

# Electrolytes for solid oxide fuel cells

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## Abstract

The high operating temperature of solid oxide fuel cells (SOFCs), as compared to polymer electrolyte membrane fuel cells (PEMFCs), improves tolerance to impurities in the fuel, but also creates challenges in the development of suitable materials for the various fuel cell components. In response to these challenges, intermediate temperature solid oxide fuel cells (IT-SOFCs) are being developed to reduce high-temperature material requirements, which will extend useful lifetime, improve durability and reduce cost, while maintaining good fuel flexibility. A major challenge in reducing the operating temperature of SOFCs is the development of solid electrolyte materials with sufficient conductivity to maintain acceptably low ohmic losses during operation. In this paper, solid electrolytes being developed for solid oxide fuel cells, including zirconia-, ceria- and lanthanum gallate-based materials, are reviewed and compared. The focus is on the conductivity, but other issues, such as compatibility with electrode materials, are also discussed.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) can provide efficient and clean energy conversion in a variety of applications ranging from small auxiliary power units to large scale power plants [1–6]. The major advantage of SOFCs over polymer electrolyte membrane fuel cells (PEMFCs) is their superior tolerance to impurities in the fuel [3–9], which allows for their operation using lower quality, thus less costly and more widely available, fuel. The superior fuel flexibility is due primarily to the higher operating temperature, which increases reaction rates in the fuel, but also increases the rates of undesired reactions and creates thermal stresses during thermal cycling. Thus, the development and fabrication of materials to meet these requirements is a major challenge for the implementation of cost effective SOFCs [10–16]. While there are materials challenges in all fuel cell components, the focus of this paper is on materials for use as the solid electrolyte.

The key requirement for the solid electrolyte is that it has good ionic conduction to minimize cell impedance, but also has little or no electronic conduction to minimize leakage currents, so control of the concentration and mobility of ionic and electronic

charge carriers is critical. Various approaches for controlling these transport properties through structure and composition of the electrolyte material have been recently reviewed [17]. The electrolyte material must also be chemically and mechanically (*e.g.* thermal expansion) compatible with other fuel cell components. This compatibility extends to fabrication processes, since some processes may need to be performed with multiple components present, which limit the range of parameters (*e.g.* temperature or pressure) to those acceptable for all components. A major impetus for the development of new electrolyte materials is in reducing the operating temperature to 500–800 °C for intermediate temperature solid oxide fuel cells (IT-SOFCs). Such an intermediate operating temperature will relax some of the requirements related to high-temperatures operation, while maintaining a sufficiently high temperature to retain good fuel flexibility. The focus of this paper is on comparison of the transport properties of electrolyte materials for solid oxide fuel cells, but other issues, such as compatibility with electrode materials, will also be discussed.

## 2. Stabilized zirconia

The most common solid electrolyte material used in solid oxide fuel cells is yttria-stabilized zirconia (YSZ). Yttria is

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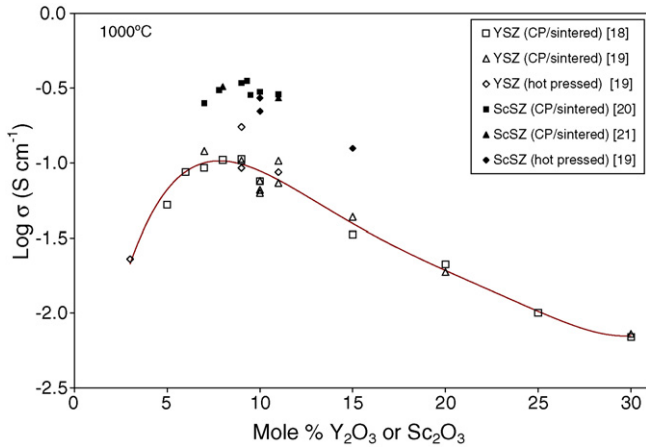


Fig. 1. Conductivity of yttria and scandia stabilized zirconia in air at 1000 °C [18–21].

added to stabilize the conductive cubic fluorite phase, as well as to increase the concentration of oxygen vacancies, and thus increase the ionic conductivity. Fig. 1 [18–21] shows that the conductivity of YSZ increases for yttria additions of up to about 8 mole% and then decreases for higher yttria contents. The decrease at higher dopant contents is due to association of point defects, which leads to a reduction in defect mobility and thus conductivity. A promising, although though less widely used, dopant for zirconia is scandia, which, as shown in Fig. 1, has a higher conductivity than YSZ. The temperature dependences of the conductivities of YSZ and scandia-stabilized zirconia (ScSZ) are shown in Fig. 2 [18,19,22–30] and Fig. 3 [20,27,31–37], respectively. To aid in comparison of the two dopants an outline of the range of conductivities for YSZ from Fig. 2 (gray lines) is included in Fig. 3 (solid black lines) and shows that the conductivity of ScSZ is higher than that of YSZ in the temperatures of interest for SOFCs.

