VARIOUS APPROACHES TO ENHANCE IONIC CONDUCTIVITY OF SELECTED OXIDE ELECTROLYTES

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ABSTRACT

The advantages of lowering the operation temperature of SOFCs have attracted great interest worldwide. One of the major barriers to decrease temperature is the ohmic loss of the electrolyte. Maximising the electrolyte ionic conductivity is of significant importance, especially in the absence of new electrolyte materials. The ionic conductivity of electrolytes can be influenced by many parameters. There is an enormous effort in the literature for the improvement of the electrolyte ionic conductivity. From practical point of view, this paper reviews various approaches to enhance the ionic conductivity for polycrystalline zirconia- and ceria-based electrolytes in light of composition, microstructure, and processing. Suggestions are given for future work.

INTRODUCTION

For reasons related to long term stability and cost, decreasing the operation temperature of solid oxide fuel cells (SOFCs) down to 500 - 700°C has attracted interest worldwide [1]. Decreasing temperature, however, requires increasing electrolyte ionic conductivity and enhancing electrode reaction activity. Maximising the electrolyte ionic conductivity is of significant importance, especially in the absence of new electrolyte materials. Understanding of various approaches that influence the ionic conductivity can help to optimise all the conditions to further improve the electrical properties of electrolytes.

There is an enormous effort in the literature for the improvement of electrolyte ionic conductivity. Zirconia-based electrolytes such as yttria-stabilized-ZrO₂ (YSZ) are the most popular materials employed as electrolyte in SOFCs because of their attractive ionic conductivity, stability in both oxidising and reducing environments and stability against electrode materials. However, their ionic conductivity is much lower than that of ceria-based electrolytes such as gadolinia-doped ceria (GDC) or lanthanum gallate based electrolytes such as La₀.₈Sr₀.₂Ga₀.₮Mg₀.₂O₃₋₅ (LSGM) at lower temperatures. Ceria-based electrolytes have been considered for lower temperature applications compared to the LSGM in terms of cost, processing, and stability. However, further enhancement of ionic conductivity and stability against reduction is still required for ceria-based electrolytes.

The electrical conductivity (σ) can be expressed as σ = nqμ, where n is the charge carrier concentration, q the charge, and μ the mobility of charge carrier. Thermodynamically and kinetically, the electrical conductivity in an oxide can be related to the temperature,
oxygen partial in the surrounding gas atmosphere, the type and concentration of dopants, and the microstructure [2-3]. The major sources of ionic carriers in oxides and their respective mobilities are summarized in figure 1, and the broken arrows indicate that large numbers of carriers generated via deviation from stoichiometry or doping may alter the carrier mobilities [2-3]. The ionic conductivity in zirconia- and ceria-based electrolytes have been discussed in many ways such as grain boundary, local structure, microdomain, grain size, composition, dopants, microstructure, impurity, and processing [4-8]. In this paper, we review the effects in terms of composition, microstructure, and processing on the electrical conductivity for polycrystalline zirconia- and ceria-based electrolytes. As we can see in the following discussion, these parameters are correlated to each other. Composition and processing conditions can change the properties of grain and grain boundary while grain and grain boundary conditions can affect the effectiveness of the dopants. Grain boundary properties can be also varied by grain size.

![Figure 1. The major sources of ionic carriers in oxides and their respective mobilities compiled from literatures.](image)

**ENHANCEMENT FROM COMPOSITION**

It is well known that ionic conductivity of electrolytes can be maximised from composition modification through selection of an appropriate aliovalent dopant and its concentration [4-8]. The doping can be either homogeneous to form solid solution or heterogeneous to form composite. For the homogeneous doping, additions of aliovalent cations to the zirconia or ceria produce oxygen vacancies, which provide the pathway for the conducting oxygen ions. The existence and the contribution of microdomain may suggest that oxygen vacancies are not a simply random distribution. The composition range is generally defined by a solid solution region and the parent cubic fluorite structure is preserved.

