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Solid electrolytes: main prospects of research and development †

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The review briefly outlines the general laws of ion transport in solid electrolytes, including the mechanisms of defect formation and proper ion transport. Various approaches used to produce solid electrolytes are considered, including the formation of solid solutions with defect structure, nanodisperse and composite materials, materials containing a liquid phase, as well as amorphous inorganic and polymeric materials. Electrolytes with high Li-ion, O-ion and proton conductivity are considered in detail as best candidates for practical applications. Specific features of ion transport in these systems, problems that make them of limited use and the possibilities of modification of these systems are analyzed.
The bibliography includes 500 references.

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I. Introduction

More than 100 years ago Turbandt and Lorenz discovered ionic conductivity in a typical solid, silver iodide (α-AgI), upon a phase transition at 420 K.[1] The phenomenon manifested itself only at rather high temperatures and therefore was not in demand for long. Intensive research in the field began only in the mid-1960s with the studies of rubidium – silver iodide $RbAg_4I_5$ (see Refs 2 and 3) and β-sodium aluminate $NaAl_{11}O_{17}$ (see Ref. 4) whose room-temperature ionic conductivity approaches a value of 0.35 and 0.1 S cm^{-1}, respectively. Relying on the results obtained, it was assumed that these compounds can be used for power cell applications. Since then, ion-conducting solid electrolytes have been among the most attractive materials in solid-state physics and chemistry.

Initially, it was assumed that high ionic conductivity is only possible in compounds containing monovalent sodium, silver and copper cations because their ionic radii are optimum for fast ion transport along the lattice channels. Besides, copper and silver ions have readily polarizable electron shells which facilitates ion transport. Large-radius ions should overcome high steric barriers when moving across narrow faces of the coordination polyhedra. Seemingly, small-radius ions should offer considerable advantages. However, they are characterized by high binding energies and low coordination numbers, which favours stronger bonding to the faces of the coordination polyhedra. As a result, both small- and large-radius ions have high activation energies for conductivity.[5]

Recently, the attention of researchers has been attracted to proton-, lithium- and oxygen-conducting materials. Materials that simultaneously exhibit ionic and electronic conductivity are also in high demand. They are used in the most promising devices of modern alternative power engineering, *viz.*, fuel cells[6–9] and Li-ion batteries.[10–12] Note that materials with unipolar conductivity are mainly used as electrolytes or membranes. Charge separation (transport of

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hydrogen, lithium and oxygen ions between electrodes) in these systems is due to the chemical potential gradient. Energy generated is consumed in the external circuit. These electrolytes have also found applications in, *e.g.*, sensorics, wastewater treatment, *etc.*).[13, 14]

Materials with bipolar conductivity (if there are two types of charge carriers, *e.g.*, ions and electrons) are inefficient as components of electrolytes. However, they are used as electrode materials for fuel cells and Li-ion batteries;[6, 7, 12, 15] and as efficient components of systems for production and purification of hydrogen and oxygen [16, 17] and in catalytic processes.[17, 18]

Recently, a large number of reviews have been published on solid electrolytes with bipolar conductivity. However, in spite of increasing flow of original articles, most reviews on solid electrolytes with unipolar conductivity have been reported more than a decade ago,[19–21] except the studies on the membrane and some composite materials.[9, 22–25] The last fifteen years are marked with the emergence of original ideas and development of methods for the synthesis of novel types of materials and modification of the existing ones. They are aimed to fabricate chemically and thermally stable materials with high conductivity of a specified type of ions, maximum possible selectivity of ion transport, admissible mechanical properties, *etc*. Ideas on the design of such materials are materialized through scientific research and applied studies.

This review concerns ion transport in solid electrolytes, methods for their fabrication and modification, as well as main types of ion-conducting systems. A single review is insufficient to cover all types of solid electrolytes with conductivity of different-type cations and anions. Therefore, we will consider only lithium-, hydrogen- and oxygen-conducting solid electrolytes. They are most widely used (see above), have different properties, and ion transport in them proceeds by different mechanisms. Indeed, transport of small lithium ions is possible in some materials at low temperatures, whereas bulky O^{2-} ions become highly mobile only at high temperatures. Finally, the proton transfer mechanisms are different from those of other ions.

II. Ion transport in solids: general

Being a solid, a perfect crystal is characterized by a close packing and large energy expenditures necessary to deform the electron shells; therefore, ions cannot exchange their positions. Ion transport in solids always occurs through defects. There are two main mechanisms of defect formation.[5] According to the Schottky mechanism, a cation and an anion are displaced from corresponding lattice sites and move to the crystal surface; as a result, cationic and anionic defects are formed simultaneously in the bulk. In the Frenkel model for defect formation, an ion is displaced from its lattice site to an interstice, thus producing a vacancy. In both cases, considering a binary crystal built of cations, A^+, and anions, X^-, one deals with the formation of a pair of defects. The formation of the Frenkel and Schottky defects in a crystal can be described by the following quasi-chemical equations:

$$A_A + V_i \rightleftharpoons A_i^* + V'_A \quad (1)$$

$$A_A + X_X \rightleftharpoons V'_A + V_X^* + A_s + X_s \quad (2)$$

where A, X and V denote the cation, anion and vacancy, respectively, and the subscript denotes the position occupied by a given species, *viz*., the subscripts 'A' and 'X' correspond to cationic and anionic positions, respectively; the subscripts 'i' and 's' denote the species in the interstitial and on the crystal surface, respectively; and the superscripts '*' and '′' respectively denote the positive and negative charge of the species relative to the stoichiometric value for the given lattice site.[26] Ions displaced on the surface complete the regular crystal lattice and are therefore most often omitted in the quasi-chemical equations

$$A_A + X_X \rightleftharpoons V'_A + V_X^* \quad (2a)$$

In ionic crystals of pure compounds, defect formation is due to the thermally activated process of intrinsic disordering. Since the enthalpy of defect formation is high, the concentration of the intrinsic lattice defects in most solids is very low. To improve the conductivity, the defectiveness of crystals is often forcedly increased by replacing a fraction of ions with different-valence ions (so-called doping). For instance, replacement of some silver ions in AgCl crystals by divalent cadmium cations causes simultaneous formation of an equivalent number of vacancies in the silver positions to maintain the electrical neutrality of the crystal

$$CdCl_2 \rightleftharpoons Cd_{Ag}^* + V'_{Ag} + 2\,Cl_{Cl} \quad (3)$$

Other defect formation mechanisms [5, 22] will be considered when necessary.

In a crystal with a vacancy, the neighbouring ions can occupy it. However, in most cases, they should at least pass across a narrow face of the coordination polyhedron ('bottleneck'); in this case, the interatomic distances are much shorter and the ion energies become much higher (Fig. 1); therefore, the residence time of ions in this position is much shorter than in the regular lattice site. One can assume that ion transport in solids occurs by fast hopping between neighbouring positions with a characteristic hop time being much shorter than the residence time of ions in the regular lattice site.

Now we will consider main relationships necessary for understanding the material presented in this review; for details of derivation, see, *e.g.*, a monograph.[5] When an

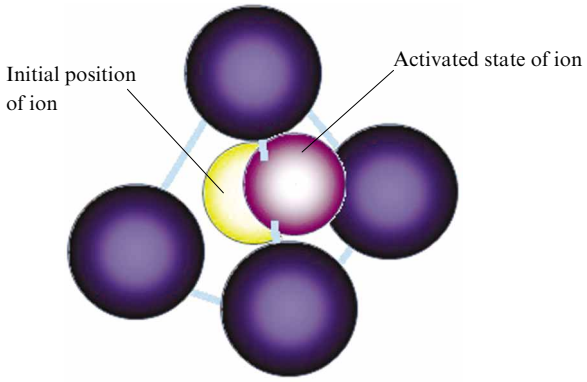


Figure 1. Scheme of the ion passing through a face of coordination polyhedron.

electric field is applied to a crystal, one deals with superposition of random ion hopping and directed ion transport. The motion of cations towards a cathode is accompanied by a decrease in energy and the frequency of the cathode-directed hops is higher than that of the hops along other directions. The ion flux (J) through a flat sample with the cross-section S and length l is

$$J = \frac{C_q S a^2 \Delta\phi v_0}{lkT} \exp\left(-\frac{E_m}{kT}\right) \quad (4)$$

where C_q is the volume concentration of electricity carriers bearing the charge q, a is the hop length along the chosen direction, $\Delta\phi$ is the electric potential drop across the hop length, v_0 is the pre-exponent determining the frequency of ion hops, E_m is the activation energy for migration, k is the Boltzmann constant and T is absolute temperature.

Since the role of current carriers is played by defects, namely, ionic vacancies or interstitials, whose concentration in corresponding pure crystals exponentially depends on temperature, the overall expression for the specific ionic conductivity in the compound A^+X^- has the form

$$\sigma = \frac{qa^2 v_0}{kT} \exp\left(\frac{\Delta S_d}{2k}\right) \exp\left(-E_m + \frac{\Delta H_d}{2kT}\right) \quad (5)$$

Generally, for ionic crystals $A^{n+}X^{m-}$ one gets

$$\sigma = \frac{qa^2 v_0}{kT} \exp\left(\frac{\Delta S_d}{(n+m)}\right) \exp\left(-E_m + \frac{\Delta H_d}{(n+m)kT}\right) \quad (5a)$$

where ΔS_d and ΔH_d are respectively the entropy and enthalpy of the defect formation process described by Eqn (1) or Eqn (2). Since this relationship is rather complicated and in most cases all parameters are difficult to determine unambiguously, it is usually simplified by reducing to the Frenkel equation

$$\sigma T = A \exp\left(-\frac{E_\sigma}{kT}\right) \quad (6)$$

or Arrhenius relation

$$\sigma = \sigma_0 \exp\left(-\frac{E_\sigma}{kT}\right) \quad (7)$$

where A and σ_0 are the pre-exponents and E_σ is the activation energy of conductivity.

