“CHAPTER 5: MICROWAVE PROCESSING AND CHARACTERIZATION OF Co DOPED Ce\text{0.80 Gd\text{0.20}O\text{1.90}}: A POTENTIAL ELECTROLYTE FOR IT-SOFC ”

“5.1. INTRODUCTION”

CGO is considered to be one of the most promising electrolytes for SOFCs to be operated below 650°C, as it has higher ionic conductivity compared to other commonly used materials such as YSZ and LSGM (La\text{0.9}Sr\text{0.1}Ga\text{0.8}Mg\text{0.2}O\text{2.85}) (Minh et al. 1993) (already discussed in chapter1-review).

Gadolinium oxide, Gd\text{2O\text{3}}, has C-type crystal structure (Mn\text{2O\text{3}} type) in which six oxygen atoms surrounds a gadolinium atom. C-type structure is obtained by removing two oxygen atoms of eight in fluorite structure in a regular manner (Nakagawa et al. 2001). Therefore, gadolinium- doped ceria (CGO) is a solid solution formed by replacing the Ce\text{4+} sites of the CeO\text{2} fluorite lattice by Gd\text{3+} cations.

The ionic conductivity of ceria resulting from oxygen vacancies depends on the dopants and their amount (Yahiro et al. 1989., Inaba et al. 1996). It increases significantly when ceria is doped with aliovalent oxides such as Y\text{2O\text{3}} and various rare earth oxides. However, an increasing amount of dopants tends to form a second phase due to the solubility limit, and this reduces the conductivity. The critical dopant concentration to achieve the total conductivity was reported to be approximately 20 mol%, which was due to the formation of microdomains (Zhang et al. 2004).

Dense ceramic bodies of CeO\text{2} are difficult to obtain since sintering of this material typically requires temperatures above 1500°C. However, these high temperatures lead to a decrease in density and microcracking. This is believed to be due to the reduction of Ce\text{4+} to Ce\text{3+} above 1300°C. Since the diffusivity of oxygen in pure CeO\text{2} is very low, the expansion effect, microcracking and thus poor sinterability is mainly attributed to the liberation of oxygen. Therefore, much research has been directed to decrease the sintering temperature of ceria based solid electrolytes.

Fully dense sintered CeO\text{2} has not been obtained prior to the work of Chen in 1993, who succeeded in sintering CeO\text{2} at temperatures <1300°C using nano powders.
Rahaman, et al (1995) found that doping CeO$_2$ with divalent and trivalent cations strongly effects the sintering and grain growth. They obtained material of > 98% density with an average grain size of 100 nm when sintering 3 mol% Y$_2$O$_3$ doped CeO$_2$ at 1150°C for two hrs.

Sirman et al (1997) studied the effect of adding 0.5 cation % Co to CGO and calcined the sample at 300°C and sintered samples at 1400°C for 50 h by isothermal heating. He found decrease in the lattice parameter and above 0.5% addition of Co there was no effect on the lattice parameter so he concluded that the solubility of Co in CGO was 0.5%

Kleinlogel (1999) reported the effect of sintering temperature and time on the conductivity of addition of 1- 2 mole% Co in CGO and found that doping the CGO below 2 mole % did not change conductivity significantly.

Lewis et al (2003) convinced with the proposal that transition metal ions act as acceptors enhancing the concentration of charge compensating oxygen vacancies and, hence, mass transport and, in turn, sinterability.

The purpose of this work was to investigate the potentiality of microwave energy in the sintering of precursor Ce$_{0.80}$Gd$_{0.20}$O$_{1.90}$ (CGO) with 1mole % of transition metal oxide CoO prepared by mixed oxide method in order to lower sintering temperature and time.