The higher conductivity of ScSZ is attributed to the smaller mismatch in size between  $Zr^{4+}$  and  $Sc^{3+}$ , as compared to that between  $Zr^{4+}$  and  $Y^{3+}$ , leading to a smaller energy for defect association, which increases mobility and thus conductivity [21,38–40]. The activation energy for conduction in ScSZ tends to increase with decreasing temperature, such that the conduc-

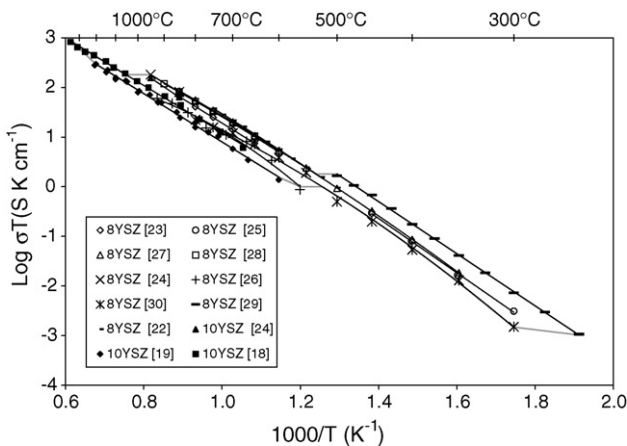


Fig. 2. Conductivity of yttria-stabilized zirconia in air [18,19,22–30].

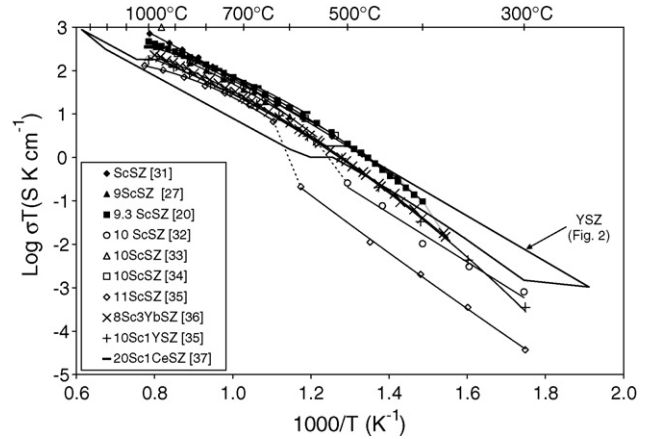


Fig. 3. Conductivity of scandia-stabilized zirconia in air [20,27,31–37]. Range of YSZ conductivities from Fig. 2.

tivity of ScSZ is similar or even lower than that of YSZ below 500 °C. This is consistent with the observed increase in the migration energy of co-doped zirconia at 380–560 °C as yttria is replaced with scandia [41]. Another issue with ScSZ is that for higher scandia contents (*e.g.* 10–12 mole%), the cubic phase transforms to a rhombohedral phase at lower temperatures. The rhombohedral phase has a lower conductivity [20,31,34,36,42], so there is a decrease in conductivity as indicated by broken lines in two of the curves in Fig. 3. The phase change can be avoided by limiting the scandia content to 8 mole% [20,31] or by co-doping with other oxides, such as those of bismuth [32] or ytterbium [36].

During operation, aging of both YSZ and ScSZ can lead to decreases in conductivity [21,31,43]. Aging in ScSZ has been attributed to the disappearance of a distorted fluorite phase [20],  $t'$ , which has a higher conductivity than the cubic phase [44]. The  $t'$  phase transforms to a tetragonal phase, the amount of which has been shown, with X-ray diffraction [43] and Raman spectroscopy [21], to increase during aging. The magnitude of the decrease in conductivity during aging is larger for YSZ than for ScSZ, such that, in one study [21], after 5000 h, the conductivity of ScSZ, which was initially about twice that of YSZ, was the same as that of YSZ. This suggests that the presence, or larger amount, of the  $t'$  phase may contribute to the higher conductivity of ScSZ relative to that of YSZ. The aging behavior in ScSZ can be improved by increasing the scandia content [21] or by co-doping with indium oxide [45].

Grain boundary conduction is also important in YSZ [27,29,46], and since the grain boundary contribution increases with decreasing temperature, it is particularly important for IT-SOFCs. For example, for YSZ materials produced by several different methods, the fraction of the total resistance due to grain boundary resistance is negligible at 900 °C, but increases to ~0–40% at 700 °C, and then further to ~10–65% at 500 °C [27]. Grain boundary transport becomes especially important for nano-structured materials due to their high proportion of grain boundary area. For example, processing YSZ to produce grain sizes less than 10 nm resulted in conductivities which were 50% higher than those of materials with larger grain sizes [23]. Thus,

