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Hybrid membranes containing inorganic nanoparticles

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Hybrid ion-exchange and gas-diffusion membranes containing the nanoparticles of inorganic components are considered. These materials, in which transfer and separation processes occur by different mechanisms, similarly changed their properties upon the introduction of dopants into them to increase the rate and selectivity of transfer processes (ionic conductivity or gas permeability).

Introduction

The development of nanotechnologies substantially affected many branches of science, in particular, membrane technologies. Membranes including a system of nanosized pores and channels belong to this class. In this case, the nanosized pores are responsible for the transport properties and practical applications of the membranes.[1,2] At the same time, the production of so-called hybrid membranes based on high-molecular-weight materials containing the nanoparticles of inorganic substances has been actively developed since the 1980s. The development of these membranes was due to the extensive prospects of their use in fuel cells[3–12] and in gas separation processes, where the systems of this type are frequently referred to as mixed matrix membranes.[13–17] These membranes have also been used in the processes of pervaporation.[18,19]

It is amazing that these completely different classes of materials, ion-exchange and gas-diffusion membranes, in which transfer and separation processes occur by completely different mechanisms, similarly change their properties upon the introduction of the nanoparticles of inorganic compounds. Correctly chosen dopants and doping methods can increase both the rate and the selectivity of transfer processes in the obtained materials.[14,20,21] For this reason, the attention of scientists in membrane technologies is focused on both ion-exchange and gas-separation membranes.

In this context, the aim of this small survey was to consider the structure and transport properties of hybrid membranes intended for ion transfer and gas fractionation.

Hybrid ion-exchange membranes

Methods of synthesis and morphology

In the first experiments on the synthesis of hybrid membranes, the simplest method of the introduction of nanodispersed particles into solution, from which a membrane was cast, was used.[4] Aggregation considerably decreases the effectiveness of modification with the use of this approach. The introduction of large particles and aggregates leads to the blocking of a part of the membrane matrix and to a dramatic worsening of its mechanical properties. Therefore, another approach related to the synthesis of nanoparticles directly in membrane pores when they serve as nanoreactors was found much more effective.[7] The pore walls restrict the reaction volume, and they can sorb initial reagents due to the presence of ion-exchange groups. The diameter of the formed nanoparticles is 2–5 nm because the characteristic nanopore size does not exceed 5 nm. Furthermore, the walls of the membranes isolate the formed particles from each other, and they can decrease surface tension forces due to additional binding. This ensures the thermodynamic stability of the formed nanoparticles.

The majority of precursors used for the synthesis of inorganic nanoparticles contain hydrophilic fragments, and they are capable of forming coordinate bonds with the functional groups of ion-exchange membranes. After the introduction of the second reagent, the formation of nanoparticles also occurs in the pores of membranes. The diffusion-limited processes of agglomeration and nucleation proceed very rapidly because of the thermodynamic

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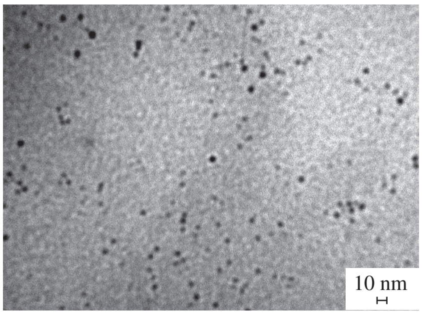

Figure 1 TEM image of SiO_2 particles in a Nafion membrane. Figure from ref. 21(*a*). ©2008 Pleiades Publishing, Ltd. Reproduced with permission.

instability of small nanoparticles, the high rate of reagent transfer inside a pore and the small length of a diffusion zone (3–4 nm). So more than one nanoparticle cannot be formed in a pore (Figure 1). This was confirmed by transmission electron microscopy data.[21(*b*)] Therefore, an increase in the number of cycles of nanoparticles synthesis and the concentration of a precursor in a membrane first leads to an increase in the size rather than the amount of nanoparticles. However, it is impossible to increase the dopant concentration above several volume percents. For this purpose, a precursor is introduced into a membrane solution followed by casting and chemical treatment. The size of the particles obtained with the aid of this approach is greater and the formation of agglomerates becomes possible.[22]

