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Oxygen Ion-Conducting Materials

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Abstract

Oxygen ionic and mixed ionic-electronic conductors find important applications in solid-state electrochemical devices, including sensors, solid oxide fuel cells, high-temperature electrolyzers, and oxygen separation membranes. This chapter presents a brief overview of oxide phases with high diffusivity of $\text{O}^{2-}$ anions, providing an introduction to this fascinating topic. Particular emphasis is centered on the comparative analysis of ionic and electronic conductivity variations in the major groups of solid oxide electrolytes and mixed conductors, such as perovskite- and fluorite-related compounds, apatite-type silicates, and derivatives of $\gamma$-Bi$_4$V$_2$O$_{11}$ and $\beta$-La$_2$Mo$_2$O$_9$. The defect chemistry mechanisms relevant to the oxygen ion migration processes are briefly discussed.

9.1 Introduction

Technologies based on the use of high-temperature electrochemical cells with oxygen anion- or mixed-conducting ceramics provide important advantages with respect to the conventional industrial processes [1–8]. In particular, solid oxide fuel cells (SOFCs) are considered as alternative electric power generation systems due to high energy-conversion efficiency, fuel flexibility, and environmental safety [1–3]. Dense ceramic membranes with mixed oxygen-ionic and electronic conductivity have an infinite theoretical separation factor with respect to oxygen, and can be used for gas separation and the partial oxidation of light hydrocarbons [4, 5, 7, 8] (these and other applications are reviewed in Chapters 12 and 13). For all types of electrochemical cells, the key properties which determine the use of a material are the partial ionic and electronic conductivities. As an example, solid electrolytes for SOFCs, oxygen pumps and electrochemical sensors should exhibit a maximum oxygen ionic conductivity, while the electronic transport should be minimal. In contrast, for SOFC electrodes...
and oxygen separation membranes, both ionic and electronic conductivities should be as high as possible (see Chapter 3). In the case of SOFC interconnectors, both minimum ionic and maximum electronic conduction are necessary.

In this chapter we present a brief overview of the major groups of solid oxide electrolytes and mixed conductors, placing special emphasis on their ion transport properties. The main features of the crystal structures enabling fast anion diffusion and the basic defect-chemistry mechanisms relevant for these materials are addressed in Chapters 2–4. Since it has been impossible to cover all promising compositions and migration-affecting factors within the chapter, priority has been given to those single-phase oxide ceramics which exhibit a high ionic conductivity sufficient for practical applications. Further information regarding conventional and new materials for high-temperature electrochemical devices is available in a variety of reviews and monographs [4, 6–17].

9.2 Oxygen Ionic Transport in Acceptor-Doped Oxide Phases: Relevant Trends

Perhaps one of the most widely studied topics in high-temperature electrochemistry is the oxygen ion conductivity of the fluorite-structured binary oxide systems. Except for the δ-phase of Bi₂O₃, these are formed by preparing solid solutions of tetravalent metal oxides (e.g., zirconia and ceria) with lower-valent metal oxides, most notably the trivalent rare earths (Ln³⁺). In these solid solutions, addition of the lower-valent cation is charge-compensated by the formation of oxygen vacancies, which are highly mobile at elevated temperatures. The combination of this ability of the fluorite lattice to accept high concentrations of vacancies with the fact that they are mobile at high temperatures is the origin of this high oxygen ion conductivity. A prominent feature seen in all investigations is the maximum in the conductivity isotherms with respect to the content of the aliovalent additive. A simple analysis [12] shows that a maximum is to be expected when the oxygen sublattice is half occupied, although experimentally this is found to occur at much lower concentrations. As an example, this concentration in Zr₁₋ₓYₓO₂₋ₓ/₂ corresponds to x ≈ 0.07–0.11, depending on temperature, preparation route, pre-history, purity, and other factors. For zirconia, this effect is complicated by the fact that it only adopts the fluorite structure (at moderate temperatures) when the dopant concentration is already high, because the small Zr⁴⁺ cation (0.84 Å in eightfold coordination) is not large enough to stabilize the fluorite structure to low temperatures. In contrast, in pure ceria the Ce⁴⁺ cation (0.97 Å in eightfold coordination) is large enough to be stable in the fluorite lattice, and thus provides an ideal opportunity for examining any effects from dilute to concentrated solid solutions. The example of ceria-based electrolytes is used in this section to illustrate the key effects of acceptor-type doping, which are observed in most fluorite- and perovskite-related phases.

For most ionic conductors, the conductivity activation energy (Eₐ) may be considered to consist of two parts, namely the enthalpy of ion migration (∆H_m) and any terms caused by the interaction of the point defects and/or by the charge carrier formation. For low concentrations of the trivalent additive in ceria lattice, the
interaction term is thought to be due to the formation of defect associates of the oxygen vacancy with the substitutional cation(s). In a simplest case, this type of defect interaction in yttria-doped ceria can be presented as

\[ \text{Y}^{\text{r}_{\text{Ce}}} + \text{V}_0^\text{**} \rightarrow \{ \text{Y}^{\text{r}_{\text{Ce}}} \text{V}_0^\text{**} \}^* \]  

(9.1)

with the association enthalpy \( \Delta H_a \). Shown here is the simple dimer, or associated pair, but it should be noted that the concentration of substitutional cations is twice that of the oxygen vacancies, and so there is a high probability of forming trimers and higher clusters as the concentration increases (a point to which we will return). If simple dimers were to form, then the activation energy for conductivity would be given by the sum \( (\Delta H_a + \Delta H_m) \). Irrespective of the association type, two vacancy concentrations can be defined: the stoichiometric concentration, which is determined by the electroneutrality condition; and the mobile or “free” vacancy concentration given by the association equilibria, which can be very different. Only the “free” vacancies are mobile and can contribute significantly to oxygen ionic transport.

What is found by experiment is that, as a general rule, at substitutional concentrations close to the maximum in the conductivity isotherms, there is a minimum in the activation energy. In an early (but very comprehensive) study of ceria solid solutions with the trivalent rare earths, Faber et al. [18] showed that the depth of the minimum, and the concentration at which it occurs, depends upon the identity of the rare earth cation (Figure 9.1). The minima have been ascribed [19] to competitive defect interactions. Initially, the effect is a weakening of the association energy of the dimers caused by an electrostatic interaction between the cluster and the unassociated substitutionals having an opposite effective charge in the lattice; note, however, that

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**Figure 9.1** Activation energy versus dopant concentration in ceria solid solutions. Data from Ref. [18].
the intrinsic vacancy-formation process cannot be neglected at low dopant concentrations. On further doping, higher-order clusters form, which act as much deeper traps for the oxygen vacancies and thus increase the association term.

