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Synthesis and impedance analysis of gadolinium-doped cerium electrolyte

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Abstract

Gadolinium-doped ceria-based electrolyte (at 20 % dopant cation) was prepared for intermediate temperature solid oxide fuel cells (ITSOFCs). The fine powder has been synthesized by a simple and fast freeze drying method at relatively low temperature. The XRD results showed that the powder has a single phase with cubic fluorite structure. The SEM results exhibited that electrolyte pellets sintered at 1100 °C was dense, and the relative density of pellet was over 96 %. Impedance spectra analysis of this electrolyte has been performed at 200–850 °C. The results displayed that $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ appeared higher conductivity at the temperature range of 550–700 °C.

Keywords: Freeze drying; IT-SOFC; Solid electrolyte; Conductivity

1. Introduction

Solid Oxide Fuel Cells technology has been undertaken a new interest in the last few years: research groups, universities and governments imply themselves in the projects of research and development of SOFC. The SOFC are now developed to generate electrical power for both stationary and mobile applications [1, 2]. SOFCs are electrochemical reaction that can directly convert a chemical fuel to electrical power with high efficiency and very low pollution [3]. Generally; the gases used are H_2, CH_4, CO as fuel in the anode and oxygen or simply air in the cathode. A solid oxide fuel cell essentially consists of two porous electrodes (cathode and anode) separated by a dense, oxygen ion conducting electrolyte.

The electrolyte for SOFCs must be stable in both reducing and oxiding environment, and must have sufficiently high ionic with low electronic conductivity at the operating temperature. Until now, Standard electrolyte materials , based on stabilised zirconia, especially yttria stabilised zirconia (YSZ), has been the must favored electrolyte [4], and require operating temperature around 1000°C to ensure sufficient ionic conductivity. Since lowering the operating temperature has many advantages [5, 6].

CeO_2-based solid electrolyte exhibits high ionic conductivity at intermediate temperature (600–800 °C), which is comparable with that of YSZ at high temperature, many researches have been focused on this system [7-10]. The ion conductivity can significant improve by increasing the oxygen vacancies by the substitution of a lower-valent metal ion for cerium, and upon substituting for Ce^{4+} are charge compensated by oxygen vacancies [11-14]. Several divalent alkaline-earth and trivalent rare-earth oxides form extensive solid solution with rare-earth doped ceria has been found [9] to be a more promising candidate as a solid electrolyte in SOFC which can be operated at intermediate temperature, these materials have potential for applications in electrolytes for SOFCs at intermediate temperatures [15, 16]. Gadolinium doped ceria (GDC) is considered to be one of the best ceria-based solid electrolytes [17, 18].

Generally, ceramic materials are synthesised by solid state reaction: the powders are mixed, milled and calcined. Since the limited diffusion of reactants, the reaction require high temperature, long heating period and intermediate milling to achieve good homogeneity. Other disadvantages of the method are the formation of undesirable phases, large grains sizes (low densification and surface area of materials) due to firing at high temperature and poor chemical homogeneity. A common feature of the new synthesis methodologies is their search for alternative reaction paths through which the cationic diffusion distances are reduced and the precursor possesses high reactivity which allows a reduction in the temperature and/or sintering time [19-21]. In this context, use of precursors obtained by freeze-drying processing of the appropriate aqueous metal salts has proved to be a very versatile method for obtaining stoichiometrically controlled complex polymetallic systems [22-25]. It is well known that the preparative route plays a critical role in governing materials properties, controlling the structure, morphology, grain size and surface area of the obtained materials.

In this work, results about a freeze drying prepared gadolinium doped ceria, $Ce_{0.80}Gd_{0.20}O_{2-\delta}$, are presented.

2. Experimental

Polycrystalline material with composition $Ce_{0.80}Gd_{0.20}O_{2-\delta}$ was prepared by the freeze drying method. The appropriate quantities of of $Ce(NO_3)_3.6H_2O$ (99.99%, Aldrich) and $Gd(NO_3)_3.6H_2O$ (99.99%, Aldrich) were dissolved in distilled water. Droplets of the resulting solution was flash frozen by projection on liquid nitrogen and then freeze-dried at a pressure of 1-10 Pa in a Heto Lyolab freeze-dryer. In this way, dried solid precursor was obtained as amorphous loose powder. The amorphous precursor powders were studied with a TG/DTA to obtain the optimum temperature of crystallisation.

X-ray powder diffraction (XRD) pattern was acquired using a Philips X'Pert Pro diffractometer, equipped with a Ge(111) primary monochromator and an X'Celerator detector. Routine pattern for phase identification was collected with a scanning step of 0.08° over the angular 2θ range 20-80° with a collection time of 5 s per step. The graphical representation concerning XRD pattern was performed using WinPlotr program [26].