In the case of zirconia-based systems, Sc$^{3+}$ cation is the most effective dopant. However, the initial high conductivity in ScSZ is followed by at first a rapid and then a gradual
drop off in conductivity. This behaviour of conductivity degradation has been attributed to the existence of a metastable t'-phase as discussed in the following section of grain boundary. Regarding doped ceria, highest conductivities have been reported for either Sm- or Gd-doped ceria. It is generally recognized that the most effective aliovalent addition appears to be defined by the relationship between the ionic radii of the additive and parent lattice [9-11]. However, there is still discrepancy to understand the relationship between the dopant properties and the ionic conductivity. Kilner has suggested that a better means of evaluating the relative ion mismatch of dopant and host would be to compare the cubic lattice parameter of the host oxide and that of the pseudocubic lattice parameter of the corresponding dopant oxide. In this way, it has been explained why Gd and Sc are excellent dopants in ceria and zirconia, respectively [12]. Kim proposed a concept of critical ionic radius of the dopant, which was an ideal dopant cation radius that would gave the same lattice constant as that of undoped electrolyte [13]. The critical ionic radius for a trivalent dopant in ceria is 1.038 Å. However, although Gd- or Sm-doped ceria have higher ionic conductivity than Y-doped one, the best match for either the ionic radius of Ce⁴⁺ (0.97 Å) [14] or the critical ionic radius in ceria is Y³⁺ (1.019 Å) rather than Gd³⁺ (1.053 Å) or Sm³⁺ (1.079 Å). Kilner et al. and Catlow explained that a smaller ionic size mismatch between the host and a dopant was preferable for obtaining a high conductivity [15-16].

In addition to the single doping in zirconia and ceria, multiple doping appears to improve the electrolyte ionic conductivity further. Several ternary systems involving yttria-stabilised zirconia have been studied from the viewpoint of structure and electrical properties with the third component being calcia, scandia, rare-earth oxide, or magnesia [17-26]. Depending on chemical and phase composition, these generally improve ionic conductivities, although in some cases deterioration of the ionic conductivity has been observed. Mucko has studied the electrical conductivity for a series of YSZ systems with the addition of calcia at 350°C [17]. They found that the ionic conductivity of YSZ with a small amount of calcia addition could be enhanced about 3 times compared to that of YSZ without calcia. This effect was was most likely due to some local structure effects. Gong et al. also observed a ionic conductivity improvement for zirconia doped with 6 mol% calcia and 4 mol% yttria at temperatures above 830°C [18]. They concluded that such improvement might be due to the increase in the concentration of oxygen vacancies linked to the low activation energy. Kaneko et al. examined the electrical conductivity of zirconia co-stabilised with 8 mol% scandia and yttria by impedance measurement [19]. The electrical conductivity increases at temperature above 370°C and decreases below this temperature when increasing scandia-doping levels. Souza and Chinelatto have studied the effect of rare earth on the electrical conductivity of impure zirconia doped with 12 wt% yttria [20]. The additions of rare earth lead to an electrical conductivity close to or higher than that of electrolytes prepared from high-purity zirconia. SEM examination of the grain boundaries indicated the enhanced impurity segregation. Souza and Chinelatto suggested that the conductivity improvement was most likely due to the increasing segregation of impurities on grain boundaries rather than the effect of dopant properties [20]. The elastic field generated by the size mismatch of dopants with the YSZ matrix might help the segregation of the small radius impurity ions. Shiratori et al added magnesia to YSZ in order to better match the TEC with other components without significant degradation of ionic conductivity [21]. It was found that when the molar fraction of magnesia was less than 0.6, the conductivities of the composites were in the same range as the conductivity of pure 3YSZ at temperatures of 700-900°C.
The effects of multiple doping on the conductivity of ceria-based electrolytes also have been reported. Ralph et al. have studied the effect of oxide additions on the total and grain boundary conductivity for Gd-doped ceria with compositions of Ce1-x-yGdxMyO2 (M = Ca, Fe, Pr; x = 0.09, 0.10, 0.18, 0.19, 0.20; y = 0.01, 0.02) [22-23]. Small amount of oxide additions significantly enhances the grain boundary conductivity compared to that of Gd-doped ceria without additions. Maricle et al. have studied similar electrolyte systems with the composition of Ce0.8Gd0.19Mo.01O2 (M = Pr, Sm) [24]. It was demonstrated that these oxide additions also extended the electrolyte domain boundary by two orders of magnitude to lower oxygen partial pressures. However, Ralph et al did not confirm the effect of second phase additives on the width of electrolyte domain for the same electrolyte composition.