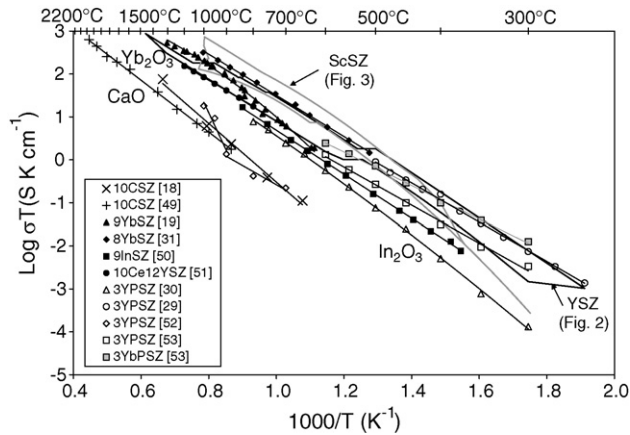


Fig. 4. Conductivity of fully- and partially-stabilized zirconia in air [18,19,29–31,49–53]. Ranges of YSZ and ScSZ conductivities from Figs. 2 and 3, respectively.

the benefits of small particle sizes in reducing processing temperatures must be balanced against increased grain boundary resistance, particularly at lower operating temperatures.

The mechanical properties of ScSZ are similar [31] or better [47] than those of YSZ. Although the strength of an electrolyte in a SOFC is of secondary importance as compared to electrochemical properties, it is important for the production of reliable long-life SOFCs. The strength and toughness can be improved with the addition of oxide dispersants, such as alumina [48] or niobates [30]. However, such additions typically reduce conductivity, so the benefits in improved strength must be balanced with any resulting increases in cell impedance.

The conductivities of zirconia stabilized with other dopants are shown in Fig. 4 [18,19,29–31,49–53]. For comparison, the ranges of conductivities for YSZ and ScSZ from Figs. 2 and 3 are represented with black and gray lines, respectively. The dopant resulting in the highest conductivity among those shown is ytterbium, which has conductivities comparable to ScSZ and YSZ. Also shown are some examples of partially stabilized zirconia (3% yttria or 3% ytterbia), some of which have conductivities that are comparable to fully stabilized zirconia. The advantage of partially stabilized zirconia is the improved mechanical properties due to toughening from the transformation of the tetragonal particles to the monoclinic phase.

Co-doping can also be used to improve the electrochemical properties. For example, the addition of calcium to YSZ can lead to a reduction in the activation energy for conduction [54]. Alumina, which as mentioned above can be used to improve mechanical properties, has been shown to both increase [48,55,56] and decrease [48,57] the conductivity of YSZ, depending on the doping level. The beneficial effects of alumina have been attributed to the alumina scavenging silica [55], while the detrimental effects have been attributed to increasing defect association [57]. Niobium additions have also been shown to increase defect association [58,59], while ceria additions have been shown to extend the yttria content at which a decrease in conductivity occurs, indicating a decrease in the amount of defect association [51]. The addition of bismuth oxide to ScSZ has been shown to increase the conductivity of ScSZ [32].

There are several potential compatibility issues for solid electrolytes in SOFCs, since the solid electrolyte is in contact with both electrodes, the sealant and, in some cases, the interconnect. Among these, for YSZ, chemical reaction with the cathode material is generally of greatest concern. The most common SOFC electrolyte–cathode combination is a YSZ electrolyte with a  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSM) cathode. Depending on the strontium content in the LSM, the YSZ and LSM can react to form the pyrochlore  $\text{La}_2\text{Zr}_2\text{O}_7$  ( $x \leq 0.2$ ) [60–80], the perovskite  $\text{SrZrO}_3$  ( $0.3 \leq x \leq 0.4$ ) [77–81], or both  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{SrZrO}_3$  ( $x \geq 0.5$ ) [77–83]. The stability of both phases at intermediate compositions is in agreement with thermodynamic calculations [84,85]. Reaction between YSZ and LSM is typically only a problem during processing at high temperatures, but  $\text{La}_2\text{Zr}_2\text{O}_7$  has been observed to form during cell operation at 900 °C [86]. The reaction layer, whether formed during processing or cell operation, is detrimental to fuel cell performance [74], because the conductivities of the reaction products are lower than those of the electrolyte and electrode materials [67,68,86–88]. The generally accepted reaction mechanism for the reaction between YSZ and LSM [60,61,65,88–90] is that preferential diffusion of manganese from LSM into the YSZ leads to an increase in the concentration of  $\text{La}_2\text{O}_3$  in the LSM. Once the concentration exceeds the solubility limit in LSM,  $\text{La}_2\text{O}_3$  reacts with YSZ to form  $\text{La}_2\text{Zr}_2\text{O}_7$ . Thus, one approach to inhibiting this reaction is to start with a higher manganese content, which will extend the time required to decrease the manganese content to the critical value. The use of A-site deficient (*i.e.* lanthanum deficient) LSM has been shown to suppress  $\text{La}_2\text{Zr}_2\text{O}_7$  formation between YSZ electrolytes and LSM electrodes [64,65,74,76,77,88,91–96] and in YSZ–LSM composites [97–99]. The approach is supported by thermodynamic calculations indicating that  $\text{La}_2\text{Zr}_2\text{O}_7$  is not in equilibrium with lanthanum-deficient LSM [84,100,101]. The behavior of other manganites is similar to that of LSM [76,83,89,102–108], although some of these materials, such as calcium-doped lanthanum manganite [76,83,89], strontium-doped gadolinium manganate [83,105] and strontium-doped yttrium manganate [106], have a weaker tendency for pyrochlore formation.