“5.2. EXPERIMENTAL”

The precursor powder was prepared by mixed oxide method corresponding to composition CoCe$_{0.80}$Gd$_{0.20}$O$_{1.90}$ (CoCGO). CeO$_2$, Gd$_2$O$_3$ were taken in stoichiometric ratio and ball milled for six hours in a vertical ball mill using zirconia balls in acetone medium. The acetone was removed by evaporation. The powder obtained was mixed with 4 % PVA solution prepared in water. 1mole % Co was added to CGO in the form of Co$_3$O$_4$ and again ball milled for six hours in a vertical ball mill using zirconia balls in acetone medium. The microwave system used in this study was a modified domestic microwave oven of 2.45 GHz having maximum 1.2 KW power output. An applicator made of microwave transparent insulating material was used for sintering. The crucible was surrounded with porous zirconia, which works as an insulator as well as susceptor. The CoCGO specimens were sintered using microwave energy at 900°C , 1000°C , 1100°C , 1200°C in, 1300°C for 10 min. soaking time period. For the
CeO₂ and Gd₂O₃ IN POWDER FORM WERE MIXED IN STOCHIOMETRIC RATIO IN POLYTHENE BOTTLES TO GET PRECURSOR Ce₀.₈Gd₀.₂O₁.₉ and Co₃O₄ WAS ADDED TO GET Co Ce₀.₈Gd₀.₂O₁.₉

POWDER WERE BALL MILLED USING ZIRCONIA BALLS AND ACETONE AS GRINDING MEDIUM FOR 8 HOURS

POWDER WERE DRIED IN OPEN AIR & WERE MIXED WITH 4% PVA BINDER

CONSOLIDATION OF POWDERS IN CYLINDRICAL PELLETS BY UNIAXIAL PRESSING

SINTERING

MICROWAVE SINTERING 900°C, 1000°C, 1100°C, 1200°C and 1300°C for 10 min

CONVENTIONAL SINTERING AT 1300°C FOR 8 HOURS

CHARACTERIZATION BY DENSITY, XRD, SEM, VICKERS HARDNESS, FRACTURE TOUGHNESS AND IMPEDANCE ANALYSIS.

“Figure 5.1. The schematic diagram of the preparation and characterization of Co Ce₀.₈Gd₀.₂O₁.₉”
comparison the green pellets were sintered conventionally also at 1300°C for 8 hrs soaking time period. The microwave sintered samples were designated as CoCGOMW and conventionally sintered samples were designated as CoCGOCON. The method in detail has been given in chapter 2. The resulting materials were characterized by XRD, SEM(fractured surface), Density measurements, Vicker’s hardness, Fracture toughness and complex Impedence analysis for the electrical conductivity measurements. The whole process is shown in the figure 5.1.

“5.3 RESULTS AND DISCUSSION”

5.3.1 XRD study

Figure 5.2 (a) shows the XRD pattern of the CoCe$_{0.80}$Gd$_{0.20}$O$_{1.90}$ (CoCGO) precursor powder. It shows the mixture of phases. Figure 5.2 (b-f) shows the XRD of CoCGO microwave sintered at 900°C for 10 min, CoCGO microwave sintered at 1000°C for 10 min, CoCGO microwave sintered at 1100°C for 10 min, CoCGO microwave sintered at 1200°C for 10 min, and CoCGO microwave sintered at 1300°C for 10 min. Figure 5.2 (g) shows the XRD pattern of the conventionally sintered CoCe$_{0.80}$Gd$_{0.20}$O$_{1.90}$ (CoCGO). The peaks of CCOCON XRD have been indexed for the cubic phase of CeO$_2$. The characteristic peaks of cubic CeO$_2$ are (111), (200), (220), (311), (222), (400), (331) and (420). The XRD patterns indicate the formation of a single-phase material in the sintered samples. The diffraction peaks of the MW CoCGO samples are essentially unchanged from that of the pure CeO$_2$ except for slight shifts towards left (i.e. decrease in $2\theta$). This has been also reflected in increase in the lattice parameter of microwave sintered CoCGO sample with increase in temperature. The lattice parameter, $a$, was determined as 5.4208 for pure CGO. We found a decrease of the cubic lattice constant in sample of CGO doped with cobalt due to the smaller sizes of the cobalt cations.