There are distinct differences between the compositional dependence of $E_a$ for each of the substitutional species, both in terms of the magnitude and shape of the dependence, even though they have the same effective charge and give rise to identical stoichiometric vacancy concentrations (see Figure 9.1). In particular, there is a further minimum here as a function of the size of the substitutional cation. This is shown much better in Figure 9.2, where the minima with concentration are plotted as a function of the dopant radius. The global minimum corresponding to the lowest total activation energy is an important feature for the technological application of ceria solid solutions. It is usually assumed that, to a first approximation, the migration enthalpy in these materials changes very little from system to system, and that the observed changes in $E_a$ reflect changes in the association term. If this is the case, then Figures 9.1 and 9.2 demonstrate that the association energy must contain terms that reflect both an electrostatic and an elastic interaction between the components of any defect cluster, as the dopant size is so important.

The explanation of the minimum in activation energy with dopant radius was initially made in terms of the elastic component of the association energy of the simple pairs – that is, in terms of the size mismatch between the host and the substitutional ion (see early references in Ref. [12]). Later computer simulations of

**Figure 9.2** The minimum activation energy in ceria-based systems (closed symbols) and calculated binding energies of vacancy substitutional pairs in ceria (open symbols) plotted against the M$^{3+}$ dopant cation radius in eightfold coordination. Data from Refs. [18, 20].
ceria-based solid solutions [20] showed that the situation is more complicated and that, in fact, the minimum is caused by the switchover of the vacancy from a first (r_{\text{ion}} \leq \text{Gd}^{3+}) to a second nearest-neighbor site (r_{\text{ion}} \geq \text{Gd}^{3+}) to the substitutional ion in the fluorite lattice, as the dopant size exceeds that of the host (see Figure 9.2). A similar dependence is operative in zirconia electrolytes [21]; moreover, the same type of size dependence could be found for larger clusters. More recent density functional calculations for ceria-based materials have confirmed this trend [22], and have shown that at the minimum in the association (binding) energy where the crossover takes place, there is a balance between the electrostatic and elastic interactions that removes the energy difference between the first- and second-neighbor configurations. It would seem, therefore, that the above-mentioned theoretical studies present a consistent account of the size dependence. However, recent calorimetric studies performed by Navrotsky et al. [23] have shown that this explanation might not yet be complete. In fact, their measurements would indicate that the vacancy is, as expected, in the first nearest-neighbor position in \text{CeO}_2-\text{Y}_2\text{O}_3, and \text{CeO}_2-\text{Gd}_2\text{O}_3, but the same seems to be true for \text{CeO}_2-\text{La}_2\text{O}_3 solid solutions, in contrast to the calculated predictions.

A word of caution is needed at this point on the above observations and following comments. It is clear from Figure 9.1 that the defect structure has a strong concentration dependence, and thus for meaningful comparisons between different materials it is necessary to compare like with like. However, the concentration dependence of the activation energy curve is different for each substitutional cation; indeed, Andersson et al. [22] showed that the interplay between the electronic and elastic component depends heavily on the dopant type. It is probably the case that the type of defect clusters observed is very dependent upon concentration, and that typically around the concentration for the minimum activation energy a change in the defect structure takes place.

In the case of mixed ionic-electronic conductors, an analysis of the lattice strain-promoted clustering phenomena becomes even more complicated as the oxygen vacancy concentration – and, consequently, the ionic conductivity – depend on both the oxygen partial pressure and cation size mismatch. In this situation, any quantitative comparison is often difficult, even when the experimental data were obtained for essentially similar materials and under identical external conditions. Nonetheless, the data available on ferrite-, cobaltite-, and nickelate-based systems with perovskite-related structures (e.g., [24–28]) seem to confirm that, when long-range ordering in the oxygen sublattices can be neglected, the ionic transport tends to increase with decreasing difference between the host and dopant cation sizes. As an example, Figure 9.3 compares the variations of partial ionic and p-type electronic conductivities in perovskite-type \text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_{3-\delta} (\text{A} = \text{Sr, Ba}) [24]. Under oxidizing conditions, increasing the mismatch between \text{Ln}^{3+} and \text{A}^{2+} radii weakens the metal–oxygen bonding, increases the oxygen nonstoichiometry, and decreases the hole concentration due the electroneutrality condition; the ionic transport then exhibits a trend opposite to the vacancy concentration variations. A similar tendency is observed for the ionic conductivity in reducing atmospheres, when the oxygen deficiency becomes similar for all \text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_{3-\delta} perovskites; the activation energy
increases with lattice strains and displays no direct correlations with the stereological parameters which might affect ion diffusivity [24].

One way to confirm the defect cluster configurations is to use localized probes such as the synchrotron-based extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopic analyses to examine the local cation coordination [29, 30]. Alternatively, electron beam-based techniques such as high-resolution electron energy loss spectroscopy (EELS) and selected-area electron diffraction (SAED) can be used [31]. Most of these techniques have been applied to materials with the acceptor-type dopant concentration >5%, where trimers and higher-order clusters are to be expected. Interestingly, even in concentrated solid solutions based on ceria, the different trivalent substitutionals show differing behaviors. The study of yttria- and gadolinia-doped CeO$_{2-\delta}$ using EXAFS and XANES [29] revealed a greater tendency towards defect association in the former system, with the most likely configurations comprising either two or four trivalent cations clustered with one or two neighboring oxygen vacancies. Similar conclusions were drawn when the study was extended to the CeO$_2$-La$_2$O$_3$ system [30]. Deguchi et al. [30] also suggested a similarity between the radial distribution functions for the

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**Figure 9.3** Oxygen nonstoichiometry at atmospheric oxygen pressure (top), and values of partial p-type electronic and ionic conductivities in air, and ionic conductivity in reducing atmospheres when the oxygen content in the perovskite lattice ($3 - \delta$) is close to 2.75 atoms per formula unit (bottom), versus the difference between A$^{2+}$ and Ln$^{3+}$ cation radii in Ln$_{0.5}$A$_{0.5}$FeO$_{3-\delta}$ (Ln = La-Sm, A = Sr, Ba) at 1223 K. Data from Ref. [24]. All A-site cation radii correspond to ninefold coordination.
dopant cations (e.g., \( R_{Ln-1} Ln \)) and those found in the corresponding rare earth sesquioxides, concluding that “... it is interesting to note that the original structure of each dopant oxide is kept even in the ceria lattice”. This theme was echoed by Ou et al. [31], who showed that the defect structure in ceria electrolytes does indeed change with the dopant content, albeit for rather concentrated materials containing 15–25% additives; these authors proposed the existence of ordered nanodomains – essentially large vacancy-dopant clusters that resemble the parent C-type structure of \( Ln_2O_3 \).

Some final comments are needed to qualify the previous analysis. For the experimental observations, it has already been stated that care must be taken to ensure that like materials are compared (although the term “like” materials is not quite clear). It is also instructive to remember that the different techniques probe the materials over different length scales, and are sensitive to the different properties of the material. The theoretical techniques also differ in their strengths and weaknesses to simulate these complex lattices, and will be more successful in their description of one aspect of the problem. However, the most problematic issue is the comparability of even the most “identical” samples.