Ionic conductivity of hybrid membranes

The introduction of nanoparticles can considerably change the proton conductivity, gas permeability, strength, thermal stability and some other parameters of the membranes. These changes depend on the synergism of the properties of individual components.[4,23,24] Therefore, the properties of a material depend on the properties of a dopant. Thus, the hydrophilic nature of the surface of nanoparticles introduced into the membrane ensures the absorption of additional water molecules and an increase in conductivity.[4] However, this cannot explain the possibility of membranes conductivity increase upon the introduction of finely dispersed hydrophobic additives and an increase in the conductivity observed in a number of cases upon decreasing the mobility of interstitial solution containing water molecules and protons formed by the dissociation of functional groups.[25] For explaining these phenomena, a model was proposed, according to which the introduction of a dopant into membrane pores leads to their expansion simultaneously with the expansion of channels, which limit the conductivity of membranes.[26] Indeed, the moisture content of the membranes is determined by the binding of water by the protons of functional groups, whose concentration insignificantly changes as a result of modification. Therefore, the water uptake of the membranes will remain almost constant or even somewhat increase due to the additional sorption of water on the surface of hydrophilic particles. The size of connecting channels also grows due to an increase in the total pore size (Figure 2). As a result, the acceleration of proton transfer through narrow channels and the conductivity of membranes as a whole was observed.

The dependence of conductivity on dopant concentration passed through a maximum at a dopant content of about 2 vol%. A further increase led to a decrease in the water uptake and the conductivity of membranes. Pressure (elastic force) proportional to the deformation of material acts on pore walls; it can be characterized by an increase in the pore radius. According to Hooke’s law, the force required for pore expansion increases with the pore size. After equilibration, the pressure of elastic forces and the osmotic pressure on the pore walls become equal.

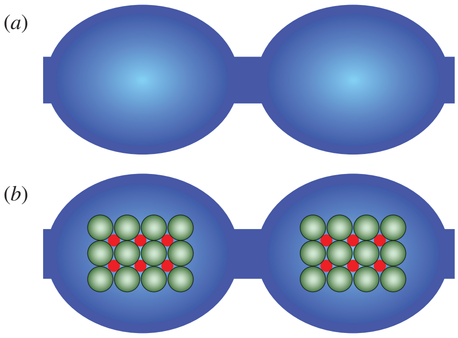

Figure 2 Schematic diagram of an increase in the size of channels connecting membrane pores upon the introduction of nanoparticles into the membranes. (*a*) Pores of initial membrane; (*b*) pores of hybrid membrane containing nanoparticles.

Thus, an increase in the elastic forces prevents the further widening of pores and facilitates a decrease in the moisture content and conductivity at a high dopant content (with a rise of the particle size).[27] The model proposed was confirmed by a comparison between NMR-spectroscopic data and the conductivity of hybrid membranes.[25]

An important advantage of hybrid membranes is the possibility of maintaining high proton conductivity at a low humidity when the conductivity of ordinary membranes is reduced by several orders of magnitude due to dehydration and a decrease in the volume of pores and channels.[28] This is especially important for fuel cells.[12] The introduction of either individual heteropoly acids[29] or their mixtures with silica or other oxides[30,31] can increase the conductivity at a low humidity. Note that the power of fuel cells at a low humidity raised by 50% due to the use of the membranes containing mesoporous zirconium phosphate.[32]

Within the scope of the above model, the reason for an increase in the conductivity of membranes with low water uptake is that a part of the membranes pore volume is occupied by dopant particles. This prevents the contraction of pores at a lowered water uptake and, as a result, increases the size of channels that join pores.[27] Furthermore, proton transfer occurs between water molecules at a high humidity, whereas the SO_3^- functional groups, which are characterized by a much lower proton affinity, do almost not participate in the transfer. In the dehydrated MF-4SK membranes, protons are contained in the form of $H_5O_2^+$ ions,[33] in which direct proton transfer is hindered at a low temperature because of the high enthalpy of the proton transfer reaction[21]

$$2\,H_5O_2^+ \rightarrow 2\,H_2O + 2\,H_3O^+. \qquad (1)$$

Note that an increase in the distance between these groups upon dehydration results in the participation of functional groups in transfer processes. This leads to the advantage of hybrid membranes, which contain a significant number of additional oxygen-containing groups capable of participating in proton transfer in pores.