The indexing of the diffraction peaks would also be consistent with the lattice planes of the fluorite structure Ce$_{0.80}$Gd$_{0.20}$O$_{1.90}$ with $a = 5.420$ Å (JCPDS database 75-0162). However, the XRD pattern could be also compatible with a CeO$_2$ in a cubic fluorite structure or with a C type Gd$_2$O$_3$ structure, since it is difficult to clearly
“Figure 5.2. XRD Pattern of (a) CoCe$_{0.80}$Gd$_{0.20}$O$_{1.90}$ (b) CoCGO (MW) sintered 900°C for 10 min. (c) CoCGO MW sintered 1000°C for 10 min. (d) CoCGO sintered 1100°C for 10 min. (e) CoCGO (MW) sintered at 1200°C for 10 min. (f) CoCGO MW sintered 1300°C for 10 min. (g) CoCGO (CON) sintered at 1300°C for 8 hours”
"Table 5.1. Lattice constant of pure ceria, precursor and conventionally and microwave sintered pellets of Co \((C_{0.80}G_{0.20}O_{1.90})\)"

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering Temperature (°C)</th>
<th>Sintering Time</th>
<th>Lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO</td>
<td>-</td>
<td>-</td>
<td>5.4208</td>
</tr>
<tr>
<td>CoCGO</td>
<td>-</td>
<td>-</td>
<td>5.4201</td>
</tr>
<tr>
<td>Co CGO (MW)</td>
<td>900</td>
<td>10min</td>
<td>5.4207</td>
</tr>
<tr>
<td>Co CGO (MW)</td>
<td>1000</td>
<td>10min</td>
<td>5.4208</td>
</tr>
<tr>
<td>Co CGO (MW)</td>
<td>1100</td>
<td>10min</td>
<td>5.4209</td>
</tr>
<tr>
<td>Co CGO (MW)</td>
<td>1200</td>
<td>10min</td>
<td>5.4211</td>
</tr>
<tr>
<td>Co CGO (MW)</td>
<td>1300</td>
<td>10min</td>
<td>5.4212</td>
</tr>
<tr>
<td>CoCGO (CON)</td>
<td>1300</td>
<td>8 hours</td>
<td>5.4209</td>
</tr>
</tbody>
</table>
distinguish between those structures and the CGO solid solution. In the fluorite unit cell structure, the Ce\(^{4+}\) cations are placed in the FCC lattice sites, while the anions (O\(^{2-}\)) are located at the eight tetrahedral sites. Four remaining octahedral sites in the FCC lattice remain vacant.

On indexing the XRD patterns it was observed that CoCGO retained the cubic symmetry of CeO\(_2\) as the ionic radii of Gd (1.05 Å) is close to that of Ce (0.97 Å). Thus, 20% of gadolinium oxide is completely dissolved into the ceria fluorite structure, which means that the Ce\(^{4+}\) ions of the lattice are partially replaced by the Gd\(^{3+}\) ions.

It has been already mentioned in chapter 1 that the microwave processing is a volumetric heating of a material. It is a material property controlled by polarization and its relaxation behavior. The presence of the substitutionally dissolved aliovalent cations in ceria results in the formation of equivalent concentration of oxygen vacancies (Etsell, 1970). It has been proposed by Klein et al (1996) and Breckridge (1952) that the relaxation behavior is observed due to vacancy-vacancy and vacancy-impurity pairs. The change in the polarizability is expected to produce observable changes in microwave absorption by the material.

### 5.3.2 Density measurements

Green pellets of CGO were sintered at 900°C, 1000°C, 1100°C, 1200°C and 1300°C for 10 min soaking time period. Figure 5.3 shows the variation in densities CGO samples microwave sintered at different temperature for 10 min of fixed time period. It shows that the densities of microwave sintered CGO samples increases with sintering temperature for a fixed time of 10 min. The highest density of 7.39 g/cm\(^3\) was achieved at 1300°C (Table 5.2). The sample of same composition was sintered by conventional heating for 8 hours at 1300°C. The density of the sample was found to be 5.02 g/cm\(^3\). Small amounts of sintering aids, e.g. transition metal oxides Co is added to increase the sintering rates so enhanced densification rates have been obtained in constant heating rates by doping CGO with 1 mol% of CoO.