Thermogravimetrical analysis (TG/DTA) was performed in a Perkin Elmer Instrument (mod. Pyris Diamond). TG/DTA curves were collected using a heating/cooling rate of 10 °C/min to study the crystallisation of the amorphous precursors.

The morphology was analysed by scanning electron microscope (Jeol, JSM-6300) operating at an accelerating voltage of 20 kV. All the preparations were covered with a thin film of gold for better image definition.

Starting freeze-dried powders were uniaxially pressed into disks of 7mm of diameter at 130MPa. Dense pellets with relative density higher than 96 % were obtained after sintered at 1100 °C for 12 h. Pellet with very high geometrical factor (thickness=3mm and diameter = 5mm) was fixed in an electrochemical setup of alumina with Pt-wires for the electrical connections and then inserted into a quartz flow-through tube furnace. To ensure good contact between the platinum wires and the samples, each side of the pellet was painted with platinum paste and baked at 950 °C for 12 h. The Solartron 1260 impedance analyzer was used for electrical characterization, including an assessment of grain boundary effects. Spectra were obtained in the frequency range from 0.1 Hz to 1MHz with an applied voltage of 25mV in the temperature range of 500–850 °C and 100mV in the range 200–500°C, which was controlled by the computer program ZPlot. Data analysis was made by equivalent circuits using the program ZView [27] allowing us to estimate the different contributions of the conductivity.

3. Results and discussion

Results of TG/DTA analysis of the amorphous precursor indicates that the decomposition of freeze-dried precursor occurs at low temperature. The main mass loss is observed between 240 and 300 °C. The oxidation complete at 450 °C.

Single fluorite-type structure has been synthesized by the freeze-dried precursor method after one thermal treatment at only 400 °C. This is an advantage to prepare nanopowder materials, which can contribute to improve the physicochemical properties of the SOFC electrolyte than those obtained by conventional solid state reaction. A more homogeneous porosity is obtained, which generally results in a better diffusion of gases towards the electrolyte and an increase of reaction sites, where electrochemical reaction occurs. All these factors generally contribute to enhance the electrochemical performance of the electrolyte. Another issue to be considered is that freeze-dried method has several advantages compared to other alternative precursor routes. For example, in sol–gel routes, the pH, cation concentration, ligand–metal ratio and gelification temperature are critical factors to be controlled and to avoid undesirable precipitation during the gelification process. On the contrary, the only parameters that affect the freeze-dried product are: the cation concentration and the pH of the starting solution, which are easier controllable. It should be also considered that freeze drying is a process which is used to dehydrate in large scale a wide variety of industrial products, e.g. foods, pharmaceuticals, etc. Therefore, the preparation of large quantities of precursor for the synthesis of almost any ceramic material is possible. In fact, the use of freeze-dried precursors has proved to be a very versatile method for obtaining different materials as mixed oxides [28, 29], metal nitrides [30], etc.

XRD patterns of powder obtained directly for the freeze drying process are shown in Figure 1. All the peaks of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ are exhibited at relatively low temperature (400 °C). However the peaks are relatively broad, whish indicated that the crystallites were very small. The size of the crystallite has been calculated from the XRD pattern by the standard Scherrer analysis of the half-width of the XRD peak [31]. Well crystallized LaB_6 was used as standard to calibrate the intrinsic width associated to the equipment. The average crystallite size was 20 nm. A qualitative analysis of the XRD dada indicated that the sample exhibited a single cubic phase (fluorite type-structure with space group Fm-3m) with a cell parameter of 5.4189 Å.