Transfer process selectivity

Selectivity is one of the important features of membranes; in the case of cation-exchange membranes, it depends on their ability to transfer cations much faster in comparison with anions or neutral molecules.[1] The selectivity of ion transfer in these membranes is determined by transfer numbers (charge fractions transferred by ions of a given charge). An increase in the transfer numbers of cations was detected for MF-4SK perfluorinated membranes modified by the nanoparticles of silica and zirconia,[34] acid zirconium phosphate,[35] silver,[36] carbon nanotubes[37] and polyaniline.[38]

The diffusion of gas and alcohol molecules in the hybrid membranes is of special interest. This is due to the fact that the power of fuel cells and the fuel efficiency depend on a ratio between the rates of proton diffusion and the crossover of fuel (hydrogen, alcohols) and oxidant (oxygen) molecules. The possibility of crossover decrease is one of the most important advantages of hybrid membranes. Thus, for instance, the hybrid perfluorinated membranes containing silica are characterized by reduced permeability to gases and methanol.[39–43] The combination of high conductivity and low permeability to methanol makes these membranes highly applicable to direct methanol fuel cells. According to published data,[44] the specific power of this fuel cell on their basis is as high as 350 mA cm^{-2}. The surface of silica nanoparticles can be additionally modified to improve the properties of hybrid membranes. The Nafion membranes containing silica nanoparticles with grafted sulfo groups[45–47] or different sulfonic acid fragments[45,47,48] exhibited increased proton conductivity and low methanol permeability. The doping of Nafion membranes with silica and phosphotungstic acid diminished the permeability to methanol to 2×10^{-7} cm^2 s^{-1},[49] and the permeability of membranes from sulfonated polyether (ether) ketone (SPEEK) doped with a heteropoly acid to methanol was found lower than that of Nafion 117 by a factor of 20.[50] The membranes modification with sulfonated zeolites makes it possible to decrease permeability to methanol with the retention of proton conductivity and a considerable increase in the power of methanol fuel cells.[51,52] Choi *et al.*[53] managed to decrease the permeability of sulfonated polyaryl ether sulfone to methanol by modification with zeolites by a factor of more than 20.

The transfer processes occur in aqueous solution localized in the system of pores and channels in cation-exchange membranes where the distribution of cations and anions is nonhomogeneous. This is determined by the negative charge of pore walls due to the presence of fixed SO_3^- ions on them; the charge of these ions is compensated by the adjacently located protons. The thickness of this Debye layer is small (about 1 nm). On the contrary, anions and nonpolar molecules are excluded from it. On the other hand, almost electrically neutral solution localized at the pore center contains cations and anions in equal amounts. It can also contain nonpolar molecules.[54] Thus, a charge distribution in the pores and channels system of the membrane can be presented by the scheme [Figure 3(*a*)].[21]

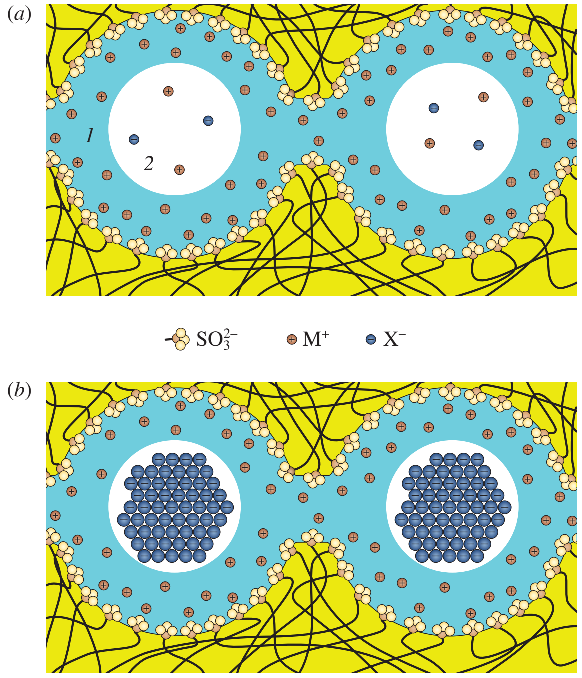

Figure 3 Diagram of the distribution of positively and negatively charged ions in the pores of (*a*) an ion-exchange membrane and (*b*) a membrane containing dopant nanoparticles: (*1*) Debye layer and (*2*) electrically neutral solution. Figure from ref. 21(*b*). ©2012 OOO ‘Park-media’. Reproduced with permission.

