Effect of Submicron Grains on Ionic Conductivity of Nanocrystalline Doped Ceria

Virendra Singh\textsuperscript{1}, Suresh Babu\textsuperscript{1}, Ajay Singh Karakoti\textsuperscript{1}, Arvind Agarwal\textsuperscript{2}, and Sudipta Seal\textsuperscript{1}\textsuperscript{*}

\textsuperscript{1}Surface Engineering and Nanotechnology Facility, Plasma Nanomanufacturing Facility, Advanced Materials Processing and Analysis Center (AMPAC), Mechanical Materials Aerospace Engineering, Engineering Building, Room \#381, P.O. Box 162455, University of Central Florida, Orlando, FL 32816, USA

\textsuperscript{2}Mechanical and Materials Engineering, Florida International University, Miami, FL 33174, USA

Doped ceria has been considered for high oxygen ion conductivity for solid oxide fuel cells. In the present study, 20 mole% samarium doped nano ceria powder was prepared by wet chemical synthesis and sintered at different temperatures to retain submicron grains (>92–96\% density). Ionic conductivity of the sintered pellets was measured using impedance spectroscopy as a function of temperature (200–800 °C). The total maximum conductivity was \(1.0 \times 10^{-2}\) S.cm\(^{-1}\) (at 600 °C) for samples sintered at 1200 °C. The activation energy at higher test temperature decreases with the decrease in the sintering temperature (by 25\%). The grain boundary, grain interior conductivity and activation energy of the electrolyte were correlated to the resulting microstructure. It has been demonstrated that use of doped nano ceria powder as precursor not only reduced the sintering temperature but also provided segregation free grain boundary for engineering higher conductivity dense electrolytes.

Keywords: Doped Ceria, Nanopowder, Conductivity.

1. INTRODUCTION

In the recent years increasing demand for efficient alternate energy resources has expedited the research on energy related materials. Solid oxide fuel cells (SOFC) are one of the attractive candidates for conversion of low cost fuels to energy. Extensive research has been done over past few decades to find suitable materials that can act as electrolytes for transfer of ions or species to the working electrode of SOFC.\textsuperscript{1–4} Conventionally yttria stabilized zirconia (YSZ) has been used as an electrolyte due to its high oxygen ion conductivity and chemical stability at higher temperatures (>900 °C). The operation at high temperature (900–1100 °C) required special interconnects, insulations and unique sealing that further increases the operational cost. Thus, there is an imminent need for SOFCs which can operate at relatively lower temperature region e.g., 450–700 °C, called intermediate temperature solid oxide fuel cells (IT-SOFC). Doped ceria as a solid electrolyte has been found as a promising candidate for high ionic conductivity at intermediate temperatures (<700 °C). As compared to the zirconia based electrolytes, ceria does not undergo any phase transformation at the operating temperature range.

Further, doping of trivalent ions such as Gd\textsuperscript{3+}, Y\textsuperscript{3+}, Sm\textsuperscript{3+}, Nd\textsuperscript{3+}, and Pr\textsuperscript{3+} increase the oxygen ion vacancies in the ceria host which further increase the ionic conductivity and power density of the doped ceria based electrolytes.\textsuperscript{2,5–7} Besides dopants, the performance of the solid electrolyte is also affected by factors such as density of the sintered electrolyte, Si or Ca impurity segregation at the grain boundary, segregation of dopants at grain boundary and the surrounding oxygen partial pressure. High density of the electrolyte is the primary requirement to avoid the reaction between the fuel (hydrogen or CO) and oxygen at the electrodes. It has been established that highly dense doped ceria electrolytes, by mixed oxide route, can only be obtained by sintering above 1500 °C for several hours. However, the high temperature sintering of doped ceria is detrimental for SOFC applications due to the following reasons: (1) It is difficult to obtain fully dense ceria based electrolytes by high temperature sintering due to the release of oxygen by reduction of cerium from Ce\textsuperscript{4+} to Ce\textsuperscript{3+} causing pin holes and micro cracks in the sintered body. (2) Solute segregation at the grain boundary from the lattice increases with higher sintering temperature; this further increases the grain boundary blocking effect for oxygen ion conductivity.