Mori et al. have proposed a concept of an effective index from the crystallographic point of view to maximize the ionic conductivity in ceria-based systems. They found that electrolyte materials do not only have improved ionic conductivity but also reduction in resistance in reducing atmospheres with high index. Analysis of HRTEM revealed that electrolyte with single doping had large microdomains over 10 nm while multiple doping could reduce the microdomain to be around 1-3 nm, suggesting that small microdomains would benefit the oxygen ion transport through the lattice. However, the stability of the small microdomains against annealing of electrolyte was not reported [25-26].

An alternative route to enhance the ionic conductivity from composition is to employ heterogeneous dopants that are insoluble or soluble with low limit in the zirconia or ceria bulk structure. Alumina has been most commonly used for such purpose in YSZ due to its limited solubility. Depending on the alumina concentration and electrolyte materials, the addition was either beneficial or detrimental to the electrical conductivity. TEM and microanalytical information revealed that the addition of alumina to zirconia, at levels beyond the solubility limit, results in an improvement primarily because of grain boundary interactions between second phase alumina particles and the silicate films [27]. EDX microanalysis using a finely focused electron probe showed that small inclusions of dark contrast within alumina were rich in silicon. The silicate phases exist as impurity in the electrolyte and can cause a significant blocking to grain boundary conductance as discussed in the next section. Drennan et al. observed that there was a strong interaction between the boundaries and the alumina that takes the form of boundary pinning, glassy pocket formation at the interface [28]. Butler et al. suggested that the grain boundary conductivity improvement only occurs at alumina levels sufficient to establish local grain boundary thermodynamic equilibrium and eliminate silica-rich liquid phases in favour of mullite or mullite in local equilibrium with free alumina [29-30]. Steele and Butler reported that there is a smaller improvement in overall conductivity when additions of alumina are made in YSZ of higher purity [31]. A.C. impedance measurements demonstrated that the effect was essentially related to improvements in the bulk conductivity due to Al3+ doping, and the improvement depended on the silicate level in the YSZ. However, Guo et al. reported that the addition of alumina in amounts of 0.4 mol% increased both grain and grain boundary resistivities [32]. The grain resistivity was increased by only 3%, whereas the grain boundary resistivity was increased by 600%. Miyayama et al. reported an alumina solubility limit of 0.6 mol% in YSZ [33]. They found grain and grain boundary conductivities decreased and grain growth was promoted below the solubility limit. Whereas the grain boundary conductivity increased.
and grain growth was inhibited above the solubility limit of alumina. Feighery and Irvine [34] also investigated the effect of alumina additions on the electrical conductivity of 8 mol% YSZ. They reported that approximately 1 wt% alumina dissolves into the structure of YSZ when sintered at 1500°C for 24 h. The high-temperature conductivity increases for 1 wt% alumina and then decreases to approximately the same conductivity as the undoped 8YSZ. The conductivity remained constant until 10 wt% alumina and subsequently decreased rapidly with further addition of alumina. Badwal and Drennan found that scandia-stabilised zirconia (ScSZ) could also benefit from the addition of alumina [35].

Analogically, addition of alumina to ceria-based also has been studied. Zhang et al. examined the effect of alumina addition to 20% Gd doped ceria and found in the 0-10% alumina range the overall conductivity was lower [36]. This was due to a slight increase in grain interior conductivity and a rapid decrease in grain boundary conductivity that can be observed with increasing alumina content. This is in contrast to previous findings that alumina-doping in YSZ leads to a slight decrease in grain interior conductivity, but a remarkable improvement in grain boundary conductivity. Increased grain interior conductivity for alumina-doped 20% GDC was postulated to be largely attributable to the solid state reaction between alumina and gadolinia, which results in a decrease in the amount of gadolinia dissolved in ceria.

