CHAPTER 4

Ionic conductivity of GDC electrolyte

4.1 Introduction

Solid oxides with fluorite structure, such as, ZrO$_2$ and CeO$_2$, when doped with aliovalent cations become oxygen ion conductor and are used as solid-oxide electrolyte in various electrochemical applications [118,159]. Rare earth oxides, such as, Gd$_2$O$_3$ and Sm$_2$O$_3$, are the most commonly used dopants in ceria. Their doping in ceria introduces vacancies in the oxygen sub-lattice as charge compensating defects. The defect reaction can be presented in Kröger-Vink notation:

\[
Gd_2O_3 - \frac{2CeO}{2} \rightarrow 2Gd_{Ce}^{\oplus} + 3O_{O}^{\ominus} + V_{O}^{\bullet\bullet} \quad \text{............... (4.1)}
\]

Oxygen ions hop through the vacancies and under a potential gradient a net flux of ions takes place resulting in ionic conductivity. The high oxygen ion conductivity has led to its use as an electrolyte material in solid oxide fuel cells. At higher temperatures and
reducing environment the valence state of cerium ions starts changing from Ce\(^{4+}\) to Ce\(^{3+}\). This phenomenon introduces electronic conductivity in the material and restricts its use at higher temperature. Nevertheless, appreciable ionic conductivity and ionic transport number in doped ceria at temperatures lower than 800 °C make it a candidate electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFC) [160,43].

The diffusion of oxygen ions through the fluorite structure is a thermally activated process and is associated with an activation barrier. The oxygen ion conductivity increases with increase in temperature following Arrhenius equation. The temperature dependent ionic conductivity is expressed as:

\[
\sigma = \sigma_0 \exp \left( \frac{-E}{kT} \right) \quad \text{........................ (4.2)}
\]

where, \(k\) is the Boltzmann’s constant, \(E\) is the activation energy for ionic conduction and \(\sigma_0\) is the pre-exponential factor.

The pre-exponential term in Eq. (4.2) increases linearly with oxygen vacancy concentration. The concentration of oxygen vacancies increases with increase in dopant concentration. It may be apparent that the conductivity will increase with dopant concentration. However, for various fluorite based electrolyte systems it is known that conductivity increases with dopant concentration, exhibits a maximum and subsequently decreases with increasing dopant concentration. This is explained as due to the opposite effects associated with increase in the number of vacancies and decrease of vacancy mobility as the dopant concentration increases. At higher dopant concentration oxygen vacancies get associated with cations forming (Gd'\(_{cc}\)-\(V^*_O\)- Gd'\(_{cc}\)) and (Gd'\(_{cc}\)-\(V^{**}_O\))\(^0\).
clusters. This association energy is a function of (a) coulombic interaction between the oxygen vacancy and the dopant cations and (b) the elastic strain field around the defect complex. The vacancies need to overcome these barriers to be mobile leading to oxygen ion conduction. Therefore, it is apparent that activation energy for ion migration increases with dopant concentration.

The ionic conductivity is also influenced by microstructure and impurities as reported by many authors for zirconia and ceria based electrolyte systems [161-166]. In zirconia based electrolyte systems it has been indicated that the grain boundary resistivity is two to three orders of magnitude higher than the bulk conductivity [161,162]. The grain-boundary resistivity originating from the space-charge layers has been discussed in detail by X. Guo [163]. With the logic of very high grain boundary resistivity as compared to the bulk resistivity, it is expected that large grained microstructure is preferable in order to achieve higher conductivity. In YSZ system Verkerk et al. [162] found that the grain boundary conductivity increases linearly with the grain size in small grained (0.3 to 2.4 \( \mu \)m) structure and is constant in large grained structure. On the contrary nanostructured YSZ fabricated by spark plasma sintering have significantly higher grain boundary conductivity in comparison with conventionally processed microcrystalline samples [164,165]. Presence of silica has been reported to affect the grain boundary conductivity significantly [165-168]. In samples having larger grains the total grain boundary area becomes less and there is a possibility that a significant part of grain boundary is covered by non-conducting impurity phase, such as, silica. Mondal et al. [168] has indicated that the specific grain boundary conductivity of the nanocrystalline samples is 1 to 2 orders of the magnitude higher than that of the microcrystalline samples. This has been attributed
to the low silica content and its grain size-dependent segregation in the nanocrystalline samples.

