topological variety of the distribution of two phases (or three phases including the Debye layer with high defect concentration).[75–77] Bunde and co-workers[76,78] calculated the conductivity of a two-phase system $LiI-Al_2O_3$ using the Monte Carlo technique. The results of calculations were illustrated taking the 2D percolation model (Fig. 7) as an example. At low concentrations of the oxide phase, the conductivity of the system increases due to the formation of high-conducting contacts (Fig. 7 *a*). If the concentration of the inert phase is higher than a threshold value (first percolation threshold), the oxide particles are in contact at any instant (Fig. 7 *b*), thus forming high-conducting chains. The second percolation threshold corresponds to such a concentration of the inert phase (Fig. 7 *c*) at which (and at all higher concentrations) the high-conducting chains break down (Fig. 7 *d*). According to calculations, in the region between these critical points the conductivity of the system approaches its maximum value and varies insignificantly.

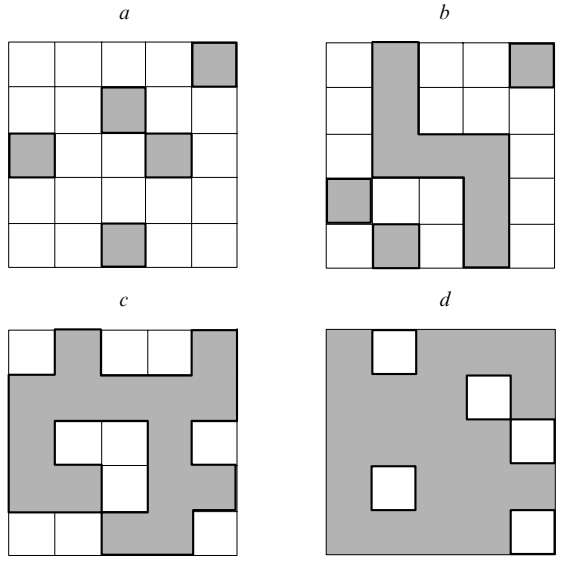



**Figure 7.** Formation of high-conducting chains in solid composite electrolyte with an increase in the content of inert phase.
For notations *a*–*d*, see text.

Having passed the second critical concentration, the conductivity of the system rapidly decreases. A similar technique was also used to describe the behaviour of the conductivity of composites containing lithium and silver salts with various oxide dopants.[79] Note that the blockage of conductivity is most pronounced in the systems based on superionic salts[65] and other ionic crystals, which are characterized by rather high intrinsic defectiveness.[80]

The experimental conductivity-*vs*.-chemical composition plots of the systems $Li_2CO_3-Al_2O_3$, $Li_2CO_3-BaTiO_3$ (Ref. 81) and $CsHSO_4-TiO_2$ (Ref. 65) are shown in Fig. 8. It follows that usually such plots for composite electrolytes pass through a maximum at a content of the highly disperse oxide phase from 20% to 40%.

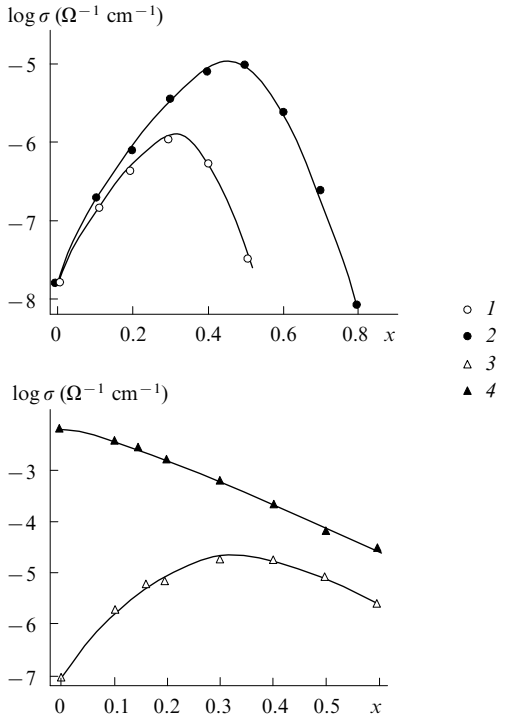



**Figure 8.** Conductivities of the systems $(1-x)\,Li_2CO_3 \cdot x\,Al_2O_3$ (*1*) and $(1-x)\,Li_2CO_3 \cdot x\,BaTiO_3$ at 250 °C (*2*),[81] and $(1-x)\,CsHSO_4 \cdot x\,TiO_2$ at 80 °C (*3*) and 170 °C (*4*) plotted *vs*. chemical composition.[65]

The temperature dependence of the ionic conductivity of solid electrolytes is described by the Frenkel equation

$$\sigma T = A\exp\left(-\frac{E_\sigma}{kT}\right), \tag{17}$$

where $A$ is the pre-exponent and $E_\sigma$ is the activation energy for conductivity. For binary crystals MX, the energy $E_\sigma$ equals the sum of the activation energy for mobility of defects ($E_a$) and the halved enthalpy of defect formation ($\Delta H$)

$$E_\sigma = E_a + \frac{1}{2}\Delta H. \tag{18}$$

Usually, heterogeneous doping of ionic crystals causes the activation energy for conductivity to decrease. In this

case, defects are formed at the interface and the enthalpy of this process becomes much lower than that of defect formation in pure (undoped) crystal. In many practically important cases, the enthalpy of adsorption of ions at the interface is negative and rather high in absolute value. Adsorption of such systems weakly depends on temperature and the activation energy for conductivity approaches $E_a$. Because of this the conductivity of heterogeneous systems considerably increases at relatively low temperatures (see Fig. 7 *a*–*c*).[28, 78, 82, 83]

The intrinsic conductivity of a crystal usually dominates at high temperatures, because it is characterized by a higher activation energy. Therefore, the presence of low-conducting dopants often leads to a decrease in conductivity at high temperatures. This is most pronounced when a compound exhibits a superionic transition. In systems such as $AgI-Al_2O_3$,[60] $CsHSO_4-SiO_2$ (Refs 68–70 and 84) and $CsHSO_4-TiO_2$ (Ref. 65) (Fig. 9), the dopants phases cause the conductivity to increase at low temperatures and to decrease at high temperatures; the corresponding activation energy decreases in the former case and remains unchanged or somewhat increases in the latter case.

