Glycine-nitrates combustion synthesis and properties of nano-sized Ce$_{1-x}$Gd$_x$O$_{2-\delta}$ solid solution for solid oxide fuel cell viewpoint

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Nanocrystalline gadolinium-doped ceria powders for solid electrolytes have been successfully prepared via glycine nitrate combustion synthesis and characterized by TGA/DTA, XRD and SEM. Using these powders; highly dense ceramics have been prepared by sintering at 1100°C which is much lower temperature than 1600°C usually required for ceria solid electrolytes prepared by conventional ceramic technique. The effect of compositions on structure and conductivity has also been studied.

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Solid oxide fuel cell (SOFCs) offers a clean, pollution free technology for the electrochemical generation of electricity at high efficiencies$^{1-3}$. Traditional SOFC with yttria-stabilized zirconia (YSZ) as electrolyte places considerable constraints on materials which can be used for interconnections and balance of plant due to high operating temperature (around 1000°C), hence limits the commercial development of SOFC. To lower the operating temperature many studies have been made on other solid electrolytes with conductivity values larger than those of zirconia based electrolytes as alternative to zirconia, e.g., Bi$_2$O$_3$-based$^4-6$ and CeO$_2$-based$^7-10$ materials. However, the application of Bi$_2$O$_3$-based materials is hindered by their limited electrolyte domain even though they have significantly higher oxide ion conductivity compared to that of yttria stabilized zirconia.

Doped ceria is the most promising high conducting solid electrolyte for SOFC. In the recent years, many investigations have been carried out on various aspects of ceria solid electrolytes mostly prepared by conventional ceramic methods, which have some limitations$^{11}$. For example, the density of the samples is less than 95% of theoretical. Moreover, the sintering temperature of 1600-1650°C renders the process costly besides allowing loss of ceria due to high mobility of Ce$^{4+}$ at these temperatures. Combustion synthesis is an important powder processing technique generally used to produce complex oxide ceramics$^{12-15}$. The products are generally more homogeneous, have less impurities and higher surface area than powders prepared by conventional solid-state methods$^{16}$. Specially, glycine nitrates combustion synthesis route has been known to produce oxide powders compositionally uniform up to atomic scale and fine enough to be readily sinterable to high densities$^{17,18}$. In this paper, the results of study on the structure, thermo-physical and electrical conductivity properties of Ce$_{1-x}$Gd$_x$O$_{2-\delta}$ ($x = 0.05$ to $0.20$) solid solutions prepared by a glycine nitrate combustion synthesis have been presented.

Experimental Procedure

Initial ingredients cerium nitrates hexahydrates (Ce(NO$_3$)$_3$.6H$_2$O), gadolinium nitrates hexahydrates (Gd(NO$_3$)$_3$.6H$_2$O) were procured in the 99.9% purity grade from Aldrich Sigma Company. According to the stoichiometric ratios of Ce$_{1-x}$Gd$_x$O$_{2-\delta}$, cerium nitrates and gadolinium nitrates solutions were weighed with the help of Mettler balance$^{163}$ AE. Stoichiometry of the redox mixture for combustion was calculated based on the total oxidizing and reducing valences of the oxidizer (O) and the fuel (F), where O and F serve as numerical coefficient so that the equivalence ratio $\phi_c$ (O/F), becomes unity$^{19,20}$. Using the concept of propellant chemistry, the valence of C = +4, H = +1, Ce = +4, Gd = +3, O = -2, N = 0 has been considered to calculate the
composition for combustion synthesis. The ingredients were thoroughly mixed and dissolved in distilled water. Calculated amount of glycine fuel added to the above solution was continuously stirred for complete homogenization. The aqueous redox solution containing metal nitrates and glycine when introduced into a muffle furnace preheated to 550°C boils, froths, ignites and catches fire. At this higher temperature, the metal nitrates decompose to metal oxides and oxides of nitrogen, which leads to a voluminous foamy combustion residue in less than 10 min and the flame persisted for about 2 min. The foam (pale yellow in color) was then lightly ground in silica basin with porcelain pestle to obtain fine powders. The powders were then transferred into a silicon crucible and calcined at 800°C for 3 h in air in order to obtain pure and well-crystallized powders. The flowchart for combustion reaction is shown in Fig. 1. The combustion reactions are given as:

(i) One mole of glycine (C\textsubscript{2}H\textsubscript{5}N\textsubscript{2}O\textsubscript{2}) as fuel, gave five moles of the following gases as per the reaction.

\[
2\text{NH}_2\text{CH}_2\text{COOH} + 2\text{O}_2 \rightarrow \text{N}_2 \uparrow + 4\text{CO}_2 \uparrow + 5\text{H}_2
\]

(ii) Theoretically equation for producing parent oxide assuming complete combustion of the redox mixture with glycine is as given below

\[
18\text{Ce(NO}_3)_3 + 30 \text{ NH}_2\text{CH}_2\text{COOH} \rightarrow 18\text{CeO}_2 - \delta (s) + 60\text{CO}_2 (g) \uparrow + 42\text{N}_2 (g) \uparrow + 75\text{H}_2\text{O}(g)
\]

\[
4\text{Gd}_5(\text{NO}_3)_{11} + 30\text{NH}_2\text{CH}_2\text{COOH} \rightarrow 20\text{GdO}_{1.5} - \delta
\]

\[
+ 60\text{CO}_2 (g) \uparrow + 22\text{N}_2 (g) \uparrow + 75\text{H}_2\text{O}(g)
\]