On the other hand, the higher surface energy and reactivity of nano crystalline powder allows sintering well
below the temperature required for the coarse grained polycrystalline micron sized powders. The use of doped nano ceria also facilitates sintering at lower temperature and therefore it can be co-sintered with electrode material, which can further lower the fabrication cost of the SOFC. Numerous techniques have been developed to synthesize nano crystalline cerium oxide powders with and without doping, such as sol-gel,\textsuperscript{1,3} precipitation,\textsuperscript{9,10} hydrothermal,\textsuperscript{11} combustion process\textsuperscript{12} microemulsion.\textsuperscript{13} The cerium oxide produced via these methods generally show higher reactivity than the coarse ones. These nanopowders grow in size upon sintering at higher temperatures resulting in electrolytes with higher grain size than the original nanoparticles. Conventional doped ceria electrolytes for IT-SOFC applications have grain sizes in the size range greater than 1.0 μm. The ionic conductivity studies on nano crystalline doped cerium oxide, in the grain size range of 10–40 nm, revealed an increase in electronic conductivity over the coarse grained electrolytes.\textsuperscript{14,15} However, limited studies are available on the effect of sub micron grains (100 nm–1 μm) of the electrolyte on ionic conductivity. In the present study we have tried to bridge the gap (between nano and micro) by studying the ionic conductivity of sub micron grain sized samarium doped ceria electrolytes. The ionic conductivity of the sintered pellets was recorded and reported as a function of sintering temperature and grain size.

2. EXPERIMENTAL DETAILS

2.1. Sample Preparation

Cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O, purity ~99.9%, Sigma–Aldrich, USA) and samarium nitrate (Sm(NO$_3$)$_3$·6H$_2$O, purity ~99.9% Sigma–Aldrich, USA) were used for nano powder preparation. Stoichiometric amount of cerium nitrate and samarium nitrate were dissolved in deionized water subsequently added 1 N ammonium hydroxide as precipitant. The particles were washed with deionized water and centrifuged to remove any adsorbed nitrate ions. Finally nano particles were dried in the vacuum oven at 80 °C and annealed at 600 °C for 2 hrs before final sintering treatment. Powders were uniaxially pressed at a compaction pressure of 240 MPa to form green pellets. Sintering temperature was varied from 1200 to 1600 °C for 3 h to study the effect of sintering temperature on ionic conductivity while sintering time was varied from 3 to 9 hrs at a fixed temperature of 1300 °C.

2.2. Structural and Microstructural Analysis

The X-Ray diffraction (XRD; Rigaku D-Max B diffractometer) pattern was collected and analyzed to identify the crystallite size and phase. The crystallite size of the doped ceria was calculated using the equation.

$$D = \frac{0.9\lambda}{\beta_{\cos \theta}}$$

where λ ~ wavelength of the X-rays, $2\theta$ ~ diffraction angle and $\beta$s ~ observed FWHM, $\beta_m$ ~ corrected FWHM of doped sample and $\beta_c$ ~ FWHM of standard ceria sample. Density of the sintered pellets was determined using Archimedes principle and relative densities were reported as a function of sintering temperature and time.

Theoretical density of Ce$_{0.9}$Sm$_{0.1}$O$_{2-δ}$ was determined using the following equation.

$$\rho_{\text{theoretical}} = \frac{3.2M_{\text{Ce}} + 7.6M_{\text{O}} + 0.8M_{\text{Sm}}}{N_a \alpha^3}$$

Where $M_{\text{Ce}}$, $M_{\text{O}}$, and $M_{\text{Sm}}$ are atomic weight of Ce, O and Sm, $N_a$ ~ Avogadro number and “α” is the lattice parameter determined from XRD. Comprehensive microstructural characterization of the sintered pellets was carried out using scanning electron microscopy (SEM; Carl Zeiss Ultra 55). High resolution transmission electron microscopy, HRTEM (Philips Tecnai F30) was used to study the particles size of the as synthesized Sm doped nano ceria.