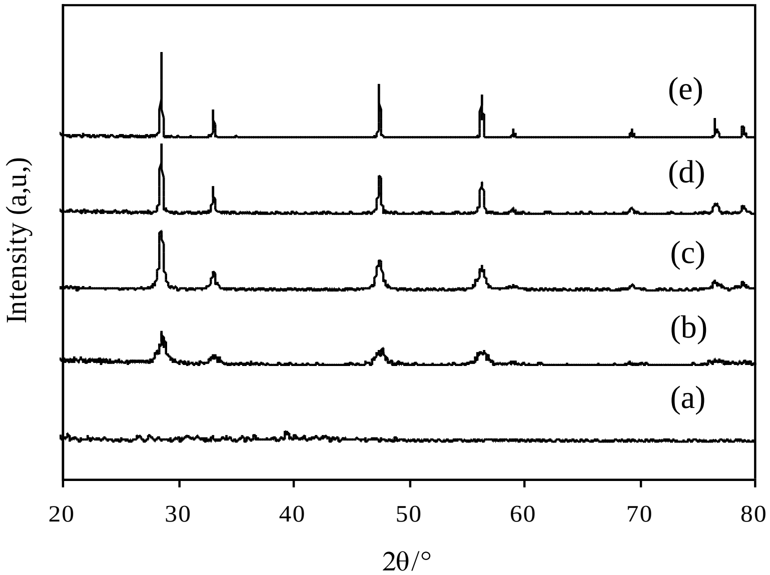

Figure 1. XRD patterns of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ powder resulting from freeze drying method at amorphous precursor (a), 400 °C (b), 600 °C (c), 800 °C (d) and 1000 °C (e)

Pellet prepared showed relative density of higher than 96 % were obtained after sintered at 1100 °C for 10 h. The main diffraction peaks do not shift significantly and moreover there are no extra diffraction peaks, which indicate the phase stability (figure 2). The average grain sizes in the sintered pellets were determined from the SEM micrographs (Figure 3) and were within the range of 1–3 μm. Sintered samples confirmed that the single cubic phase was preserved with an increase in grain size and crystallinity.

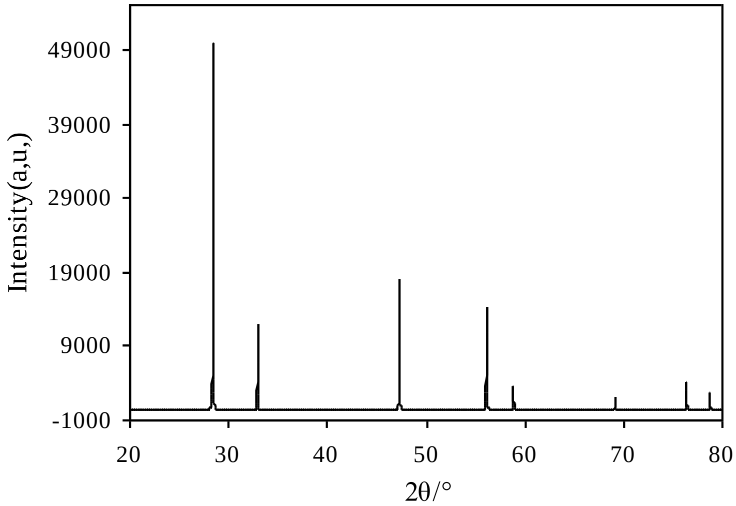

Figure 2. XRD pattern of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ pellet sintered at 1100 °C for 10 h

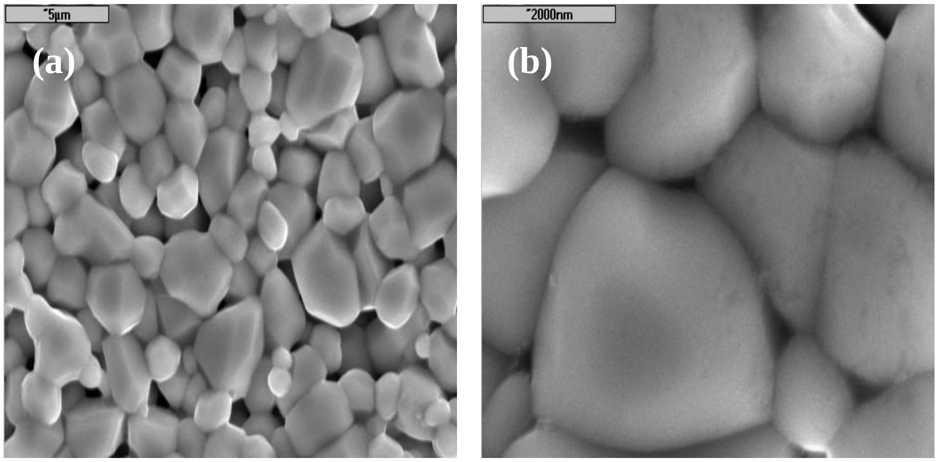

Figure 3. SEM images showing the microstructure of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ pellet sintered for 10 h at 1100 °C. Scale bars corresponds to 5 µm (a) and 2000 nm (b)

The impedance spectra have been widely used for the measurement of the electrical conductivities of solid materials. The impedance were fitted to the conventional equivalent electronic circuit containing three Resistance-Constant Phase Element (R-CPE) subcircuits in series which, at low temperatures three successive semicircles can normally be resolved on the Nyquist plots corresponding to polarizations of the electrode, grain boundary and grain interior, respectively [32]. Figure 4 shows one typical plot of impedance spectroscopy measurements for $Ce_{0.80}Gd_{0.20}O_{2-\delta}$ taken at 250°C.