The proton conductivity of the membranes is predominantly determined by transfer in the Debye layer along pore walls, but anions and nonpolar molecules mainly moved through free solution localized at the centers of pores. The formation of nanoparticles occurs directly in the membrane pores. Moreover, as follows from the above examples, their surface most frequently manifests acidic properties, and it will be charged negatively. Therefore, the localization of such particles near the walls of a channel is unfavorable in terms of electrostatics. Hence, such particles primarily displace free solution from the center of membrane pores without affecting the thin Debye layer localized near the walls [Figure 3(*b*)].[21,55] This leads to a decrease in the concentration of anions and neutral molecules like hydrogen or alcohols in the membrane (this is important in the use of the membranes in fuel cells). Therefore, their transfer becomes substantially slower, while the cation conductivity of hybrid membranes remains at the same level or increases.

Effect of the surface of dopant particles

It is obvious that the nature of a dopant can substantially affect the membranes water uptake (hydrophilicity or hydrophobicity) and the concentration of carriers (proton-acceptor ability). In turn, these parameters essentially influence the membrane conductivity.[56] The essential effect of the hydrophilicity of a dopant on the properties of membranes was noted.[4,57] Thus, for instance, the influence of the surface hydrophilicity of silica,[58,59] zirconium oxide[60–63] and zirconium phosphate[35,41,57,64–67] was considered.

Upon the introduction of hydrophobic particles (carbon, silicon carbide and fullerenes) into a membrane, its water uptake decreases, but the conductivity can also somewhat increase at a low dopant content or weakly change with decelerating of anions and neutral molecules transfer and raising the selectivity. A small improvement in the transport properties of Nafion membranes was noted only upon the membranes modification with C_{60} fullerene and fullerenol,[68] whereas modification with carbon nanotubes did not improve the conductivity of the membranes as well as the power of fuel cells.[69]

The influence of carrier concentrations can be even more important. The transfer of protons in the membranes is carried along the system of hydrogen bonds between water molecules and oxonium ions by the Grotthus mechanism.[28] The protons of acidic groups, whose concentration is proportional to the conductivity, are the current carrier. For increasing their number, it is reasonable to increase the acidity of a dopant by its acidic functionalization.

Indeed, the Nafion membranes doped with silica nanoparticles with a sulfonated surface were found very effective for fuel cells due to their higher proton conductivity and low methanol permeability.[45–47,70] Similar results were obtained upon the modification of membranes with the silica particles modified by different sulfonic acid fragments[45,48] or by metal oxides with sorbed heteropoly acids[49,71–76] or their salts[72,77–79] on their surface. The proton conductivity of the Nafion membranes with the additives of silicotungstic, phosphotungstic and phosphomolybdic heteropoly acids increased to 1.5×10^{-2}–9.5×10^{-2} Ω^{-1} cm^{-1}.[29,30] Good results were also obtained for other membranes doped by heteropoly acids.[80–83] Their conductivity at room temperature reached 9×10^{-2} Ω^{-1} cm^{-1}, and the permeability of membranes from sulfonated polyether (ether) ketone doped with a heteropoly acid was lower than that of Nafion 117 by a factor of more than 20.[50] The surface functionalization of single-wall carbon nanotubes (0.05 wt%) with sulfo groups made it possible to noticeably increase the proton conductivity of the Nafion membranes.[84]

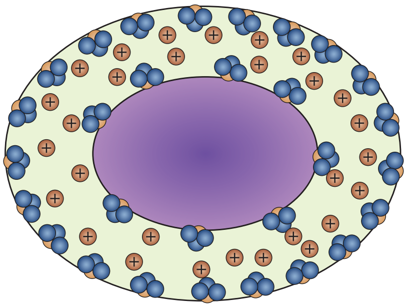

Figure 4 Distribution of ions in the pores of an ion-exchange membrane containing dopant nanoparticles whose surface contains groups with acidic properties.

Note that the membranes water uptake is assigned by osmotic pressure, which is determined by the number of acidic groups in its matrix. Therefore, the acidic modification of a dopant unavoidably leads to an increase in the water uptake of hybrid membranes.[21] At a low humidity, dopant particles actively participate in proton transfer, and nanoparticles whose surface has a clearly pronounced acid function also become most preferred.[31]

Surface modification also leads to a change in the selectivity of transport processes, as confirmed by a decrease in the permeability of neutral molecules and anions in the hybrid cation-exchange membranes with dopants whose surface is characterized by acidic properties.[45–52,84,85] It was noted above that an increase in the selectivity of hybrid membranes depends on the displacement of free solution, in which neutral molecules and anions are predominantly localized, from the pore center by dopant particles. Simultaneously, the negative charge of fixed ions localized on the pores walls prevents transfer of neutral molecules and anions in the thin Debye layer. The introduction of dopant nanoparticles whose surface contains groups with acidic properties results in the formation of an additional Debye layer (Figure 4), which decreases the concentration of anions and nonpolar molecules in the pore. This is responsible for a higher selectivity of transport processes in the membrane.