In most oxygen ion-conducting materials used for practical applications, the lattice diffusivity of the cations is particularly sluggish. This brings its own problems for understanding the microscopic mechanisms and materials optimization. Usually, the distribution of dopant cations is assumed to be random among the available lattice sites – indeed, this is the aim of the (mainly solution based) fabrication processes designed to maximize cation mixing. Yet, this is far from the case in the ceramic samples that are subsequently investigated. The computer simulations show that there is an energetic advantage for the formation of clusters. However, these need to form from the initial random distribution imposed by fabrication and thermal prehistory; the redistribution kinetics may be very slow, and it is unlikely that a true “equilibrium” structure will result. Whichever metastable cation distribution results from the prehistory, the oxygen sublattice will rapidly adjust to it. It is probable, therefore, that subtle differences in the observed defect cluster structure can occur between ostensibly similar materials, and this should be taken into account when evaluating the experimental data relating to this fascinating topic.

9.3 Stabilized Zirconia Electrolytes

The maximum ionic conductivity in \( \text{ZrO}_2 \)-based systems is observed when the content of acceptor-type dopant cations with the smallest radii (Sc, Yb, Y) is close to the minimum necessary to completely stabilize the cubic fluorite-type phase in the operating temperature range [9, 11, 16, 32–35]. This concentration (often referred to as the low stabilization limit) and the conductivity of the ceramic electrolytes are dependent, to a finite extent, on the pre-history and various microstructural features. In addition to the metastable states discussed above, critical microstructural factors
include the dopant segregation at grain boundaries, impurities, porosity, and the formation of ordered microdomains. Nevertheless, despite minor contradictions still existing in the literature, for most important systems the dopant concentration ranges providing maximum ionic transport are well established. For example, the highest conductivity in Zr$_{1-x}$Y$_x$O$_{2-x/2}$ and Zr$_{1-x}$Sc$_x$O$_{2-x/2}$ is observed at $x = 0.07$–0.11 and 0.09–0.11, respectively. Although further additions decrease the ionic conduction due to progressive defect clustering, typical dopant concentrations in the solid electrolyte ceramics used for most practical applications are moderately higher, for example, $x \approx 0.15$ in Zr$_{1-x}$Y$_x$O$_{2-x/2}$ (8 mol.% Y$_2$O$_3$). This doping strategy aims, in particular, to partly suppress ageing at 900–1300 K associated with kinetically limited phase changes and time degradation of the conductivity. In the case of scandia-stabilized zirconia (SSZ), where a relatively fast decomposition of metastable cubic and rhombohedral solid solutions and/or partial ordering occur at moderate temperatures, this strategy is less effective compared to Y-containing analogues. Taking into account the precursor costs, yttria-stabilized zirconia (YSZ) is among the most commonly used solid electrolytes to date. Numerous attempts have been made to identify new electrolyte compositions in ternary systems, particularly to increase the conductivity by optimizing the average size of dopant cations, to increase the stability of Sc-containing materials by co-doping, or to decrease the cost of Ln$^{3+}$-stabilized phases by mixing rare- and alkaline-earth dopants [33]. However, no worthwhile improvement has been observed. Figure 9.4a displays typical values of the total conductivity (predominantly ionic) for selected ZrO$_2$-based phases and one YSZ-Al$_2$O$_3$ composite. Small additions of highly dispersed alumina make it possible to improve the mechanical strength and to reduce the grain-boundary resistance due to the "scavenging" of silica-rich phases [45–47]; this approach has been used successfully to prepare a variety of solid electrolyte ceramics (e.g., [48–50]).

Another necessary comment is that, if compared to other oxide electrolytes, stabilized zirconia ceramics without variable-valence additives exhibit, as an average, a minimum electronic contribution to total conductivity in the oxygen partial pressure range most important for practical applications [1, 6, 10, 11, 13, 14, 16, 33]. This approximate $P_{O_2}$ range is from 100–200 atm (oxygen compressors, impurity sensors in oxygen, high-pressure SOFCs) down to $10^{-25}$–$10^{-20}$ atm (standard SOFC systems, water vapor electrolyzers, exhaust gas sensors). Whilst in reducing environments, the n-type electronic transport in ThO$_2$- and LaGaO$_3$-based electrolytes is lower than that of stabilized ZrO$_2$ zirconia, the latter shows lower p-type electronic conduction and, thus, a higher performance under oxidizing conditions. It should be noted also that the performance of lanthanum gallate at low $P_{O_2}$ is limited by Ga$^{3+}$ reduction and gallium oxide volatilization, rather than the n-type electronic conductivity. For applications in oxygen-separation membranes and SOFC electrodes, the electronic transport in stabilized zirconias can be moderately enhanced by incorporating variable-valence cations (e.g., Ti, Nb, Cr, Tb, Pr) into the fluorite-type lattice [4, 9, 17, 33, 51, 52]. However, such doping leads usually to decreasing ionic conductivity, the solubility of transition metal cations is relatively low and temperature-dependent, whereas the addition of praseodymium oxide causes thermomechanical instability.
9.4 Doped Ceria

The main advantages of fluorite-type Ce(Ln)O$_2$–δ [38, 53–61] include a faster oxygen-ionic transport with respect to stabilized ZrO$_2$, a lower cost than that of La(Sr)Ga(Mg)O$_{1–δ}$ (LSGM) ceramics, and modest reactivity and volatility of the components in

![Figure 9.4](image-url)
comparison with LaGaO$_3$, La$_{10}$Si$_6$O$_{27}$, and Bi$_2$O$_3$-based materials. In addition, the superior catalytic properties of ceria are advantageous for increasing the exchange currents of the SOFC anodes. Among CeO$_2$-based phases, the highest level of ionic conduction is characteristic of the solid solutions Ce$_{1-x}$M$_x$O$_{2-d}$ (M = Gd or Sm; $x = 0.10$–$0.20$) and their analogues obtained by co-doping, where the concentrations of substitutional cations are adjusted to optimize the average radius and hence, to minimize the tendency to vacancy clustering. Selected data on the total conductivity, which is predominantly ionic under oxidizing conditions, are shown in Figure 9.4b. As with all ceramic electrolytes, the grain boundaries are partially blocking to ionic transport across them; this is an extra contribution to the total resistance that is dependent on impurities and dopants that segregate to the boundaries, and is therefore highly variable from one source to another. This has been an origin of numerous contradictions in the reported data, particularly that relating to the optimum ceria-based compositions. Thus, while Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ has the highest lattice conductivity, Ce$_{0.8}$Gd$_{0.2}$O$_{1.90}$ often has higher total conductivity because its grain boundary contribution seems to be more tolerant to impurities [57]. Due to the dopant segregation and interaction with impurities, analogous discrepancies can also be found on the effects of co-doping (e.g., Refs [60–62] and references cited therein).