There was also an effort to make ceria-zirconia composite electrolytes to either improve the ionic conductivity or take the advantages of both components in terms of stability and conductivity. Luo et al. prepared GDC-YSZ composite from powders and sintered over a temperature range of 1400 to 1600°C [37]; they found that the ionic conductivity of the electrolyte decreased with the 10-50 wt% addition of GDC to YSZ. XRD examination of the composites revealed formation of a solid solution that led to the reduced conductivity. Horita et al examined films using a thin layer of YSZ sandwiched between two layers of GDC and found poor electrical conductivity compared with theoretical values due to the formation of a solid solution phase [38]. The solid solution phase likely reduced the ionic conductivity of the GDC-YSZ-GDC composite and raised the activation energy for ionic conduction. In addition, pores formed at the interface of the GDC-YSZ layers and this could have contributed to reduction of conductivity. Low conductivity by an order of magnitude over either YSZ or CGO was also found for a composite electrolyte of SZ-CGO0.5YSZ0.5-CGO [39]. Again, pores were found between the layers. Most recently, Zhou et al. studied the interaction between GDC and YSZ [40]. XRD analysis showed a phase change for GDC and YSZ powder sintered at different temperatures, indicating that the interaction started around 1200°C. Studies on the solid solution revealed that it was a n-type electronic conductor instead of a ionic conductor in the oxygen partial pressure of $1 - 10^{-18}$ atm at 800°C. The solid solution has lower conductivity and larger reduction expansion than that of GDC or YSZ.

**ENHANCEMENT FROM MICROSTRUCTURE**

**Effects of Grain Boundaries**

The electrical conductivities of polycrystalline materials are greatly influenced by their nature of microstructure, i.e. the properties of grain and grain boundary. Grain
boundaries are the crystallographic mismatch zones whose properties are determined by mismatch of the lattices, impurities or second phase segregation, space charge, micro cracks, or a combination of these effects. In many polycrystalline materials grain boundaries provide a region of relatively rapid mass transport compared to the bulk properties of the crystallites. However in zirconia- or ceria-based electrolytes the grain boundaries can potentially decrease the effective charge carrier concentration, or result in a highly resistive grain boundary phase. A.C impedance spectroscopy is widely employed to obtain information relating to the electrical behaviour of both the bulk (grain interiors) and to the grain boundaries. For a sample with a length of L and cross-section area of A, the bulk conductivity, $\sigma_b$, $\sigma$ and the total grain boundary conductivity, $\sigma_{gb}$, can be expressed as $\sigma = L/AR_b$ and $\sigma_{gb} = L/AR_{gb}$, where $R_b$ and $R_{gb}$ is bulk and grain boundary resistance, respectively. Then, the total electrical conductivity, $\sigma_T$, can be calculated from equation $1/\sigma_T = 1/\sigma_b + 1/\sigma_{gb}$ [41]. Assuming that all the grains are cubic with the equal size of $d_g$; the grain size is much smaller grain boundary thickness, $\delta_{gb}$; and the contribution to the conductivity parallel to the grain boundaries is negligible, then the specific grain boundary conductivity can be estimated by the following equation [42].

$$\sigma_{gb}^{sp} = \sigma_{gb}^{T} \delta_{gb}$$

Assuming reasonable values for the grain boundary thickness, order of magnitude estimates of specific grain boundary conductivity have been reported [43]. Nearly all impedance studies on both micro-structured and nano-structured YSZ showed that the electrical conductivity in grain boundaries is 2-3 orders of magnitude smaller than in the crystallite volume. Correspondingly, the activation energy of the electrical conduction at interfaces with values in the range of 1.0 to 1.2 eV is significantly higher than the values of 0.84-0.93 eV observed for the bulk conductivity [43-44]. When temperature is high enough, the grain boundary resistance appears to become negligible in comparison to the grain resistance. This temperature varies with dopant types and concentrations in zirconia or ceria. Nowick et al. observed that the grain boundary effect becomes negligible above a dopant concentration of 15 mol% regardless of the dopant type in ceria [45-46]. Therefore, the impact of grain boundary on the ionic conductivity of electrolyte is especially important for lower-temperature applications. Hon et al. also found that the grain boundary contribution to the resistivity in ceria generally decreased with increasing dopant levels. They found that the temperature above which the grain boundary effect appears to become negligible for ceria doped with 9 mol% Gd$_2$O$_3$, Sm$_2$O$_3$, or La$_2$O$_3$ is 725°C, 775°C, and 650°C, respectively [47].