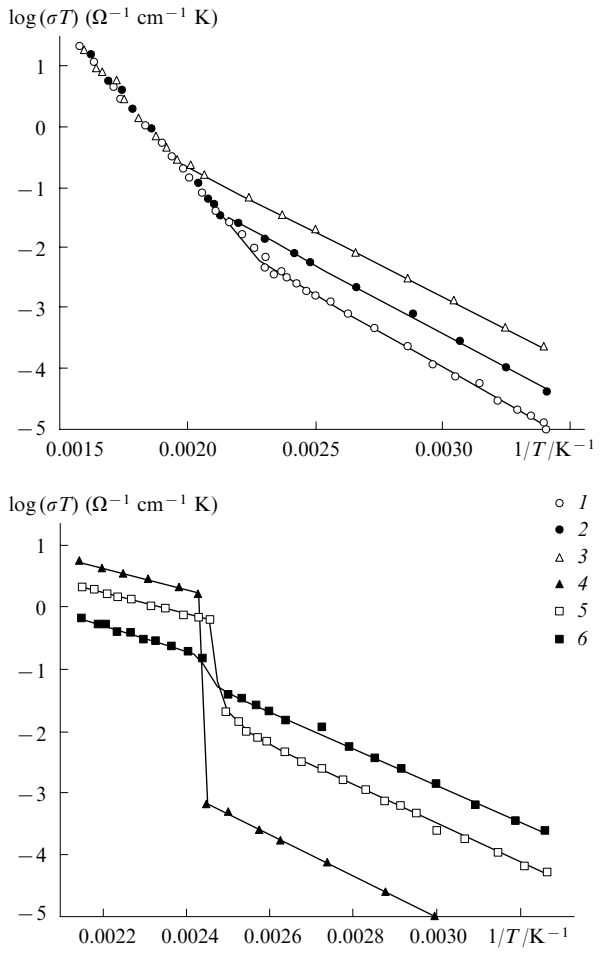



**Figure 9.** Conductivities of the systems $(1-x)\,CuBr\cdot x\,TiO_2$ (*1*, *2*, *3*)[7] and $(1-x)\,CsHSO_4\cdot x\,TiO_2$ (*4*, *5*, *6*)[65] plotted *vs.* temperature in the coordinates of Eqn (17).
$x$ = 0 (*1*, *4*), 0.199 (*2*), 0.2 (*5*), 0.212 (*3*) and 0.5 (*6*).

## V. Ionic conductivity of composite materials based on solid electrolytes

Based on the aforesaid, one can conclude that theoretical models for the description of changes in ionic conductivity of solid composite electrolytes have been formulated to date. At the same time, the conductivity of a particular composite cannot be predicted with certainty. The main reason is that sorption phenomena at interfaces have been poorly studied so far. In addition, the conductivity of a composite depends on a number of factors including the degree of dispersion of the ionic crystal and the inert phase, the pore size and shape in the inert phase, the degree of homogenization of the mixture of both components, temperature and other mixture treatment conditions, which strongly affect the formation of the structure of the interface.

In this connection, research to extend the range of chemical compounds to be used in the design of composite materials has been carried out continuously. Traditionally utilized objects include systems based on lithium, copper and silver chlorides, bromides and iodides. Recently, composites containing lithium salts (fluoride,[82] carbonate,[81, 82, 85] sulfate,[69, 86] perchlorate[87] and phosphate[82]) have been intensively studied. Considerable attention is also paid to investigations of composites based on alkali metal nitrates[59, 61, 88–91] and other salts with cationic conductivity including silver sulfate,[92] sodium carbonate,[93] caesium chloride[63] and many other compounds. Mention may be made of some composites with anionic conductivity; among them, systems based on calcium[33, 45, 94] and lead[32, 44] halides receive great attention. The formation of near-surface phases with unusual transport properties in ceramic composites based on potassium tungstates and $WO_3$ was reported.[95, 96]

Attempts to improve the properties of proton-conducting solid electrolytes by the formation of composites have failed for long. It seems likely that high polarizing effect of protons should favour their intense adsorption on the surface of various oxides. However, efforts to enhance the conductivity of zirconium hydrogen phosphate,[97, 98] hydrated antimony oxide[99] or heteropolyacids[100] by doping with zeolites or highly disperse oxides of polyvalent elements were unsuccessful. From the standpoint of the theory of conductivity of composite materials the main reason consists in the use of starting materials with high degree of cation disorder, which can hardly be increased by adding heterogeneous compounds. For the first two systems, this is due to high dispersion of zirconium hydrogen phosphate and hydrated antimony oxide (their conductivities were determined by the surface component in the starting materials); for heteropolyacids, this is due to their abnormally high conductivity.