The nitrogen-containing groups of such species as amines and polyaniline are capable of binding the protons of SO_3H groups by strong hydrogen bonds.[86] This reduces the concentration of current carriers, the hydrophilicity and water uptake of the membranes.[38] Meantime, the conductivity of the membranes can be somewhat increased at a low polyaniline content[86] due to a change in the size of the pores and channels system. The modification of silica with hydrocarbon fragments containing the basic nitrogen atoms leads to the same effect.[87] Upon the introduction of these particles, their surface can be positively charged to form a Debye layer with an increased anions concentration. At the same time, their surface is bound to the walls of pores to decrease the volume of interstitial solution and to make it close to the Debye layer volume. This, on the contrary, provides a higher selectivity of transport processes.[87]

Hybrid materials for membrane gas separation

The development of hybrid membrane materials for gas separation was preceded by long-term works on filled polymers (*e.g.*, see ref. 88). The introduction of impenetrable inorganic particles (for example, SiO_2, Al_2O_3 and salts) into polymeric matrices increased the tortuosity of diffusion paths and, therefore, reduced the coefficients of diffusion and gas permeability without a gain in the selectivity of gas permeability. However, principally different results were obtained more recently with the use of much smaller particles (10–100 nm). This effect was convincingly demonstrated in a study of gas transport in polymethylpentyne with the additives of fumed silica (SiO_2) and other particles.[89] It was found that the permeability coefficients did not decrease upon the introduction of nanoadditives in accordance with the Maxwell model[90] for filled polymers; on the contrary, they noticeably raised. Moreover, this increase was more significant for particles with minimal sizes of introduced particles (SiO_2, soot and Al_2O_3):

Particle size, nm	500	30	15	12
Relative increase in permeability, P/P_0	1.05	1.25	1.6	1.9

These results were confirmed in numerous subsequent works. The permeability coefficients grew due to an increase in the free volume near phase boundaries and, consequently, by an increase in the diffusion coefficients.[91,92] An increase in the free volume was demonstrated by the positron annihilation method.[93,94] Meanwhile, in some cases, the introduction of nanoparticles is accompanied by a reduction of the coefficients of permeability and diffusion, and this behavior was explained by the densification of macrochains near the phase boundary.[95]

Two principally distinguished types of nanoparticles introduced into polymeric matrices were used. The nonporous nanoparticles include different oxides; the additives of SiO_2, TiO_2 and MgO were studied in most detail. The additives of porous nanoparticles are more diverse: interesting results were obtained for hybrid membrane materials containing carbon nanotubes, organometallic skeleton structures and zeolites.

The dependence of the permeability coefficients on additive concentration is important. In the overwhelming majority of cases, this dependence is nonlinear: at small additive concentrations, the permeability to different gases weakly depends on the amount of introduced nanoparticles; then, a sharp increase in the permeability is observed starting from concentrations of 30–35%.[96,97] This behaviour can be accounted for in terms the Takahashi–Paul model,[98] according to which a sharp increase in the diffusion and permeability coefficients begins after the formation of large clusters with an enhanced free volume at the interfaces. In some cases, the permeability passes through a minimum at the small concentrations of additives (*e.g.*, in the polytrimethylsilylpropyne–TiO_2 system[99]).

Hybrid systems with SiO_2 additives

Different behaviour in terms of the transport properties was observed upon the introduction of SiO_2 additives into glassy polymers and highly elastic polymers. Thus, for matrices based on the polymer with intrinsic microporosity (PIM-1)[96] or polysulfone,[97] an increase in the permeability with reducing different separation factors, for example, $\alpha(O_2/N_2)$, was observed (Figure 5).[97,100]

At the same time, the permeability decreased as a result of the introduction of a SiO_2 additive into highly elastic matrices (polyurethane, polydimethylsiloxane).[101,102] In terms of the Moore–Koros model,[95] this can be indicative of phase densification at the interfaces.