Comparing Eqns (6), (7) and Eqn (5a), one gets for a pure ionic compound:

$$E_\sigma = E_m + \frac{\Delta H_d}{n+m} \quad (8)$$

i.e., the activation energy of conductivity in, *e.g.*, compound A^+X^-, includes the activation energy for migration of ions in the lattice and half the enthalpy of defect formation. If the defect concentration considerably increases upon doping the material with impurity ions or is governed by the dopant concentration, it is temperature-independent. In this case, the activation energy of conductivity equals E_m.

Structural features of materials, *e.g.*, vacancies and conduction channels connecting them, as well as the channel size, are of great importance. Since most materials are polycrystalline, random packing of crystals causes elongation of the diffusion path length of ions in systems with rapid unidirectional ion transport. In this respect, materials with intercrossing system of conduction channels or with the possibility of ion transport across a certain plane (this is typical of layered materials) offer considerable advantages.[5,25] Small coordination numbers of ions, all other things considered, lead to enlargement of faces of the coordination polyhedra and facilitate ion transport. Even at equal coordination numbers, the formation of the coordination polyhedra in the form of trigonal pyramids is energetically more favourable than the formation of octahedral coordination polyhedra because some triangular faces are transformed into larger rectangular faces.[5,19] In some highly conducting solid electrolytes, mobile ions are disordered over various positions even at low temperatures, so main sites and interstitials become almost indistinguishable.[5]

The room-temperature ionic conductivity in most solids is relatively low, being at most 10^{-10}–10^{-14} S cm^{-1}. However, there are dozens of materials with high ionic conductivity from 10^{-3} S cm^{-1} to a few S cm^{-1} at relatively low temperatures.[27] Materials with high ionic conductivity are often classified as so-called superionic conductors containing a large proportion of delocalized cations (or anions). For instance, only ~70% of lithium ions were located in a neutron diffraction study[28] of the high-temperature rhombohedral modification of lithium–zirconium double phosphate $LiZr_2(PO_4)_3$, other ions were delocalized within conduction channels. The structure can be treated as two-component one, with the mobile cations as highly mobile pseudoliquid component and the ions in fixed positions as a rigid framework determining the mechanical properties of the sample. Considering them altogether, one deals with a kind of a sponge filled with water (*i.e.*, mobile cations).[5] By analogy, metals consist of a cationic core and 'electron gas' delocalized over the lattice.

It should be noted that the highly mobile component is mainly formed by singly charged cations having relatively small radii. This is due to the lower binding energies of the singly charged ions and to their ability to penetrate faces of small coordination polyhedra with relative ease (low activation energy for hopping). However, too small cationic radii most often also cause the activation energy of conduction to increase[5] because of strengthening of the ionic bonds and, in some cases, displacement of the mobile ions towards a corner or a face of the polyhedron where the ion resides for a longer time. There is an analogy with the fact that small wheels make it less-than-ideal for rugged country roads. As mentioned above, there exists an optimum size of the mobile ion, *viz.*, ~1 Å for most materials. In this respect, the closest singly charged cations are Na^+, Cu^+ and Ag^+. However, researchers are focused on practically valuable lithium-, proton- or oxygen-conducting materials, although Li^+ and H^+ are much smaller, while O^{2-} is much larger than the optimum size.[10,11,29,30]

Large cations usually have very low mobility. However, their rather high conductivity can manifest itself provided that the structure of solids contains 3D conduction channels. In particular, Burmakin, Shekhtman and co-workers reported that orthophosphates,[31–34] aluminates,[35,36] gal-

lates[37] and ferrites[38–43] doped with the multiply charged ions can exhibit high potassium-, rubidium- and caesium-ion conductivity (up to 10^{-2}–1 S cm^{-1}). They also reported a trivalent ionic conductivity.[44] The size of conduction channels in ionic crystals is usually governed by the close packing of anions, being a fraction of the size of the anions; therefore, wide channels are difficult to create. The best results can be obtained using a close packing of bulky anions (sulfur or iodine) with rather high polarizabilities of their electron shells to facilitate cation transport. However, sulfur- or iodine-based materials have low chemical stabilities which makes them of limited use.

High anionic conductivity is very rare. The attention of researchers is mainly focused on transport of two smallest species, fluorine and oxygen anions with ionic radii of 1.36 and 1.4 Å, respectively.[15,17,45–49] High anionic conductivity, especially oxygen-ion conductivity, manifests itself at rather high temperatures.[6,50] This is due to the fact that the ionic radius of the relatively 'small' O^{2-} anions is comparable with that of the relatively 'large' potassium cations and it is difficult to find a crystal lattice without considerable steric hindrances to transport of fluorine or oxygen ions. In addition, high strength of bonds formed by the doubly charged oxygen should be taken into account. Sulfur-conducting materials have been less studied.[47,51–53] The ionic radius of sulfur is even larger (1.84 Å), but the electron shells of sulfur ions are more polarizable.

III. Solid solutions with defect structure

As mentioned above, the mobility of all ions (except protons) in the structure of solids is determined by the presence of conduction channels with sufficiently large size of faces of the coordination polyhedra. Ions should overcome these barriers to move from one position to another. However, this is not a sufficient condition for high ionic conductivity in a material because the concentration of electricity carriers (ionic defects or disordered ions) should also be rather high. This is a key feature of the so-called superionic conductors. However, a considerable defect concentration in individual compounds is rare to occur. An example is provided by niobium monoxide where 25% of the total number of cationic and anionic positions are vacant, all vacancies being ordered with the formation of a new superstructure and remain low-mobile.[5]

The monoclinic phase of zirconium oxide is characterized by a much lower intrinsic defectiveness. However, a relatively high mobility of oxygen ions in the high-temperature cubic phase of this material makes it the most widely known oxygen-conducting solid electrolyte. The high-temperature cubic phase of ZrO_2 is stable at > 2640 K[54] and is characterized by a higher defect concentration compared with the low-temperature phases. This phase can be stabilized at lower temperatures by partial replacement of zirconium by low-valence elements (scandium, yttrium, calcium ions, *etc.*).[47,50] Additional defects are generated in the following quasi-chemical process:

$$Y_2O_3/ZrO_2 \longrightarrow 2\,Y'_{Zr} + 3\,O_O + V_O^{**} \qquad (9)$$

Surprisingly, cerium also appeared to be a good dopant despite the fact that this tetravalent ion should not increase the defect concentration. Its efficiency upon doping is explained by transition to the trivalent state on the surface of the oxide phase.[55,56]

The ionic conductivity of some other materials can be significantly improved by varying the defect concentration. For instance, it is convenient to use double phosphates with the NASICON‡ $[M^I_xA_2(BO_4)_3]$ structure for heterovalent substitution. Depending on the charge of the dopant, one can increase the concentration of lithium ions in the interstitials or that of lithium vacancies and thus considerably improve the ionic conductivity of these materials.[25,57–59]

Most often, one deals with partial replacement by cations whose charge differs by unity because the solubility appreciably decreases almost to zero if the charges differ to a greater extent. In some cases, doping with ions with greater charge difference is possible (*e.g.*, solid solutions of the general formula $Rb_{2-2x}Ga_{2-x}A_xO_4$ (A = P, V, Nb, Ta) based on rubidium gallate $RbGaO_2$[37] and on rubidium ferrate, $Rb_{2-2x}Fe_{2-x}P_xO_4$).[42] High caesium-ion conductivity in $Cs_{2-2x}Fe_{2-x}A_xO_4$ (A = P, V) is $\sim 3\times10^{-2}$ S cm^{-1} at 300 °C and $\sim 3\times10^{-1}$ S cm^{-1} at 700 °C.[42]

If the dopant concentration is low, the conductivity of materials varies linearly in proportion to it. However, if the dopant concentration increases, the conductivity increases much slower due to association of defects and ordering processes that can lead to formation of a new phase.[5] In the case of continuous solid solutions, the conductivity passes through a maximum at some intermediate compositions.

In systems with isovalent substitution the dependence of conductivity on the composition usually deviates from linear as a result of variation of the mobility of electricity carriers. These phenomena were studied in detail taking glasses and crystalline materials containing singly charged cations as examples. When A^+-ions are replaced by B^+-ions, their mobility decreases as the concentration of A^+ decreases and the larger the difference between the cationic radii the greater the conductivity drop.[60] In the case of alkali metal compounds, the phenomenon is termed 'mixed alkali effect'.[61,62]

IV. Specific features of ion transport in nanodisperse and composite materials

Surface diffusion in solids proceeds much faster than diffusion in the bulk because of large free volume and the existence of uncompensated bonds. Usually, the activation energy for surface diffusion of ions or molecules is about 10% of the heat of sorption,[63] being only 15–20 kJ mol^{-1} even for the carbon monoxide molecules strongly chemisorbed on the surface of platinum group metals.[64] The surface diffusion coefficients of atoms are, as a rule, a few orders of magnitude higher than for diffusion in the bulk.[65] It is equally important that the near-surface layer always contains a higher defect concentration.[66] In this connection, surface (or interfacial) diffusion most often makes the major contribution to the transport properties of finely disperse materials characterized by a large fraction of ions located on the developed surface.[67]

There are four types of ionic defects in binary ionic crystals M^+X^-, namely, cationic and anionic vacancies and interstitials. Pure compounds most often contain two

‡ Na Super Ionic CONductor.

types of defects, either cationic and anionic vacancies or cationic vacancies and interstitials. The condition for electrical neutrality is met in the case of equal defect concentrations in the bulk. However, the situation on the surface is usually characterized by preferred sorption of same-type ions; consequently, the defect concentrations become different and an electrical double layer is formed. The surface is still covered with the same-type ions, *e.g.*, M^+. A thin near-surface Debye layer 1 – 2 nm thick contains an increased concentration of the other type of ions (X^-) or cationic vacancies (V'_M). As a result, the surface concentration of defects increases. For nanomaterials, the effect can extend to the whole bulk;[22, 66 – 69] therefore, the ionic conductivity of nanomaterials considerably increases. Besides, the conductivity of many solid electrolytes depends on the particle size.[70, 71] Since a number of reviews on the subject are available (see, *e.g.*, Refs 22 and 72 – 74), no detailed consideration of the problem will be given below.