Only in 1999, Ponomareva *et al.*[68] succeeded in stabilizing the high-conducting phase of caesium hydrogen sulfate by doping with heterogeneous additives. More recently, they prepared high-conducting composites in the systems based on caesium, rubidium, potassium and ammonium hydrogen sulfates doped with highly disperse silica and titania.[60, 68, 69, 101–105] Similar experiments were also reported by other authors.[106–108] Studies on the search for composite solid electrolytes based on acid alkali metal phosphates of somewhat different chemical composition are also available.[109–111]

Novel composite electrolytes based on $TaH(PO_4)_2 \cdot 2H_2O$ and $SiO_2$ were prepared.[112] The proton conductivity of acid iron and indium sulfates was enhanced by doping with finely dispersed silica or zirconia.[27, 113, 114]

The degree of dispersion of the oxide phase unambiguously affects the properties of composite electrolytes,[65, 81, 82, 115] namely, the higher the degree of dispersion the larger the change in the conductivity of a composite and the stronger the ionic current blockage.[79] The properties of composites also depend on the pore size. The reason consists in changes in pore selectivity to sorption of different cations and in the ability to dispersion of ionic salts. The maximum conductivity of $MHSO_4-SiO_2$ composites was attained at pore sizes ranging from 3.5 to 10 nm.[69, 70, 84]

Traditional method of synthesis of composites involves the use of all (or at least one) starting compounds in the nanodisperse state followed by heat treatment of the material. To attain a maximum effect, the heat treatment temperature is chosen to be similar to (or even higher than) the melting point of the component with ionic conductivity.

At the same time, elaboration of methods for preparation of nanocomposites using various physical or chemical approaches is in progress. For instance, a new method for enhancement of ionic conductivity of solid electrolytes by chemical modification of thin surface layer was proposed.[116] The conductivity of crystalline zirconium hydrogen phosphate was enhanced upon the formation of a surface layer of ion exchange products. If the thickness of this layer is of the order of a few nanometres (within the limits of the thickness of the Debye layer), the conductivity of the system dramatically increases. However, an increase in the degree of substitution (thickness of the layer of the new phase) again led to blockage of the Debye layer by the exchange products and the system conductivity decreased.[117] An essentially similar approach to the formation of high-conducting nanocomposites by successive deposition of calcium and barium fluoride layers was elaborated by Sata *et al.*[118, 119]

Promising methods include filling of porous matrices with conducting components. For instance, a conducting composite was prepared by introducing silver iodide into porous alumina.[120] Composites were also prepared in mesoporous oxides (pore size 2–10 nm).[121]

## VI. Polymeric membranes and hybrid materials

Prior to going to the description of composite materials based on ion-exchange membranes, it is appropriate to briefly outline some structural features of the starting materials. Polymeric ion-exchange membranes are built of flexible polymer (hydrocarbon or perfluorinated) chains whose repeating units contain functional groups ($SO_3H$, $PO_3H$, COOH, $NH_3OH$, *etc.*). Protons in cation-exchange membranes and OH groups in anion-exchange ones can be replaced by ions present in solutions contacting the membrane. At present, the number of available membrane materials is rather large, but only a few of them are produced on a large scale. Some membranes are fabricated for mainly research purposes (this category continuously extends). Information on the chemical composition and structure of such membranes can be found in, *e.g.*, reviews.[122, 123]

In terms of their structure, ion-exchange membranes can be divided into two main types, homogeneous and heterogeneous. The former are fabricated by polymerization or copolymerization of monomers and the corresponding reaction products are quite homogeneous. The latter comprise particles of different materials.

Fragments of a homogeneous membrane are of various nature. Hydrocarbon or perfluorinated chains are hydrophobic; contrary to this, functional groups are hydrophilic. The formation of membranes containing flexible polymer chains is accompanied by self-organization processes. Hydrocarbon or perfluorinated chains form the core of a membrane, while functional groups form small clusters a few nanometres in size depending on the chain flexibility and on the concentration of ionogenic groups. In studies on the subject, these small objects are often called 'phases' or 'nanophases'.[124]

The conclusion that the membrane structure contains clusters arranged in ordered manner was based on the presence of reflections in the region of small-angle X-ray scattering in sulfonic acid membranes.[125, 126] A structural model for Nafion perfluorinated sulfonic acid membranes proposed by Gierke *et al.*[127, 128] is now considered as a generalized structural model for homogeneous ion-exchange membranes. According to this model, fixed acid residues are arranged in the peripheral area of the cluster, whereas the interior of the cluster is filled with an aqueous solution containing protons (with oxonium ions as counterions) that are formed upon dissociation of functional groups (Fig. 10).

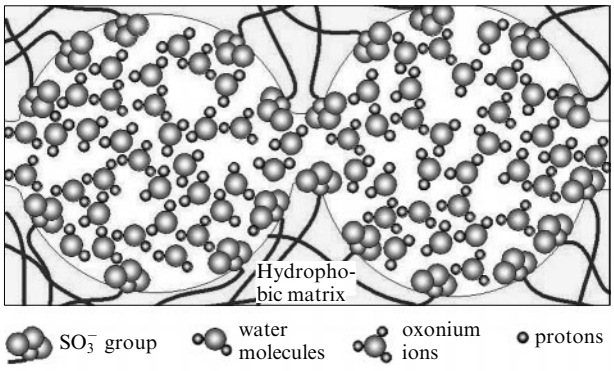



**Figure 10.** Structure of pores in polymeric cation-exchange membrane (hydrogen form).

Clusters are a few nanometres in size, which allows membranes to be treated as nanostructured objects.[123] This type of structural nano-organization provides an explanation for the key (first of all, transport) properties of ion-exchange membranes.[122, 123, 129] The membrane pores containing hydrophilic functional groups can be readily hydrated. For instance, even well-dried sulfonic acid membranes contain two water molecules per proton of sulfonic group.[130] Hydration of ions and hydrophilic areas of the polymer matrix cause swelling of ion exchanger and, as a consequence, enlargement of clusters.[124, 127, 131]