The introduction of SiO_2 additives makes the glassy matrix more loosely packed; this manifests itself in the transport properties of hydrocarbons with different molecular weights in polyacetylenes. It is well known that these highly permeable polyacetylenes exhibit so-called thermodynamic (solubility controlled) selectivity: an increase in the permeability coefficients with the molecular weight of a C_1–C_4 penetrant due to an increase in their solubility.[103] The introduction of SiO_2 nanoparticles into polytrimethylsilylpropyne and polymethylpentyne[104] increases the permeability coefficients of all of the hydrocarbons with the retention of thermodynamic selectivity. This is caused by raising diffusion coefficients since the sorption isotherms of gases and vapors in the hybrid systems do not depend on the concentration of SiO_2 added. An interesting result was obtained for other highly

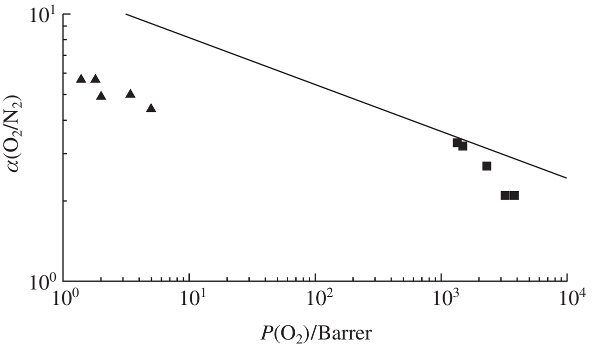

Figure 5 Permeability–selectivity relationship for the (squares) PIM-1–SiO_2 and (triangles) polysulfone–SiO_2 systems.The left and right points of the arrays correspond to pure polymers and maximum additive contents, respectively. The straight line corresponds to the upper boundary of the Robeson diagram (2008), which characterizes a maximum gas separation selectivity [$\alpha(O_2/N_2)$] at a given permeability [$P(O_2)$].

permeable polymer, amorphous Teflon AF2400, which has diffusion (size sieving) selectivity for the transport of the hydrocarbons: $P(CH_4) > P(C_4H_{10})$. The introduction of SiO_2 additives into this glass matrix made its structure much looser; as a result of this, the thermodynamic selectivity was observed: $P(CH_4) < P(C_4H_{10})$.[93] Thus, the introduction of nanoparticles can qualitatively change the regularities and mechanism of gas transport.

Hybrid membranes with carbon nanotube additives

Carbon nanotubes (CNTs) differ significantly from other nanoparticles introduced into the hybrid gas-separating membranes. First, they have large shape anisotropy (length-to-diameter ratio). Furthermore, there are both multiwall and single-wall CNTs. Unlike other nanoadditives, they were successfully used as membrane construction elements. In membranes of this kind, the CNT arrays are oriented perpendicularly to the base layer.[105] In this case, the Knudsen mechanism of transport occurred with very high parameters caused by the smooth walls of CNTs.[106] However, these systems with a very high throughput are low selective, and the mouths of CNTs should be functionalized for their use as membranes; in turn, this functionalization will affect the permeability. An additional special feature of CNTs is related to the fact that transport in the systems containing CNTs can occur not only through a matrix with changed properties but also through the channels of CNTs. Therefore, different properties are observed in CNTs with open and closed mouths. The role of transport through the channels of CNTs can be revealed by comparing experiments performed with compositions containing CNTs with closed and open ends. Thus, the introduction of CNTs with closed ends into a polyimide matrix led to a significant decrease in permeability.[107] This can be interpreted as an indication of the lengthening of diffusion paths in the membrane and the appearance of a closer packing at the interface. At the same time, the introduction of CNTs with open channels led to an increase in the permeability due to rapid transport inside the channels. It was found that, in the presence of functionalized CNTs, the permeability coefficients of gases in the systems based on PIM-1 polymer with intrinsic microporosity increased even at the small concentrations of an additive.[108]

CNT concentration (wt%)	0	1	2	3
Permeability to CO_2/Barrer	6210	7810	12270	4820

Studies on the transport of gases (N_2, O_2, CH_4 and C_3H_8) in the hybrid membranes based on glassy polyvinyltrimethylsilane with the small (0.3–3 wt%) additives of multiwall CNTs showed that, starting at a concentration of 0.4 wt%, the system passed through a threshold of percolation; thereafter, transport through the channels of CNTs, which is characterized by large flows and low selectivity, was predominant; that is, the Knudsen diffusion occurred.[109]