The higher densities obtained in all the microwave processed samples i.e. CoCGO reflect the volumetric heating as well as higher diffusion that has occurred during microwave sintering which is attributed to the microwave effect. The enhanced
Table 5.2. Densities of microwave processed Co\(\text{Ce}_{0.80}\text{Gd}_{0.20}\text{O}_{1.90}\) at different sintering temperatures with soaking time period of 10 min

<table>
<thead>
<tr>
<th>Composition (\text{Co(Ce}<em>{0.80}\text{Gd}</em>{0.20}\text{O}_{1.90}))</th>
<th>Sintering Temperature (\degree\text{C})</th>
<th>Sintering Time</th>
<th>Sintered Density(\text{g/cm}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co CGO(\text{MW})</td>
<td>900</td>
<td>10min</td>
<td>5.04</td>
</tr>
<tr>
<td>Co CGO(\text{MW})</td>
<td>1000</td>
<td>10min</td>
<td>5.64</td>
</tr>
<tr>
<td>Co CGO(\text{MW})</td>
<td>1100</td>
<td>10min</td>
<td>5.98</td>
</tr>
<tr>
<td>Co CGO(\text{MW})</td>
<td>1200</td>
<td>10min</td>
<td>6.89</td>
</tr>
<tr>
<td>Co CGO(\text{MW})</td>
<td>1300</td>
<td>10min</td>
<td>7.39</td>
</tr>
<tr>
<td>Co CGO(\text{CON})</td>
<td>1300</td>
<td>8 hrs</td>
<td>5.02</td>
</tr>
</tbody>
</table>
“Figure 5.3. Variation of densities of CoCe\textsubscript{0.8}Gd\textsubscript{0.2}O\textsubscript{1.9} for microwave sintered at different temperatures with soaking time period of 10 min”
densification of the ceramic material due to the microwave heating has been observed in many studies. Rothman (1994) confirms the microwave enhanced diffusion in his critical review. He indicates that the enhanced diffusion observed by Janney and Kimry (1991) in sapphire single crystal and Fathi et al (1992) in silicate glass is due to the volume bulk diffusion, since there is no grain boundaries in these cases.

For polycrystalline materials, the microwave enhancement cannot be simply attributed to the volume diffusion because of the presence of the grain boundaries with various defects. According to Freeman et al (1993) the ionic mobility along grain boundary can be three to four orders of magnitude greater than in the bulk and so the grain boundary diffusion is mainly responsible for the densification of ceramic after sintering. Also, it has been emphasized by Fang (1994) that the grain boundaries couple with microwave more strongly than the bulk thus, the enhancement in diffusion during the sintering may be attributed to the enhancement in grain boundary diffusion. Meek (1987) and Brooske et al (1991,1992) have attempted to interpret the microwave enhanced densification, but no satisfactory theory has been developed. Further Co has been added as a sintering aid to the CGO resulting in the formation of multiphase CoCGO. The Co is a magnetic material therefore more susceptible to microwave absorption compared to cerium and gadolinium. The higher susceptibility of Co for microwave absorption will lead to anisothermal diffusion in the CoCGO system which results in the faster sintering with better densification. However, in the conventional sintering isothermal diffusion occurs resulting in the delayed sintering and poor densification.

5.3.3 Microstructure study: SEM

The scanning electron microscopy of the samples was carried out for the understanding of their microstructures. Scanning electron micrographs (SEM) of sample CoCe$_{0.80}$Gd$_{0.20}$O$_{1.90}$ (CoCGO) microwave sintered at 1200ºC for 10 min. soaking time period and SEM of the sample CoCGO microwave sintered at 1300ºC for 10 min soaking time period is shown in the figure 5.4 and figure 5.5 respectively. The SEM of sample conventionally sintered at 1300ºC for 8 hours is shown in the figure 5.6. Comparing the SEM in figure 5.4 and 5.5 reveals that CoCGO microwave sintered at 1200ºC for 10 min. (fig.5.4) has poor grain growth and high porosity and
“Figure 5.4. SEM Micrographs Co(Ce<sub>0.80</sub>Gd<sub>0.20</sub>O<sub>1.90</sub>) microwave sintered at 1200°C for 10 min”