The thermo-chemical properties such as dehydration, dissociation, decomposition, phase transformation and purity of synthesized powder were investigated by means of differential thermal analysis (DTA) and thermogravimetric analysis (TGA), which was carried out in the temperature range 30-1000°C by TA instrument TA-4000 with a heating rate of 20°C/min in air. The room temperature X-ray diffraction was carried on the calcined powders for phase identification and crystallite size estimation using a Rigaku X-ray diffractometer with CuK\textsubscript{α} radiation. The reflection from the (111) plane was used for the determination of the average crystallite size. The average crystallite size, \(D\), of the prepared powder was calculated from the Scherrer formula

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the wavelength of the X-rays, \(\beta\) is the corrected half width, \(\beta_m\) is the observed half width of the (111) reflections in samples of Ce\textsubscript{1-x}Gd\textsubscript{x}O\textsubscript{2-δ} and \(\beta_s\) is that of a standard sample of CeO\textsubscript{2}.

The microstructures of the sintered specimens at different sintering temperature were observed by scanning electron microscope (SEM). The AC conductivity of sintered pellets was observed by two-probe impedance spectroscopy using an HP make Impedance Analyzer Model-4192, 5 Hz to 13 MHz, in the temperature range 200-650°C in air. Platinum was sputtered onto either side of the sintered GDC pellets to act as an electrode.

**Result and Discussion**

Figures 2(a-e) show the TGA and DTA plots obtained for the synthesized powder. Accompanying the changes seen in the DTA curve, the TGA curves exhibit that in almost all samples a gradual weight loss from room temperature to 800°C. Total weight loss is 6-7%. DTA curves show that all complexes lose the water of absorbed hydration initially at approximately 50°C. Endothermic peaks are observed at around 250-400°C. These are not associated with any sudden change in weight loss, indicative of no phase transition and direct formation of solid solution. Endothermic peaks are related to the loss of water of crystallization and inorganic residues left during combustion synthesis. In all samples, above 800°C, no prominent change in TGA/DTA curves was observed, suggesting that perfect crystallization had taken place in all combustion synthesis powders by calcinations at 800°C.

![Flowchart](image-url)
In order to compare with the DTA/TGA data, the fluorite phase evolution during the combustion process as a function of heat treatment temperature was examined by XRD technique for Ce$_{1-x}$Gd$_x$O$_{2-δ}$ (Fig. 3). The powder calcined at 800°C show no evidence of impurity with wide peak width, which is indicative for smallest particle size. The XRD pattern of CeO$_2$ powder calcined at 1200°C is observed to be narrower than that of powder calcined at 800°C (Fig. 4). This suggests that the calcinations temperature increases the particle size.

The average crystallite size, \(D\), of calcium-substituted ceria powder, calculated by Scherrer formula from XRD data were between 6 nm and 15 nm, (Table 1).
The colossal surface area of the ultra-fine powder enhances greatly the rate of sintering due to the shortened path of diffusion between particles. All these factors contribute to accelerate the course of sintering. The ultra-fine substituted ceria powders, sintered into pellets at 1100°C, have apparent densities of over 95% of the theoretical value, while ceria solid electrolytes, prepared by conventional ceramic techniques, require over 1600°C for sintering.

The theoretical densities of the sintered pellets were calculated using $\rho = \frac{M}{V}$

$$M = \text{Mass of U.C.} = \frac{N(1-x)M_{\text{Ce}} + xM_{\text{Gd}} + (2-x/2)M_o}{N_A}$$

where, $M_A$ is atomic weight of element, $N_A$ is Avagadro’s number and $V$ is volume of U.C. = $a^3$.

The apparent density of each sintered pellet was determined by measuring diameter, thickness and weight of specimen.

Relative density$= \frac{\text{Apparent density}}{\text{Calculated density}} \times 100\%$

Table 1—Lattice parameter, crystallite size, relative density and free volume of Gd-doped system

<table>
<thead>
<tr>
<th>Dopant content (Å)</th>
<th>Lattice parameter (Å)</th>
<th>Average crystallite size (nm)</th>
<th>Relative density (%)</th>
<th>Free volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.3679</td>
<td>10.40</td>
<td>94</td>
<td>49.712</td>
</tr>
<tr>
<td>0.05</td>
<td>5.3728</td>
<td>6.87</td>
<td>95</td>
<td>50.822</td>
</tr>
<tr>
<td>0.1</td>
<td>5.3764</td>
<td>6.87</td>
<td>96</td>
<td>51.822</td>
</tr>
<tr>
<td>0.15</td>
<td>5.3839</td>
<td>9.84</td>
<td>96</td>
<td>53.042</td>
</tr>
<tr>
<td>0.2</td>
<td>5.3875</td>
<td>12.95</td>
<td>96</td>
<td>54.156</td>
</tr>
</tbody>
</table>

The extent of agglomeration of the starting powders, which allows good compaction uniformity in the green bodies and sintering kinetics. The low sintering temperature of our oxide powders suggests that the densification mainly proceeds through grain boundary diffusion, which is much faster than lattice diffusion at lower temperatures. Sintering of nano-sized CeO₂ powder was found recently controlled by such a diffusion mechanism.