Hybrid systems with zeolite additives

Zeolites were the first to attract the attention of researchers as nanoadditives. Thus, Paul and Kemp[110] proposed an idea related to the more recent studies of hybrid membranes: zeolite introduced into siloxane simulated free volume elements in the glassy polymers. Zeolites are available and cheap feedstock, and this makes them useful additives in combination with different polymers. The geometric parameters of the porous crystal structure of zeolites are well known; thus, it seems possible to match specific zeolites for the selective sorption of particular components from a separated gas mixture. Figure 6 compares the pore sizes of some zeolites with the gas-kinetic sizes of some molecules.[111] This offers the possibility of the size sieving separation of specific gas mixtures. Note that numerous experimental data did not completely confirm expectations of this kind.

Various zeolites were considered as additives to different gas-separating membranes: SAPO-34, zeolites 3A and 4A, ZSM-5 (MFI), *etc*. They were introduced into polyvinyl acetate, Ultem polyesterimide, polycarbonate, polyethersulfone and other polymers. Zeolite additives do not principally differ from metal-organic frameworks (MOF) structures or nonporous nanoparticles (for example, SiO_2) by the type of their action.

On the one hand, as expected in accordance with the relative molecular dimensions of gases and pores in zeolites, the introduction of zeolite additives in a number of cases led to an increase in selectivity for pairs such as H_2/CH_4 and H_2/CO_2. For example, this occurred in the polyethersulfone–SAPO-34[112] and polycarbonate–zeolite 4A[113] systems. In some cases, both selectivity and permeability increased.[112] At the same time, in certain examples, the introduction of zeolite nanoadditives into polymers led to a decrease in selectivity: this was observed in the polyethersulfone–zeolite 4A[114] (for the pair CO_2/CH_4), polyether ether ketone–zeolite NaA[115] and polymethylmethacrylate–zeolite 4A (for the pair O_2/N_2).[116]

Defects appear at the interfaces between inorganic zeolite particles and an organic polymer matrix, and they can be responsible for a dramatic decrease in selectivity. To overcome these problems, third components, namely, organic molecules capable of improving the compatibility of zeolite nanoparticles and the matrix, are frequently introduced into the hybrid membranes containing zeolites. 2-Hydroxy-5-aniline, aminopropyltriethoxysilane and other substances were used as such additives.[117,118] Indeed, a simultaneous growth of permeability and selectivity is sometimes observed in ternary systems,[112] but this effect is absent from classical binary systems. Meantime, the introduced organic additives can partially block the pores of zeolites to decrease the permeability.[117]

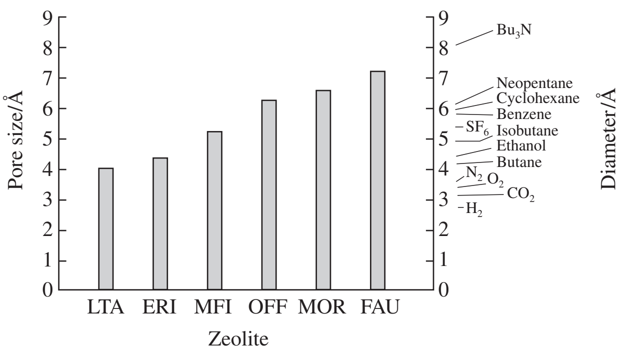

Figure 6 Correlation between the zeolite pore size and the molecular dimensions of gases and vapors.

In spite of the expected advantages of hybrid membranes containing zeolites, in the majority of studies of this type, even an increase in the permeability and selectivity does not provide a considerable improvement in the separating properties. As a result, in the Robeson diagrams,[100] which characterize maximum gas separation selectivity at a given permeability, the majority of the obtained systems lies considerably lower than the record values from Upper Bound. The reason for this is related to insufficiently high level of permeability and selectivity of the used polymer matrices.[112,113,115–117,119] Gorgojo *et al.*,[120] who introduced exfoliated zeolite Nu-6(2) into co-polyimide prepared based on 6FDA-containing dianhydrides, reported a rare example when the barrier of an upper boundary was overcome. The reason for this behavior of a system of this type is probably related to the fact that the representing points for the polymer matrix without additives are already located near upper boundaries of the Robeson diagram.