Figure 5.5. SEM Micrographs Co(Ce<sub>0.80</sub>Gd<sub>0.20</sub>O<sub>1.90</sub>) microwave sintered at 1300°C for 10 min”
“Figure 5.6. SEM Micrographs Co(Ce_{0.80}Gd_{0.20}O_{1.90}) conventionally sintered at 1300°C for 8 hours”
the samples sintered at 1300°C for 10 min. has higher grain growth and low porosity (fig. 5.5). This reveals that with the increase in temperature for the same soaking time period the grain size has increased and density has also increased with increase in temperature. However SEM of conventionally sintered sample shows large grain growth having large number of pores which is revealed in its poor densification. It reveals that during conventional sintering the diffusion of particles is poor leading to poor densification but due to prolonged sintering (8 hrs) at 1300°C leads to the grain growth locally.

**5.3.4 Vickers hardness**

Figure 5.7 shows the Vickers indentation images of samples Co(Ce<sub>0.80</sub>Gd<sub>0.20</sub>O<sub>1.90</sub>) microwave sintered at 1300°C for 10 min and Co(Ce<sub>0.80</sub>Gd<sub>0.20</sub>O<sub>1.90</sub>) conventionally sintered at 1300°C for 8 hrs. Co (Ce<sub>0.80</sub>Gd<sub>0.20</sub>O<sub>1.90</sub>) microwave sintered at 1300°C for 10 min shows the Vickers hardness 6.87 GPa. The lower hardness of sample (4.38GPa) which is sintered conventionally at 1300°C for 8 hours was due to high porosity.

Table 5.3 shows the Vickers hardness of sample of CoCGO sintered by microwave processing at 900°C, 1000°C, 1100°C, 1200°C and 1300°C for 10 min and conventionally sintered at 1300°C for 8 hours. Further during microwave processing as the sintering temperature increases from 900°C to 1300°C for 10 min soaking time period, the Vickers hardness increases. It is evident from the table 5.3 that hardness of CoCGO microwave processed at 1300°C for 10 min is higher than that of conventionally sintered samples.

According to the literatures, grain size is the other important factor that can affect hardness of ceramic materials. However, due to the superseding effect of density on the hardness, this trend was not very obvious here. The direct effect of density on the hardness of ceramics also has been reported by some others (Jahromi et al, 2009).

Table 5.3 shows the values of Fracture toughness (K<sub>IC</sub>) obtained by applying Vickers indentation at a load of 0.5 Kg. In general, K<sub>IC</sub> decreased with the increase of hardness and density and this is well reflected from the values given in the table. Sample microwave sintered at 1300°C for soaking time period of 10 min with the
“Figure 5.7. Vickers indentation images of samples in Co(Ce$_{0.80}$Gd$_{0.20}$O$_{1.90}$)

(a) MW sintered at 1300°C for 10 min (b) Co(Ce$_{0.80}$Gd$_{0.20}$O$_{1.90}$)

Conventionally fired at 1300°C for 8 hrs”
“Table 5.3. Vickers hardness in Co Ce<sub>0.80</sub>Gd<sub>0.20</sub>O<sub>1.90</sub> MW and CON sintered at 1300ºC for 10 min with 0.5 Kg load applied”