The p-type electronic conductivity of gadolinia-doped ceria (CGO) in air is 0.5 to 3.0-fold lower than that of LSGM, and this difference increases with decreasing temperature (Figure 9.5). The main problems in using doped ceria as an SOFC electrolyte arise, however, from the partial reduction of Ce$^{4+}$ to Ce$^{3+}$ under the reducing conditions of the anode [11, 13, 16, 55, 57, 69]. This has two main effects: (i) it produces n-type electronic conductivity, which causes a partial internal electronic short circuit in a cell; and (ii) it generates oxygen deficiency and an expansion of the lattice, which can lead to mechanical failure. For Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$, the electronic conductivity at the anode side is greater than the ionic conductivity for temperatures higher than about 823 K (inset in Figure 9.4). Such properties mean that ceria electrolytes are viable only for low-temperature operation; at the same time, the appearance of significant mixed conductivity in reducing environments is advantageous for ceria-containing anodes. The behavior of doped CeO$_{2-\delta}$ with respect to variable-valence additives which have been incorporated to further enhance electronic transport in electrodes and ceramic membranes, is generally similar to other fluorite-type oxides, such as zirconia [4, 7, 8, 17, 40, 70–73]. In particular, maximum oxygen permeability is achieved in those systems with the highest solubility of variable-valence cations, such as Pr$^{4+/3+}$ [73]; however, the thermomechanical stability of such ceramic materials remains an open issue.

9.5 Anion Conductors Based on Bi$_2$O$_3$

Oxide phases derived from Bi$_2$O$_3$ are particularly interesting due to their high ionic conductivity in comparison to other solid electrolytes [4, 74–78]. The maximum ionic transport is known for stabilized $\delta$-Bi$_2$O$_3$ with a highly oxygen-deficient fluorite
structure, and for one member of the Aurivillius series, \( \gamma \)-Bi\(_4\)V\(_2\)O\(_{11}\), which is the parent compound of the so-called BIMEVOX family. Unfortunately, Bi\(_2\)O\(_3\)-based materials exhibit a number of disadvantages that hamper their practical application, notably a very high thermal expansion, instability in reducing atmospheres, volatilization of bismuth oxide, a high corrosion activity, and low mechanical strength.

Figure 9.5 Comparison of the oxygen ionic (a) and electronic (p- and n-type) (b) conductivity of selected solid electrolytes and mixed conductors under oxidizing conditions. The partial ionic conductivity of perovskite-type \( \text{Sr}_{0.7}\text{Ce}_{0.3}\text{Mn}_{0.9}\text{Al}_{0.1}\text{O}_{3-a} \) [63] correspond to the oxygen partial pressure gradient of 0.21/0.021 atm; data on electronic conduction in other materials correspond to \( P_{O_2} \) range of 1.0/0.21 atm. All other data [36, 40, 64–68] correspond to \( P_{O_2} = 0.21 \) atm. The ionic conductivity of 8 mol\% yttria-stabilized zirconia (YSZ) [36] is shown for comparison.
Stabilization of the high-diffusivity $\delta$-$\text{Bi}_2\text{O}_3$ phase down to intermediate and low temperatures can be achieved by doping with rare-earth and/or higher-valency cations, such as Y, Dy, Er, W, or Nb [11, 13, 74–76]. Figure 9.6 displays representative data on the total conductivity (mainly ionic) for two $\delta$-$\text{Bi}_2\text{O}_3$-based compositions. As with zirconia and hafnia electrolytes, the highest ionic transport is observed for materials containing the minimum addition necessary to stabilize the $\delta$-polymorph; further doping decreases oxygen ion mobility due to a decreasing unit cell volume and increasing the average energy of the metal–oxygen bonding. As $\text{Bi}^{3+}$ cations are relatively large, at a given doping level the ionic transport increases with increasing $\text{Ln}^{3+}$ radius. However, the minimum stabilization limit also increases with $\text{Ln}^{3+}$ size, and this leads to a decrease in the maximum ionic conductivity with increasing radius of the stabilizing cation. As a result, the highest conductivity in the $\text{Bi}_2\text{O}_3$-$\text{Ln}_2\text{O}_3$ systems is observed for Er- and Y-containing solid solutions, namely $\text{Bi}_{1-x}\text{Er}_x\text{O}_{1.5}$ ($x \approx 0.20$) and $\text{Bi}_{1-x}\text{Y}_x\text{O}_{1.5}$ ($x = 0.23–0.25$). It should be noted, however, that all known $\delta$-$\text{Bi}_2\text{O}_3$-based phases with the disordered fluorite structure are metastable at temperatures below 770–870 K, and exhibit a slow degradation in conductivity with time due to sluggish polymorphic transformations. The solid

![Figure 9.6](image)

**Figure 9.6** Total conductivity of $\text{Bi}_2\text{O}_3$-based [64, 75, 79, 80] and $\text{La}_2\text{Mo}_2\text{O}_9$-based [81] materials in air, compared to the ionic transport in 8 mol% yttria-stabilized zirconia (YSZ) [36]. The inset presents the conductivity data on undoped $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{La}_{1.7}\text{Bi}_{0.3}\text{Mo}_2\text{O}_9$ [65], for comparison.
solutions based on $\gamma$-Bi$_4$V$_2$O$_{11}$ [49, 77, 78, 82, 83] stabilized by the substitution of 7–15% vanadium with transition metal cations such as Cu, Ni, or Co, possess a better phase stability at moderate temperatures, superior ionic conductivity and oxygen ion transference numbers ($t_0$) close to unity below 900 K under oxidizing conditions (Figures 9.5 and 9.6). The electrolytic domain of BIMEVOX ceramics is, however, very narrow. For example, decreasing the $P_{O_2}$ to $10^{-2}$ atm results in the electron transference numbers of Bi$_2$V$_{0.9}$Cu$_{0.1}$O$_{5.5}$ increasing to 0.05 at 908 K (inset in Figure 9.7); any further reduction will cause phase decomposition.

9.6 Transport Properties of Other Fluorite-Related Phases: Selected Examples

The pyrochlore-type compounds, where the crystal structure is usually considered as a cation-ordered fluorite derivative with $\frac{1}{2}$ vacant oxygen site per fluorite formula unit, constitute another large family of oxygen anion conductors [9, 33, 41–43, 84–88]. The unoccupied sites provide pathways for oxygen migration; furthermore, the $A_2B_2O_7$ pyrochlore structure may tolerate formation of cation and anion vacancies, doping in both cation sublattices, and antistructural cation disorder. Regardless of these factors,
the oxide pyrochlores possess, in general, worse transport properties compared to the fluorite-type compounds (Figures 9.4 and 9.5). At elevated temperatures (typically up to 1650–2500 K), most pyrochlores disorder into fluorite polymorphs. A decreasing A-site cation radius favors this transition. As a rule, partially cation-disordered pyrochlores exhibit relatively high activation energies for anion transport in the intermediate-temperature range; the maximum ionic conductivity (which can be further enhanced by acceptor-type doping within the solid solution formation limits) occurs for cation stoichiometry, for example, Gd$_2$Ti$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$. Until now, the highest values of oxygen ion diffusivity in pyrochlore-type compounds have been achieved for Gd$_{2-x}$Ca$_x$Ti$_2$O$_7$ with $x \approx 0.2$ [42, 84]. These materials also display a significant electronic contribution to the total conductivity under oxidizing and strongly reducing conditions, close to the upper limit acceptable for solid electrolytes (Figure 9.5). However, due to the limited solubility of variable-valence cations in most pyrochlore phases, the electronic transport cannot be further enhanced by doping to a substantial extent, as for the fluorite-type solid electrolytes.