Heterogeneous membranes represent composites comprising ion-exchange resins and fillers. They have a somewhat more complicated structure (Fig. 11). In particular, a cation-exchange membrane MK-40 is a composite made of polystyrene sulfate and polyethylene particles (the latter compound and the reinforcing network ensures mechanical strength of the membrane). The pore size distribution in

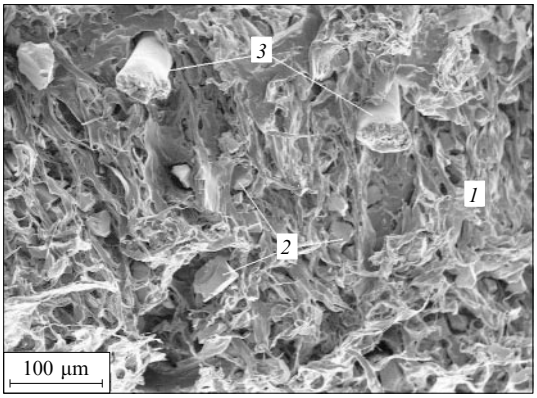



**Figure 11.** Section of MK-40 membrane: a micrograph. Polystyrene sulfate fibres (*1*), polyethylene (*2*) and reinforcing network (*3*).

these membranes is bimodal and its maxima correspond to nanopores of radius from a few nanometres to tens of nanometres and to macropores with a characteristic size of about 1000 nm.[132, 133] The first type of pores is localized within particles of the ion-exchange resin, while the second type of pores represents the inter-particle space between the resin and polyethylene binder. The total volume of large pores is an order of magnitude smaller than that of small pores.[133]

Although a variety of ion-exchange membranes are available at the moment, they do not meet increasing demands of science and industry. For instance, mixture separation techniques require high selectivity of transfer, while fuel cell applications require membranes with high conductivity at different humidity values, low gas permeability and high thermal stability.[5, 122, 134–138] In this connection, recently intensive research on the synthesis of hybrid materials based on polymeric membranes containing inorganic nanoparticles has been carried out.[136, 137]

One of the most evident methods for improvement of transport properties of membranes involves their modification. This makes it possible to vary the properties of a relatively small number of commercially available materials and can be done in different manner.[123, 136]

## 1. Modification of membrane surface

The first barrier to ions moving through a membrane is the surface of the membrane, which plays an important role in transport processes.[122, 139] For instance, the surface of heterogeneous membranes MK-40 and MA-40 is covered with a polyethylene film, which is formed in the course of hot pressing and reduces the diffusion permeability. The simplest way is profiling of membranes, which makes it possible to increase the active surface area, enhance the conductivity of membranes and provides high transport number of counterions in the course of electrodialysis.[140]

The most promising are the approaches involving modification of membrane surface with an additional component imparting specific properties. For instance, modification of the surface of commercially available cation-exchange membranes with a thin layer of chitosan significantly improves their selectivity. The transport numbers of metal cations in binary systems ($H^+/Zn^{2+}$ and $H^+/Al^{3+}$) considerably decrease.[141] Presumably, this is due to electrostatic factors and steric hindrances.

In the course of electrodialysis of aqueous solutions, heterogeneous anion-exchange membranes are coated with a hydrophilic coating, which leads to a decrease in resistance and power consumption.[142] Composite cation-exchange membranes with thin urethane acrylate layer exhibit enhanced selectivity and conductivity. A possible reason consists in resonance stabilization of urethane groups possessing the properties of a weak acid.[143]

The surface of heterogeneous cation-exchange membranes MK-40 can be activated by coating with a thin layer of homogeneous membranes MF-4SK, either undoped[144] or doped with inorganic dopants.[145] The transport properties of such membranes are significantly improved and approach those of much more expensive homogeneous membranes MF-4SK.

Modification of the surface of cation-exchange membranes by various amines leads to enhancement of their conductivity and to improvement of their permeability compared to singly charged cations.[146–149] Examples of modification of the membrane surface with thin layers of other compounds can be found in the literature.[150–157]

Thin layers of chemical compounds on the surface of membranes are often formed by plasma treatment. In some cases such layers improve the selectivity of membranes[158] or reduce their gas permeability.[159]

## 2. Modification of the bulk of ion-exchange membranes by oxide and salt nanoparticles

In most cases, modifiers are introduced into the bulk of membrane materials.[6, 136, 137, 160] Considerable recent progress in this field is first of all due to the fact that hybrid organic/inorganic membranes appeared to be quite attractive for fuel cell applications. Particles of inorganic compounds dispersed in a polymer matrix can either produce mobile ions upon dissociation or be inert compounds.[6, 136] Most often, the latter group of compounds includes oxides of polyvalent elements (silicon, aluminium, zirconium). The most widely reported advantages of hybrid membranes include improvement of mechanical properties and enhancement of selectivity and ionic conductivity.[136, 146]

Inorganic nanoparticles can incorporate into materials when membranes are formed from solutions containing nanodisperse additives[136, 137, 161] or in the case of *in situ* synthesis of nanoparticles.[137, 162] The first method is more simple and attractive, but often leads to undesired results because nanodisperse particles are prone to aggregation that can be rather stable in solution. This significantly reduces the efficiency of doping and in some cases causes the loss of mechanical strength and an increase in macroporosity and gas permeability of the membrane. Stabilization of nanoparticles by various surfactants seems to be very attractive.[163, 164] However, in this case one should remove the surfactants from the membrane upon completion of the synthetic procedure.