<table>
<thead>
<tr>
<th>Co Ce&lt;sub&gt;0.80&lt;/sub&gt;Gd&lt;sub&gt;0.20&lt;/sub&gt;O&lt;sub&gt;1.90&lt;/sub&gt;</th>
<th>Sintering Temperature(ºC)</th>
<th>Sintering Time</th>
<th>Vickers Hardness(GPa)</th>
<th>Fracture Toughness (MPa.m&lt;sup&gt;1/2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCGO (MW)</td>
<td>900</td>
<td>10 min</td>
<td>4.96</td>
<td>3.7</td>
</tr>
<tr>
<td>CoCGO (MW)</td>
<td>1000</td>
<td>10 min</td>
<td>5.07</td>
<td>3.5</td>
</tr>
<tr>
<td>CoCGO (MW)</td>
<td>1100</td>
<td>10 min</td>
<td>5.47</td>
<td>3.4</td>
</tr>
<tr>
<td>CoCGO (MW)</td>
<td>1200</td>
<td>10 min</td>
<td>6.07</td>
<td>3.2</td>
</tr>
<tr>
<td>CoCGO (MW)</td>
<td>1300</td>
<td>10 min</td>
<td>6.87</td>
<td>2.9</td>
</tr>
<tr>
<td>CoCGO (CON)</td>
<td>1300</td>
<td>8 hours</td>
<td>4.38</td>
<td>3.8</td>
</tr>
</tbody>
</table>
maximum values of hardness and density revealed the lowest $K_{IC}$ of 2.9 MPa.m$^{1/2}$. Briefly, these mechanisms explain that, presence of any micro crack, defect, or porosity inside the material would result in the increase of Gc or strain energy release rate by extension of micro cracks and redistribution of stress ahead of the crack tip or by modifying the crack path. In summary, decrease of density, which results in the increase of porosities or defects fraction inside the material will increase the Gc and $K_{IC}$ of samples as a result. In the optimum condition, the $K_{IC}$ of 3.7 MPa.m$^{1/2}$, HV of 4.96 G Pa were obtained for the CoCGO samples having density 5.04g/cm$^3$ microwave sintered at 900°C. The $K_{IC}$ value obtained in our samples was larger than the reported $K_{IC}$ of 1 to 2 MPa.m$^{1/2}$ for the undoped ceria. According to Wang et al, 2007 density would affect the value of fracture toughness by activating micro crack formation and extension, or deflection toughening (in the case of larger fraction of porosity) mechanisms.

A comparison of data from literature show that cobalt codoped CGO has slightly worse mechanical properties as compared to 8YSZ electrolyte for high temperature SOFC.

### 5.3.5 Electrical conductivity study

The bulk electrical conductivity of the microwave and the conventionally processed CGO samples were evaluated from their complex admittance plots in the temperature range of 350°C to 700°C. It is reported (Petot et al 1998) that both the bulk electrical conductivity and the overall electrical conductivity (due to the transport process, in the bulk and in the grains) do not depend on the oxygen partial pressure. Therefore, the bulk electrical conductivity measurements were performed in the air only.

Figure 5.8 (a and b ) shows the typical admittance plots of the microwave processed (1300°C) CoCGO at 650°C and 700°C. It shows two dispersion curves, the intercept of which on real axis (G-axis) gives the bulk electrical conductivity of the samples. The higher frequency dispersion curve is steeper and it indicates that the grain boundary resistance of the samples is smaller. The conductivity of the CoCGO samples microwave sintered at 1300°C for 10 min was higher than that for the
samples microwave sintered at 1200°C for 10 min and conventional sintered samples at 1300°C for 8 hours.

Figure 5.9 shows the temperature variation of the electrical conductivity of CoCGOMW samples in the temperature range of 350 to 700°C. It is evident from figure 5.9 that the conductivity of CoCGOMW samples increases with increasing temperature and becomes maximum at 650°C. CoCe$_{0.80}$Gd$_{0.20}$O$_{1.90}$ was found to have the highest conductivity $6.9 \times 10^{-2}$ at 650 °C (Ω cm)$^{-1}$ at 700°C conductivity is found to be almost same but in case of samples of CoCGO conventionally processed conductivity is found to be $9.8 \times 10^{-3}$ at 650 °C (Ω cm)$^{-1}$ is very low.

The variations in the bulk electrical conductivity of the microwave processed CGOMW and conventionally processed CGO samples deduced from the complex admittance plot in the temperature range of 350°C to 700°C. These plots show Arrhenius behavior represented by the equation (Nowick 1984; Kilner 1981)

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

(5.3.1)

where $E_a$ is the activation energy for the conduction of the charge carrier (ions) and the pre-exponential factor $\sigma_0$ is a material constant. Since equation (5.3.1) predicts that there is a linear relationship between log $\sigma$ (or log $\sigma T$) and $1/T$, a single straight line is obtained usually referred to as the Arrhenius plot. From the slope of each Arrhenius plot (Figure 5.10), the value of the activation energy ($E_a$) and the pre-exponential factor ($\sigma_0$) were calculated as given in table 5.4.