Among other ion-conducting phases with fluorite-like structures, note should be taken of Y$_4$NbO$_{8.5}$, (Y,Nb,Zr)O$_{2-\delta}$ solid solutions, and their derivatives (see Refs. [89–91] and references cited therein). The total conductivity of Y$_4$NbO$_{8.5-\delta}$ is essentially independent of the oxygen partial pressure, which may suggest a dominant ionic transport [90]. However, the conductivity level in this system is rather low, and similar to that in pyrochlore-type titanates and zirconates, although some improvements can be achieved by the addition of zirconia.

9.7 Perovskite-Type LnBO$_3$ ($B =$ Ga, Al, In, Sc, Y) and their Derivatives

Perovskite-type phases derived from LaGaO$_3$ via acceptor-type doping into both cation sublattices of the ABO$_3$ perovskite structure exhibit a higher ionic conductivity than that of stabilized zirconia, and are thus promising materials for electrochemical cells operating in the intermediate-temperature range (Figures 9.5, 9.8 and 9.9). In oxidizing atmospheres, the p-type electronic transport in the gallate solid electrolytes is moderately higher with respect to CeO$_2$-based solid solutions (Figure 9.5), but the electrolytic domain of doped LaGaO$_3$ extends to substantially lower oxygen chemical potentials. Following the principle of minimum strain giving maximum oxygen ion mobility, doping with Sr$^{2+}$ leads to a higher ionic conductivity in comparison with either Ca$^{2+}$ or Ba$^{2+}$ [104–106]. As for the fluorite-type electrolytes, there is an optimum concentration of acceptor cations, depending on their size; further additions result in progressive vacancy association processes. In the case of the La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ (LSGM) series, the maximum ionic transport is achieved at $x = 0.10–0.20$ and $y = 0.15–0.20$, whilst the introduction of smaller Ln$^{3+}$ cations and the creation of an A-site deficiency decrease the ionic conduction [103–108]. It should be noted that qualitatively similar trends are known for numerous perovskite-type systems with either predominant ionic transport or mixed conductivity, such as rare-earth aluminates [109, 110], ferrites, and cobaltites [24–28, 98, 102, 111],
although the optimum concentrations of acceptor-type dopants are always unique for each system.

The introduction of small amounts of variable-valence cations, such as iron or cobalt, into the B sites increases ionic conduction in the gallate-based electrolytes and
their analogues, and produces only a small increase in the electronic conductivity [95, 112, 113]. However, the concentration of transition metal dopants in the solid electrolyte ceramics should be limited to below 3–7% due to rising electronic transport. Also, in many cases the ionic conductivity of heavily doped gallates is lower than that of LSGM, particularly in the intermediate-temperature range and under oxidizing conditions, when the average oxidation state of transition metal cations is higher than 3+ (Figure 9.8). Nevertheless, optimization of the acceptor-type and variable-valence dopants content makes it possible to develop mixed-conducting membranes with a high oxygen permeability and improved dimensional stability [114–117]. The disadvantages of LaGaO$_3$-based electrolytes and membrane materials include the possible reduction and volatilization of gallium oxide, the relatively high cost of gallium, and significant reactivity with electrodes and catalysts.

Perovskite-type aluminates based on acceptor-substituted LnAlO$_3$ [93, 94, 106, 109, 110, 118, 119] possess a better stability with respect to reduction and volatilization as compared to doped CeO$_2$–5 and LaGaO$_3$–5, and also moderate thermal expansion and relatively low cost. Their major disadvantages relate to a rather low level of oxygen ionic transport, a significant p-type electronic conductivity under oxidizing conditions, and, in many cases, poor sinterability. Although the published data are somewhat contradictory due to microstructural differences and high grain-boundary resistivity of aluminate ceramics, the highest ionic conduction is known for compositions close to La$_{0.9}$Sr$_{0.1}$AlO$_{3–5}$, possibly substituted with less than 10% Mg$^{2+}$ on
the B sublattice. Other materials of this large family comprising perovskite-like LnBO₃ (B = In, Sc, Y) and their derivatives [93, 94, 106, 120–124], represent mainly academic interest, although a considerable level of protonic conduction in several LaYO₃, and LaScO₃-based phases might also be of interest for some applications. The oxygen ionic conductivity of In-, Sc-, and Y-containing perovskites is comparable or even lower than that of aluminates, while the costs are substantially higher. In addition, these perovskites exhibit a high electron-hole contribution to total conductivity under oxidizing conditions, as for aluminates.

Similar properties are also known for brownmillerite- and perovskite-type phases derived from Ba₂In₂O₅ and having a substantially high electrical conductivity [125–132]. The conductivity is typically oxygen-ionic in dry atmospheres with moderate \( P_{O_2} \), mixed ionic and p-type electronic under oxidizing conditions, and protonic in \( H_2O \)-containing gas mixtures. The parent compound, brownmillerite-like Ba₂In₂O₅, exhibits a mixed conductivity with a dominant oxygen ionic transport in dry air; the ion transference number at 773 K is approximately 0.93. Heating up to 1140–1230 K causes a transition into the disordered perovskite phase, which leads to a drastic increase in the anion conduction. Doping with higher-valence cations (e.g., \( Zr^{4+}, Ce^{3+}, Sn^{4+} \) or \( Hf^{4+} \) in the indium sites, or \( La^{3+} \) in the barium sublattice) makes it possible to stabilize the disordered cubic perovskite structure, and thus to increase the ionic conductivity in the intermediate temperature range (Figure 9.10);

![Figure 9.10 Comparison of the oxygen ionic conductivity of several ferrite-based materials with layered, perovskite and garnet structures [68, 133, 134], and total conductivity of Ba₂In₂O₅-based ceramics [125, 127, 129]. Data for Ba₂In₂O₅ [125] correspond to \( P_{O_2} = 10^{-6} \) atm, where the conductivity is predominantly oxygen ionic. The ionic conductivity of SrFeO₃ and Sr₃Fe₂O₆ [134] correspond to moderately reducing conditions, where the average oxidation state of iron cations is \( 3^+ \). All other data correspond to dry air.](image-url)
the substitution with transition metal cations (V$^{5+}$, W$^{6+}$, Mo$^{6+}$) promotes hole transport. Another important advantage is related to the high protonic conductivity under SOFC operation conditions [128, 129]. However, due to the instability of Ba$_2$In$_2$O$_5$-based ceramics in humid atmospheres, high reactivity with CO$_2$ and easy reducibility [127, 129, 130, 132], it is difficult to imagine practical applications, taking into account that both the stability and ionic conductivity of LSGM are higher [126]. Again, the easy hydration and phase instability are also typical for analogous compounds, such as Ba$_2$Sc$_2$O$_5$ [135].