Contradictory results have also been reported in ceria based electrolyte systems. Zhou et al.[169] indicated that Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ with finest grain size possessed highest grain boundary resistance. On the contrary, Christie and van Berkel [170] measured significantly low overall grain boundary resistance in Ce$_{0.8}$Gd$_{0.2}$O$_{1.90}$ samples with sub-micron mean grain size. Enhanced ionic conductivity in nanocrystalline solid electrolyte thin film has also been reported by many authors [171-174]. It has also been reported that decreasing grain size induces electronic conductivity [175]. This makes the generalization more difficult. As discussed by Belleno et al.[176], the electronic conductivity in nanocrystalline undoped or lightly doped ceria is attributed to the formation of space charge layer close to the grain boundary region. The width of the space charge region is inversely proportional to the root of the concentration of ionic defects. Thus, in heavily doped ceria the space charge region is very small and the space charge model is not much relevant [176].

In GDC system maximum conductivity has been reported for 12 mol% Gd$_2$O$_3$ content [118]. As mentioned above the conductivity is influenced by microstructure. From the above examples, it seems that the literature is not definitive on the issue of the effect of grain size on ionic conductivity. In order to address this issue, the present investigation is aimed at studying the effect of grain size on the bulk and grain boundary ion conduction behavior in gadolinia doped ceria. GDC containing 12 mol% Gd$_2$O$_3$ (12GDC) has been
chosen for this study. It has been reported that in heavily doped ceria samples when measurements are taken in oxidizing atmosphere (air, $p_{O_2} = 0.2$ atm.) the electronic contribution in the conductivity is not significant and ionic transport number can be considered close to unity [118]. For studying the effect of grain size on conductivity it is important to produce samples with high density and at the same time with different grain size. It has been discussed in the previous chapter that dense microstructure of gadolinia doped ceria can be obtained by low temperature sintering of doped ceria powder produced by gel combustion route. Grain size can be changed by post-firing the dense samples at higher temperatures. In the present investigation different microstructures of 12 mol% gadolinia doped ceria samples have been generated by adopting different firing schedule. The ionic conductivity has been determined from ac impedance data. Impedance spectra of the bulk and grain boundary have been analysed in order to discuss the influence of grain size on the ionic conductivity.

As discussed in Chapter 3, GDC nano-powders of different gadolinia content have been synthesized by solution synthesis routes and the powders have been sintered at 1250 °C to get near theoretical density. This low temperature sintering of electrolyte material has added advantage in fabricating SOFC cell by co-firing route. As the conductivity dependents on composition and microstructure it is prudent to measure the conductivities of GDC samples of different compositions but prepared under a set of processing condition (starting powders and processing parameters, particularly, sintering parameters). The above investigation on optimization of composition has also been included in the present work.
4.2 Experimental

Gadolinia doped ceria powders with different level of gadolinia doping, synthesized by gel combustion method were used for this study. Pellets of 12 mm diameter were pressed in a uniaxial die and sintered at predetermined temperatures. Few pellets of 12GDC were sintered at 1200 °C for 3 h. Out of these pellets one set of pellets were further fired at 1400 °C and another set was fired at 1500 °C to generate microstructures of different grain sizes. 12 GDC samples sintered at 1200, 1400 and 1500 °C are referred as GDC12, GDC14 and GDC 15, respectively. Densities of the sintered pellets were determined by water displacement method. The micrographs of the sintered pellet were taken by SEM (Seron Technology, Korea). The SEM images were analyzed to estimate the average grain size by linear intercept method. GDC pellets of different compositions (nGDC, where n = 0, 3, 4, 6, 8, 10, 12, 15 and 18 mol% Gd₂O₃ doped in CeO₂) were also prepared by die pressing followed by sintering at 1250 °C. The densities of the sintered pellets were measured by water displacement methods and recorded.