The addition of cobalt to LSM increases reactivity [107,108], a tendency that is continued in another SOFC cathode material,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  (LSC). Like LSM, LSC reacts to form  $\text{La}_2\text{Zr}_2\text{O}_7$  and/or  $\text{SrZrO}_3$ , depending on strontium content [69–72,109–114]. LSC reacts more strongly than LSM with YSZ, and  $\text{SrZrO}_3$  [115,116], as well as increases in cell resistance [117,118], have been observed during fuel cell operation. The reaction between LSC and YSZ can also affect fabrication by inhibiting sintering [119]. Other lanthanide cobaltites behave similarly [69–72,107], but some less strongly [120] as compared to LSC. Another cathode material  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  (LSF) does not typically react with YSZ [69–72,113,121,122]. As might be expected,  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$  (LSCF), and cobaltite ferrites of other lanthanide and rare-earth elements, react similarly to LSC, but to a lesser extent [69–72,107,123–126], presumably due to the lower cobalt oxide activity. Finally, another SOFC cathode material,  $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$  (LNF), reacts with YSZ to form  $\text{La}_2\text{Zr}_2\text{O}_7$  [70,127–130].

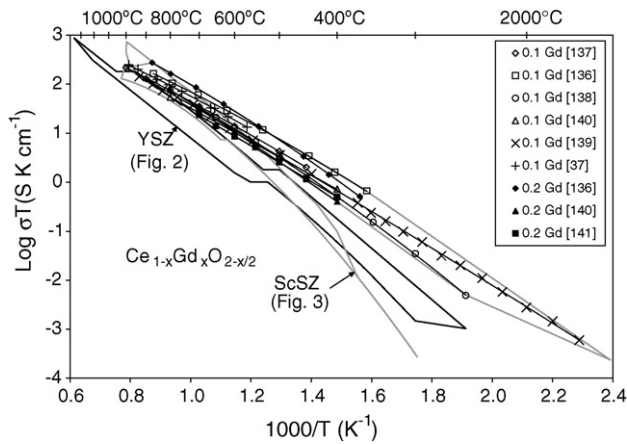


Fig. 5. Conductivity of  $Ce_{1-x}Gd_xO_{2-x/2}$  in air [37,136–141]. Ranges of YSZ and ScSZ conductivities from Figs. 2 and 3, respectively.

### 3. Doped ceria

Like zirconia, ceria forms the fluorite structure and is a common electrolyte material for SOFCs. As compared to zirconia, ceria has a higher conductivity, particularly at low temperatures, and a lower polarization resistance [131]. The primary disadvantage of ceria is electronic conduction at low oxygen partial pressures [37,38,131,132]. Like zirconia, ceria is doped to increase conductivity, and, also like zirconia, the highest conductivity occurs for ions with the lowest size mismatch, which for cerium is gadolinium and samarium [133–135]. The conductivity of the most widely used ceria-based electrolyte,  $Ce_{1-x}Gd_xO_2$  (CGO) [37,136–141], is compared with those of YSZ (from Fig. 2) and ScSZ (from Fig. 3) in Fig. 5. Below 600 °C, the conductivities of CGO are consistently higher than those of YSZ or ScSZ. Like zirconia, the conductivity increases with increasing dopant concentration to a maximum (e.g. 0.20–0.25 Gd [141]) and then decreases. There is a report [142] of very high conductivity for 0.6 Gd, but the sample in that study was deposited as low temperature, and not subsequently treated at a higher temperature, so the stability of the structure is not certain. The range of conductivities in Fig. 5 for  $Ce_{0.9}Gd_{0.1}O_2$  and  $Ce_{0.8}Gd_{0.2}O_2$  are similar, and  $Ce_{0.9}Gd_{0.1}O_2$  has been shown to have better stability than  $Ce_{0.8}Gd_{0.2}O_2$  at low oxygen partial pressure [136]. Performance of the electrolyte at low oxygen partial pressures is important [131,135,137,143,144], so both compositions are used.

In addition to gadolinium and samarium [26,135,145–154], other dopants for ceria include lanthanum [155–157], yttrium [38,135,158–160], ytterbium [161] and neodymium [153,162,163]. Fig. 6 [26,135,145–151,155,156,160,161] shows that the conductivities of  $Ce_{1-x}Sm_xO_2$  (CSO) are similar to, but in the lower range of, the conductivities of CGO (represented by the gray line). The conductivities of ceria with the other dopants are typically lower than those of CGO or CSO. As with zirconia, co-doping can be used for improving properties. For example, the addition of praseodymium (replaces cerium) and samarium (replaces gadolinium) increases the conductivity of CGO [164].  $Ce_{1-x}Y_xO_2$  (CYO) is particularly amenable to co-doping as benefits of co-doping of yttria with samarium [147], cal-