The increase in the ionic conductivity due to preferred sorption of particular type of ions on the surface of particle can be enhanced through formation of nanodisperse composites. These materials usually consist of solid electrolyte and particles having high affinity to the mobile ions from the electrolyte that can be sorbed on the particle surface. First of all, these are nanodisperse alumina, silica, titania and oxides of some other multivalent elements.[72] The enthalpy of defect formation at the interfaces decreases as the enthalpy of sorption processes increases; this causes an appreciable decrease in the activation energy of conductivity.[65] At high temperatures, the concentration of the defects originating from intrinsic disorder is usually higher than the concentration of the defects formed as a result of sorption at the interface. The temperature dependence of the ionic conductivity of nanoscale systems plotted in the coordinates of either Arrhenius equation ($\log\sigma - 1/T$) or Frenkel equation ($\log\sigma T - 1/T$) exhibits two linear branches with different activation energies, *viz.*, a high-temperature branch and a low-temperature one.[5, 75]

V. Heterogeneous materials containing a liquid phase

In some cases, specific features of solid electrolytes make these systems of limited use. For instance, the design of solid oxide fuel cells requires materials with high oxygen-ion conductivity. However, a practically valuable conductivity in such systems can be achieved only at 800 – 900 °C. Therefore, a considerable energy expenditure is necessary for heating to the operating temperature. Switching on such a fuel cell takes a long time (a few hours), so the device should be in continuous operation. Besides, the selectivity of catalysts abruptly decreases at high temperatures and problems related to carbonization of the anode space upon the oxidation of carbon-containing fuel arise (the possibility to use carbon-containing fuels is a key advantage of the solid oxide fuel cells). In this connection, considrable efforts of researchers are aimed to search for materials with high oxygen-ion conductivity at lower temperatures.

High ionic conductivity in liquid solutions at relatively low temperatures, which much exceeds the conductivity of solids, is determined by intrinsic disorder and high molecular mobility. However, a too high mobility, short-range ordering and the lack of other mechanical properties typical of solid compounds make solutions inapplicable for utilization in most devices. In this connection, it seems natural to use highly porous media filled with electrolyte solutions. It is just this approach that was employed in the design of the first alkali fuel cells for power supply in spacecrafts. The role of membranes was played by asbestos soaked in an alkali solution. Similar materials are often used in the Li-ion batteries where the separator is filled with a solution of lithium salts containing bulky anions. Ideally, the separator can not only reinforce the construction, but also preclude the growth of lithium dendrites through the electrolyte, which leads to the battery short circuit.[76]

Recently, there has been intensive research into fabrication of thin films in order to reduce the ohmic losses in power cells[77] and into electrolytes with high ionic conductivity at reduced temperatures (600 – 800 °C) in order to make solid oxide fuel cells more efficient and commercially attractive.[78, 79] For instance, a promising approach involves fabrication of composite materials with one component in the molten state at the operating temperatures. Examples are provided by composites consisting of eutectic carbonate melt[80, 81] as well as molten bismuth oxides[82, 83] or vanadium oxides.[84]

VI. Amorphous inorganic and polymeric materials

Various amorphous systems in glassy or rubbery state represent yet another class of materials with enhanced ion mobility. Irregular mutual arrangement of coordination polyhedra or polymer chains in these systems lead to violation of long-range order and to changes in the ion transport conditions, namely, distances between possible ion positions and the face size of the coordination polyhedra that should be overcome by the ion.[85] Strengthening of certain bonds and weakening of some other bonds can significantly reduce the energy of defect formation and increase the concentration of defects in the materials. Also, the energy of ion transport can decrease and increase in activation segments. The overall activation energy for ion transport in the materials with 1D conduction channels should decrease. However, most often one deals with a system of intercrossing conduction channels, so an ion can choose an optimum direction to overcome the lowest energy barriers. Taking into account a decrease in the enthalpy of defect formation, this facilitates ion transport in glassy systems, and the conductivity of glasses is usually much higher than that of crystals. In this connection, there is considerable literature on glassy solid electrolytes.[86 – 93]

This class of materials also includes polymeric ion-conducting electrolytes. They can be divided into two large subclasses. One of them comprises ion-exchange membranes containing functional groups that dissociate to cations or anions. The other includes a variety of polymers containing dissolved ionic salts or acids. To meet the necessary condition for their solubility, the polymer should contain a high amount of polar groups capable of forming complexes with cations or anions. The higher the solubility of the latter the higher the concentration of charge carriers and the conductivity in such systems. On the other hand, an increase in the salt concentration usually leads to ordering and reduced fragmental mobility of the polymer owing to an increase in the contribution of ionic interactions (they are stronger than van der Waals interactions).[5] On the contrary, this is accompanied by a decrease in the conductivity.[94] The former effect dominates in the initial steps of doping,

whereas the latter manifests itself as the concentration of ionic salt increases. The maximum conductivity is usually attained at low dopant concentrations. Good results can be obtained using copolymers with violated periodicity, where the fragmental mobility of polymers is not suppressed.[95,96]

A promising avenue of research is to use composite systems consisting of a polymer, a dissolved ionic component and a highly porous or highly disperse filler. Often, the polymer is incorporated into the porous matrix. Other systems contain inserted fragments (most often, silica gel). Here, steric hindrances complicate crystallization and can cause an increase in the ion mobility. Examples are provided by materials containing a highly porous silica-based matrix (formed by sol–gel synthesis) with incorporated polymers and functional components.[46,97–101]

The materials mentioned above are mainly designed for chemical power cell applications, first of all, Li-ion batteries that are mainly based on systems with organic solvent and lithium salts with bulky anions.[102–105] Recently, considerable attention has been paid to polymeric electrolytes.[46,106–109]

Noteworthy is high interest in polybenzimidazoles (PBI) widely used as solid electrolytes for fuel cell applications. Undoped PBI are characterized by low conductivity; however, they can contain large amounts of phosphoric acid owing to the presence of nitrogen atoms. Acid-doped PBI membranes seem to be a very good alternative to Nafion membranes (see below) for fuel cell applications[110,111] because they are relatively cheap and exhibit high thermal stability;[112] in addition, these membranes demonstrate high proton conductivity (0.13 S cm^{-1} at 160 °C) up to 160–200 °C.[113–118]

The next important class of conducting polymers includes electrolytes based on ion-exchange membranes. They are built of high-molecular-mass polymers with functional ion-exchange groups in the side chains. Cation-exchange membranes contain, most often, fixed SO_3^- and PO_3^- ions, while anion-exchange membranes contain NR_3^+ or NR_2H^+ ions produced upon dissociation of functional groups (SO_3H, NR_3OH, *etc.*). Dissociation is accompanied by simultaneous formation of mobile ions (counterions — H^+, OH^-, *etc.*) whose charge is opposite in sign to the charge of the fixed ion. These membranes exhibit rather high ionic conductivity due to the high concentration and mobility of counterions;[23] the counterions can be readily exchanged by the likely charged ions and, thus, change the type of the major electricity carrier. To ensure good mechanical properties of certain polymers, they are used to fabricate heterogeneous composite, membranes consisting of ion-exchange resins and fillers.[23]

High proton conductivity of ion-exchange membranes is due to self-organization processes resulting in the formation of the membrane matrix from hydrophobic polymer chains and clustering of hydrophilic functional groups that uptake a large amount of water (Fig. 2). As a result, a system of pores filled with an aqueous solution containing mobile ions is formed. The most widely known perfluorinated membranes Nafion have pore diameter of 4–5 nm at 100% humidity.[119] Pores form an interconnected system of channels ~1–2 nm in diameter[120,121] and thus ensure high conductivity. An alternative model for a comb-like pore structure in a membrane was proposed by Ozerin *et al.*[122]

Membrane walls are covered with fixed ions (SO_3^-, PO_3^-, NR_3^+). This leads to localization of most counterions in the

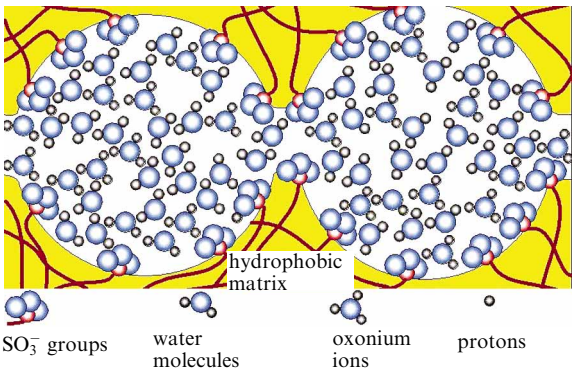


Figure 2. Pore structure in polymeric cation-exchange membrane (hydrogen form).[23]

Debye layer ~1 nm thick near the membrane walls.[123] The central regions of pores are filled with almost electrically neutral solution. When a membrane contacts an electrolyte solution, both cations and anions move to this region and enable the transport of not only counterions, but also co-ions (the co-ions and fixed ions are likely charged) across the membrane. However, the conductivity with respect to counterions is usually much higher (by more than an order of magnitude). The fraction of the total charge transferred by a particular type of ions in an electrolyte is called the transport number.[13] It characterizes the selectivity of transport processes in the membrane.

According to NMR data, the diffusion coefficient of water in different ionic forms of the Nafion membranes decreases in the following order of singly charged cations:[124]

$$H^+ > Cs^+ > Rb^+ > Na^+ > Li^+$$

An increase in the diffusion coefficient with the cationic radius in the lithium–caesium series is due to the low binding energy between water and bulky cations. Only protons deviate from this dependence because they become involved in the translational diffusion detected by ^{1}H NMR spectroscopy as both charged species and constituents of water molecules.