Mechanical properties of hybrid membranes

It is often assumed that the mechanical properties of high-molecular ion exchange membranes are among their prime advantages. A number of authors noted an improvement in the mechanical properties of hybrid membranes due to the synergism of their properties.[4] However, the modification of membranes with nanoparticles more frequently led to an inverse effect especially at high dopant contents.[21] This result is quite reasonable. It is well known that a decrease in the strength of solids is determined by the presence of extended defects (nanosized cracks) in their structures. The greater the size of a crack, the smaller the load at which its expansion occurs and the lower the mechanical strength of material as a whole.[121] The nanopores of membranes play the role of such cracks. From this point of view, it is possible to conclude that the higher the dopant concentration, the greater the pore size and the lower the membrane strength.

In the case of hybrid ion-exchange membranes, osmotic pressure inside pores becomes insufficient for compensating the elastic deformation forces of the walls at a large size of introduced particles; this diminishes the moisture content of the membranes. In this case, the concentration of protons in the interstitial solution and the osmotic pressure, which deforms the membrane from the inside, increase.[21]

Numerous studies of gas-separating membranes with the additives of nanoparticles also showed that the introduction of nanoparticles into different polymer matrices leads to a considerable worsening in the mechanical properties of composites. Some examples are represented in Table 1. As a result of the introduction of nanoadditives, polymer matrices become more brittle: both the tensile strength and ultimate elongation decrease. Note that low mechanical properties are a crucial factor that impedes the introduction of large dopant quantities. Analogous behavior was noted for both dense films and hollow-fiber membranes (*e.g.*, see refs. 126, 127).

On the other hand, based on the above theory of the solids destruction,[121] strengthening can be expected only upon the introduction of extensive one-dimensional nanoparticles, which are characterized by high strength, for example, CNTs, into the membranes. These dopants can be an analogue of nonwoven reinforcing material for the membrane to impart it a higher strength. Indeed, the introduction of a small quantity of single-wall CNTs into the membranes results in an essential improvement in their mechanical properties.[37,69,108] Thus, the doping of Nafion ion-exchange membranes with 1 wt% carbon nanotubes leads to an increase in their Young modulus by a factor of about 2 (from 50 to 110 N mm^{-2}) and the tensile stress from 8–10 to 13–15 MPa.[37] Analogously, a rise of the tensile strength and ultimate elongation was observed at small (up to 2%) concentrations of CNTs introduced into the PIM-1 polymer.[108] This fact can be considered as a confirmation of the formation of an additional extensive nanosized network from dopant particles, which increases the strength of the membrane. Note that a similar tendency is also observed upon the introduction of CNT additives into different polymers.[128] However, the mechanical properties of the membranes dramatically decrease with the concentration of CNTs.[37]

Table 1 Effect of the concentration of an introduced additive on the mechanical properties of the resulting hybrid membrane materials.

Polymer	Dopant	Dopant concentration (%)	Tensile strength/ MPa	Ultimate elongation (%)	Ref.
Polyimide Matrimid	MOF Cu-BPY-HFS	0	87	21.0	122
		10	75	6.6	
		20	69	4.6	
		30	53	3.0	
	MOF ZIF8	0	109		123
		20	98		
		30	93		
		60	47		
Polyimide 6FDA-ODA	MOF MIL53	0		12.0	124
		20		3.3	
		30		2.6	
		36		0.8	
Brominated poly(2,6-diphenyl-1,4-phenylene oxide)PPO	CNTs (single-wall)	0		4	125
		5		2	

Note that the problems of improving the mechanical properties of hybrid membranes have been inadequately considered in the literature. An obvious approach can assume crosslinking. However, this can be made only with the fabricated matrices; as a consequence, the technology of membrane preparation can become more expensive.

Conclusions

The above data show that, in a number of cases, the introduction of nanoparticles can lead to an essential improvement in the properties of the hybrid membranes, among which an increase in the proton conductivity of ion-exchange membranes and the permeability of gas-diffusion membranes can be noted. In addition, the selectivity of transport processes in many of them grows. Due to these facts, hybrid membranes can find a broad application in actual practice. Thus, the above data indicate that they are in wide current use for the construction of fuel cells with improved operational parameters and for gas separation processes. Furthermore, an increase in the selectivity of transport processes is responsible for their effective use in water purification processes,[129–131] for drug delivery[132] and as sensor materials.[133]

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