Platinum paste was applied on both the flat sides of the sintered samples and baked at 1000 °C. Electrical measurements were carried out in a frequency response analyzer (Solatron 1260) in the frequency range 0.1 Hz to 10 MHz and in the temperature range 225 – 1000 °C in air. Resistance offered by different processes for oxygen ion conduction has been determined from complex impedance plots ($Z''$ vs. $Z'$). The ac electrical data have been analyzed using Z-view software to separate the contribution of bulk and grain boundary. Arrhenius plot for conductivity values were plotted and activation energies
were calculated for different samples. The impedance data are plotted in form of Bode plots (plot of $Z''$ vs. log frequency) and oxygen ion jump frequency have been evaluated.

## 4.3 Results and Discussion

### 4.3.1 Densities and microstructures of the sintered 12GDC pellets

The densities of the 12GDC pellets obtained after sintering at 1200 °C were in the range of 95 – 96% of theoretical density. The theoretical density of 12GDC has been taken as 7.22 g.cm$^{-3}$ [177-178]. High value of sintered density is in agreement with high sinterability of the combustion synthesized powder. On further firing at 1400 and 1500 °C there was a marginal (less than 1.0%) increment in density. Thus in all the three samples used in this study the densities remained in the range of 95 – 97% of theoretical density. The SEM micrographs of the samples fired at 1200, 1400 and 1500 °C are shown in Fig. 4.1. Significant grain growth with increase in firing temperature is evident from the micrographs. The dark/bright contrast in these microstructures is due to surface topography. Energy dispersive X-ray spectra (EDS) do not show the presence of any impurity element. The average grain sizes as estimated by linear intercept method are 0.2, 0.9 and 1.2 μm for the samples fired at 1200, 1400 and 1500 °C respectively.

### 4.3.2 Complex impedance plot: Determination of bulk, grain boundary and total conductivity

The ac impedance data have been plotted in the form of complex impedance curve (plot of imaginary impedance vs. real impedance) and impedance spectra (plot of imaginary
Fig. 4.1: SEM micrographs of the samples fired at (a) 1200, (b) 1400 and (c) 1500 °C
impedance vs. frequency) in order to analyze the ion conduction behavior of bulk and grain boundary in GDC samples. In general the relaxation time for the oxygen ion transfer through bulk, grain boundary and electrode are well separated and hence distinct arcs are expected for each process in the complex impedance plot [179]. In correlation with the relaxation times the arcs correspond to bulk, grain boundary and electrode properties are in order of decreasing frequency. Resistance of bulk or grain boundary is calculated from the difference between the low and high frequency intercepts of the corresponding arc (extrapolated on fitted semicircle using ZView software) with the real impedance axis. To calculate bulk and grain boundary conductivities, total thickness of all the grains and that of all the grain boundaries are required to be known separately. The grain boundary thickness is considered to be of few nm. Hence, the total thickness of grains can be approximately taken as that of the sample. However, the total thickness of grain boundary is difficult to estimate. Hence, apparent grain boundary conductivity has been used to compare the data. In this the total sample thickness is considered instead of only grain boundary thickness. It may be mentioned here that all the arcs are not necessarily to appear in the impedance plot depending on temperature and the experimental frequency range. As the temperature increases the relaxation time for a process decreases and the response shifts to higher frequency. Also at higher temperature as the sample impedance decreases the inductive component of the circuit dominates at high frequency. Because of the above two factors high frequency responses may not appear in the impedance plots made using experimental data.
Fig. 4.2: Complex impedance plot of different samples (GDC12, GDC14 and GDC15) at (a) 300 °C, (b) 500 °C and (c) 1000 °C
The complex impedance plots of the three samples at temperatures 300, 500 and 1000 °C have been presented in Fig. 4.2(a-c). As shown in Fig. 4.2(a), the impedance plots at 300 °C, bulk and grain boundary arcs are distinct along with rising electrode arcs for GDC14 and GDC15 samples. In GDC12 sample, a broad curve appears instead of two distinct arcs for bulk and grain boundary. In this sample the low frequency intercept of the semicircle with the real impedance axis has been taken as the total resistance. Bulk resistances and grain boundary resistances have been determined separately for GDC14 and GDC15 samples. In the impedance plots at 500 °C (Fig. 4.2b) the responses from the bulk do not appear and hence, in this case only grain boundary resistances have been determined. Total resistances have been calculated from the low frequency intercept of the grain boundary arcs. At still higher temperature, both the responses from bulk and grain boundary are missed out as seen from the impedance plots at 1000 °C (Fig. 4.2c). In such cases, the high frequency intercept of electrode arc has been taken as the total resistance.