9.8 Perovskite-Related Mixed Conductors: A Short Overview

The complex phase diagrams and rich crystal chemistry of the transition metal-containing oxide systems, and great diversity in the defect chemistry and transport properties of mixed-conducting materials known in these systems, make it impossible to systematize all promising compositions in a brief survey. The primary attention here is therefore centered on the comparison of major families of the oxide mixed conductors used for dense ceramic membranes and porous electrodes of SOFCs and other high-temperature electrochemical devices.

Perovskite-type manganites (Ln, A)MnO$_3$ (Ln = La–Yb or Y; A = Ca, Sr, Ba, Pb) and their derivatives possess a high electronic conductivity, substantial electrocatalytic activity towards oxygen reduction at temperatures above 1000–1100 K, and moderate thermal expansion coefficients (TECs) that are compatible with commonly used solid electrolytes such as YSZ [1–4, 11, 136–138]. Although the total conductivity of manganites is lower compared to their Co- and Ni-containing analogues (Figure 9.11), the latter perovskite families exhibit other important disadvantages, including excessively high TECs and/or limited thermodynamic stability, even under oxidizing conditions. In fact, (La$_{1-x}$Sr$_x$)$_1$MnO$_3$ (LSM) and LSM-based composites are still considered as state-of-the-art cathode materials for SOFCs operating at 1070–1270 K. All perovskite-related manganites exhibit a predominant electronic conduction in combination with low oxygen ion diffusivity; their transport properties and electrochemical activity are heavily dependent on the oxygen nonstoichiometry. In particular, the electrocatalytic behavior under high cathodic polarization and the specific oxygen permeability, which are limited by both surface exchange kinetics and bulk ionic conduction, are usually correlated with oxygen vacancy generation at the manganite surface [136, 137, 148–152]. At atmospheric $P_{O_2}$ and temperatures below 1270 K, La$_{1-x}$Sr$_x$MnO$_3$ perovskites are oxygen-hyperstoichiometric at $x \leq 0.2$, and become deficient on further doping [152, 153]. The p-type electronic conductivity of Ln$_{1-x}$A$_x$MnO$_3$ at moderate A$^{2+}$ concentrations increases with $x$ as the Mn$^{4+}$ fraction increases; the maximum lies in the range $x = 0.2–0.5$ and shifts towards a lower dopant content on heating. This feature is qualitatively similar to most other perovskite systems with predominant hole transport, whilst the acceptor-type dopant concentrations corresponding to maximum conductivity are unique for each solid solution and depend on
temperature and oxygen chemical potential. In the case of Ln$_{0.7}$Sr$_{0.3}$MnO$_3$ (Ln = La-Gd) series, the highest conductivity was reported for Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ above 760 K and for Pr$_{0.7}$Sr$_{0.3}$MnO$_3$ at lower temperatures [154]. The minimum polarization resistance of manganite cathodes at 1070–1270 K, observed in the range $x = 0.3$–0.7, also tends to shift towards lower dopant concentrations when the temperature increases, and is close enough to the conductivity maximum. The introduction of an A-site cation deficiency increases the electrode performance due to a suppressed reactivity with zirconia electrolytes, a higher oxygen-vacancy content and, often, a faster ionic conduction [139, 151, 155, 156].

The number of iron-containing oxide phases with a significant mixed conductivity, which are stable under the operating conditions of SOFC cathodes and ceramic membranes, is larger than that in the manganite systems. These primarily include perovskite-like (Ln,A)FeO$_{3-\delta}$ and their derivatives existing in all Ln-A-Fe-O systems, A$_2$Fe$_2$O$_{5-\delta}$ brownmillerites, (Ln,A)$_3$Fe$_5$O$_{12-\delta}$ garnets in the systems with relatively small Ln$^{3+}$ cations, Ruddlesden–Popper series (Ln,A)$_{n+1}$Fe$_n$O$_{3n+2}$, and a variety of other intergrowth compounds such as Sr$_4$Fe$_5$O$_{13-\delta}$ (see Refs [4, 8, 17, 98, 134, 152, 157–168] and references cited therein). However, due to structural

Figure 9.11 Total conductivity of various mixed-conducting materials in air [68, 101, 133, 139–147].
constrains and defect chemistry features limiting both ionic and electronic transport, in most cases an extensive iron substitution is necessary to achieve the total conductivity higher than 10–30 S cm$^{-1}$ and partial ionic conductivity higher than 0.1 S cm$^{-1}$ at temperatures above 700 K. For B-site-undoped ferrites, the maximum conductivity is characteristic of perovskite-related solid solutions, such as Ln$_{1-x}$Sr$_x$FeO$_{3-\delta}$, where the highest level of electronic and ionic transport is known for Ln = La and x $\approx$ 0.5. Selected data on the ionic conductivity of these perovskites are presented in Figures 9.3, 9.8 and 9.9. Figure 9.12 compares the steady-state oxygen permeation fluxes through dense ceramic membranes of various perovskite-related compounds with predominant electronic conductivity. For most materials the oxygen fluxes are governed by both surface exchange and bulk ionic conduction, but can still be used to evaluate variations of the ionic transport properties in different systems due to the well-known correlations between the exchange kinetics and ion diffusivity [173–175]. It should also be noted that, in the

Figure 9.12 Temperature dependence of the oxygen permeation fluxes through various mixed-conducting membranes, made of perovskite-related compounds with predominant electronic conductivity, under fixed oxygen chemical potential gradients $p_1 = 0.066$ atm and $p_2 = 0.21$ atm. $p_1$ and $p_2$ are the oxygen partial pressures at the membrane permeate and feed sides, respectively. All data correspond to the ceramic membranes without surface modification.

\[
\begin{align*}
\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} & \quad p_1 = 0.066 \text{ atm} \\
\text{SrCo}_{0.7}\text{Ce}_{0.3}\text{MnO}_3 & \quad p_2 = 0.21 \text{ atm} \\
\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_3 & \quad d = 1.00 \text{ mm} \\
\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3 & \\
\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_3 & \\
\text{La}_{1.9}\text{Sr}_{0.1}\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_4 & \\
\text{Pr}_2\text{CuO}_4 & \\
\end{align*}
\]
Ruddlesden–Popper series, the partial electronic and ionic conductivities tend to decrease when the concentration of rock salt-type \((\text{Ln},\text{A})_2\text{O}_2\) layers increases; the general trends observed on acceptor doping are similar to those in the perovskite systems (e.g., Refs \[134, 165, 167, 168]\). If compared to manganite electrode materials, one important disadvantage of perovskite-related ferrites relates to a high chemical expansion, which provides a critical contribution to the apparent TECs due to oxygen losses at elevated temperatures, and may lead to a thermomechanical incompatibility with common solid electrolytes \[117, 162, 176, 177]\.