Contrary to this, the ionic conductivity of different salt forms of membranes decreases with increasing cationic radius. As the cation size decreases from caesium to lithium, steric hindrances to ion transport also decrease.[5] The conductivity of the proton form appears to be even higher because it proceeds by the Grotthuss mechanism through cooperative effects. In addition, protons introduced into the system violate tetrahedral coordination of water molecules and enhance their rotational mobility necessary for the proton conductivity to occur.[20,125]

Having considered general approaches to the formation of various ion-conducting solid electrolytes and methods for improvement of ionic conductivity, we will analyze lithium-, oxygen- and proton-conducting systems. They are significantly different from one another in the ion transport mechanisms and methods for fabrication of highly conducting systems.

VII. Lithium-conducting materials

By comparing the ionic conductivities of two solid electrolytes based on structurally similar inorganic materials (NASICON, β-aluminates, *etc.*) one can show with ease that in most cases the Na-ion conductivity in them will be higher than the Li-ion conductivity. Besides, sodium is much more abundant than lithium and cheap. Nevertheless, high interest in lithium-conducting electrolytes is due to the demand for Li-ion batteries.[126] Considering compounds with rather high Li-ion conductivity at moderate temperatures, mention should be made of such a specific material, as lithium nitride (Fig. 3, line *4*). It consists of the Li_2N and lithium layers. In the former, lithium forms a hexagonal graphite-like network with nitrogen ions located in the voids. Nitrogen ions in the neighbouring layers are stacked and connected to a lithium ion which occupies a central site between the Li_2N layers.[129] The ionic conductivity of the material reaches a value of 5×10^{-4} S cm^{-1} at 30 °C,[130] the in-plane conductivity being more than two orders of magnitude higher than in the perpendicular direction.[131] According to structural data, transport of lithium ions occurs in the Li_2N layers in spite of their much closer packing.[132] The conductivity can be improved to the greatest extent by doping with hydrogen.[133] The effect is quite understandable because a proton is located within the electron shell of nitrogen and creates 'lithium vacancies' without imposing limitations on the motion of lithium ions, although the lithium affinity of these vacancies decreases. Besides, one can assume a decrease in the charge of the nitrogen ion and in the energy of electrostatic interactions in the lattice. Among materials with high lithium mobility, mention may also be made of β-lithium aluminate characterized by a Li-ion conductivity of 4×10^{-3} S cm^{-1} at 300 °C.[134]

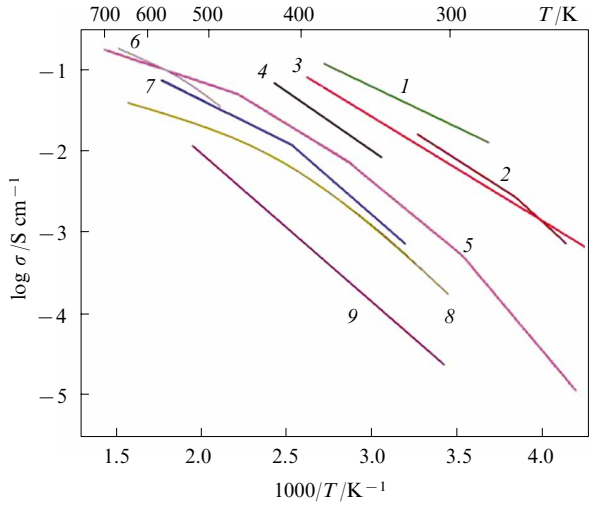


Figure 3. Ionic conductivity in lithium electrolytes plotted *vs.* temperature using data taken from Refs 124, 127 and 128.
Electrolyte: Nafion (lithium form) (*1*), $7Li_2S \cdot 3P_2S_5$ (*2*), $Li_{10}GeP_2S_{12}$ (*3*), $Li_{3-x}H_xN$ (*4*), $Li_{0.34}La_{0.51}TiO_{4-x}$ (*5*), $Li_{14}Zn(GeO_4)_4$ (*6*), $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (*7*), $Li_7La_3Zr_2O_{12}$ (*8*) and $Li_6BaLa_2Ta_2O_{12}$ (*9*).

However, the materials listed above are not in demand because of low stability (Li_2N) and inadmissible mechanical properties of pressed samples (β-lithium aluminate). Lithium-conducting solid electrolytes with tetrahedral anions, *i.e.*, lithium phosphates, silicates and germanates attract much more attention. Among them, germanate-based materials of the general composition $Li_{2+2x}Zn_{1-x}GeO_4$ are well known. They are abbreviated as LISICON (Lithium Super Ionic CONductor) and have a relatively low conductivity of 10^{-6} S cm^{-1} at 25 °C.[135, 136] However, their analogues with oxygen atoms replaced by sulfur have much higher conductivities of the order of $10^{-4} - 10^{-3}$ S cm^{-1} at 25 °C (see Fig. 3).[126, 137, 138] In particular, solid solutions $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ have a conductivity of 2.2×10^{-3} S cm^{-1},[138] whereas that of the tin-containing materials approaches a value of 4×10^{-3} S cm^{-1} (see Ref. 139). Such a high conductivity is due to a high polarizability of sulfur ions. Even higher conductivity was found in sulfur-containing glassy ceramics, namely, 10^{-2} S cm^{-1} in $Li_{10}GeP_2S_{12}$ (see Ref. 140) and 1.7×10^{-2} S cm^{-1} in $Li_2S - P_2S_5$ at room temperature.[141]

Yet another type of solid electrolytes includes materials with the NASICON structure. This is an abbreviation for complex sodium – zirconium silicophosphates with very high ionic conductivity, namely, to 10^{-1} S cm^{-1} at 300 °C.[26] Despite the fact that the Li-ion conductivity of the NASICON materials was at least three orders of magnitude lower than the Na-ion conductivity,[142] the possibility of utilizing them as solid electrolyte or cathode materials for Li-ion batteries attracts considerable attention of researchers.[11, 127, 143 – 146]

The 3D framework in the structure of the NASICON materials of the general formula $M^I_xA_2(BO_4)_3$ is formed by the alternating AO_6 octahedra and BO_4 tetrahedra. Three-dimensional conduction channels formed between them are partially or completely filled with the M^+ cations.[25] The A-sites can be occupied by ions of tri-, tetra- and pentavalent elements,[147] while the B-sites are occupied by phosphorus, silicon, vanadium and niobium ions.[148] The maximum conductivity was found in the high-temperature (rhombohedral or hexagonal) forms of these materials; therefore, their polymorphous transformations are studied thoroughly. In the low-temperature triclinic form, lithium ions are distributed between two positions with occupancies of 71% and 29%.[148] The highly conducting phase $LiZr_2(PO_4)_3$ is formed after an order – disorder transition near 310 K. This is to some extent unconventional transition because it occurs in a certain temperature range rather than at a particular temperature and exhibits a hysteresis (different fractions of the phases co-existing at the same temperature during the heating – cooling cycles).[147] In the high-temperature rhombohedral form, 30% of lithium ions were not located even by neutron diffraction analysis.[28]

Higher conductivity is, as a rule, observed in the materials with the A-sites occupied by the quadruply charged cations. It is noteworthy that structural features and high synthesis temperature of the NASICON materials allow heterovalent substitution in the A- and B-sites to occur. Heterovalent substitution is accompanied by the appearance of cationic vacancies in the alkali-metal sites and insertion of extra lithium ions into interstices; as a consequence, the transition temperature gradually decreases and the ionic conductivity increases.[20, 57, 147, 149 – 151] The

room temperature conductivity of a $Li_{1.2}Zr_{1.9}Ca_{0.1}(PO_4)_3$ sample was as high as 5×10^{-5} S cm^{-1}.[152]

The defect concentration can be varied using materials with the A-sites occupied by the tri- and pentavalent ions, *e.g.*, $Li_{3-2x}Nb_xIn_{2-x}(PO_4)_3$ and $LiTaAl(PO_4)_3$;[153–155] partial replacement of phosphorus by silicon is also used.[156]

Recently, considerable attention has been paid to the double lithium–titanium phosphate with the NASICON structure, including samples doped with tri- and pentavalent elements.[59,157–164] In particular, the room-temperature conductivities of the best samples of the $Li_{1+x}Cr_xTi_{2-x}(PO_4)_3$ solid solutions approached a value of 10^{-3} S cm^{-1}.[165] Phosphates containing cerium[166] and (especially) germanium also attract the attention of researchers. A wide range of materials based on the lithium–germanium phosphate and doped with trivalent cations (Al, Cr, Ga, Fe, Sc, In) was studied.[167] A number of more recent studies were devoted to Al-doped glassy ceramic materials. The maximum conductivity values, namely, $(1.0–5.8)\times10^{-4}$ S cm^{-1} at room temperature, were determined for the $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ samples with $x = 0.4–0.7$.[168–173] However, the authors of another study[174] reported a room-temperature conductivity of 5.08×10^{-3} S cm^{-1}. The activation energies for mobility of lithium ions and lithium ion conduction determined from NMR data (30 and 30.6 kJ mol^{-1}, respectively) are almost equal.[172] This suggests that the enthalpy of defect formation does not contribute largely to the activation energy of conductivity, the conductivity being almost completely governed by the impurity defects.