Fig. 4.3(a) and 4.3(b) show the variation of bulk and grain boundary conductivities with temperature in the form of Arrhenius plot for the samples GDC14 and GDC15. The bulk conductivity is found to be higher in GDC15 sample. The apparent grain boundary conductivities of GDC 14 and GDC15 are very close. The activation energy values for corresponding bulk and grain boundary are given in Table 4.1.
Fig. 4.3 Variation of (a) bulk conductivity and (b) effective grain boundary conductivity with temperature presented in the form of Arrhenius plot

Table 4.1 Activation energies for the bulk and the grain boundary conduction

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy (eV) for oxygen ion conduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in bulk</td>
</tr>
<tr>
<td>GDC14</td>
<td>0.94</td>
</tr>
<tr>
<td>GDC15</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Fig. 4.4: Variation of total conductivity with temperature (a) in lower temperature range, (b) in higher temperature range

Fig. 4.4 shows the variation of total conductivity with temperature in the form of Arrhenius plot. In the lower temperature range, as shown in Fig. 4.4(a), the total
conductivity increases with decrease in grain size. In the higher temperature range, as shown in Fig. 4.4(b), the total conductivity increases with increase in grain size. The total conductivity remains almost unaffected with firing temperature in the measurement temperature range 400 – 600 °C. It has been mentioned in the previous paragraph that the bulk conductivity of GDC15 is higher than that of GDC14. Thus the bulk effect is dominant in the higher temperature range. The reverse trend in the lower temperature range may be attributed to higher apparent grain boundary conductivity as the grain size decreases. As the grain size decreases the grain boundary path for ion conduction is believed to be more. Thus the actual grain boundary conductivity increases significantly with decrease in grain size.

4.3.3 Analysis of imaginary impedance spectra

The above observed phenomena can be better understood from the analysis of the imaginary impedance spectra. In the impedance spectra, the frequency corresponding to a peak of imaginary impedance (−Z″) can be correlated to successful jump frequency of the oxygen ions [180]. This frequency is characteristics of composition and structural arrangement of atoms. Hence analysis of impedance spectra is expected to give information on oxygen ion hopping through the grain / grain boundary. As the relaxation frequency of bulk is more than that of grain boundary two distinct peaks corresponding to the bulk and grain boundary are expected to appear in the imaginary impedance spectra. It may be mentioned here that presence of impurity phases like silica can change the
Fig. 4.5 Imaginary impedance spectra of different samples (GDC12, GDC14 and GDC15) at (a) 300 °C, (b) 500 °C and (c) 1000 °C
overall grain boundary resistance by reducing the effective conducting path across the grain boundary. Hence, analysis of measured conductivity data may not reflect true oxygen conduction behavior through the grain boundary. Thus, it will be interesting to analyze the characteristic frequency from the impedance spectra to avoid the complexity arising from partial coverage of grain boundary.

Fig. 4.5 shows the impedance spectra of the samples at 300, 500, and 1000 °C. The characteristic frequency is found to be influenced by the microstructure. The peaks can be distinguished for the samples GDC14 and GDC15. However, the peak is overlapped in case of GDC12. As shown in Fig. 4.5(a) the characteristics frequency corresponding to bulk in GDC14 is smaller than that of GDC 15 sample. However in the grain boundary the characteristic frequency is more in case of GDC14 sample. At an intermediate temperature, say at 500 °C as shown in Fig. 4.5(b), the bulk behavior does not appear. Observation of the grain boundary behavior shows that the characteristic frequency of GDC14 sample is more than that of GDC15 sample.