The attraction of the second technique is due to the fact that membranes represent unique matrices for the synthesis of nanoparticles. Functional groups in pores can sorb a particular starting reactant, *e.g.*, cations of polyvalent elements or molecules of organometallic compounds. Then, nanoparticles can be synthesized in the same pores provided that other reactants are somehow delivered. The pores act as nanoreactors, because they confine the reaction volume and the particle size. In addition, membrane walls efficiently separate the particles from one another and reduce the surface tension, thus ensuring thermodynamic

stability of nanoparticles. Thus, the synthesis of nanoparticles directly in the pores of a membrane can be considered as a promising method of preparation of nanoparticles and hybrid materials.[136, 137]

The synthesis of hybrid membranes has been reported quite recently;[136, 165] however, the number of studies on the subject rapidly increases. It should be noted that modification of homogeneous and heterogeneous membranes with inorganic particles leads to fundamentally different results. For instance, an attempt to synthesize zirconium hydrogen phosphate nanoparticles in a matrix of heterogeneous membrane MK-40 has failed.[166] In this case, enhancement of ionic conductivity is accompanied by an increase in the diffusion permeability of the membranes due to enhanced anion mobility, and the main result of modification consists in reduction of the selectivity of ion transfer.

Basically different results were obtained in the course of modification of Nafion homogeneous ion-exchange membranes (MF-4SK) by inorganic particles. In this case, one can not only enhance the ionic conductivity, but also improve the selectivity of ion transfer.[162, 167–183] The reason for these differences can be understood by considering the key factors leading to changes in the transport properties of membranes. As mentioned above, the size of nanoparticles synthesized within homogeneous membranes is first of all governed by the pore size, being usually 2–5 nm,[162, 170] as indicated by, *e.g.*, electron microscopy (Fig. 12), powder X-ray diffraction, microprobe analysis and high-resolution NMR spectroscopy data.

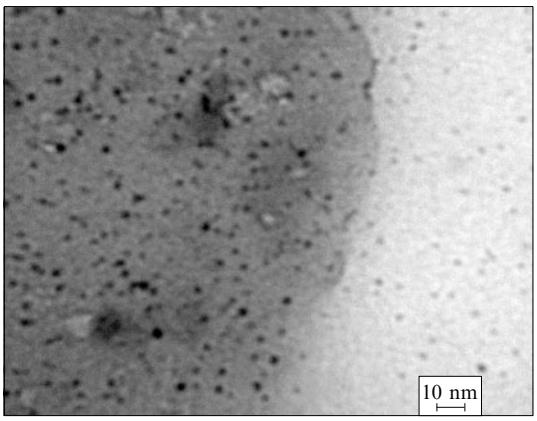



**Figure 12.** Electron micrograph of MF-4CK membrane with hydrated silica synthesized inside the membrane.[169]

Heterogeneous membranes MK-40 have both nanopores and large pores ($\sim$1000 nm in size). Therefore, the average particle size of zirconium hydrogen phosphate determined by power X-ray diffraction (about 10 nm) is much larger than when using the MF-4SK membranes. The key factor leading to intensification of transport processes is the sorption–desorption processes at the interface.[6, 30, 37, 43] This causes an increase in the concentration of defects within the thin Debye layer near the interface and enhancement of ion mobility. An important role is also played by high ion mobility near grain boundaries.[43] Finally, some contribution may come from an increase in the total moisture content owing to introduction of hydrophilic particles into the membrane.[136, 171, 172] Some additives cause an increase in the moisture content and enhancement of the ionic conductivity of membranes at low humidity.[171]

When large particles are formed in macropores of heterogeneous membranes between ion-exchange resins and inert binder, the surface area of the dopant/ion exchanger interface decreases considerably. This significantly reduces the efficiency of the membrane modification procedure. In addition, high temperature at which zirconium hydrogen phosphate is synthesized may induce structural degradation of the MK-40 membranes characterized by much lower thermal stability compared to the Nafion and MF-4SK homogeneous membranes. This is indicated by reduction of the mechanical strength and an increase in the fraction of the solution localized within the pores.[166]

A number of hybrid proton-conducting membranes containing nanoparticles of various modifications of silica were synthesized using tetraethoxysilane and other organosilicon compounds as starting reactants. The Nafion/$SiO_2$ hybrid membranes have been best studied.[162, 173–181] In some cases, the conductivity of these materials enhanced, but in other cases it reduced.[176–179] Different results can be explained by the influence of such factors, as, first of all, the concentration of additives, the particle size of the additive and the procedure used to form the hybrid membranes. An increase in the permeability of membranes towards hydrogen and methanol was also reported,[176] although most often these parameters decrease.[177–180] This type of hybrid membranes is characterized by higher mechanical strength.[182] Related composite materials based on other polymeric membranes were also prepared.[136, 183–185] For instance, the conductivity of membranes based on sulfonated polyether ether ketone can be about four times higher upon doping with mesoporous silica.[184, 185]

In a number of studies, the surface of silica particles was chemically modified to improve the properties of composite membranes. The simplest way is sulfonation of $SiO_2$ particles. In particular, the Nafion membranes doped with $SiO_2/SO_3H$ differ from the corresponding undoped membranes by high proton conductivity and lower gas permeability.[186] Similar results were obtained for membranes containing silica particles modified by some perfluoroalkyl sulfonic acids,[187] diphenyldimethoxysilane with grafted $SO_3H$ groups[188] and other alkoxide groups.[189]

A grave disadvantage of silica as a material for modification of membranes is relatively low acidity. In this connection, the addition of strong acids seems to be appropriate. Among the strongest inorganic acids, there are heteropolyacids, which were used in some studies.[168, 190–192] The distinctive features of this type of composite membranes include increased moisture content. Their proton conductivity is typical of the Nafion membranes, but is attained at much lower humidity.[168] Similar results were also obtained for a number of salts of heteropolyacids.[193] Composite membranes containing some tetravalent metal oxides and heteropolyacids were studied.[194] The proton conductivity was as high as $1.6 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 120 °C and a relative humidity of 35%.