Double phosphates with the NASICON structure were used as both electrode materials and electrolytes for Li-ion batteries.[144,173–176] Information on phosphates with the NASICON structure is available in reviews.[25,57]

Materials with high Li-ion conductivity also include lithium–lanthanum titanates $Li_{3x}La_{(2/3)-x}TiO_3$ with the perovskite structure.[177–179] Their room-temperature conductivity reaches a value of 10^{-3} S cm^{-1} (see Fig. 3). Particular attention is paid to improvement of grain-boundary conductivity[180,181] by doping with, *e.g.*, silicon,[182] zirconium,[183,184] niobium[185] and silver.[186]

Yet another important class of lithium electrolytes of the general formula $Li_5La_3M_2O_{12}$ (M = Ta, Nb) has the structure of a garnet.[187–189] The room-temperature conductivity can be as high as 10^{-6} S cm^{-1} for $Li_5La_3Nb_2O_{12}$,[190] being even higher for $Li_6BaLa_2Ta_2O_{12}$ (1.3×10^{-5} S cm^{-1}).[191] An efficient method for improving the conductivity is to replace a fraction of niobium or tantalum atoms by indium or yttrium ones.[187,192] A zirconium-based material $Li_7La_3Zr_2O_{12}$ is structurally similar and has a conductivity to 2×10^{-4} S cm^{-1} at room temperature.[146,193–196] To make the highly conducting cubic polymorph more stable, it was doped with aluminium,[197,198] gallium and tantalum.[199] High electrochemical stability of these materials allowed them to be used as electrolytes for Li-ion batteries.[200–202]

Glassy materials often exhibit a higher conductivity that crystalline ones, thus being quite attractive.[5,203] The highest conductivity was reported for sulfides.[204,205] To improve the conductivity of these materials, anionic substitution is performed.[206–208] An interesting technique is to use composites which simultaneously contain a glassy phase and a crystalline phase. If the latter is formed by nanoparticles, the conductivity of the glass remains unchanged. These materials with high grain-boundary conductivity seem to offer considerable advantages.[138,209] In this respect, mention may be made of an increasing attention to the systems whose compositions are similar to those of the NASICON materials.[210–213]

The greatest research efforts are aimed at fabricating materials for Li-ion batteries. Considering electrolytes, they more often represent liquid systems based on organic solvents and lithium salts with a bulky anion characterized by a low charge density ($LiPF_6$, $LiClO_4$).[11,102,103] However, this poses problems associated with an increase in the pressure on heating (observed in the case of fast charge-discharge of batteries), possible case breakdown, risk of fire and environmental problems in the case of disposal. In this connection, considerable attention has been paid recently to research into polymeric electrolytes.[11,106–109,214,215] First of all, these are systems similar to the solutions described above. They are based on polymers bearing various groups containing electronegative atoms capable of coordinating cations of the salt and maintaining the solubility of the salt and rather fast charge transfer. Recently, these has been considerable interest in the lithium form of ion-exchange polymers. Most often, these systems are in the hydrated state,[23] which excludes their use in Li-ion batteries. However, utilizing aprotic solvents instead of water offers prospects for these materials.[216,217] On the other hand, high stability of solid electrolytes allows them to be used more widely in the design of new-generation Li-ion batteries[127,144,145,200] and as electrode materials that simultaneously exhibit high Li-ion conductivity and electronic conductivity (for details, see a review[12]).

VIII. Oxygen-conducting materials

The oxygen ion is not the best candidate for fast charge transfer applications. It has a slightly deformable electron shell and a rather large radius (1.4 Å). This hampers migration of O^{2-} ions from one crystallographic position to another because of the need to go through a number of bottlenecks formed by the electron shells of other ions. Besides, a charge of 2− and a high covalency determine a rather high strength of the bonds formed by the oxygen ion in the crystal lattice. As a result, one deals with a high activation energy of ionic conductivity, so that a relatively high oxygen conductivity in most solid electrolytes is attained only at 700–1000 °C.[44,218]

The most widely known oxygen-conducting solid electrolytes are based on zirconium oxide.[219] Their conductivity is determined by the relatively high concentration of oxygen vacancies in the high-temperature cubic phase of zirconium oxide (fluorite structure). However, this polymorph is stable only at temperatures above 2000 °C. It is stabilized by doping with tri- and divalent cations (Sc^{3+}, Y^{3+}, Ca^{2+}, *etc.*).[220–222] Smaller charges of these cations are compensated by producing vacancies at the oxygen site following the quasi-chemical reaction

$$Sc_2O_3/ZrO_2 \longrightarrow 2\,Sc'_{Zr} + 3\,O_O + V_O^{**} \qquad (10)$$

It is the presence of oxygen vacancies and oxygen-ion disorder that are responsible for stabilization of the high-temperature phase. These materials are most often used as oxygen-conducting solid electrolytes at temperatures above 700 °C (see Refs 6, 7, 223–227 and Fig. 4, line *4*). Materials

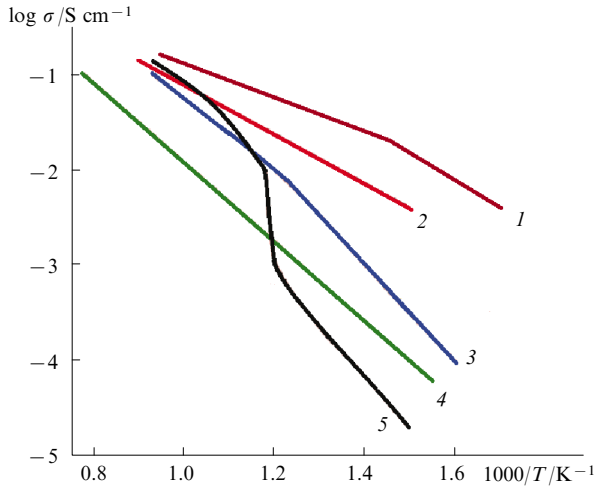


Figure 4. Total conductivity in selected solid oxygen-conducting electrolytes plotted *vs.* temperature using data taken from Refs 7, 228 and 229.
Electrolyte: $Bi_2V_{1.9}Cu_{0.1}O_{5.35}$ (*1*), $Ge_{0.8}Gd_{0.2}O_{1.9}$ (*2*), $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (*3*), $Zr_{0.86}Y_{0.14}O_{1.93}$ (*4*) and $La_2Mo_2O_9$ (*5*).

with partial replacement of oxygen atoms by nitrogens were also reported.[230] The possibility of co-doping with two metals to improve the conductivity and stability of the high-temperature modification of zirconium oxide has also been studied intensively.[231–237]

As mentioned above, the defectness is to a great extent determined by the state of the surface of the materials; therefore, the stability of the high-temperature forms depends on the oxide particle size (on the synthesis temperature of the oxides).[238]

The MO_2 oxides containing larger cations (cerium, thorium and uranium) form the cubic structure much more easily. They are also doped to increase the defect concentration and to improve the oxygen conductivity, but only the materials based on cerium oxide are used in practice.[239–242] For instance, the gadolinium-doped material exhibits high conductivity (see Fig. 4, line *2*), but a large proportion of cerium is reduced at low partial pressure of oxygen and temperatures above 600 °C and the contribution of electronic conductivity becomes very large.[243,244] At low concentrations of impurity cations, the conductivity of such systems increases with increasing dopant concentration to 10%–14% and then decreases again owing to association of defects.[245–247] It should be noted that solid solutions of cerium oxide and zirconium oxide also exhibit high conductivity.[56,248]

Oxygen-conducting electrolytes based on δ-Bi_2O_3 also belong to the fluorite structure type. At low temperatures, they are stabilized by doping with niobium, tungsten, rhenium and some rare-earth element ions. In some cases, high conductivity is attained at relatively low temperatures.[249]

A material called BIMEVOX (Bi–M–V–Oxygen) consisting of complex bismuth oxides based on the $Bi_4V_2O_{11}$ structure (see. Fig. 4, line *1*) is more widely known. It can undergo a chain of polymorphous transformations, but only the high-temperature polymorph is characterized by high ionic conductivity. Doping with some metals allows one to stabilize this polymorph and to attain a rather high oxygen-ion conductivity.[250–255] Note that this group of materials often demonstrates a sufficiently high electronic conductivity.

Oxygen-conducting materials belonging to the perovskite structure type are also available. Among a large family of solid solutions of the general formula $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (here, divalent strontium and magnesium replace trivalent cations, thus producing vacancies in the oxygen sublattice), of particular importance is the solid solution $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ whose conductivity is higher than that of yttrium-stabilized zirconia.[228,256,257] Compound $Gd_{0.85}Ca_{0.15}AlO_{2.925}$ has a somewhat lower conductivity.[258] Good results were reported for the gallates $La_{1-x}Ba_{1+x}GaO_{4-x/2}$;[259] the maximum conductivity corresponding to an oxygen ion transport number of 0.95 was obtained at $x = 0.55–0.56$.[260–262]

Lanthanum molybdate demonstrates quite attractive properties. High ionic conductivity of the material take place after a first-order phase transition at 580 °C.[263,264] According to neutron diffraction data for the high-temperature phase, oxygen ions partially occupy two lattice sites, being strongly disordered over the structure of the material.[265,266] Interestingly, partial replacement of lanthanum by alkali metals or alkaline-earth elements stabilizes the high-temperature phase, but has almost no effect on the conductivity of these materials.[267–270]

The ionic conductivity and stability of materials based on hydroxyapatite $Ln_{9.33}(SiO_4)_6O_2$ can be improved in a variety of ways, *e.g.*, by increasing the lanthanum content,[271] using heterovalent substitution,[272,273] homo- and heterovalent substitution[274] and partial replacement of oxygen atoms by nitrogen ones.[275]

Considerable research efforts are aimed to develop methods for decreasing the operating temperature of the oxygen-conducting solid electrolytes in order to significantly improve the efficiency of solid oxide fuel cells.[6,78] For instance, various methods for fabrication of thin films in order to reduce the ohmic losses by decreasing the thickness of the electrolyte layer[77,276] and nanomaterials with a large contribution of grain-boundary ion transport[277] were studied.