The variations of characteristic frequency with temperature for both bulk and grain boundary are shown in Fig. 4.6. In the overlapped peak of the GDC12 sample (Fig. 4.5(a)) the peak does not extend to the frequency corresponding to the grain boundary arc. Therefore, the grain boundary relaxation takes place at much higher frequency than that of other two samples fired at higher temperature. The peak frequency is in between the characteristic frequencies of bulk and grain boundary for GDC14 and GDC15 samples. This behavior indicates that the characteristics frequency of the bulk decreases and that of the grain boundary increases in GDC12 in comparison with GDC14 and
GDC15 samples. From the above analysis it can be said that characteristics frequency of the bulk decreases as the grain size decreases. Also the grain boundary characteristic frequency increases with decrease in grain size.

Fig. 4.6 Variation of hopping frequency with temperature (a) bulk and (b) grain boundary
Minute observation of Figure 11 of an article by Chen et. al. [164] reveals the trend of increase in grain boundary relaxation time (i.e. decrease in grain boundary characteristics frequency) with increasing sintering temperature in the range of 1200 to 1500 °C. The grain size was reported to increase with increase in sintering temperature as usually expected.

4.3.4 Grain size effect

The change in characteristic frequency can occur due to change in composition in the bulk / grain boundary by partitioning of solute at different firing temperatures. However the change in characteristic frequency is very significant in case of GDC12 sample having very fine grained structure. It is difficult to explain the significant shift of the grain boundary characteristic frequency by compositional changes due to partitioning of dopant. The shift towards higher frequency as the grain size decreases may be attributed to low angle grain boundary in nanostructured material. The change in the characteristic frequency of the bulk with grain size is also consistent. From the basic conductivity equation it can be seen that the characteristic frequency is related to the lattice vibration frequency. The results are indicative that the lattice vibration frequency is influenced by the grain size. Overall the bulk characteristic frequency decreases and grain boundary characteristic frequency increases with grain size in the fine grained structure.

4.3.5 Variation of conductivity with composition

Bulk and grain boundary ionic conductivities have been evaluated separately along with total conductivity for GDC samples of varying gadolinia content. Fig 4.7 shows the
variation of bulk ionic conductivity values ($\sigma$) of different compositions at various temperatures. At lower level of gadolinia concentration the bulk conductivity is found to increase sharply with gadolinia substitution. There is a plateau in the conductivity maxima at a doping level of 10 to 12 mol% gadolinia. On further gadolinia doping a regular decrease in the conductivity value is observed.

\[
\ln \sigma_{gi} (\text{in S.cm}^{-1}) \quad \text{Gd}_2\text{O}_3 (\text{mol %})
\]

Fig 4.7: Variation of lattice conductivity with composition at different temperatures

Similar to the previous section in the analysis of grain boundary conductivity, ‘apparent grain boundary’ or ‘effective grain boundary conductivity’ has been used to present the data. While calculating the apparent grain boundary conductivity, the total thickness of the sample is taken into consideration. Fig. 4.8 shows the variation of grain boundary conductivity with composition. A very high grain boundary resistance is observed in the dilute region. For pure CeO$_2$ the apparent grain boundary resistance value is 1000 times
Fig. 4.8: Variation of grain boundary conductivity with composition at different temperatures.

higher compared to 3GDC. It has been reported that the thickness of the grain boundary and effective grain boundary area decreases with gadolinia substitution [183]. Hence, the resistance contribution from the grain boundary decreases with gadolinia doping. There is a sharp increase in the grain boundary conductivity up to 6GDC and then the increase in conductivity is not significant. A plateau in the grain boundary conductivity was observed above 15GDC.