Figure 5 presents the Arrhenius plots of total conductivity derived from these impedance spectra. For each of these, data is presented for the sintered pellet at 1100 °C for 10 h measured in air for the relevant intermediate temperature range 200–850°C. The powder synthesized by freeze drying process can significantly decrease the sintering temperature, compared to that above 1550 °C required for ceria solid electrolytes prepared by solid state reaction.

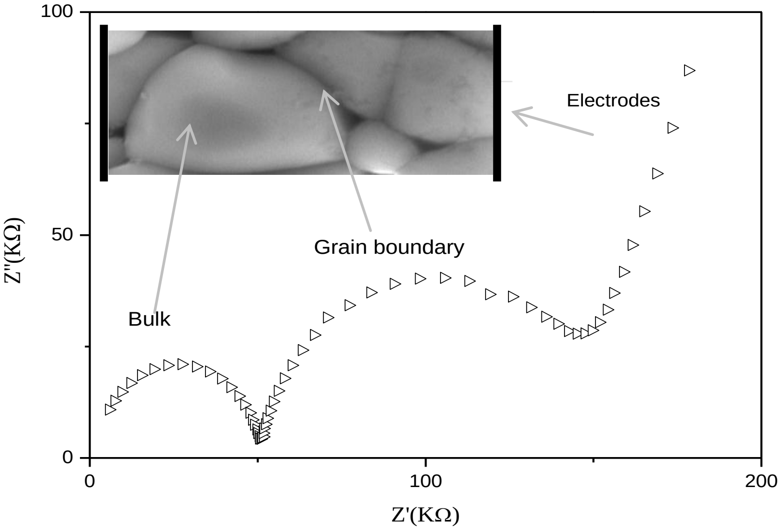

Figure 4. Typical impedance spectra obtained at 250 °C of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ pellet

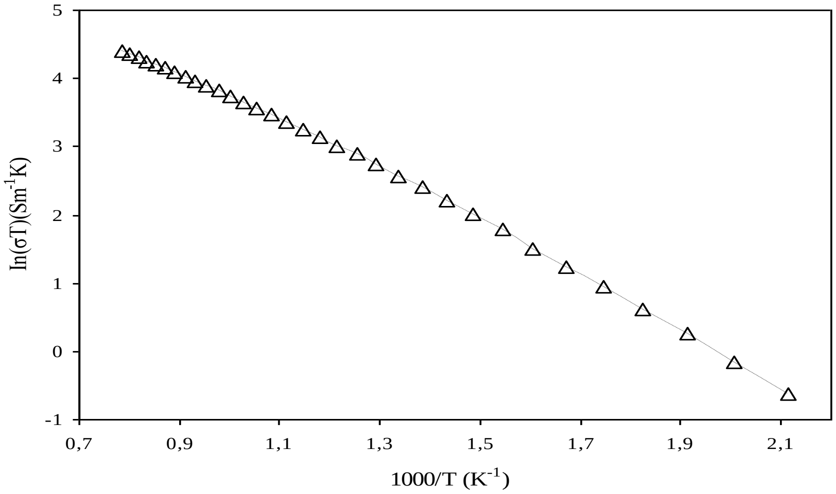

Figure 5. Arrhenius plot of total conductivities of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ sample

It indicates that at lower temperatures, the slopes of the Arrhenius plots are linearly dependent on the temperature. However, at higher temperatures (approximately from 400 °C upwards), it is possible to see that the gradient of the curves gradually. This curvature has previously been found for numerous ceria based solid solutions [33-35]. It is important to emphasize that the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ electrolyte prepared by freeze drying process had high conductivities, about 3.03 10^{-2} Scm^{-1} at 650°C. These values are slightly higher than the best results reported by other authors [36-38] and they were considerably higher than that of the electrolytes prepared from conventional solid-state reaction.

Conclusion

Nanopowder $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ material with the fluorite structure was prepared by the freeze drying process. Average particle size was estimated from the peak broadening in the XRD pattern. Because of the small particle size of the doped ceria, the sintering temperature needed to obtain a dense ceramic pellet was reduced to 1100 °C. It demonstrated that $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ material prepared by the freeze drying method could be easy to sinter at lower temperature and obtain dense ceramic electrolyte with better electrical property. Generally, Over the complete temperature range the conductivities at 1100 °C sintered temperature was 3.03 10^{-2} Scm^{-1} at 650°C.

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