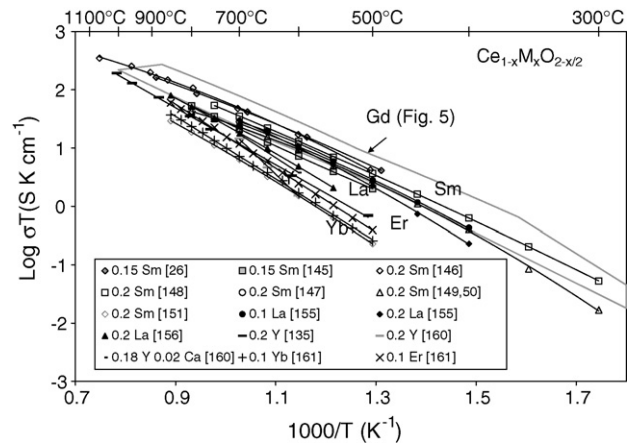


Fig. 6. Conductivity of  $Ce_{1-x}M_xO_{2-x/2}$  in air [26,135,145–151,155,156,160,161]. Range of CGO conductivities from Fig. 5.

cium [160], lithium + cesium [160] and dysprosium [165] have been reported. Dopants can also indirectly improve properties through their effects on processing, such as improving sinterability [166,167].

As with zirconia, grain boundary conduction is important [46,168]. For example, reduction of grain size has been shown to lead to lower total conductivity of CSO [148] and higher hole conductivity in CGO [163], both of which are detrimental to performance. In addition, small grained materials are more susceptible to reduction in low oxygen partial pressures [37]. Thus, any benefits of reduced grain sizes in processing must be balanced with possible detrimental effects on materials properties.

The importance of interfaces on transport properties is also evident in a nanostructured material consisting of alternating layers of ceria and zirconia, which has a conductivity higher than those of either of the two constituents indicating that the conduction is dominated by the interfacial layers [169]. Although the mechanism is not completely understood, the high conductivity was attributed to strain enhancing ionic mobility. As mentioned above, ceria additions can be used as a co-dopant with yttria. In addition, zirconia–ceria solutions can be used as SOFC anode materials in which the electronic conduction due to reduction of  $Ce^{4+}$  is desirable [170].

Although the stability of ceria in low oxygen partial pressures is inferior to that of zirconia, the chemical stability of ceria with cathode materials is superior to that of zirconia. CGO has been shown to be stable with a wide variety of electrodes, including all the common cathode materials discussed above, LSM, LSC, LSF, LSCF, LNF [69–72,123,171,172]. Because of this excellent stability with cathode materials, ceria-based interlayers are applied between YSZ and the cathode to prevent reaction [114,117,121,173–179]. CGO is most commonly used, but CSO or CYO are also effective. One exception to the good stability of ceria is that an unidentified phase has been observed between bismuth-doped ceria and LSCF [180]. The good stability of CGO has led to its use in composites cathodes with LSM [181–183], which improves oxygen transport in the cathode. When used as an interlayer between YSZ and the cathode, the interface at which interaction occurs is the YSZ–ceria interface [70,72,117,121,178,184,185]. Since both phases form the same

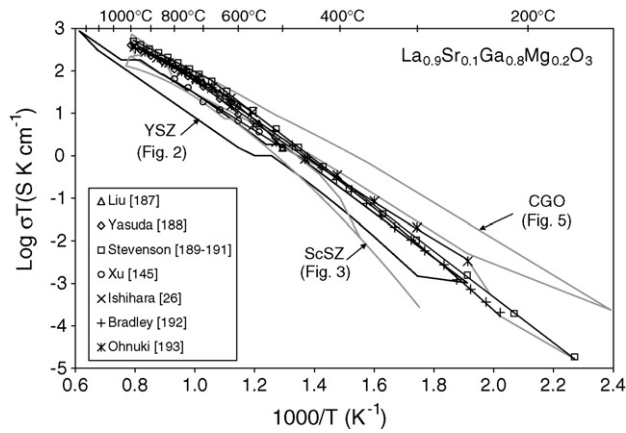


Fig. 7. Conductivity of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  in air [26,145,187–193]. Ranges of YSZ, ScSZ and CGO conductivities from Figs. 2, 3 and 5, respectively.

cubic fluorite structure, interdiffusion can occur and results in the formation of a region with low conductivity due to ordering of cations.