A recently proposed approach involves fabrication of composite electrolytes containing a component capable of readily going to a molten state with high oxygen-ion conductivity. Often, one deals with a molten eutectic rather than a single component. For instance, composite electrolytes based on doped cerium dioxide and a binary molten carbonate eutectic[81,278–282] exhibit high ionic conductivity at lower temperatures. They were used to design a direct carbon fuel cell.[283] Detailed information on this group of electrolytes is available in the review.[79]

Yet another important class of materials includes those with mixed ionic-electronic conductivity. They allow for the oxygen extraction from air[284] or for the partial oxidation of hydrocarbons by atmospheric oxygen to produce synthesis gas or for catalytic oxidative coupling of methane.[18,285] To attain high mixed conductivity, the oxide structures should contain oxygen defects and neighbouring transition metal ions in different oxidation states.[65] The highest oxygen-ion conductivity was reported for oxides with the $ABO_{3-\delta}$ (B = Co, Fe) perovskite structure, *e.g.*, $La_{1-x}Sr_xCoO_{3-\delta}$ (Ref. 286) and $La_{1-2\delta}Sr_{2\delta}FeO_{3-\delta}$.[17] According to Möss-

bauer spectroscopy data, the oxides $SrFe_{1-x}M_xO_{3-\delta}$ (M = Al, Ga) represent vacancy-ordered phases with the brownmillerite structure.[287] High oxygen conductivity can be achieved by fabricating nanomaterials with large contribution of grain-boundary transport of oxygen ions.[288] Oxygen diffusion in these materials and the kinetics of oxygen exchange on the surface of oxygen-conducting oxides have been studied in detail.[289–293] Additional information on the systems with mixed oxygen-electronic conductivity can be found in the review.[17]

IX. Proton-conducting materials

IX.1. Specific features of proton transport in solids

Proton transfer is of great importance for various chemical, physical and biological processes including diffusion-controlled reactions, ion exchange[294,295] and life support.[296] Proton conductors are widely used in production of electrolyzers, fuel cells, sensors and other devices.[9,297–299]

The mechanisms of proton conductivity are the most complicated ones. Proton transfer proceeds by specific mechanisms because, unlike all other ions, protons are elementary particles with an extremely small radius. In contrast to electrons, which can move with ease in many materials owing to repulsion from the electron shells of atoms and ions, protons are trapped by these shells with high efficiency and the transport process slows down.[300] In this sense, proton transport is also essentially complicated when compared to transport of all other ions having individual electron shells. Hypothetical transport of protons, as small-radius particles, by the conventional hopping mechanism should be characterized by enormously high activation energy.[5]

The ionic radius of oxygen is 1.4 Å and the O–H distance in the case of a polar covalent bond is 1.0 Å; therefore, in all the proton conductor structures considered below the H^+ ions mainly reside within the electron shells of the charged ions. In this connection, it should be noted that protons in the proton-conducting materials usually form a hydrogen bond with one or two electronegative atoms. Protons execute fast hops between two energy minima along the direction of the hydrogen bond

$$O-H\cdots O \rightleftharpoons O\cdots H-O \qquad (10)$$

In most structures, the minima have different energies and oscillations may occur by the tunnelling mechanism provided short hydrogen bonds.[20]

Proton hops along the line of the hydrogen bond can only cause polarization of the system, whereas the onset of proton conductivity requires a chain of proton hops and rotation of the proton-containing groups.[301,302] There are three classes of proton-conducting materials with significantly different proton transfer mechanisms. With respect to the ranges of operating temperatures, these are low-temperature (to 100–120 °C), high-temperature (500–800 °C) and moderate-temperature materials. The ranges of operating temperatures for the third class of materials reported by different authors are significantly different, but their boundaries can be estimated with ease using the corresponding data for the other two classes of materials (Fig. 5).

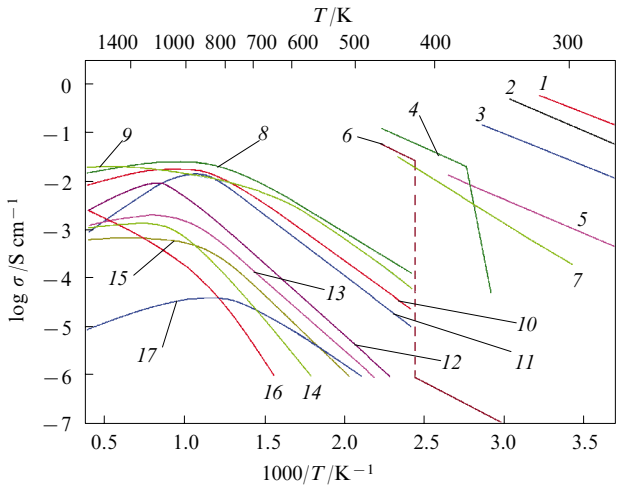


Figure 5. Proton conductivity in selected solid proton-conducting electrolytes plotted *vs.* temperature using data taken from Refs 21, 298 and 303.
Electrolyte: 1 M HCl (*1*), $H_3PW_{12}O_{40}\cdot 29\,H_2O$ (*2*), Nafion (*3*), KOH/NaOH (*4*), $H_5O_2Ta(PO_4)_2$ (*5*), $CsHSO_4$ (*6*), $KOH\cdot H_2O$ (*7*), $BaZrO_3$ (*8*), $BaTbO_3$ (*9*), $Ba_2SnYO_{4.5}$ (*10*), $BaCeO_3$ (*11*), $SrCeO_3$ (*12*), Gd_2O_3 (*13*), $LaScO_3$ (*14*), $La_2Zr_2O_7$ (*15*), $LaPO_4$ (*16*) and $SrZrO_3$ (*17*).
For the high-temperature electrolytes, the dopant concentration (dopant is not shown as in the original study[21]) is 10% and the water vapour pressure is 30 GPa.

IX.2. Hydrated proton-conducting solid electrolytes

Among low-temperature proton conductors, acid hydrates, acid salt hydrates and base hydrates are preferred, the last-mentioned compounds being used much more rarely. In this case, an important role is played by rotation of water molecules or $H(H_2O)_n^+$ ions involved in the formation of hydrogen bonds.[20,304,305] This may give rise to yet another, specific type of defectiveness called orientational disorder. According to Bjerrum, there are two types of orientational defects, *viz.*, short O–O contacts with no protons (L-defects) and with two protons (D-defects). An analysis of the structure of a large number of inorganic acid hydrates and acid salt hydrates[306] revealed high concentrations of L-defects.

It was assumed for long that rotational mobility of proton-containing groups requires that all hydrogen bonds they form be broken. However, actually, rotation of these groups is accompanied by a gradual decrease in the energy of the hydrogen bond. For instance, rotation of the O–H bond by 45° and ~90° about the line connecting two oxygen atoms causes the energy of this bond to be halved in the former and to decrease to almost zero in the latter case.[300]

It seems likely that the rotational mobility of water molecules should decrease upon the introduction of strong acids due to the formation of strong hydrogen bonds in proton hydrates. Indeed, an oxonium ion can form three strong hydrogen bonds with energies lying between 80 and 150 kJ mol^{-1} (see Ref. 307; *cf.* 15–25 kJ mol^{-1} for the energies of the hydrogen bonds in ice and in liquid water with tetrahedral coordination of water molecules in both cases). However, it is the ice and liquid water structures that require simultaneous cleavage of at least three out of the

four hydrogen bonds for rotation of a water molecule to occur.[308]

The rotational mobility of $H(H_2O)_n^+$ ions in solid acid hydrates and acid salt hydrates is usually higher than that of water molecules in conventional solid hydrates[309] due to, in particular, a low proton-acceptor ability of the anions (X^-) as constituents of the materials. Indeed, hydration of protons in solids is possible only if the proton-acceptor ability of the anions is lower than that of water molecules, and the $H(H_2O)_n^+ - X^-$ hydrogen bonds thus appear to be sufficiently weak. At the same time, the systems with a hydrated proton unavoidably contain oxygen atoms with incomplete octahedral environment, which participate in the formation of only three hydrogen bonds. A positive charge of H_3O^+ ions prevents the oxygen atoms from being acceptors of the additional hydrogen bonds. In this connection, the environment of the oxonium ion has the geometry of a contracted trigonal pyramid with the H_3O^+ ion in its apex. It is energetically favourable to place an additional electronegative atom in the unoccupied fourth vertex (Fig. 6 *a*) with the formation of a Bjerrum L-defect, as was confirmed by structural data for various acid hydrates and acid salt hydrates.[310] Therefore, rotation of the OH_2 unit of the H_3O^+ ion about the short hydrogen bond may lead to formation of two new hydrogen bonds which, along with the other two bonds that are cleaved upon rotation, gradually weaken and then become stronger again (Fig. 6 *b*). Their rotational mobility considerably increases while the energy of the activated state[300] containing the Y-shaped hydrogen bond (see Fig. 6 *b*) decreases.

A important role in unfreezing the rotational mobility is played by cooperative effects.[311] If a proton-containing group becomes rotationally mobile, all hydrogen bonds between this group and its nearest neighbours break, thus facilitating rotation of the neighbours. In particular, a number of hydrogen bonds formed by water molecule and proton hydrates in $H_3PW_{12}O_{40} \cdot 29\,H_2O$, where oxygen atoms of the anion with low proton-acceptor ability act as donors, appear to be very weak. High rotational mobility of these fragments acting as acceptors of other H-bonds extends to the entire proton hydrate sublattice; therefore, its transition to the highly mobile state occurs at very low temperatures.[309]

Proton transport also requires proton hopping along the direction of the A – H···B hydrogen bond (see. Fig. 6 *c*). The activation energy for proton hopping is determined by the distance between the donor (A) and acceptor (B) and by the difference between their proton-acceptor abilities. Proton hops usually occur concertedly with the vibrational mobility of the lattice, when the distance between the electronegative atoms becomes the shortest possible, whereas the H-bond breaks necessary to unfreeze rotation of the proton-containing groups mainly occur when the electronegative atoms are separated by the longest distance.[312] These cooperative effects are particularly pronounced in the systems containing a plenty of water molecules, some of them being connected to the excess protons or HO^- ions. The mechanism of proton transfer in such systems is called the Grotthuss mechanism.[20]

The activation energies of proton conductivity obtained for different types of the environment of the proton-containing groups, different hydrogen bond lengths, various proton-acceptor ability differences and for additional potential acceptors of the hydrogen bond in the environment can be found in the literature.[300, 302] The highest conductivity can be achieved when the proton-acceptor ability of the anion is close to or much lower than that of water molecules. The first type of materials includes a few compounds, *e.g.*, acid sulfates of trivalent metals[313] and acid tantalum phosphate[314] (see Fig. 5, line *5*); here, the proton-acceptor ability of the anion is reduced owing to coordination to the multiply charged cations.[300]

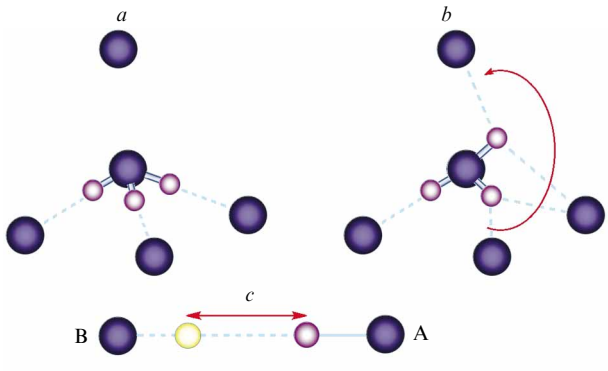


Figure 6. Typical environment of oxonium ions in the structure of acid hydrates and acid salt hydrates (*a*), formation of Y-shaped hydrogen bonds upon rotation of oxonium ion (*b*) and proton hops between two electronegative atoms with two energy minima (*c*). Open circles denote hydrogen atoms while solid circles denote electronegative atoms (most often, oxygen).