2.3. Impedance Measurement

The sintered pellets were polished from both sides and coated with Pt paste (CL, Heraeus), connected with a Pt wire (99.9 pure, diameter ~0.3 mm) and cured at 900 °C for 1 hr. The ionic conductivities of the sintered pellets were measured using impedance spectroscopy (Solartron 1260). Impedance measurement was conducted at different temperatures (200 to 800 °C) in air. At each temperature, electrolyte sample was soaked in the furnace for half an hour before impedance measurement. The imaginary and real part of the impedance was measured in the frequency range of 0.1 to 10 MHz with a 100 mV AC excitation signal. An equivalent circuit model was generated using Zview® software to fit impedance spectra of the electrolyte. To minimize the inductive effect (at high temperature) of the instrument and Pt wire connections, an extra inductor (L) was used in the equivalent circuit during impedance data fitting.

3. RESULTS AND DISCUSSION

3.1. Electrolyte Synthesis and Characterization

Nano structured 20 mol% samarium doped ceria was prepared using a simple wet chemical precipitation technique. HRTEM and XRD confirm the nano morphology of the
Effect of Submicron Grains on Ionic Conductivity of Nanocrystalline Doped Ceria

The selected area electron diffraction (SAED) patterns depict the fluorite phase of the particles (inset of Fig. 1). The powder was subsequently compacted to pellet and sintered at different temperatures. Surface cracks and porosity were observed in the pellet due to the evaporation of the retained nitrate and hydroxyl groups during the initial stages of sintering. Thus the as-prepared nano powder was annealed at 600 °C for 2 hrs to ensure complete removal of the volatile matter before compaction. The XRD patterns of the dried and annealed powders showed broader peaks indicating the nanocrystalline nature of the as-prepared powder. The observed planes in XRD can be indexed to ceria (JCPDS # 34-0394) and no phase separation into samaria was observed from the XRD pattern. The crystallite size calculated from Debye-Scherrer formula from the (111) peak indicate an increase in size from 6.5 nm to 14 nm upon annealing. The pellets were subsequently sintered at 1200 to 1600 °C for different sintering times. XRD pattern of the sintered pellet is shown in Figure 1(c, iii), indicates sharp peaks due to the coarsening of the nano particles. Doping of Sm in cerium oxide leads to the expansion of the cerium oxide lattice to 0.544 nm with a theoretical density of 7.12 g/cm³ calculated by Eq. (2). The effect of sintering temperature on density and grain size of the pellets are shown in Figure 2. The density increases with an increase in sintering temperature until 1400 °C and decreases at 1500 and 1600 °C. This decrease in density can be attributed to the reduction of Ce⁴⁺ to Ce³⁺ according to the following reaction, that releases oxygen from the samples during sintering and generates pin holes and surface cracks which is evident from the SEM results (Fig. 3). Additional, Inaba et al. demonstrated that the densification of doped nano ceria depends upon the diffusion of oxygen from the pores and diffusion rate of oxygen is the rate determining step in densification. This phenomenon was observed especially with nano ceria (5–15 nm) powders sintered at higher temperature (≥1500 °C) and is consistent with the reported literature.

![HRTEM of 20 mol% doped cerium oxide nano particles](image)

**Fig. 1.** HRTEM of 20 mol% doped cerium oxide nano particles (a) As prepared and dried at 120 °C (b) powder annealed at 600 °C for 2 h reveals nano particles growth up to 16 nm. (c) X-ray diffraction pattern (i) As prepared nano powder dried at 120 °C, broad peaks indicate the nano-crystalline nature of the powder (average particle size~6.5 nm) (ii) As prepared powder annealed at 600 °C for 2 h (average particle size~14 nm) (iii) Sintered pellet at 1400 °C for 3 h shows sharp peaks, attributed to the coarsening of nano grain.
3.2. Sintering Time and Temperature Correlation to Microstructural Evolution