From table 5.4, it is evident that as the sintering temperature is increased from 900°C for 10 min to 1300°C for 10 min the activation energy of microwave processed samples of CoCGO decreases and the pre-exponential factor of microwave processed CGO samples increased. It is reported that at the low temperatures (below 700°C), most of the oxygen vacancies in the doped CGO are associated with the doping cations and the measured activation energy for the electrical conduction is the sum of the formation and the migration energies of the oxygen vacancies (Nowick, 1984). The increase in the bulk activation energy with increase in sintering temperature is an indication of defect clustering (Nowick, 1984). The activation energy of CGO MW samples has been calculated in the range of 0.66eV and 1.1eV. The increase in the pre-exponential factor with the CGO may be attributed due to increase in the charge
“Figure 5.8. (a) Admittance curve of CoCGO at 650°C microwave sintered at 1300°C
(b) CoCGO at 700°C microwave sintered at 1300°C”
“Figure 5.9. Variation in electrical conductivity of CoCGO MW and CoCGOCON with temperature”
“Figure 5.10. Variation in the bulk electrical conductivity of CoCe$_{0.8}$Gd$_{0.2}$O$_{1.9}$ microwave sintered at 900°C for 10 min, 1000°C for 10 min, 1100°C for 10 min, 1200°C for 10 min and 1300°C for 10 min and CoCe$_{0.8}$Gd$_{0.2}$O$_{1.9}$ conventionally sintered at 1300°C for 8 hours”
carrier concentration which may lead to the increase in bulk electrical conductivity (Nowick, 1984, Kilner 1981). Table 5.4 shows the variation in the activation energies of the CGO sample microwave sintered samples. CGO sintered at 1300°C for 10 min show activation energy 0.74 eV. Activation energy decreases from 1.1 eV to 6.6eV for the CGO samples when sintered at 900°C for 10 min to 1300°C for 10 min. The
CGO sample conventionally sintered at 1300°C for soaking time period of 8 hours showed the activation energy of 1.1 eV.

“5.3. CONCLUSION”

The results show that sintering of gadolinium doped CeO2-solid solutions in presence of transition metal cobalt has a profound effect on densification and microstructure. It has been shown that doping of CGO with 1 mol% CoO gives rise to > 95% dense ceramic material. Factors affecting solid solution formation include ionic radius and valence. It is well known however, that CeO2 and CoO do not react to form a compound, and that the ionic radius of Co2+ is 0.90, close to that of Ce4+ with 0.97. From this we expect a high solubility of Co within the CeO2 lattice chemical affinity and structural similarity. The sintering temperature for CGO after adding cobalt as an sintering aid has decreased from 1600°C to 1300°C. For 1 mol% cobalt addition we obtained dense samples having density 7.39 g/cm³ at 1300°C for 10 min soaking time period. After sintering started the rate of densification increases with increase in sintering temperature. Poor densification is obtained for samples sintered conventionally at 1300 °C for 8 hours. The activation energies determined from the slope of the curves in the plot for the samples microwave sintered at 1300°C for 10 min is 0.66eV and CoCe0.8Gd0.2O1.90 was found to have the highest conductivity (6.9× 10⁻² at 650 °C (Ω cm)⁻¹ whereas Chiodelli et al, 2005 investigated conductivity value of 2.6× 10⁻² at 700°C (Ω cm)⁻¹ for Ce0.8Gd0.2O1.9 which is very lower value as compared to our studies. The electrical properties of the products are improved by microwave sintering than that of products made by the conventional ceramic route. In addition, by appropriate selection of doping level of sintering aid in ceria solid solution, sintering temperature and heating rate the opportunity is given to co-sinter cathode, anode and electrolyte in solid oxide fuel cell applications in a single step thereby reducing thermal stresses, chemical reactions of the components and fabrication costs. CoO doped Ce0.8Gd0.2O1.9 ceramics sintered at temperatures as low as 1300°C for soaking time period of only 10 min. are promising candidates for electrolytes in SOFCs which can be operated at intermediate temperatures with high power output.