The second type of materials with low proton-acceptor ability of the anion is much more representative. The highest room-temperature proton conductivity was attained for high-water heteropolyacid hydrates, $H_3PW_{12}O_{40} \cdot 29\,H_2O$ with a conductivity of ~ 0.18 S cm^{-1} (see Ref. 315 and Fig. 5, line *2*) being the best known. Heteropolyanions with highly symmetrical Keggin structure are located in them in a highly mobile water environment containing extra protons produced upon dissociation of the acid. Other acids with the phosphorus atom replaced by atoms of other penta-, tetra- or trivalent elements and a molybdenum atom instead of the tungsten one are available. Numerous attempts to synthesize novel materials with tungsten partially replaced by other ions were reported. These are materials containing, *e.g.*, vanadium,[316 – 322] chromium, iron and cobalt.[322 – 325] The central phosphorus atom is often replaced by silicon or germanium and more rarely by other cations (aluminium, gallium, titanium, *etc.*).[320, 326 – 328] The structure of the heteropolyanion can differ from the Keggin structure.[327, 329, 330] High conductivity of these systems is governed by their acidity and by the large number of water molecules. They have low mechanical strength and low chemical and thermal stability. Heteropolyacid hydrates lose a large amount of water even if simply exposed to air; this causes an abrupt decrease in the proton conductivity.[331] Therefore, they are used rarely, although being promising solid electrolytes for, *e.g.*, fuel cell applications and electrochemical capacitors.[332 – 335]

Heteropolyacids can be stabilized through formation of insoluble salts. Most heteropolyacid salts are well soluble due to the low lattice energy determined by the large anionic radius. Unexpectedly, the salts containing a bulky alkali metal cation (K^+, Rb^+, Cs^+) or Tl^+ appeared to be

insoluble. Singly charged cations in these salts are localized in voids of the close packing of heteropolyanions. In nanodisperse materials, a large proportion of these cations is on the surface and can be readily replaced by protons, as was shown in a Tl NMR study of $Tl_3PW_{12}O_{40}$.[336] Depending on the particle size, protons replace up to 40% of thallium ions, the remaining cations being responsible for the core structure.[337] Water sorbed on the surface of such particles ensures high proton conductivity of the material (up to 10^{-2} S cm^{-1}).[337, 338]

Yet another well-known approach is to fabricate composites with, *e.g.*, silica,[339, 340] zeolites,[341] mesoporous silica [342, 343] or activated carbon.[344] The proton conductivity of these materials exceeds a value of 10^{-2} S cm^{-1} at room temperature.[340, 341] Fabrication of polymeric proton-conducting membranes based on an inert high-molecular-mass matrix containing heteropolyacids was reported.[345 – 350] More complex systems containing silica and other additives as the third component were also synthesized; their conductivity can be higher than that of the initial heteropolyacids.[351 – 353]

Detailed description of other good low-temperature proton conductors seems to be senseless because most of them were obtained long ago;[354] mention may be made only of the fact that their properties can often be improved by heterogeneous doping.[71, 355] In this case, sorption at interfaces leads to formation of the Debye layer with high defect concentration responsible for an abrupt (by up to a few orders of magnitude) increase in the ionic conductivity of materials.

At the same time, mention should be made of a wide use of ion-exchange membranes in, *e.g.*, wastewater treatment, separation and power engineering.[117, 356 – 360] Among them, the Nafion membranes seem to be the most widely known. They contain perfluorinated polymer chains and perfluorinated side chains terminated by highly acidic SO_3H groups. The properties of the Nafion membranes including the ionic conductivity are well described.[121, 360, 361]

The properties of proton-conducting membranes are mainly improved by modification,[359] first of all, by the synthesis of hybrid materials based on them. Pores of hybrid membranes contain nanoparticles of dopants (usually, inorganic compounds).[8, 24, 362 – 364] In contrast to the conducting composite materials described above, the increase in the proton conductivity of hybrid membranes cannot be explained by high defect concentration. All protons in the initial membranes are dissociated, and the oxonium ions themselves are defects in the aqueous solution containing a characteristic tetrahedral network of hydrogen bonds. The introduction of nanoparticles is accompanied by widening of pores and corresponding enlargement of channels connecting them. Since it is the channels that govern the membrane conductivity, the proton conductivity increases.[365] The best results can be obtained if dissociation of groups localized on the surface of dopant nanoparticles produces extra protons and thus increases the concentration of charge carriers.[123]

IX.3. Anhydrous proton-conducting materials

The design of proton-conducting materials capable of operating at elevated temperatures is topical. At low temperatures, irreversible sorption of CO by catalysts for fuel cells occurs. This excludes the use of relatively cheap hydrogen [8] produced by conversion of hydrocarbons or alcohols [17, 18] in low-temperature fuel cells. On the other hand, hydrated compounds, including heteropolyacid hydrates and membranes, are thermally unstable. They readily lose water and, therefore, high ionic conductivity when heated to 100 °C. In this connection, the search for materials suitable for operation at temperatures above 120 °C is in progress.

First of all, membranes based on PBI doped with phosphoric acid are thermally stable up to 140 – 180 °C [113, 114, 118, 366] and thus seem to be promising for fuel cell application at elevated temperatures.[367 – 370] They have a drawback, namely, a ready loss of phosphoric acid during the fuel cell operation. The negative effect can be reduced by doping with nanoparticles of multivalent element oxides.[116, 370] In addition, hybrid membranes often exhibit high conductivity.[371 – 373] A possible alternative is provided by oligosiloxanes doped with phosphoric acid.[374]

In the temperature range of 130 – 300 °C, some phases of solid electrolytes based on acid salts of alkali metals and ammonium $M_nH_m(XO_4)_p$ [375 – 377] demonstrate high proton conductivity up to 6×10^{-2} S cm^{-1}.[378] Intensive research into the properties of these materials began after the discovery of a phase transition of $CsHSO_4$ at 141 °C. This transition is accompanied by an increase in the proton conductivity by more than three orders of magnitude (see Ref. 379 and Fig. 5). Transition to the superionic state is accompanied by an increase in the crystal symmetry and by dynamic disorder of the system of hydrogen bonds.[380] The electron density maps constructed for the $MHSO_4$, $M_3H(SO_4)_2$ and $M_5H_3(SO_4)_4$ single crystals demonstrate high proton disordering.[381] For instance, $CsHSO_4$ undergoes two phase transitions, at 318 and at 414 K.[382 – 384] Proton transfer in this type of structures occurs in two stages, *viz.*, proton hopping along the direction of the hydrogen bond between two HSO_4^- groups and reorientation or librations of SO_4^{2-} tetrahedra.[385] The first stage is the limiting one in the superionic phases. In the low-temperature phase of $CsHSO_4$, chains of hydrogen bonds 2.572 Å long are formed between the SO_4^{2-} tetrahedra [386] where the proton is distributed over two equivalent positions. In the superionic phase, the SO_4^{2-} tetrahedra may have four equivalent crystallographic orientations, the hydrogen bonds being dynamically disordered. This type of disorder also exists in other sulfates and phosphates.

Attempts to carry out heterovalent substitution in these systems seem to be very attractive. Indeed, partial replacement of sulfur atoms by phosphorus atoms may result in close-size, structurally similar tetrahedral anions that have identical properties and bear charges differing by unity. This strategy leads to higher degree of disordering of the system of hydrogen bonds as well as to higher transition temperatures and low-temperature conductivity.[376] Besides, the formation of various individual mixed-anion compounds, *e.g.*, $Cs_2(HSO_4)(H_2PO_4)$,[387] $Cs_5(HSO_4)_3(H_2PO_4)_2$, $Cs_3(HSO_4)_2(H_2PO_4)$ [388] and $Cs_3(HSO_4)_{2.5}(H_2PO_4)_{0.5}$,[389] as well as series of solid solutions based on them is possible.