Fig. 5 shows densification behaviour of gadolinium-doped ceria as function of sintering temperature for holding time 8 h. The plot exhibits that gadolinium doping accelerates densification. It was satisfactorily rationalized on the basis of the free volume through which lattice expansion takes place. The ‘free volume’, defined as the difference between the ceria unit cell volume (as calculated from the U.C. lattice parameters) and the total volume occupied by all ions present within the unit cell (calculated from the effective ionic radii), tends to increases with increasing Gd substitution (Table 1). Thus, densification accelerates with Gd substitution.
SEM of Ce$_{0.90}$Gd$_{0.10}$O$_{1.90}$ sample at different sintering temperature are shown in Figs 6a-6e. The surface view of the pellets prepared from calcined powder (Fig. 6a) shows that nano-sized particles are only loosely agglomerated. The particle size observed from micrographs (10.54 nm) approximately agreed with (6.87 nm) those determined by XRD. The micrographs of pellets sintered at 800°C for 3 h (Fig. 6b) exhibit that particles are still loosely agglomerated but particle size is coarsened from 10.54 to 62.5 nm (calculated relative density ~ 83.75). For the specimen sintered at 1100°C for 3 h (Fig. 6c) results sub-micrometer grain size, these are grown from 62.5 nm to 130 nm but no sharp grain boundary is observed (~86.83 density). Figs 6d and 6e depict micrographs of fractured pellets sintered at 1100°C for 5 h and 8 h respectively. Fig. 6d reveals that grains are non-uniform in size and shape, and there is no evidence of exaggerated grain growth. Grain size is increased from 130 nm (for 3 h sintering) to 266 nm with calculated relative density 92.25. The micrograph (Fig. 6e) of specimen sintered for 8 h shows that negligible porosity with grains has grown by a factor of approximately 2 (405 nm) compared to specimens sintered for 5 h. There is non-homogeneous distribution of grain sizes. SEM microstructure indicates that densification proceeds with elimination of interconnect porosity through grain diffusion.

Pure ceria oxide is basically a poor oxide ion conductors ($\sigma_{600°C} = 10^{-5}$ S cm$^{-1}$). Fig. 7 shows that the ionic conductivities are significantly enhanced in Ce$_{1-x}$Gd$_x$O$_{2-\delta}$ solid electrolytes by increasing the oxygen vacancies $V'_o$.

$$\text{Gd}_2\text{O}_3 \xrightarrow{\text{CeO}_2} 2\text{Gd}^{3+}_{\text{Ce}} - V'_o - 3\text{O}'_o.$$ 

Moreover, the linear Arrhenius plots, ln($\sigma$,$T$) = ln $A$ – $E_a/kT$, over a wide temperature range indicate the presence of only one mode of oxide ion conduction in the substitution range of Gd. The isothermal dopant content versus conductivity plot (Fig. 8) shows that Ce$_{0.90}$Gd$_{0.10}$O$_{1.90}$ solid solution exhibits highest
conductivity at all temperature ranges. The ionic conductivity of the Ce\(_{1-x}\)Gd\(_x\)O\(_{2-\delta}\) system increases systematically with increasing gadolinium substitution and reaches a maximum at \(x = 0.10\). The formation of defect association cluster \([\text{Gd}'+\text{Ce} - \ldots \text{O}^-]\) at higher concentration of \(\text{O}^-\) leads to the lowering of conductivity for \(x > 0.10\). The highest ionic conductivity is observed for the composition \(x = 0.10\) (\(\sigma_{600 \, ^\circ C} = 0.058 \, \text{Scm}^{-1}\) and \(E_a = 0.79 \, \text{eV}\)).

Conclusions

A glycine-nitrate combustion route to synthesize Ce\(_{1-x}\)Gd\(_x\)O\(_{2-\delta}\) (\(x = 0.05-0.20\)) solid solution has been investigated. Ultra-fine particles of uniform crystallite dimensions \(\sim 6-15 \, \text{nm}\), were formed by this synthesis method. Because of the small particle size of the doped ceria, the sintering temperature needed to obtain a dense ceramic pellet was reduced substantially from 1600\(^\circ\)C, required in conventional solid state methods, to 1100\(^\circ\)C. TGA/DTA patterns showed that crystallization takes place at 800\(^\circ\)C. X-ray diffraction measurements indicate the expansion in lattice constant with dopant content. Densification behaviour is found to increase with dopant content due to the increase of free volume of system through which lattice expansion takes place. SEM microstructure indicates that densification proceeds with elimination of interconnect porosity through grain diffusion. The highest conductivity was found for the \(x = 0.1\) dopant content at 600\(^\circ\)C.

References