#### 4. Strontium/magnesium-doped lanthanum gallate

The perovskite,  $\text{LaGaO}_3$ , can be doped with strontium and magnesium,  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$  (LSGM), to produce a material with good low-temperature oxygen-ion conductivity [186]. The conductivities of one composition,  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ , from several sources are shown, along with the ranges of conductivities of YSZ (from Fig. 2), ScSZ (from Fig. 3) and CGO (from Fig. 5), in Fig. 7 [26,145,187–193]. The conductivity of LSGM is higher than those of YSZ and ScSZ and similar to or lower than that of CGO. However, LSGM does not have an easily reducible ion, like  $\text{Ce}^{4+}$ , and thus is superior to CGO for use in low oxygen partial pressures. The conductivity of LSGM depends on dopant concentration and comparison of 27 different compositions indicated the maximum conductivity was for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  [187]. Fig. 8 [187,189–191,194–200] compares the conductivities of several LSGM compositions. Most of these conductivities (including the maximum values reports by Liu et al. [187]) are

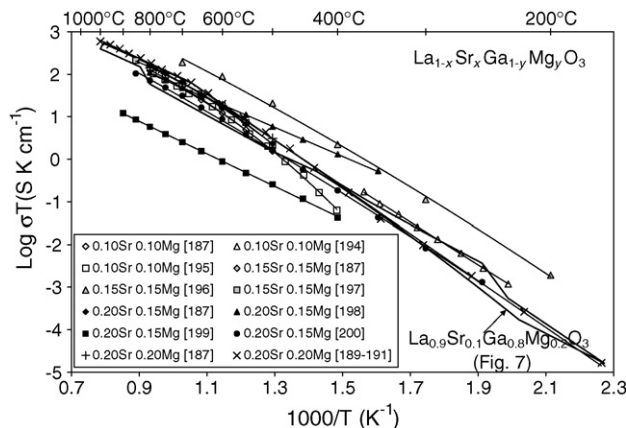


Fig. 8. Conductivity of  $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$  in air [187,189–191,194–200]. Range of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  conductivities from Fig. 7.

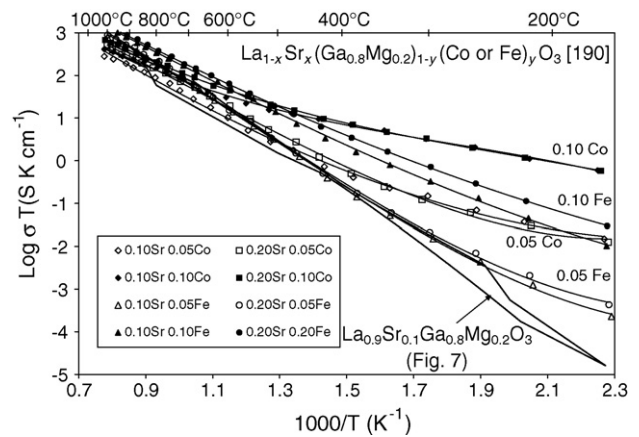


Fig. 9. Conductivity of  $\text{La}_{1-x}\text{Sr}_x(\text{Ga}_{0.8}\text{Mg}_{0.2})_{1-y}(\text{Co or Fe})_y\text{O}_3$  in air [190].

in the same range as those for  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  in Fig. 7, but there are a few values above and below this range. For comparison with other materials in subsequent figures, the range from Fig. 7 will be used to represent LSGM, since most values fall in this range.

One of the approaches to increasing the conductivity of LSGM is to add transition metal dopants, such as cobalt [26,190,199,201,202] and iron [26,190,203]. Fig. 9 [190] shows that both dopants increase the conductivity, especially at low temperatures, with cobalt being more effective than iron. However, both dopants also decrease the hole conductivity, which is detrimental to fuel cell performance. Fig. 10 [199,201] shows that the hole contribution in cobalt-doped LSGM increases with doping, particularly at higher temperatures, but the marginal improvement decreases with increasing dopant level. For example, at 700–800 °C, when the cobalt concentration is increased from 0.05 to 0.10, there is a significant increase in hole conductivity with very little change in ionic conductivity. Thus, the optimal addition of dopant depends on a balance between reducing impedance by increasing dopant level and reducing leakage current by decreasing dopant level. For example, while 0.4 Fe has the largest oxygen permeation rate [204], because of the increase in hole conductivity with increasing iron content, 0.2 Fe has the largest improvement in power density, [205]. Other

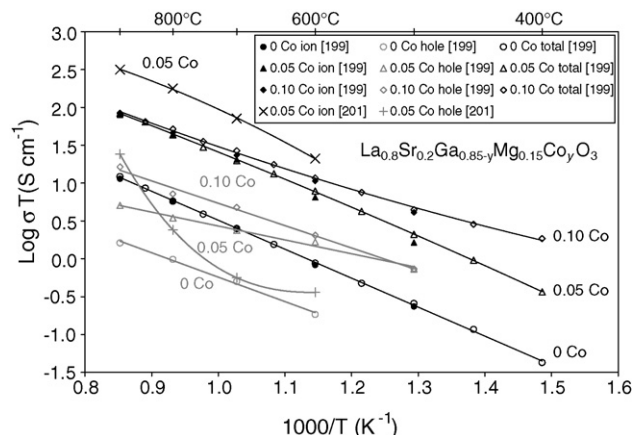


Fig. 10. Conductivity of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85-y}\text{Mg}_{0.15}\text{Co}_y\text{O}_3$  in air [199,201].

parameters may need to be adjusted when doping the LSGM electrolyte. For example, the electrolyte thickness for optimal efficiency increases with increasing cobalt dopant level [206]. By balancing these parameters, efficient fuel cells with cobalt-doped LSGM electrolyte have been produced [207,208]. Nickel has also been used as a dopant for LSGM [209,210] and behaves similarly to cobalt. A similar approach of doping with transition metals has been used to improve the performance of cubic fluorite based electrolytes. For example, cobalt has been added to CGO [136,139], CSO [211] and YSZ [212], and iron has been added to CGO [138] to improve processing and conductivity. Additions of iron and cobalt introduced through interaction with the electrode materials have been shown to enhance sintering of CGO [126].

