Structural and Ionic Conductivity Studies of Doped Ceria Electrolyte

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The present study reports synthesis, XRD, Impedance spectroscopy and ionic conductivity of Ce$_{1-x}$(Gd$_x$Pr$_{0.5}$)$_x$O$_2$ ($x = 0-0.24$) system. These samples were synthesized through the sol-gel process followed by low temperature combustion. The samples were sintered at 1300 °C to obtain dense ceramics (over 98%). XRD confirms the single phase with a cubic structure. The two-probe a.c. impedance spectroscopy was used to study the ionic conductivity of doped ceria samples. The Ce$_{0.88}$(Gd$_{0.5}$Pr$_{0.5}$)$_{0.12}$O$_2$, C$_{60,0}$(Gd$_{0.5}$Pr$_{0.5}$)$_{0.16}$O$_2$ compositions showed highest grain ionic conductivity values i.e., 1.012 × 10$^{-2}$ S/cm and 1.059 × 10$^{-2}$ S/cm respectively at 200°C.

The synthesized powders were calcined at 600 °C for 2 h. The oxidation of Ce$^{3+}$ to Ce$^{4+}$ occurred during this stage. The powders were pressed uni-axially using hydraulic press under a continuous pressure of 5 MPa into a circular pellet using a stainless steel die of dimensions 10 mm × 2 mm and then pellets were sintered in air at 1300 °C for 10 h with a programmed heating rate of 5 °C/min. Densities of the sintered samples were measured in water using the Archimedes method and the calculated densities of sintered samples were found to be more than 98% of the theoretical density. XRD patterns of the samples were obtained by BRUKER D8 using Cu Kα radiation at room temperature. XRD performed on samples sintered in air at 1300°C for 10 h. Lattice parameter was calculated using BRUKER-TOPOZ Reitveld refinement software. The sintered pellets were polished, thermally etched and gold coated for microstructure analysis using the scanning electron microscope ZEISS (FE-SEM) equipped with an energy dispersive X-ray spectrometer (EDX) analyzer.

A.C. Impedance spectra of the samples were recorded using Agilent precision impedance analyzer (4294 A) as a function of temperatures (150–700°C) in air in the measuring frequency range from 40 Hz to 5 MHz. ZSimpiwin software was used to fit the impedance data into corresponding equivalent circuits. Silver paste was brushed to each side of the samples, which was subsequently dried (at 600°C for 20 min.) producing solid silver electrode on both sides of the pellet.

**Results and Discussion**

Fig. 1 shows XRD patterns of Ce$_{1-x}$(Gd$_{0.5}$Pr$_{0.5}$)$_x$O$_2$ system. It can be seen that the samples contain only a cubic structure with the space group Fm3m (ICPDS File No. 01-081-0792). The introduction of Gd$^{3+}$ and Pr$^{3+}$ into Ce$^{4+}$ can cause a small shift in the ceria peaks (Fig. 1). This shift is indicative of a change in the lattice parameter. This is due to the difference in ionic radii of Ce$^{4+}$ (0.967 Å), Gd$^{3+}$ (1.053 Å) and Pr$^{3+}$ (1.126 Å) in an oxide solid solution. The shift indicates the change in the lattice parameter as larger ionic radii Gd$^{3+}$ and Pr$^{3+}$ ions doped into smaller ionic radii Ce$^{4+}$ (0.967 Å). This causes expansion of lattice volume. Lattice parameter was in the range 5.4122–5.4256 Å. Similar lattice expansion was observed in Sm$_{2}$Nd$_{2}$Ce$_{1-x}$O$_{2-x}$, Sm$_{2}$Nd$_{2}$Ce$_{1-x}$O$_{2-x}$, Sm$_{2}$Nd$_{2}$Ce$_{1-x}$O$_{2-x}$, Sm$_{2}$Nd$_{2}$Ce$_{1-x}$O$_{2-x}$, and Sm$_{2}$Nd$_{2}$Ce$_{1-x}$O$_{2-x}$ systems.

A.C. Impedance spectroscopy is an important tool to study the electrical properties of solid electrolytes and to study the grain, grain boundary and electrode contribution to the overall ionic conductivity. High frequency semi-circle corresponds to grain resistance ($R_g$), intermediate frequency semi-circle corresponds to grain boundary resistance ($R_b$) and low frequency incomplete arc corresponds to electrode resistance ($R_e$). As shown in Fig. 2, the equivalent circuit (R-CPE) was used to fit the impedance data to calculate grain ($R_g$) and grain-boundary resistance ($R_b$). The use of simple capacitor is not sufficient to model the electrical response of the materials due to depression of arcs in some cases. For this
Figure 1. XRD patterns of Ce$_{1-x}$(Gd$_{0.5}$Pr$_{0.5}$)$_x$O$_2$ system.

Figure 2. Nyquist plot of Ce$_{0.84}$Gd$_{0.08}$Pr$_{0.08}$O$_2$ sample measured in air at 300°C.