Since the nanocrystalline material contains very high fraction of atoms at the grain boundaries, thus the various interfaces facilitate enhanced diffusivity. An important consequence of high diffusivity is that sintering of powders can occur at temperatures much lower than those required for coarse grained polycrystalline powders. The microstructural changes during sintering are shown in the Figures 3(a–c) and 4(a–d). The compact density of the sintered pellet increases to 96.5% for samples sintered at 1400 °C (Fig. 2). Substantial grain growth was observed for pellets sintered at higher temperatures (Fig. 4). Doped ceria grains were well connected in the selected sintering temperature range with reduced porosity. Temperature plays a vital role in coarsening the grain rather than the duration of annealing at a fixed temperature. The pellets sintered at 1300 °C for longer sintering time showed marginal grain growth from 330 to 470 nm due to the reduction in grain surface energy (Figs. 3(a–c)). Faster grain growth was observed for the pellets sintered above 1300 °C. It can be concluded that the effect of sintering temperature on designing microstructure is more pronounced than the duration of sintering. Furthermore the micrograph of samples sintered at lower temperatures (such as 1200 and 1300 °C for 3 hrs) show angular grains with non-interconnected porosity. The microstructure do not show surface relaxation at the grain boundary for these samples indicating that the sintering occurred through lattice diffusion. Higher sintering temperatures (1400–1600 °C) lead to complete grain relaxation which can be seen as small grain boundary curvature and near equilibrium configuration at the triple point (Figs. 4(b–d)).

Therefore higher sintering temperature promotes the lattice, surface and grain boundary diffusion for densification and grain growth. However complete densification is difficult since residual porosities cannot be removed through grain growth mechanism due to longer diffusion distance for mass transport is required to eliminate closed pores. Moreover any change in the oxidation state of cerium often releases oxygen during high temperature sintering leading to increased porosity. It was observed that the small pores often remain in the final microstructure of the doped nano ceria (< 15 nm) which can be attributed to the release of oxygen gas due to the redox reaction.

Fig. 2. Showing effect of sintering temperature (1200–1600 °C) and sintering time (3–9 h, shown in box) at constant temperature (1300 °C) on grain size and relative density of sintered 20 mol% Sm doped ceria electrolyte pellet. Continuous grain growth observed with sintering temperature. Density increase up to 1400 °C then start decreasing.

Fig. 3. SEM of 20 mol% Sm doped ceria electrolyte sintered at 1300 for (a) 3 h (b) 6 h (c) 9 h, show grain relaxation with time and growth from 330 nm to 470 nm.
Effect of Submicron Grains on Ionic Conductivity of Nanocrystalline Doped Ceria

Fig. 4. SEM of \( \text{Ce}_0\text{Sm}_{0.1}\text{O}_{1.9} \) pallets sintered at various temperature for 3 h (a) 1200 °C (b) 1400 °C (c) 1500 °C (d) 1600 °C, where grain grows to micron size and retained porosity in the samples (>1500 °C).

\((\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+})\) and may hinder the densification at relatively higher temperatures.\(^{18,22}\)

3.3. Ionic Conductivity and Activation Energy of Electrolyte

The ionic conductivity of the doped electrolyte was determined by AC impedance spectroscopy. In the present study the grain interior (GI), grain boundary (GB) and total conductivities of the Sm doped ceria electrolyte was measured at temperatures varying from 200 to 800 °C at an interval of 50 °C in ambient air. A typical Nyquist plot, \( -Z'' \) versus \( Z' \) is shown in Figure 5. It comprises of three arcs. The high frequency arc corresponds to the grain polarization, second semi circle corresponds to the grain boundary polarization and low frequency arc indicates electrode polarization. It was possible to distinguish the arcs for GI, GB and electrode polarization (EP) at low temperature (<450 °C) over the measured frequency range however, at higher temperatures it was difficult to distinguish between the GI and GB conductivity arcs at higher frequencies (>50 KHz). The time constants associated with the GI and GB impedances are much lower than those associated with the electrode interface\(^{23}\) making it difficult to resolve. Thus the impedance spectra at higher temperatures (500-800 °C) show arcs for grain boundary and electrode polarization behavior as in Figure 6(b). Furthermore the arcs are shifted towards higher frequencies which cause the disappearance of the GI and GB arcs. The inductive response of the instrument and experimental test setup are responsible for the negative \(-Z''\) values at higher frequencies an effect that was suppressed by adding external inductor in the equivalent circuit while modeling the

J. Nanosci. Nanotechnol. 10, 1–9, 2010
Effect of Submicron Grains on Ionic Conductivity of Nanocrystalline Doped Ceria

Fig. 6. Impedance plot of 20 mol% Sm doped Ceria, sintered at 1400 °C measured (a) At low temperature (250 °C), this discern the impedance contribution due to grain boundary, grain interior and electrode in selected test frequency range (b) At high temperature (500 °C) and high frequency, the contribution from grain boundary and grain interior are not distinguishable.