It has been widely reported that impurities such as silica greatly decrease the grain-boundary conductivity in zirconia and ceria [44, 48-52]. Badwal and Rajendran found that the addition of only 0.2 wt% silica was sufficient to decrease the grain-boundary conductivity of YSZ by a factor greater than 15 [51]. Therefore, eliminating the effect of impurities on the grain boundary can benefit the ionic conductivity of electrolyte. A number of strategies have been suggested to control the silica-rich grain boundary, including specialised heat treatments, application of pressure, and various additives [44, 48-52]. Varying grain size at concentrations low enough that a discrete siliceous film does not form can systematically vary the boundary coverage of silicon. Experimental studies on fully dense, highly pure specimens of nano- and micro-crystalline calcia or yttria doped zirconia showed a significant increase of the conductivity at interfaces with
decreasing crystallite size down to nm size [44, 53]. Ralph, et al., reported that ionic conductivity could be enhanced by trapping impurities through formation of low temperature compounds with small amount of second phase additives [54]. Some oxides can form eutectic compounds with impurities in grain boundary. These compounds may have eutectic temperatures below the electrolyte sintering temperatures, which can be trapped to certain areas in the grain boundary upon cooling.

However, the grain boundary conductivity remained lower than the bulk value, even for highly pure electrolyte materials where the grain boundary had no significant amount of silica-covering [43]. Therefore, the grain boundary blocking in YSZ was also ascribed to an intrinsic property due to the formation of electric space charge layers at grain boundary, which was supported by the segregation behaviour of dopant cations [55-56]. The strain and electrostatic energies of the electrolyte could be reduced through segregation of charged species such as impurities and/or defects in the grain boundaries, leading to a positive or negative potential. Positive space charge potentials of ~0.3 to 0.5 V have been obtained for polycrystalline yttria-doped zirconia and ceria [49, 57]. Therefore, positively charged ionic defects will be depleted while those with opposite charge will be accumulated in the space charge region in zirconia- or ceria-based electrolytes. Electrochemical and theoretical studies by Guo and Maier [49] on microcrystalline zirconia doped with 2 to 8 mol% yttria indicate the presence of an ~5 nm wide, poor conduction layer at interfaces. Both analytic studies by means of HRTEM and EELS and atomistic modeling showed a significant segregation of Y$^{3+}$ depleted zones, a negative space charge and a very low concentration of oxygen vacancies prevails on the length scale corresponding to the Debye length of a few nm [49, 53, 58-59].

Many researchers have also demonstrated the effect of different microdomain or local lattice structure from different dopants on the ionic conductivity. For instance, enhanced ionic conductivity in ScSZ has been ascribed to the existence of a metastable tetragonal phase known as the t'-phase [60-61]. The formation of the t'-phase in yttria-stabilised zirconia requires very fast quenching from the melt, while the t'-phase can be easily formed in ScSZ in the cubic phase field and quenched by simply removing the sample from the furnace. This phase has a characteristic microstructure described as banding. These bands occur as the phase changes from cubic to tetragonal and the resulting strain is accommodated by the formation of twin bands. This banding rapidly disappears if the sample is annealed and the usual mottled grain structure develops, resulting a degradation of ionic conductivity [62]. The t'-phase contains high dopant concentration, but is obviously in a metastable state at the normal operating temperature for the SOFC applications. Yoshida et al. have investigated the local structures of doped ceria by extended X-ray absorption fine structure (EXAFS) measurements, and showed that the ionic conductivity is remarkably affected by the local structures of dopant and Ce$^{4+}$ ions [63]. The high ionic conductivity of LSGM has also been observed to be due to a microstructural feature with internal interface structures [64-65]. Further understanding of the formation and properties of microdomain with respect to conductivity may provide a valuable insight into the design or improvement of oxygen ion conductors.