The layered ferrite phases – particularly the Ruddlesden–Popper series and brownmillerites – display modest stoichiometry changes and better thermomechanical properties compared to the perovskite compounds, although their compatibility with electrolyte ceramics is still limited \[133, 134, 165, 167, 168, 178]\.

For the membrane reactor materials, the thermomechanical and thermodynamic instabilities typical for undoped ferrite ceramics require extensive compositional modifications, such as the substitution of more than 20–30% iron with other cations (e.g., Ti, Cr, Ga, Al) and/or the fabrication of ferrite-based composites containing dimensionally stable components \[4, 7, 8, 17, 102, 114–117, 152, 157, 162–166]\.

Perovskite-related cobaltites exhibit substantially better transport properties and electrochemical activity in comparison with their ferrite and manganite analogues, but possess also a lower thermodynamic stability and higher thermal and chemical expansion \[4, 8, 27, 101, 111, 136, 138, 152, 156, 157, 159, 168, 179]\.

The layered cobaltites where the state of Co cations is often more stable with respect to disordered perovskite phases and the TECs are lower; important compositional families are \(\text{LnBaCo}_2\text{O}_{5+\delta}\) (\(\text{Ln} = \text{Pr}, \text{Gd}, \text{Ho}, \text{Y}\)), \(\text{LnBaCo}_4\text{O}_{7+\delta}\) (\(\text{Ln} = \text{Dy}, \text{Yb}, \text{Y}\)), and also Ruddlesden–Popper type \((\text{Ln},\text{A})_4\text{Co}_3\text{O}_{10–\delta}\) and \((\text{Ln},\text{A})_2\text{Co}_4\text{O}_{4+\delta}\) (\(\text{Ln} = \text{La–Nd}\)) existing at moderately reduced oxygen pressures (see Refs \[179–184\] and references cited therein). Information on the long-term performance of such materials under SOFC cathodic conditions is, however, scarce. In the well-studied \(\text{Ln}_{1–x}\text{A}_x\text{CoO}_3–\delta\) systems, the maximum total conductivity at 800–1300 K is observed for \(\text{Ln} = \text{La–Sm}, \text{A} = \text{Sr and } x = 0.25–0.50\), shifting towards a lower \(x\) on heating; the highest level of the oxygen ionic transport corresponds to \(x = 0.65–0.70\) and \(\text{Ln} = \text{La}\). The level of ionic conduction in cubic \((\text{Sr,La})\text{CoO}_3–\delta\) is not exceptional, but lies close to the maximum known for the oxide mixed conductors where a higher oxygen permeability was only reported for \(\text{Bi}_2\text{O}_3\)-containing composites and for perovskite-like phases derived from \(\text{A(Co,Fe)O}_{3–\delta}\) (\(\text{A} = \text{Sr, Ba}\)). The roles of \(\text{A}^{2+}\) cation size and its matching to \(\text{Ln}^{3+}\) radius in these complex systems, where long- and short-range vacancy ordering in the highly oxygen-deficient lattices is often observed even at elevated temperatures, are still disputed. In addition to experimental limitations associated with the partial conductivity measurements when the ion transference numbers are as low as \(10^{-7}–10^{-5}\); the discrepancies in the available published data may partly originate from local ordering, cation demixing under nonequilibrium conditions, and phase separation in the intermediate-temperature range \[4, 185–188\]. Analogously to ferrite-based systems, these phenomena are all affected by the
cobaltites thermodynamic properties correlating with the tolerance factors and A-site cation radii, and also by the material’s microstructure. As a consequence, whilst the positive impact of Ba\(^{2+}\) doping on oxygen reduction kinetics was established by numerous research groups [24, 184, 189–192], data on the ionic transport in (Ba,Sr) (Co,Fe)O\(_3\) perovskites are quite contradictory (see Refs. [193–196] and references therein). On the other hand, an extensive Ba\(^{2+}\) substitution for Sr\(^{2+}\) in the electrode and membrane materials may lead to a fast degradation due to reactions with CO\(_2\) and water vapor present in the air [197, 198].

At oxygen pressures close to atmospheric, perovskite-type LaNiO\(_3\) is only stable below 1130–1250 K; further heating leads to the decomposition into K\(_2\)NiF\(_4\)-type La\(_2\)NiO\(_4\) and NiO via the separation of Ruddlesden–Popper-type La\(_4\)Ni\(_3\)O\(_{10}\) and La\(_3\)Ni\(_2\)O\(_7\) phases at intermediate stages [152, 199, 200]. As for LaNiO\(_3\), these layered compounds display attractive electrochemical and transport properties, but suffer from an insufficient phase stability in the range of temperatures and oxygen chemical potentials necessary for practical applications [199–203]. Decreasing the Ln\(^{3+}\) cation radius and acceptor-type doping both have a negative influence on the stability of the nickelate. The highest stability in ternary Ln-M-O (Ln = La, Pr, Nd; M = Ni, Cu) systems is observed for the K\(_2\)NiF\(_4\)-type compounds, which attract significant interest due to their moderate thermal and chemical expansion, in combination with a relatively high ionic conductivity. The total conductivity of the K\(_2\)NiF\(_4\)-type nickelates remains predominantly p-type electronic over the entire \(P_{O_2}\) range where these phases exist; the hole transport is lower than that in the perovskite analogues, but still sufficient for practical applications (see Figures 9.11 and 9.13). A moderate A\(^{2+}\) doping leads usually to a higher electronic conductivity and a lower oxygen content in Ln\(_2\)NiO\(_4\), with a negative impact on the oxygen diffusivity which is substantially determined by the interstitial anion migration [28, 206–210]. On the other hand, although the substitution of nickel with higher-valence cations raises the interstitials’ concentration, an increase in the transport is only observed at temperatures above 1100 K. Within the operating temperature range of SOFCs and ceramic membranes, maximum ionic conduction in the Ln\(_2\)NiO\(_4\)-based systems is thus characteristic of the compositions with a modest dopant content, particularly for the parent nickelate phases. The corresponding values of the ionic conductivity and oxygen permeability are 4 to 12-fold lower if compared to highly oxygen-deficient SrCo(Fe)O\(_3\) and Sr(La)CoO\(_3\) perovskites, but are quite similar to those in (La,Sr)FeO\(_3\). Again, the number of high-conductivity cuprates that are stable under SOFC cathodic conditions is not very large, including primarily the K\(_2\)NiF\(_4\)-type (Ln,A)\(_2\) CuO\(_4\), \((Ln = La–Sm; Ln = Sr, Ba)\) and various derivatives of layered LnA\(_2\)Cu\(_3\)O\(_7\) formed in the systems with Y\(^{3+}\) and smallest lanthanide cations. The total conductivity of La\(_2\)CuO\(_4\), which exhibits a small oxygen excess in air, has a pseudometalllic character and is considerably lower than that of lanthanum nickelate (see Figure 9.11); moderate acceptor-type doping enhances the p-type electronic transport, whereas decreasing the Ln\(^{3+}\) size has an opposite effect. The oxygen diffusion and surface exchange in all cuprates are rather slow, and tend to decrease when the Ln\(^{3+}\) radius decreases [36, 204, 220–225]. In the case of La\(_{2–x}\)Sr\(_x\)CuO\(_{4\pm\delta}\), the ion diffusivity
becomes slightly higher on modest Sr doping ($x < 0.1$) and drops with further additions. The substitution of copper with higher-valence cations often has positive effects on the ionic transport, thus indicating the relevance of both vacancy and interstitial migration mechanisms. It should be noted that increasing the oxygen...
content in another well-known cuprate, YBa$_2$Cu$_3$O$_{7-\delta}$, also results in a higher oxygen permeability and ionic conductivity [213].