Figure 3. Arrhenius plots for total ionic conductivity of Ce$_{1-x}$(Gd$_{0.5}$ Pr$_{0.5}$)$_x$O$_2$ system.

In general, the total conductivity ($\sigma$) of rare-earth element doped ceria is the sum of ionic conductivity ($\sigma_i$) and electronic conductivity ($\sigma_e$). The main contribution of the conductivity of ceria-based compounds in air is the ionic conductivity and contribution of the electronic conductivity is negligible ($\sigma_i \approx 10^{-2}$ S/cm; $\sigma_e \approx 10^{-5}$ S/cm $< 800\,^{\circ}\mathrm{C}$).2, 3

Fig. 3 shows the Arrhenius plots for the total ionic conductivity of Ce$_{1-x}$(Gd$_{0.5}$Pr$_{0.5}$)$_x$O$_2$ system. It can be seen from the Fig. 3 that Gd$^{3+}$ and Pr$^{3+}$ co-doped ceria samples showed higher conductivities for the composition Ce$_{1-x}$(Gd$_{0.5}$Pr$_{0.5}$)$_x$O$_2$ ($x = 0.12$ and 0.16) than Ce$_{0.9}$Gd$_{0.1}$O$_2$. From Fig. 3, the total ionic conductivity of Ce$_{1-x}$(Gd$_{0.5}$Pr$_{0.5}$)$_x$O$_2$ increases up to dopant concentration ($x = 0.16$). After that, the total ionic conductivity decreases with increase in dopant concentration, which is related to the formation of local defect structures, which lowers the mobile oxygen vacancy concentration.6 It is observed that there is a change of slope at 500°C in Arrhenius plot, which indicates the presence of two activation energies ($\Delta H_a + \Delta H_m$, $\Delta H_a$). In the case of low temperature range (150–500°C), the oxygen vacancy, which is associated with the dopant is trapped and the activation energy ($E_a$) is the sum of association and migration enthalpy (i.e., $\Delta H_a + \Delta H_m$), while in the high temperature range (500–700°C), the activation energy is equal to migration energy ($\Delta H_m$) because most of the oxygen vacancies are free to migrate. Further, the total ionic conductivity of Ce$_{0.88}$Gd$_{0.06}$Pr$_{0.06}$O$_2$ and Ce$_{0.85}$Gd$_{0.05}$Pr$_{0.05}$O$_2$ is 1.712 $\times$ $10^{-2}$ S/cm (0.77 eV) and 1.923 $\times$ $10^{-2}$ S/cm (0.79 eV) respectively at 600°C. The grain ionic conductivity of Ce$_{0.88}$Gd$_{0.06}$Pr$_{0.06}$O$_2$ and Ce$_{0.84}$Gd$_{0.08}$Pr$_{0.08}$O$_2$ is 1.012 $\times$ $10^{-2}$ S/cm (0.59 eV) and 1.059 $\times$ $10^{-2}$ S/cm (0.62 eV) respectively at 500°C. The grain ionic conductivity of Ce$_{0.88}$Gd$_{0.06}$Pr$_{0.06}$O$_2$ and Ce$_{0.85}$Gd$_{0.05}$Pr$_{0.05}$O$_2$ is 6.2% and 11.5%, respectively, higher than Ce$_{0.9}$Gd$_{0.1}$O$_2$ (0.95 $\times$ $10^{-2}$ S/cm). The grain ionic conductivity of Ce$_{0.88}$Gd$_{0.06}$Pr$_{0.06}$O$_2$ and Ce$_{0.85}$Gd$_{0.05}$Pr$_{0.05}$O$_2$ is 1.83 $\times$ $10^{-2}$ S/cm at 550°C sintered at 1300°C for 10 h can be compared to that of Omer et al.6 (1.4 $\times$ $10^{-2}$ S/cm at 550°C) in Ce$_{0.85}$Sm$_{0.075}$Nd$_{0.075}$O$_{2-\delta}$ ceramics sintered at higher temperatures (1550°C for 10 h) with a relative density 98%. These results show the efficiency of the sol-gel process with low temperature combustion of Gd and Pr co-doped ceria ceramics as candidates to be used as electrolytes in IT-SOFC applications.

In conclusion, the sol-gel process followed by low temperature combustion decrease the sintering temperature (250°C) with respect to the general solid-state method with densities higher than 98% at relatively low temperature (1300°C) for Gd-Pr-doped ceria ceramics. Codopants were used to decrease the activation energy and consequently to improve the ionic conductivity. Codopants were selected based on Density Functional Theory, which suggests using co-dopant with an average atomic number, which lies in between 61–62. The addition of Gd$^{3+}$ and Pr$^{3+}$ dopants into ceria would create vacancies and also these dopants minimize interaction with these vacancies. The composition Ce$_{0.88}$Gd$_{0.06}$Pr$_{0.06}$O$_2$ showed highest grain ionic conductivity, which was 11.5% higher than the GDC. Thus codoping based on average atomic number (61.5) results in the improvement of ionic conductivity.
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References