The electronic contribution of the electrolyte to the overall conductivity was assumed to be negligible since all the measurements were done in air up to 800 °C. On the other hand the electronic conductivity in doped ceria arises due to the reduction of Ce⁴⁺ to Ce³⁺, that occurs in reducing atmosphere and at higher temperatures (≥ 1000 °C), beyond the scope of the present study. The equivalent electrical circuit model was applied to reproduce such impedance spectra consists of parallel resistance–constant phase element (R–CPE) blocks connected in series (Fig. 5 inset). The typical impedance spectra of Sm doped ceria (sintered at 1400 °C) at 250 and 500 °C are presented in Figures. 6(a, b). GI resistance (R_GI) and GB resistance (R_GB) can be distinguished easily at lower test temperatures (Fig. 6(a)), whereas R_GI and R_GB can not be separated at high temperature. Thus the GI resistance was calculated by fitting the impedance with the analog equivalent circuit. Effect of sintering temperature on grain boundary resistance measured at 300 °C in air is illustrated in Figure 7. The grain boundary impedance was smaller for the samples sintered at lower temperature (1200–1300 °C) and increased with sintering temperature. The difference in the electrical behavior can be attributed to the different characteristic of the grain boundary and solute segregation. The unrelaxed surface and diffused grain boundary for the samples sintered at 1200 and 1300 °C for 3 hrs reduced the grain boundary blocking effect as shown in Figures 3(a) and 4(a). This effect can be attributed to the ease of oxygen ion migration through GB in case of the electrolyte sintered at lower temperature. Moreover high sintering temperature and longer processing enhance the possibility of solute (Sm) migration at the grain boundary leading to a reduced total ionic conductivity. This effect can be seen in the Figure 8, where Arrhenius plots of grain interior and grain boundary conductivities are represented at temperature lower than 450 °C. Activation energies, E_LGB and E_LGI correspond to the grain boundary conductivity (σ_GB) and grain interior conductivity (σ_GI) respectively in low temperature range, were determined from the linear fit of the Arrhenius curves (Fig. 8). It can be observed (Fig. 8) that GB conductivity increases while the activation energy decreases (E_LGB~1.03 ev to 0.80 ev) with decrease in sintering temperature due to the reduced GB blocking effect caused by the solute segregation. The samples sintered at lower sintering temperature 1200–1400 °C exhibit smaller grain sizes (0.21 μm to 0.89 μm ) as compared to the samples sintered at higher temperatures (1500, 1600 °C) thereby increasing the GB area to GI ratio which helps in diluting impurities and solutes at the grain boundaries by spreading them over a large GB area per unit volume and promote the oxygen ion migration across the GB. Furthermore it is well established that 20 mol% Sm...
RESEARCH ARTICLE

Effect of Submicron Grains on Ionic Conductivity of Nanocrystalline Doped Ceria

Fig. 8. Arrhenius plots of grain interior and grain boundary conductivity (below $T^*$) for Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ electrolyte sintered at different temperature (1200–1600 °C), showing a decreasing trend in grain boundary activation energy ($E_{GB}$) with decrease in sintering temperature. Activation energies are shown in eV in Figure 8a and 8b.

doped ceria shows high ionic conductivity, therefore to control the distribution of dopant in heavily doped electrolyte is indispensable during sintering. Although higher sintering temperature and time provide dense electrolyte but enhance the grain growth and increase the diffusion kinetics for the dopants. The increased diffusion causes the segregation at grain boundaries and increased the GB impedance this hypothesis is supported by the impedance spectra (see GB semicircles) presented in Figure 7. This exhibits the fine grain (sub-micron) electrolyte has lower resistance than the coarse grained electrolyte.

As mentioned earlier that the relaxation frequencies increases with test temperature, which prevents separation of the GI and GB contribution at high temperature, however, it has been observed that the grain boundary resistance contributes less at higher temperatures and only the bulk resistance is responsible for total conductivity. Thus the total conductivity was also calculated along with the activation energy for low and high test temperature range.