**Effects of Grain Size**

In recent years a growing interest has been observed to explore whether the ionic conductivity can be further enhanced by reducing the grain size down to nano-scale in the
electrolytes [43, 66-67]. Nanocrystallinity introduces such a high density of interfaces that the conduction properties may become interfacial controlled. Many researchers have investigated the grain size dependence of conductivity in polycrystalline solid electrolytes. For nanocrystalline zirconia-based materials, Tien reported an increased electrical conductivity with decreased grain size for Zr$_{0.84}$Ca$_{0.16}$O$_{1.84}$ at low temperatures below 800°C [68]. The specimens of smaller grain size exhibited higher activation energy for grain boundary conduction. This value was found to be about 0.96 eV, whereas the activation energy for the specimen with large grain size lies in the range 1.24 to 1.30 eV. Anderson’s group has studied a series of nanostructured thin film materials spin-coated on alumina substrate, including YSZ and ceria-based electrolyte. The studies of Kosacki et al. on thin films of 16 mol% YSZ reported a remarkably enhanced conductivity and a lower activation enthalpy in nanocrystalline films with average grain size of 20 nm than in coarse-grained polycrystals [69]. Nanocrystalline YSZ exhibits about 2-3 orders of magnitude increase in the electrical conductivity as compared to microcrystalline specimen. Activation energy is 1.23 and 0.93 eV for micro and nanocrystalline specimens, respectively, which is close to calcia-doped zirconia investigated by Tien [68].

For the nanocrystalline ceria-based electrolytes, Tschope and Birringer have compiled the experimental results on the electrical conductivity and their activation energy as a function of grain size [70]. The results showed that nanocrystalline ceria possesses an increased electrical conductivity and decreased activation energy when decreasing grain size. The quoted authors by Tschope and Birringer also concluded that nanocrystalline cerium oxide was found to be electronic conductive while microcrystalline cerium oxide exhibits predominantly ionic conductivity under the same temperature, oxygen partial pressure, and doping level [70].

However, there was a discrepancy in the literature regarding the effect of grain size on the electrical conductivity in zirconia-based or ceria-based electrolyte. Ioffe, et al., have prepared 5.7mol% YSZ specimens by hot-pressing at 1200°C and investigated the effect of grain size between ~0.2 and ~18 μm on the conductivity of YSZ polycrystalline materials. [71]. Dijk and Burggraaf investigated the effect of grain size between 0.4 to 20 μm on the ionic conductivity of Gd$_2$Zr$_{(1-x)}$O$_{(2-0.5x)}$ [72]. Verkerk, et al., explored the effect of grain size on grain boundary conductivity of YSZ [73]. Badwal, et al. and Chen, et al also investigated the variation of electrical conductivity of YSZ as a function of grain size. [74-75]. All of the authors above have observed a decrease in conductivity with decrease grain size. Under this category, impedance measurement generally revealed a constant or slightly increased bulk conductivity and a decreased total grain boundary conductivity associated with the decrease of grain size [42, 69]. However, many researchers have found an increase of specific grain boundary conductivity, which were probably due to defect and impurity segregation phenomena [42, 69]. Aoki, et al., found that the specific grain boundary conductivity decreased rapidly with increasing grain size to a nearly constant value at grain sizes larger than a few micrometers [42].

A brick-layer model has been employed to correlate the microstructure with the grain and grain boundary conductivity and to explain the variation of ionic and electronic conductivity in electrolytes as a function of grain size [72, 76-77]. It is assumed that the ceramic samples consist of grains with a high conductivity, separated by relatively thin, uniform grain boundaries. For a positive space charge potential, positive carriers such as
oxygen vacancies and electron holes are depleted and negative carriers such as $e'$ are enhanced in grain boundaries. The relative depletion of oxygen vacancies is equal to the square of the relative enhancement of $e'$, leading to an increased n-type conductivity. A positive space charge potential of 0.3 and 0.25V was obtained for polycrystalline ceria and YSZ, respectively [49, 57]. Guo and Maier reported that the magnitude of ~0.3 V for ceria is sufficient to cause an n-type conductivity enhancement of the observed order of magnitude. As a consequence, a transition from predominantly ionic to electronic conductivity could occur at a grain size of about 60 nm in ceria [70].

The variations in the electrical properties can be the result of many factors such as band structure modification due to spatial modulation of the lattice, quantum confinement of charge carriers, and dominant contributions from largely defective and strained grain boundaries in nanostructured materials [78-79]. More direct measurements of electronic and ionic conductivity for nanocrystalline electrolyte are required for further understanding the grain size effects.