Heteropolyacids were used for modification of composite membranes and as a sole additive.[195] In particular, composite materials based on Nafion membranes and phosphotungstic (NaPTA), silicotungstic (NaSTA) and phosphomolybdic (NaPMA) heteropolyacids were investigated. The moisture content (%) of these membranes increased as follows:

Nafion-117 (27) < NaSTA (60) < NaPTA (70) < NaPMA (95),

and their ionic conductivity ($\times 10^{-2}$, $\Omega^{-1}$ cm$^{-1}$) changed as follows:

Nafion-117 (1.3) < NaPMA (1.5) < NaPTA (2.5) < NaSTA (9.5),

thus increasing by almost an order of magnitude.[196] The conductivity of these membranes at 120 °C and a relative humidity of 35% reached a value of 0.015 $\Omega^{-1}$ cm$^{-1}$ (Ref. 197). The Nafion membranes were also modified by phosphotungstic acid, its salts and Teflon.[198,199]

Modification by heteropolyacids makes it also possible to improve the properties of other membrane materials, such as sulfonated polyether ether ketone,[200–202] sulfonic acids based on polyether,[203] polystyrene[204] and other materials.[90,205] The conductivities of membranes thus prepared reached values in the range $(1-9)\times 10^{-2}$ $\Omega^{-1}$ cm$^{-1}$. The methanol permeability of the membranes modified with phosphotungstic acid was about 20 times lower compared to the Nafion-117 membranes.[206]

Membrane materials are often modified by zirconium hydrogen phosphate. Most often, the Nafion membranes are doped by this compound to increase the moisture content and thermal stability.[167,169,179,207–215] Usually, the proton conductivity of such materials appears to be lower compared to the starting membranes[207,210,213,214] and decreases as the content of zirconium phosphate increases.[212] A neutron scattering study revealed that the mobility of water in the Nafion membranes remains almost unchanged in the presence of zirconium phosphate nanoparticles.[215] The most significant effect consists in enhancement of the conductivity of these membranes at high temperatures. At the same time, doping of MF-4SK membranes with small amounts of zirconium hydrogen phosphate (1%–5%) causes an appreciable increase in their conductivity even at low temperatures.[167] Other important results include improved strength of the composite membranes[211,212] and, in some cases, enhancement of their selectivity.[167,213] Membranes with similar properties containing zirconium hydrogen phosphate and Teflon additives were also prepared.[216,217] Zirconium hydrogen phosphate favours enhancement of the conductivity of the membranes based on sulfonated polyether ether ketone[218–220] and polyvinyl alcohol.[221]

Zirconia and nanoscale titania (including corresponding nanotubes) were used to modify the Nafion membranes, polyether ether ketone, *etc*.[222–235] Other oxides, namely, $Al_2O_3$,[225,230] $HfO_2$,[229] $Ta_2O_5$,[229] ZnO[230] and $WO_3$ (Refs 229 and 236) are more rarely used for modification. Experiments with more complex materials based on oxides of polyvalent elements including sulfonated titania[237,238] and zirconia,[239,240] binary oxides $ZrO_2-SiO_2$,[241] various zeolites,[226,242–250] clays,[251] diphenyl silicate[252] and phosphate–silicate gels[253] were also carried out. The Nafion membranes containing gels $SiO_2-P_2O_5-ZrO_2$ (Ref. 254) or zirconium sulfophenyl phosphate[255] showed enhanced proton conductivity above 100 °C.

Mention may be made that in spite of considerable recent literature on hybrid membranes, information on their properties is often ambiguous. The possible reasons are as follows: differences between starting membranes, different doping techniques, different degrees of dispersion of the dopants, *etc*. Moreover, experimental results are not always reproducible because membranes are very labile systems. The reason for the changes in the conducting properties of such materials is still a moot question. The case in point is that perfluorinated sulfonic acid materials of the Nafion type are very strong acids. Large number of water molecules present near these membranes causes almost complete dissociation of functional groups. Therefore, consideration of additional defect formation for this type of membranes is not quite correct. Often, it is believed that enhancement of conductivity is determined by an increase in the moisture content. However, our data show that these parameters do not always correlate. For instance, in some cases the conductivity can be enhanced at a constant moisture content and, *vice versa*, an increase in the moisture content in membranes upon doping not always unambiguously leads to increase in conductivity. A large proportion of water molecules may in some cases be localized in macropores formed during treatment of the membrane. It has been proved reliably that nanodisperse additives of certain inorganic compounds lead to enhancement of conductivity at low humidity. A possible reason is the possibility for proton transfer to follow alternative routes, *e.g*., across the surface of hydrophilic dopant particles.

Reduction of the gas permeability of membranes is most probably due to the fact that nanoparticles of additives block a proportion of pores in the bulk and channels. In this case, the choice of correct synthetic procedures that do not induce degradation of membranes becomes crucially important. Additional information on the synthesis of hybrid membranes can be found in recent reviews on the subject (see, *e.g*., Refs 136, 165, 247 and 256).