Heterogeneous doping with oxides of multivalent elements is yet another promising method for reducing the transition temperature.[372, 390] As the dopant concentration increases, the low-temperature conductivity of the composites increases and reaches maximum values at 30 vol.% – 50 vol.%. The transition temperature decreases and corresponding endothermic effects gradually disappear as a result of transition of the conducting phase to the amorphous state.[75] IR spectroscopy studies of these com-

posites showed that protons of the salt interact with OH groups on the oxide surface.[391–393] The conductivity of the composites increases due to the formation of highly conducting Debye layer at the interface. The formation of the region of spatial charge with high mobility of charge carriers was confirmed by NMR spectroscopy.[394] The concentration of defects and the conductivity in the composite abruptly increase with decreasing particle size.[395, 396] Pores in the oxide structure near the interface also participate in sorption processes. The maximum conductivity in the $CsHSO_4/SiO_2$ system was achieved at SiO_2 pore sizes between 3.0 and 10 nm.[397, 398]

The possibility of fabrication of moderate-temperature hydrogen/air fuel cells and methanol fuel cells with caesium hydrogen sulfate membranes was demonstrated.[399–401] However, these fuel cells undergo gradual degradation due to the reduction of sulfur and poisoning of the platinum catalyst with hydrogen sulfide.[399, 402] In this respect, phosphates appeared to be much more stable.[403] Therefore, fuel cells based on caesium hydrogen phosphates and on composites based on them have been studied.[404–406] An increase in the operating temperature of a fuel cell to 200 – 250 °C allows one to significantly improve its tolerance to CO, a side product of hydrogen production.[405] On the other hand, problems related to the mechanical properties and gas permeability of the thin membranes persist.

Usually, the moderate-temperature proton-conducting solid electrolytes decompose at 250 – 300 °C. On the other hand, high-temperature solid electrolytes operate at temperatures of at least 600 °C. Thus, the temperature range from 300 to 600 °C remains uncovered. Among a few proton-conducting materials that do not decompose in this temperature interval, there is zirconium hydrogen phosphate $HZr_2(PO_4)_3$ with the NASICON structure. The high thermal stability of this system is due to the fact that all oxygen ions are equivalent and form two strong bonds with phosphorus and zirconium.[25] As a consequence, O – H bonds are weak, protons being highly acidic and mobile.[407] Paradoxically, protons involved in the formation of weak bonds hold tightly in a structure because they can leave the structure only as part of water molecules along with the oxygen ions participating in the formation of very strong bonds. Therefore, $HZr_2(PO_4)_3$ decomposes only at temperatures above 550 °C; the proton conductivity of this phosphate reaches a value of 3×10^{-5} S cm^{-1}.[408] However, the material is of limited use because its conductivity is not too high and this metastable structure is difficult-to-synthesize.[409, 410] A related compound, hafnium phosphate, has a much lower conductivity.[411]

The ionic conductivity of some alkalis in the temperature range 320 – 430 K can be as high as 10^{-2} S cm^{-1}.[303, 412–414] Unfortunately, these compounds are also chemically unstable in humid atmosphere and in the presence of carbon dioxide. In addition, alkali metal cations can contribute largely to ion transport in them.[415]

IX.4. Oxide-based proton-conducting solid electrolytes

In humid atmosphere, lanthanum aluminate, lanthanum yttrate and strontium zirconate doped with acceptor impurities undergo transformation from oxygen-conducting to proton-conducting electrolytes.[416] Unfortunately, their proton conductivity appeared to be low. More recently, strontium cerates and barium cerates with higher proton conductivity in humid atmosphere were discovered.[417, 418] The best results were obtained with barium zirconate.[21, 419]

It is of crucial importance to answer the question what is the reason for the appearance of proton defects that should not exist in this material. When zirconium is partially replaced by, *e.g.*, yttrium, oxygen vacancies are formed in accordance with the following quasi-chemical reaction:

$$(2\,BaO + Y_2O_3)/BaZrO_3 \longrightarrow 2\,Ba_{Ba} + 2\,Y'_{Zr} + 5\,O_O + V_O^{**} \quad (11)$$

When the material is treated with water vapour at elevated temperatures, it absorbs water and the water molecules occupy oxygen vacancies [420–422]

$$V_O^{**} + H_2O \longrightarrow O_O + 2\,H_i^{*} \quad (12)$$

Protons appear in interstitials, thus forming OH groups in the bulk of the sample. As in zirconium phosphate (see above), protons cannot form strong bonds because all oxygen atoms are simultaneously involved in the strong bonds with barium and zirconium atoms. Consequently, almost unhindered interstitial diffusion of protons becomes possible. Raising the temperature causes the concentration of charge carriers to rapidly decrease due to dehydration, although in some materials the carriers still may exist at temperatures above 1000 – 1200 °C. On the contrary, the proton mobility abruptly increases. As a result, the proton conductivity reaches a maximum value (to 0.1 S cm^{-1}) at temperatures in the 600 – 900 °C range (see Fig. 4).[21, 419, 420, 423]

The best-studied proton conductors are the oxides $AB_{1-x}M_xO_{3-\delta}$ (A = Ba, Sr, Ca; B = Zr^{4+}, Ce^{4+}; M = Y^{3+}, In^{3+}, *etc.*) with the perovskite-type structure.[16, 21, 424–446] Considerable attention is paid to the description of defect formation processes in proton conductors[447–451] and to the relationships between the bulk conductivity and interfacial conductivity.[452–454] A chemically stable system consisting of two layers of stable $BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-\delta}$ to sandwich a layer of unstable $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ was proposed[455] and stable oxide films[456, 457] were proposed.

Materials based on the doped barium and strontium cerates and zirconates have attracted the greatest attention because of high conductivity which, however, is also achieved only at high temperatures (see Fig. 5). A severe problem consists in that the materials are chemically unstable in the presence of carbon dioxide and water; this makes them of limited use for the fuel cell and other electrochemical applications.[458, 459] In the course of search for novel, more stable solid electrolytes[460, 461] researchers focused on the materials based on complex oxides with disordered structure. These systems usually allow one to choose coordinatively unsaturated transition-metal polyhedra that can be completed using sorbed water and produce mobile protons following reaction (12). The simplest, although to some extent atypical, representative of this class of materials is ceria, CeO_2. It is characterized by rather high oxygen defectiveness, being a poor proton conductor at temperatures >500 °C. Experiments with highly porous CeO_2 films demonstrated a marked improvement of the proton conductivity at ~300 °C.[462]

This property is more typical of the materials whose structures are derived from the perovskite structure. In particular, materials with the brownmillerite structure

$A_2BB'O_5$ ($A_2BB'O_5[V_O^*]$) exhibit a considerable oxygen deficiency. An example is provided by barium indate $Ba_2In_2O_5$ which can reversibly uptake water (up to 1 mole). The proton conductivity of $Ba_2In_2O_5$ manifests itself at temperatures < 500 °C, being relatively low due to the ordering of structural defects.[463] At moderate temperatures, it can be improved using heterovalent substitution.[464 – 470] Similar properties were reported for, *e.g.*, $Ba_4(Ba_2Nb_2)O_{11}$.[471]

A research group from the Ural Federal University named after the First President of Russia B N Yeltzin contributed largely to the development of this field. They investigated niobates,[472 – 476] tantalates,[472, 477, 478] tungstates[479, 480] and zirconates[481] of alkaline-earth metals and showed that the proton conductivity of oxygen-deficient fluorine-containing materials based on barium indates[482 – 487] and barium indates – zirconates[488] increases at low content of fluorine.

However, the presence of alkaline-earth metal cations also makes these systems unstable in the presence of carbon dioxide and water vapour.[489] In this connection, systems containing no alkaline-earth metals and based on, in particular, $LaNbO_4$,[490, 491] Ln_6WO_{12},[492, 493] $La_2Mo_2O_9$ (Ref. 494) and $La_3Ga_{5.5}Ta_{0.5}O_{14}$ (Ref. 495) attracted the attention of researchers (see Fig. 4).

High-temperature proton-conducting materials are used in solid oxide hydrogen fuel cells operating at temperatures 500 – 800 °C.[496 – 499] The design of complex oxide fuel cells operating at temperatures below 500 °C is in the early stage of development.[7, 500]

X. Conclusion

Research progress in the synthesis and properties of materials with high Li-ion, oxygen-ion and proton conductivity is first of all determined by the prospects of wide use of these systems in the design of Li-ion batteries and fuel cells for alternative power engineering. Ion transport in these structures proceeds by different mechanisms. In the case of lithium and oxygen ions, one deals with ion hopping from one crystallographic position to another; proton transfer involves at least two stages, namely, rotation of proton-containing groups and proton hops between them. Common to all systems is the requirement of sufficiently high concentration of structural defects.

Among the lithium-conducting electrolytes, those exhibiting a rather high room-temperature conductivity are the most in-demand ones. These include polymeric, ceramic and glassy systems that are most often formed by heterovalent doping or by fabricating composites. Considering oxygen-conducting electrolytes, small ionic radius and high charge (twice as high as that of lithium) predetermine a low mobility of oxygen ions. It can be increased only at high temperatures. Currently, the most in-demand materials are based on the stabilized high-temperature phase of zirconium oxide and some other ceramic systems. However, attempts to improve the oxygen conductivity at relatively low temperatures are first of all associated with fabrication of films and composite materials containing a component in the molten state at the operating temperatures. Systems with mixed-type (electronic/oxygen-ion or electronic/Li-ion) conductivity are widely used as electrode materials, for gas separation and in catalysis.

Proton-conducting solid electrolytes can be divided into three classes, *viz.*, low-, moderate- and high-temperature ones. The first class mainly consists of acid hydrates and acid salt hydrates that can exist in the crystalline, polymeric or composite form. Yet another promising research avenue is to design moderate-temperature proton-conducting electrolytes, first of all, anhydrous acid salts and composites based on them, as well as thermally stable (*e.g.*, PBI-based) polymers containing incorporated acid molecules. High-temperature proton-conducting electrolytes include oxide systems with rather high concentrations of oxygen vacancies. Treatment with water vapour causes the water molecules to occupy oxygen vacancies and then dissociate with the formation of mobile protons. Materials with the perovskite-type structure (most often, based on cerates and zirconates of alkaline-earth metals) are also widely used. They are characterized by partial replacement of tetravalent cations by trivalent ones to obtain defect structures. Recently, systems based on structurally disordered complex oxides have been intensively studied.

The demand for the solid electrolytes described above is first of all due to power engineering needs. This offers prospects for the design of novel materials with high ionic conductivity.

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