The reaction of LSGM with SOFC cathodes is different from that of zirconia or ceria, because most of the common cathode materials form the perovskite structure. Thus, rather than forming a separate phase, the interaction typically occurs through interdiffusion. For example, when used with an LSM cathode, some diffusion of manganese into LSGM occurs [213]. However, the most common diffusing species is cobalt [213–221], which is the primary diffusing species even if the cobalt is not the major species in the cathode (*e.g.* (Ln,Sr)Mn<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> [215–217]). Interdiffusion also occurs between LSGM and LSCF [217,222,223] and lanthanum nickelate [224] cathodes. Since small amounts of cobalt, iron and nickel can be beneficial to electrolyte performance, and no highly resistive layer is formed at the electrolyte–cathode interface, interdiffusion is not necessarily detrimental to fuel cell performance. Nonetheless, excessive interdiffusion would eventually degrade the properties of both components, so a ceria layer has been applied to prevent cobalt diffusion from LSC into LSGM [225]. However, a resistive phase can form between CGO and LSGM and degrade fuel cell performance [226,227].

The most common anode material is a nickel-YSZ cermet, so interaction anode–electrolyte interaction is not a problem with YSZ electrolytes. However, for a LSGM electrolyte, a resistive phase can form between the LSGM and a Ni-containing anode [186]. Alternative anode materials are being developed, including perovskite oxides, which could, as in reaction with perovskite cathode, result in interdiffusion rather than formation of a new phase. For example, interdiffusion between LSGM and a (La,Sr)(Cr,Mn)O<sub>3</sub> anode material during processing can lead to resistive phase. Such degradation can be avoided by limiting the sintering time and temperature [228]. However, restrictions on the processing conditions can be a problem for LSGM, because formation of a single-phase perovskite structure can be difficult, so one of the challenges for LSGM electrolytes is the development of cost-effective processes for fabricating the desired single-phase microstructures.

## 5. Other electrolytes

The existence of two differently-sized cation sites in the perovskite structure expands the range of possible dopants. For example, although strontium and magnesium are the most common dopants for lanthanum gallate, the lanthanum site can also

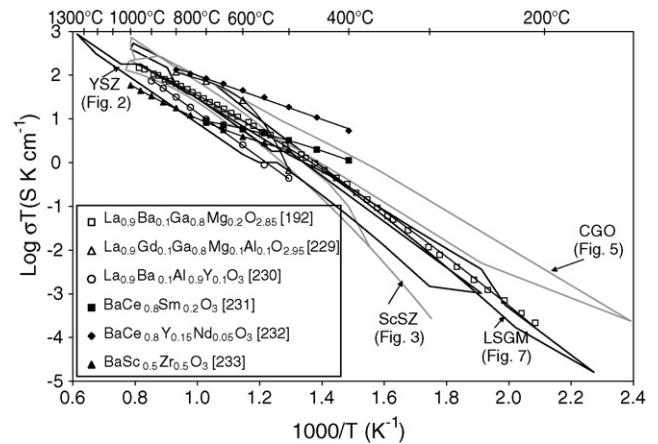


Fig. 11. Conductivity of perovskite oxides in air [192,229–233]. Ranges of YSZ, ScSZ, CGO and LSGM conductivities from Figs. 2, 3, 5 and 7, respectively.

be doped with barium [191,192] or gadolinium [229]. Doping with barium, rather than strontium, affects the octahedral tilt angle, which reduces the activation energy, such that at high temperatures the conductivity of La<sub>0.9</sub>Ba<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>2.85</sub> is lower than that of La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>2.85</sub>, but the reverse is the case at lower temperatures [191,192]. The conductivity of La<sub>0.9</sub>Ba<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>2.85</sub> and other perovskite materials are shown in Fig. 11 [192,229–233]. Other lanthanum-based perovskites, including LaScO<sub>3</sub>-, LaInO<sub>3</sub>- and LaYO<sub>3</sub>-based materials are oxygen ion conductors [38] and thus potential electrolyte materials. Due to the lower cost of aluminum relative to gallium, LaAlO<sub>3</sub>-based materials are particularly attractive as electrolytes for solid oxide fuel cells [230]. Although the stability of aluminates is very good, their conductivity is lower than other potential materials (*e.g.* La<sub>0.9</sub>Ba<sub>0.1</sub>Al<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub> in Fig. 11).