## 3. Modification of the bulk of ion-exchange membranes by nanoparticles of metals or organic compounds

Yet another important type of hybrid materials are ion-exchange materials containing metal nanoparticles. They are prepared for various purposes including the synthesis of metal nanoparticles with specific physical properties,[257] for catalytic and electrocatalytic applications and for redox sorption (synchronous sorption of ions and reduction of, *e.g*., oxygen).[258–261] These materials are also utilized for fabrication of a transient conducting layer in ion selective electrodes to get a stable potentiometric signal.[262,263]

Hybrid materials containing metal nanoparticles are usually prepared by introducing metal cations into ion exchange matrix followed by reduction of the cations.[257,264–269] Usually, metal particles in the MF-4SK membranes are $\sim 1-5$ nm in size. The total concentration of the metal can be as high as $10^{22}$ atoms per gramme of the membrane material.[257,269] The small size predetermines specific properties of metals in such systems. Transition metal nanoparticles in membrane matrices exhibit superparamagnetic properties.[257,264–267] Conducting polymers containing metal particles can be used to design highly efficient sensors, artificial muscles, *etc*.[270]

At the same time, metal nanoparticles are highly reactive.[271] Their reducing activity in the systems in question enhances owing to high concentration of protons in sulfonic acid ion exchange and membranes, which reduce the overvoltage of reduction of molecular oxygen. Inert metal (copper, silver, *etc*.) nanoparticles in ion exchange matrices are readily oxidized by oxygen.[272–274] Palladium-containing fibrous sorbents can be used for catalytic reduction of oxygen dissolved in water.[275,276] Similar membranes are used in other types of catalysis.[277–279]

Recently, nanocomposites based on ion-exchange membranes containing nanoparticles of organic substance, *e.g*.,

polyaniline have been intensively studied. Composites can be prepared either by aniline polymerization in the membrane matrix [280] or in a matrix solution followed by the membrane formation.[281] In the latter case, the size of polyaniline (or polyaniline/Nafion interpolyelectrolyte complex) particles is not limited by the pore size and varies from a few to tens of nanometres depending on the concentration of solutions used for the synthesis and on the procedure for membrane fabrication.

Composite membranes based on MF-4SK and polyaniline exhibit mixed ion-electron conductivity. The contribution of electron conductivity can be as high as 60%–70% (Ref. 280) if polyaniline is synthesized by polymerization in the membrane matrix; in this case the proton conductivity decreases. At the same time the proton conductivity of membranes prepared by casting after aniline polymerization in MF-4SK solutions passes through a maximum at a low concentration of polyaniline.[281] Subsequent increase in the polyaniline concentration causes reduction of the proton conductivity and degradation of mechanical properties of the membranes. Probably, the introduction of a small amount of polyaniline improves the microstructure of the membrane and leads to an increase in the number of centres that can participate in the transport process. However, an increase in the polyaniline concentration is also accompanied by a decrease in the number of active current carriers owing to participation of the membrane protons in the formation of strong hydrogen bonds $SO_3-H-N$. Large polyaniline particles can block certain conductivity channels.[281] In addition, the diffusion permeability of the membranes just prepared changes compared to that of the starting material. Also, the transport number of water (number of singly charged water molecules involved in the transport process) decreases because of reduction of the hydrophilicity of the polyaniline modified membranes.[282, 283]

Particular attention should be paid to the problem of asymmetry of the transport processes in membrane materials, which offers new fields of application. Membranes with asymmetric permeability were prepared by doping with oxide nanoparticles characterized by nonuniform thickness distribution of the dopant. The diffusion permeabilities along different axes differed by 40%.[162, 168] Composite membranes based on MF-4SK with nonuniform polyaniline distribution were reported.[281, 284] They also exhibit the diffusion permeability and ionic conductivity anisotropy. Similar properties exhibit the MK-40 and MA-41 membranes modified with tetrabutylammonium and dodecyl sulfate.[285, 286]

Incorporation of nanoparticles or molecules of compounds containing mobile ions into non-conducting polymers can be considered as yet another method of formation of 'composite' membranes with ionic conductivity.[136, 137] Strictly speaking, many of these systems are not composites because in some cases complete dissolution of dopants occurs. To ensure the affinity to the incorporated ionic dopants, the polymer should contain electronegative atoms. Therefore, most polymeric electrolytes contain oxygen-containing compounds [poly(ethylene oxide), poly(propylene oxide), polysiloxane, polyvinyl alcohol, *etc.*].[43, 287] Dissociation of salts or acids in these matrices provides a high concentration of mobile ions and leads to high ionic conductivity of materials. Ion transfer occurs by cation migration from one group of electronegative atoms to another against the background of intense segmental mobility of the polymer matrix, which ensures reorganization of the coordination polyhedra.[288, 289] Such membranes with high ionic conductivity are often used in lithium cells.[290–294] Materials with high proton conductivity can be prepared by, *e.g.*, polybenzimidazole doping with phosphoric acid.[294, 295] Proton-conducting membranes based on polyvinyl alcohol doped with phenylsulfonic acid were reported.[296, 297]

## VII. Utilization of composite materials in hydrogen power engineering

One of the key fields of application of composite materials is hydrogen power engineering, which has been rapidly progressing recently based on prerequisites that appeared at the end of the 20th century. Initially, the aim of fuel cell production was to meet the demands of spacecraft industry [298] and, more recently, automotive industry. According to EC forecasts, the percentage of hydrogen fuel driven motor vehicles will be about 25% in the year 2030.[2] Owing to high efficiency and low environmental pollution, fuel cells are considered as a major energy source in the 21st century. The idea of 'hydrogen economics' has been discussed in mass media and in scientific literature.[3, 299, 300]

Figure 13 presents a schematic of a fuel cell.[301] The key element is the proton-conducting membrane *1*. Hydrogen or hydrogen-containing gases are adsorbed at anode *2* (platinum catalyst), then dissociate and lose their charges with the formation of protons, which pass through the membrane under the action of a chemical potential gradient. At the cathode, protons interact with oxygen to give water molecules.