The Arrhenius plots of total ionic conductivity ($\sigma_{total}$) are shown in Figure 9 for Sm doped ceria sintered at 1200–1600 °C. It is obvious from these plots that the Arrhenius plots of $\sigma_{total}$ versus temperature cannot be fitted by a straight line. These plots exhibit curvature near temperature, $T^* - 500 \pm 50$ °C for all the samples which separates the plots into two distinct regions. The $T^*$ can be defined as a critical temperature that changes the activation energy of oxygen vacancy at low and high temperature due to interaction of defects with dopant. The apparent values of $T^*$ are estimated by slopes intersection in Figure 9 because the change in curvature of Arrhenius plots, for conductivity, are not sharp. Kilner and Steele have shown that the oxygen ionic conductivity in rare earth doped ceria can be shown by the following expression depending on the temperature:

$$\sigma T = \sigma_0 \exp \left( - \frac{\Delta H_m + \Delta H_a}{kT} \right) \quad (T < T^*)$$

$$\sigma T = \sigma_0 \exp \left( - \frac{\Delta H_m}{kT} \right) \quad (T > T^*)$$

Where $\Delta H_m$ is the migration enthalpy of $O^{2-}$, $\Delta H_a$ is the defect association enthalpy of defect complex (Sm$^{3+}$Ce-$V_O$), $\sigma$ is the ionic conductivity and $\sigma_0$ is pre-exponential factor which remain constant at a certain temperature range. According to Huang et al. dopant ion (Sm$^{3+}$) acts not only as a trap for isolated oxygen vacancies, but also as nucleating centers for the formation of ordered oxygen vacancy cluster. The nucleation centers have critical temperature $T^*$ below which the oxygen vacancies are progressively trapped out into the clusters with decreasing temperature while above $T^*$, the vacancies are dissolved into the matrix of oxygen sites. Furthermore this effect was not observed for low dopant concentration (1–5 mol%). The increase in the dopant concentration enhances the association enthalpy of the defects complex and these complexes dissociate at higher temperature, consequently activation energy then depends only on $\Delta H_m$ (Eq. (5)). Association enthalpy can be calculated by combining the slopes of the Arrhenius plots of grain conductivity (Eq. (4) and (5)), i.e.,

$$\Delta H_a = E_{GB} - E_{GI}$$
Effect of Submicron Grains on Ionic Conductivity of Nanocrystalline Doped Ceria