The variation total conductivity with composition is given in Fig. 4.9. There is a smooth increase in conductivity value with increase in gadolinia content. In the dilute region the conductivity was controlled by the grain boundary conductivity. The ratio of grain boundary resistance to the total resistance decreases from 95% to 58% as gadolinium content varies from 0 to 6 mol%. It has been observed that highest conductivity is
obtained in the composition range of 10GDC to 12GDC. However at higher gadolinia concentration, defect association leads to lowering of the effective concentration of oxygen vacancies. At higher doping level the bulk conductivity dominates. Hence, increase in gadolinia content leads to decrease in the overall conductivity.

Fig. 4.9 Variation of total conductivity with composition

4.3.6 Activation energies for ionic conduction

The conductivity values at different temperature are represented by Arrhenius plots. Arrhenius equation for conductivity is expressed as follows,

$$\sigma = \sigma_0 \exp\left(\frac{-E}{kT}\right) \quad \ldots \ (4.2)$$

Taking natural logarithm of both sides, the equations (4.2) become:
\[ \ln(\sigma) = \ln(\sigma_0) - \frac{E}{kT} \quad \cdots (4.3) \]

Graph of \(\ln(\sigma)\) vs \(1/T\) is plotted to calculate the value of activation energy. The variation of activation energy for bulk and grain boundary conduction with varying composition of gadolinia doping is shown in Fig. 4.10. It has been observed that for bulk conduction, there is no appreciable change in the activation energy up to 5mol\% Gd\(_2\)O\(_3\) doping. On further doping of Gd\(_2\)O\(_3\) the activation energy increases. This increase in activation energy is attributed to the association of the oxygen vacancy with the dopant metal cations. The activation energy for grain boundary conduction in the dilute region is very high. This higher activation energy is attributed to very high grain boundary thickness [183]. There is a rapid decrease in the activation energy for grain boundary conduction and a minimum is observed in the range 10GDC to 15GDC. Increase in activation energy is observed on further increase of gadolinia content. From the work of Avila-Paredes et al.[183] it has been seen that with gadolinia doping the thickness of the grain boundary decreases and hence the activation energy decreases. At still higher doping level there is increase in activation energy due to increased space charge layer thickness [183].

The Arrhenius plot for total conductivity is not linear over the entire temperature range. At intermediate temperature region the activation energy has two parts namely association enthalpy and migration enthalpy. At higher temperature region dissociation of vacancies takes place. The activation energy at high temperature known as migration enthalpy is not varies much with composition, whereas the association enthalpy varies
with composition. The curve of activation energy with composition is shown in Fig. 4.11. This shows a minimum at around 10-12 mol% doping.

![Graph showing variation of activation energy with composition](image)

**Fig. 4.10** Variation of activation energy of grain and grain boundary with composition

![Graph showing variation of activation energy with composition](image)

**Fig. 4.11** Variation of activation energy with composition
4.4 Summary

Gadolinia substituted ceria with dense and fine grained microstructure can be prepared by low temperature sintering of combustion synthesized powder. The grain boundary conductivity increases and bulk conductivity decreases as grain size becomes finer. As a consequence, at lower temperature maximum conductivity is obtained with fine grained structure and at higher temperature conductivity is more with coarse grained structure. Thus from technological point of view fine grained microstructure is preferable for application at lower temperatures. The analysis of impedance spectra reveals that the relaxation frequency is influenced by the grain size. The relaxation frequency of the bulk decreases and that of grain boundary increases with grain size in the fine grained structure. Gadolinia doping in cerium oxide produces oxygen vacancies responsible for the ionic conductivity. With increase in gadolinia doping conductivity increases and reaches a maximum value at 10 to 12 mol% doping. On further substitution of gadolinia, conductivity decreases. Lattice/ grain interior conductivity follows the same pattern as total conductivity. However, grain boundary conductivity decreases rapidly with gadolinia doping and remains almost same for 6GDC to 15GDC. The activation energy for total conduction have a minimum for 10-12GDC. Activation energy for lattice conductivity remains same up to 6GDC and increases on further substitution. Activation energy for grain boundary conductivity decreases rapidly and attains a minimum at 10GDC.