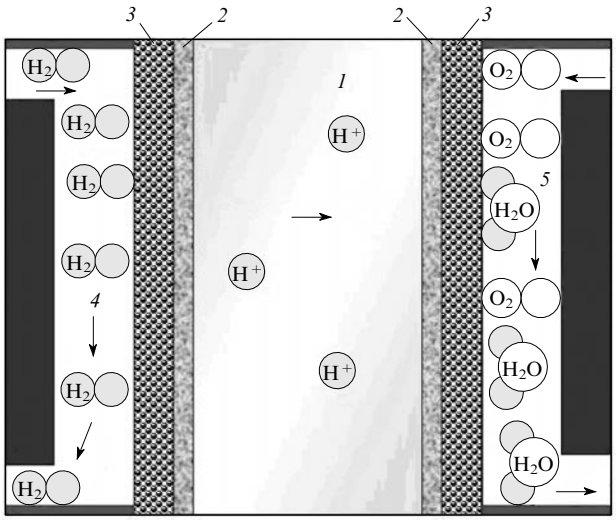



**Figure 13.** Schema of a fuel cell.
Proton-conducting membrane (*1*); catalyst (*1*); gas diffusion layer (*3*); and the anodic and cathodic gas flow channels (*4* and *5*).

In this review there is no sense to dwell on the specific features of fuel cell production and operation. We will consider only composite proton-conducting materials used in these devices. As mentioned above, composites based on lithium-containing salts have rather long been utilized in lithium cells.[11] Proton-conducting composites based on inorganic compounds are much less used. Researchers from the USA succeeded in utilizing composites based on caesium hydrogen sulfate doped with oxides or caesium

hydrogen phosphate in fuel cells.[302–306] A major drawback of proton-conducting composites is that fabrication of thin and simultaneously stable plates made of these materials is difficult.

At present, the emphasis is placed on fuel cells with polymeric membranes (most often, the Nafion membranes and polybenzimidazole are used).[5,294] Passage to composites based on the Nafion membranes is first of all due to the need to remove limitations on the range of operating temperatures (to 100 °C) and to function at reduced humidity ( < 95%).

Raising the operating temperatures to 120 °C and more will help avoid degradation of platinum catalysts owing to irreversible sorption of carbon monoxide. Fuel cells based on silica-modified Nafion membranes can operate at temperatures to 140 °C.[307,308] Utilization of these membranes at a relative humidity of 18% provides a peak power five times higher than that attained using, *e.g.*, the Nafion-1135 membranes.[309] In addition, doping with silica significantly reduces methanol diffusion through membranes.[182,309,310] This is the reason for wide use of silica-doped membranes in the design of direct methanol fuel cells.[170,179] In addition, degradation of such membranes in fuel cells is 20 times lower compared to Nafion-212 membranes.[170]

Good results were also obtained when the Nafion membranes modified with sulfonated silica were utilized in methanol fuel cells. Their conductivity increases while the methanol diffusion is suppressed (usually, by 30% – 50%) compared to the corresponding parameters of commercially available membranes.[177,186–188,252] This improves the operation of fuel cells, especially at high methanol concentration (10 mol litre$^{-1}$).[186,187,252]

Membranes modified by various heteropolyacids are also used in fuel cells;[196,197] the highest current density was attained using a Nafion – phosphotungstic acid system.[197] To prevent dissolution of the membranes, they were simultaneously doped with silica.[190] This made it possible to raise the operating temperature of the fuel cells to 200 °C (see Ref. 191) and to utilize them at a relative humidity of less than 50%.[194]

To reduce the humidity and to increase the operating temperature of fuel cells, hybrid membranes based on Nafion and zirconium phosphate were used.[209,210,216,217] This made it possible to increase the current density in hydrogen – oxygen fuel cells to 1000 – 1500 mA cm$^{-2}$ at 130 °C [209] (*cf.* a much smaller value of 250 mA cm$^{-2}$ for the starting Nafion membrane under identical conditions). Somewhat less impressive results were obtained when Nafion membranes were modified by zirconium sulfophenyl phosphate.[255]

Polycondensation membranes based on polybenzimidazoles are more promising for fuel cells operating at temperatures above 100 °C.[294,295,311,312] They exhibit high thermal stability (to 160 – 200 °C) and good mechanical properties. Nitrogen atoms present in the structure suggest the possibility of sorption of phosphoric acid. Examples of utilization of such membranes in fuel cells were reported in a review.[313] Experiments with other types of membranes containing inorganic dopants in the design of fuel cells have also been documented (see, *e.g.*, Refs 159, 183, 185, 202, 246 and 314).

## VIII. Conclusion

Although the number of synthesized inorganic and organic compounds continuously increases, it is a finite number and only a few compounds find particular practical applications. In addition, novel compounds are synthesized using increasingly more complicated procedures. At the same time, in this review we have shown that in some cases the preparation of composites allows one to fabricate novel materials with improved properties. By varying the chemical composition of the composite materials one can improve such important parameters as the strength, elasticity, electron and ionic conductivity, *etc*. In addition, by varying the percentage of components it is possible to vary the properties of materials and moreover fabricate materials with exactly specified properties (when needed).

This allows composites to be considered as future materials whose design is particularly important for progress in high-tech areas, such as the design of novel energy sources, ultrasensitive sensors, *etc*. This is directly related to environmental protection, which has become increasingly more important recently.

Going back to the subject of this review, mention may be made that composite materials with ionic conductivity are widely used in the design of various electrochemical devices including water cleaning systems, product separation facilities, electrochemical synthesis, fuel cells, electrolyzers for water steam splitting, sensors and many other. Undoubtedly, research in this field will progress rapidly.

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