Finally, it should be noted that numerous perovskite-related materials with relatively low oxygen ionic conductivity at 700–1200 K have been excluded from consideration in this brief survey, but may have potential electrochemical applications in fuel cell anodes, current collectors, sensors, and catalytic reactors. Further information on these applications is available elsewhere [1–4, 11, 159, 217–219].

9.9 La$_2$Mo$_2$O$_9$-Based Electrolytes

Another group of oxygen ionic conductors (the so-called LAMOX series) is based on the high-temperature polymorph of lanthanum molybdate, β-La$_2$Mo$_2$O$_9$, having a cubic lattice which is isostructural with β-SnWO$_4$ [13, 16, 65, 81, 220–225]. The fast anion migration in β-La$_2$Mo$_2$O$_9$ was explained by the lone-pair substitution concept [81, 220, 221] by which lone electron pairs of cations could stabilize oxygen vacancies. In particular, the outer electrons of Sn$^{2+}$ in β-SnWO$_4$ project into a vacant oxygen site, whereas the La$^{3+}$ cations have no lone-pair electrons and half of the sites occupied by lone pairs in β-SnWO$_4$ are vacant in lanthanum molybdate. Whatever the microscopic mechanisms of anion diffusion, the partial substitution of La$^{3+}$ with Bi$^{3+}$ and smaller rare-earth cations (Gd, Dy, Y) and/or the incorporation of V$^{5+}$ or W$^{6+}$ in the molybdenum sublattice can suppress the β→α transition, which normally occurs at approximately 853 K and results from long-range oxygen vacancy ordering. Examples of the cubic solid solutions with highest conductivity and stability in these systems are La$_2$–$_x$LnxMo$_2$–$_y$W$_y$O$_{9-\delta}$ (Ln = Y, Gd; x = 0.1–0.3; y = 0.3–0.6), La$_{1.7}$Bi$_{0.3}$Mo$_2$O$_{9-\delta}$, and La$_2$Mo$_{1.95}$V$_{0.05}$O$_{9-\delta}$. Figures 9.5–9.7 and 9.13 compare the transport properties of La$_2$Mo$_2$O$_9$-based materials and other solid electrolytes. The disadvantages of LAMOX include a relatively high electronic contribution to the total conductivity under ambient conditions, degradation in moderately reducing atmospheres, high TECs, and reactivity with electrode materials [65, 222, 225–228]. These problems are less prominent if compared to the Bi$_2$O$_3$-based compositions, but the ionic conductivity of LAMOX is also lower. The electronic conduction in LAMOX, mainly n-type, is comparable to the p-type transport in LSGM; the electron transfer numbers are, however, considerably higher for the former family and further increase with temperature and with reducing $P_{O_2}$.

9.10 Solid Electrolytes with Apatite Structure

Due to non-negligible levels of the oxygen ionic and/or protonic conduction in numerous crystalline and amorphous silicates and germanates free of alkaline metal cations [229–244], the electrochemical and transport phenomena in these materials has become a focus of research interest since the 1930s. However, extensive studies of
the apatite-type phases \((\text{Ln}, \text{A})_{10-\chi} \text{M}_\chi \text{O}_{26+\chi}\), where \(\text{M} = \text{Si} \) or \(\text{Ge}\), and their derivatives began only during the 1990s [204, 205, 245–257]. The germanate apatites exhibit better ion transport properties compared to their Si-containing analogues, but seem unlikely to find practical applications due to high volatilization, a tendency to glass formation, and the high costs of \(\text{GeO}_2\). These disadvantages are less pronounced for the apatite-type silicates, which may be of practical interest owing to low cost and substantial ionic conductivity comparable to that of stabilized zirconia (Figures 9.5, 9.13 and 9.14). The oxygen ionic transport in \(\text{Ln}_{10} \text{Si}_6 \text{O}_{27}\) (\(\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}\)) increases with increasing radius of \(\text{Ln}^{3+}\) cations, being maximum for the La-containing phase [245, 246]. Irrespective of the wide scatter among experimental data associated with relatively poor sintering and different processing routes, the highest ionic conductivity is observed for the apatite phases containing more than 26 oxygen ions per unit formula. This tendency suggests a significant role for the interstitial migration mechanism, in agreement with computer simulations [258, 259]. Other important factors which influence oxygen diffusion include the deficiency of Ln-sublattice and Si-site doping, which affect the unit cell volume and may promote the formation of ionic charge carriers via the Frenkel disorder mechanism. Decreasing the oxygen concentration below a stoichiometric value leads to the vacancy mechanism becoming dominant, and there is also a considerable drop in ionic conductivity. Similar effects are typical for transition metal-containing apatites at low oxygen pressures (see

Figure 9.14 Total conductivity of several apatite-type phases in air [204, 205, 247–249]. Data for 8 mol% yttria-stabilized zirconia [36], \(\text{Ce}_{0.5} \text{Gd}_{0.5} \text{O}_{2-\chi}\) [40] and \((\text{La}_{0.9} \text{Sr}_{0.1})_{0.98} \text{Ga}_{0.8} \text{Mg}_{0.2} \text{O}_{3-\chi}\) [66] electrolytes are shown for comparison.
Figure 9.13), although degradation in reducing atmospheres is also contributed by the silicon oxide volatilization and local surface decomposition [253, 254]. The latter factor, and the fast surface diffusion of silica blocking interfacial reactions, result in a poor electrochemical performance of porous electrodes in contact with the silicate solid electrolytes [256, 260].

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