Table I. Total conductivity, activation energy and association enthalpy of Ce0.8Sm0.2O1.9. Conductivity values (in S cm\(^{-1}\)) are reported at 600 °C and activation energy (in eV) for low and high temperature range.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(\sigma_{\text{rel}}) at 600 °C</th>
<th>(E_{\text{act}}^L)</th>
<th>(E_{\text{act}}^H)</th>
<th>(H_{\text{a}})</th>
<th>3 hrs</th>
<th>9 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200 °C</td>
<td>1.00</td>
<td>0.694</td>
<td>0.64</td>
<td>0.56</td>
<td>0.14</td>
<td>0.19</td>
</tr>
<tr>
<td>1300 °C</td>
<td>0.98</td>
<td>0.697</td>
<td>0.89</td>
<td>0.67</td>
<td>0.19</td>
<td>0.20</td>
</tr>
<tr>
<td>1400 °C</td>
<td>0.96</td>
<td>0.717</td>
<td>0.93</td>
<td>0.60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1500 °C</td>
<td>0.76</td>
<td>0.708</td>
<td>0.96</td>
<td>0.53</td>
<td>—</td>
<td>0.69</td>
</tr>
<tr>
<td>1600 °C</td>
<td>0.60</td>
<td>0.708</td>
<td>0.98</td>
<td>—</td>
<td>—</td>
<td>0.27</td>
</tr>
<tr>
<td>1300 °C/6 h</td>
<td>0.89</td>
<td>0.827</td>
<td>0.97</td>
<td>0.69</td>
<td>—</td>
<td>0.31</td>
</tr>
<tr>
<td>1300 °C/9 h</td>
<td>0.82</td>
<td>0.277</td>
<td>0.31</td>
<td>0.29</td>
<td>0.21</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Where \(E_{\text{act}}^L\) and \(E_{\text{act}}^H\) are activation energy for the grain conductivity at low and high temperatures respectively. The ionic conductivity at 600 °C, association enthalpy and activation energy for different sintered samples are shown in Table I. The total conductivity (\(\sigma_{\text{rel}}\)) values were higher (\(>0.01\) S cm at 600 °C) for samples sintered at 1200 and 1300 °C for 3 hrs. The conductivity values are in good agreement with the values presented in the literature for the same test temperature.\(^{16,21}\) The sintering temperature and time in earlier studies were higher (1500/5 h\(^3\) and 1640/8 h\(^3\)) whereas, similar conductivity values are achieved at lower sintering temperature for submicron grains in the present study probably due to the finer sizes of the precursor powders which influences the ionic conductivity. The conductivity values at 600 °C decrease with increase in sintering temperature (Fig. 10). Higher sintering temperature and time enhances the grain growth and dopant segregation at grain boundary that might decrease the total conductivity value. The increase in sintering temperature promotes the densification of electrolytes but can also increase the probability of diffusion of solute and impurities at the GB, specially heavily doped (>10 mol%) oxides.\(^{22}\) Various models have been proposed to explain the increased grain boundary resistance due to impurity and dopant segregation. The “brick layer model” demonstrates the effect of high dopant concentration in ceria which ascribe the increasing grain boundary resistance to the formation of space charge layer due to dopant segregation.\(^{28}\) There are limited studies available on the effect of grain size on the association enthalpy because association enthalpy is mainly affected by the dopant concentration. Although increasing acceptor dopant concentration promotes the oxygen ion vacancy concentration but it also increases the dopant cation-oxygen vacancy complexes.\(^{26,29}\) Increasing dopant concentration increases elastic strain energy of the system which is the major contributor to the association enthalpy and this term is minimized when the size mismatch between the host and dopant atom is the least.\(^{26}\) In the present study dopant concentration remained constant (20 mol% Sm) and only sintering temperature and time was varied. Thus the association enthalpy arises only due to the strain energy produced by 20 mol% dopant. The effect of sintering temperature on association enthalpy is illustrated in Table I and indicates a marginal change with sintering temperature (0.14 eV for 1200 °C against 0.20 eV for 1500 °C). In contrast, the association enthalpy showed dependence on sintering time. The association enthalpy for the sample sintered at 1300 °C for 9 hrs increased from 0.19 to 0.31 eV as compared to the sample sintered for 3 hrs at same temperature. This could be attributed to the diffusion of dopant (Sm\(^{3+}\)) from the lattice to the GB due to higher soaking time. Similar segregation of dopant at the GB can occur during high temperature sintering. During sintering the solute elements are carried with the moving grain boundary due to grain growth. Usually diffusion coefficient of solute near GB is slower than the intrinsic host atoms therefore solute drag causes the increased grain boundary resistivity. Thus the sintering temperature and time significantly affect the distribution of solutes in the electrolyte that finally control the total ionic conductivity.

4. CONCLUSIONS

For solid 20 mol% Sm doped cerium oxide electrolyte, high density (>92%) can be achieved at relatively lower temperatures by using precursor electrolyte materials in nano size regime. Doped nano ceria facilitates low temperature sintering, whereas micron size powder required high temperature sintering (1500–1700 °C) to achieve high density ceria based electrolyte. Higher ionic conductivity was observed for samples sintered at 1200 and 1300 °C because of lower grain boundary resistance. Marginal...
change in association enthalpy ($\Delta H_a \sim 0.177 \pm 0.03$ eV) was observed with increase in sintering temperature from 1200–1600 °C whereas association enthalpy was increased from 0.19 to 0.31 eV for the sample sintered for longer time. The low temperature GB activation energy decreased ($E_{GB} \sim 1.03$ eV to 0.80 eV) with decrease in the sintering temperature owing to reduced solute segregation in samples sintered at 1200–1300 °C. The lower sintering temperature exhibits submicroscopic grain with increased GB area that results in diluting solutes and impurity segregation at the GB and increasing total ionic conductivity.

Acknowledgments: The financial support from NASA (Grant No. 16266038-1) at University of central Florida is gratefully acknowledged.

References and Notes


Received: 21 September 2009. Accepted: 29 October 2009.