Proton-conducting or mixed-ion-conducting oxides have been investigated as electrolytes in fuel cells [234]. One of the advantages of such fuel cells is that, since hydrogen is transported through the electrolyte, the fuel is not diluted with water vapor. The most common proton-conducting oxide is BaCeO<sub>3</sub>, which has been doped with various oxides, including those of samarium [231], neodymium [232,235] and ytterbium [236], for use in SOFCs. Fig. 11 shows that the conductivity of neodymium–yttria co-doped barium cerate is particularly high. Other proton-conducting oxides for potential use in solid oxide fuel cells include BaSc<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>3</sub> [233], (La,Pr)<sub>0.9</sub>Ba<sub>1.1</sub>GaO<sub>3.95</sub> [237] and Nd<sub>0.9</sub>Ba<sub>1.1</sub>GaO<sub>3.95</sub> [237].

Bismuth oxide has high ionic conductivity, but decomposes at low oxygen partial pressures, which prevents it from being used in solid oxide fuel cells. One approach to overcoming this limitation is to combine doped bismuth oxide with a ceria-based electrolyte, such that the ceria is at the anode and the bismuth oxide is at the cathode [149,150,238]. If the thicknesses are selected appropriately, the bismuth oxide will remain above its decomposition oxygen partial pressure and the electronic conduction in the ceria will be blocked by the bismuth oxide. Bismuth oxide can also be doped to stabilize the conductive phase to lower oxygen partial pressures and temperatures. The conductivity of one such phase, Bi<sub>3</sub>Nb<sub>0.1</sub>Zr<sub>0.9</sub>O<sub>6.55</sub> [239] is

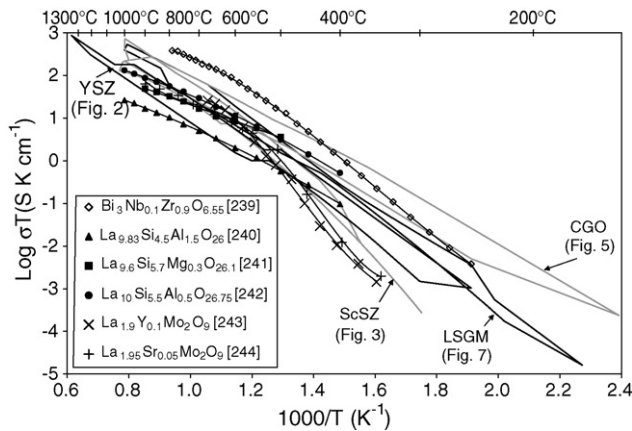


Fig. 12. Conductivity of various oxides in air [239–244]. Ranges of YSZ, ScSZ, CGO and LSGM conductivities from Figs. 2, 3, 5 and 7, respectively.

shown in Fig. 12. The phase is stable to lower temperatures than  $\delta$ - $\text{Bi}_2\text{O}_3$ , but the low oxygen partial pressure stability needs to be evaluated.

Also shown in Fig. 12 are three materials with the apatite structure based on doping  $\text{La}_{10}\text{Si}_6\text{O}_{27}$  with aluminum or magnesium. The conductivity of materials with this structure increases with increasing oxygen stoichiometry, which suggests an interstitial conduction mechanism [38]. The three examples in Fig. 12 [240–242] illustrate this trend as the conductivity increases as the oxygen coefficient increases from 26 to 26.1 to 26.75.

Another class of solid electrolytes are materials based on  $\text{La}_2\text{Mo}_2\text{O}_9$ . The two examples shown in Fig. 12 [243,244] have good conductivity at 600–700 °C, but the conductivity decreases dramatically with decreasing temperature. The possibility of electronic conduction at low oxygen partial pressures may also be a problem.

Another structure that has been investigated for potential electrolyte materials is the pyrochlore structure. The similarity of this structure with the cubic fluorite structure (*i.e.* essentially the same structure with one oxygen missing per unit cell) suggests that it may be a good oxygen ion conductor. However, the most highly conductive materials with the pyrochlore are titanates and thus exhibit electronic conduction. As mentioned above,  $\text{La}_2\text{Zr}_2\text{O}_7$  forms from the reaction of YSZ and several different electrodes and has a low conductivity relatively to YSZ. Nonetheless, electrolytes with the pyrochlore structure are being investigated for use in SOFCs [245,246].

## 6. Conclusions

The two most widely used alternatives to YSZ as electrolytes in IT SOFCs are doped ceria and doped lanthanum gallate. Ceria has the highest conductivity and the best stability with cathode materials, but suffers from stability in low oxygen partial pressures. LSGM has higher conductivity than YSZ, but is less stable with the anode and more difficult to prepare than YSZ. Fuel cell designs with layered structures can combine the advantages of the different materials, but simple structures are preferred to reduce cost and improve reliability. The required conductivity depends on the fuel cell design (*e.g.* electrolyte-supported *versus*

anode supported), and compatibility (chemical and mechanical) depends on the materials used for other components, so these factors, must be considered in the selection of the optimal electrolyte material for a particular application.

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