**ENHANCEMENT FROM PROCESSING**

Processing condition is another parameter that can greatly influence the electrical conductivity of electrolytes. The influence of processing on the ionic conductivity of the electrolyte can help to optimize the sintering conditions and further improve the electrical properties of the electrolyte. Different sintering conditions will result in diverse characteristics in the microstructures of the electrolyte such as grain size, grain boundary phases, and relative density. The ionic conductivity varies strongly with the sintering conditions of the electrolyte [80]. Kleitz et al. [81] and Dessemond et al. [82] observed high values of grain boundary resistance at sintering temperatures below 1300°C because of the low relative density of the electrolyte. Gibson also observed a linear correlation between grain boundary conductivity and porosity [83]. Microstructure with full density is therefore essential prerequisites for a high performance ionic conductor.

The processing methods also have an effect on the conductivity through grain boundary. Shelmilt et al. prepared dry-pressed and compression-molded pellets of samaria-doped ceria (SDC) with identical powder [84] and found the grain boundary activation energy higher for compression-molded sample than that for dry-pressed one with 98% theoretical density. Different levels of impurities from two different routes might lead to the observed results. Therefore, the optimized processing should have less additives and steps to avoid possible introduction of impurities into the electrolyte grain boundary. Aoki et al. reported that the quenched calcia-doped zirconia exhibited higher boundary conductivity than the same sample after slow cooling [42], most likely due to the microdomain effect as mentioned in the previous section. Hirano et al. have investigated the conductivity of 3-7 mol% ScSZ sintered at 1300°C followed by hot isostatic pressing [85]. They found a significant improvement for both the fracture strength and the electrical conductivity. Most recently, Mori et al. reported an influence of particle morphology from starting materials on the formation of microdomain and electrical conductivity in SDC [86]. They found that the electrical conductivity of sintered SDC prepared with different starting morphologies was different. The conductivity of materials prepared from round shape particles was much higher than that of ones from...
The maximum ionic conductivity can be achieved through optimising the electrolyte composition, microstructure, and processing condition. The following methods have been reported and reviewed for the enhancement of electrical conductivity.

a) Doping of aliovalent cation into zirconia or ceria is an effective approach to improve ionic conductivity.

b) Multiple doping has been demonstrated to enhance ionic conductivity and chemical stability further.

c) The composite electrolyte by introducing second phase may change the grain boundary condition and therefore vary the electrical conductivity of the electrolytes.

d) Properties of grain boundary in electrolyte such as impurity segregation and space charge play an important role for the ionic conductivity, especially at low temperatures. Certain additives can be used to scavenge the grain boundaries to enhance the ionic conductivity. The resistive grain boundaries for high purity grain boundaries have been explained on the basis of space charges and depletion of oxygen vacancies in the vicinity of grain boundaries. The space charge layer in the electrolyte as an intrinsic property does not appear to be an effective route to improving the electrical conductivity yet.

e) The existence of microdomains has been demonstrated to have a great influence on ionic conductivity. Engineering of microdomain would provide a new approach for achieving an enhancement in ionic conductivity of solid electrolytes.

f) Many researchers have revealed the dependence of electrical conductivity on grain size, particularly, the increase of specific grain boundary conductivity. However, this increase seems to be the increase of electronic conductivity in stead of ionic conductivity. The brick-layer model has predicted a decrease of ionic conductivity and increase of electronic conductivity when decreasing grain size. There also exists a discrepancy regarding the effects of grain size on the electrical conductivity. More direct measurements for the ionic conductivity are required to better understand the grain size influence on the ionic conductivity.

g) Processing condition also influences the final ionic conductivity depending on the specimen density, the level of impurities, thermal history, and the formation of microdomain.

Further improvement of the ionic conductivity in the zirconia- or ceria based electrolytes may be realised by introducing a liquid phase either in the grain boundaries or by forming a composite electrolytes. Most recently, Fu et al. have examined the electrical conductivity of ceria-chloride composite electrolytes containing GDC-LiCl-SrCl₂ [87]. The hot pressed composite showed superionic conductivity 2-10 times higher than GDC itself at temperatures of 400-600°C with reduced electronic conduction.
ACKNOWLEDGMENTS

This work is part of the solid oxide fuel cell project within the NRC Fuel Cell and Hydrogen Program.

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