

Plasma-sprayed gadolinium-doped ceria (GDC) for intermediate temperature solid electrolyte

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10 mol% gadolinium-doped cerium (IV) oxide was prepared by solid-state reaction route and deposited as a thick film using thermal (plasma) spray technique. The phase development, microstructure and topography were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The mechanical strength of the deposited film was determined by pull-off adhesion test. The plasma-sprayed GDC was characterized for its electrical properties by dc four-probe conductivity experiments. The maximum conductivity for plasma-sprayed GDC was found to be $3.60 \times 10^{-2} \text{ Scm}^{-1}$, which was lesser than $2.25 \times 10^{-1} \text{ Scm}^{-1}$ for the CIP-sintered GDC at 1000 °C and $p\text{O}_2 = 0.21 \text{ atm}$. The decrease in the conductivity is attributed to the larger intergranular spaces and uneven networking observed in the microstructure resulted in higher activation energy and low conductivity.

Key words: Thermal spray coating, GDC, Electrolyte, Ionic conductivity.

Introduction

Doped cerium oxide (CeO_2) is well recognized for its high oxygen ion conductivity in the intermediate-temperature range. Precisely, gadolinium-doped ceria (GDC) has progressively replaced yttrium-stabilized-zirconia (YSZ) that was the traditional electrolyte for SOFCs at high operating temperatures [1]. The higher ionic conductivity of GDC compared to YSZ is considered to have originated from the smaller enthalpy associated between the Gd^{3+} and the oxygen vacancy of ceria because of the higher ionic radius of Gd^{3+} as compared to Ce^{4+} [2–4]. Thus, the high oxygen ion migration is facilitated by the additional oxygen vacancies created by doping with acceptor gadolinium.

YSZ has a chemically stable structure even when exposed to highly reducing atmosphere but in case of GDC, Ce^{4+} ion is reduced to Ce^{3+} and the material becomes n-type semiconductor in such conditions [5–6]. It was found to be beneficial to apply GDC on the cathode side for enhancing the catalytic activity. Thus, recently much work has come into account towards developing a GDC/YSZ based bilayer for fuel cell application [7–9]. However, the difference in the sintering temperatures (relatively low sintering temperature of GDC in comparison to YSZ) leads to a porous GDC

layer over YSZ and results in lower ionic conduction and less charge transport because of the reduced contact area between electrolyte and electrode. Therefore, it necessary to prepare dense GDC layer on the top of YSZ. Accordingly, the high sintering temperatures required to achieve dense GDC electrolyte (1400–1600 °C) have inspired many researchers to investigate some sintering aid that can facilitate the purpose. Some of them are transition metal oxides such as CoO , Co_2O_3 , Co_3O_4 , TiO_2 , FeO , MnO_2 , Fe_2O_3 , Mn_2O_3 etc. which have been successfully co-doped in gadolinium-doped cerium oxide [10–13]; however, their effect on the conductivity and microstructure is still not fully understood. Several specialized fabrication techniques have been employed for the preparation of dense GDC electrolytes without involving sintering aids. Oh et al. have demonstrated the fabrication of thin-film GDC by chemical-solution deposition (CSD) technique [14]. GDC thin-film comprising columnar grain microstructure were prepared successfully by Hong et al. [15] and Kim et al. [16] by employing electron beam deposition and RF-sputtering techniques, respectively.

Plasma-spray coating has numerous advantages over abovementioned techniques in terms of ease of processing, significantly higher deposition rates and control over composition, porosity and microstructure [17]. Despite the favourable features, not much work has been reported about the fabrication of GDC electrolyte with this technique. Therefore, in this present work; we have demonstrated a schematic approach towards

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fabrication of plasma-sprayed and studied its physico-electrical properties considering it as a potential electrolyte material.

Experimental

Powder synthesis

10 mol% gadolinium-doped ceria (GDC) was synthesized by solid state reaction route using cerium(IV) oxide (CeO_2) and gadolinium (III) oxide (Gd_2O_3) precursors (Sewon Chemical Co. Ltd., South Korea) having analytical grade quality without any further purification. The oxide powders, in appropriate stoichiometric amount were put into the ball mill along with de-ionized water as solvent and zirconia based balls (diameter: 5–10 mm) and milled for 20 hrs. After primary milling, 0.3 wt.% of poly-vinyl alcohol (PVA) as a binder and 0.02 wt.% of sodium hydroxide (NaOH) as cohesive agent were added to the slurry and further milled for 4 hrs. The slurry was aged for 1 hr and then subjected to spray drying in a spray dryer (FOC series spray dryer, Ohkawara Kakohki Co. Ltd., Japan) having disc rotation at 16000 rpm, powder flow rate of 30 g/min and hot-air inlet temperature of 180 °C. This spray dried powder was calcined at 1300 °C for 4 hrs in air atmosphere having heating and cooling rate of 5 °C/min and finally used for plasma spray coating.

Sample Preparation

Thermal plasma spray coating technique was employed to deposit a thick film of GDC on an alumina substrate. The calcined GDC powder was fed into the spray gun provided 30 g/min powder flow rate. The spray gun was operated at a speed of 1000 mm/s given by a power supply of 102 V and 500 A. Plasma-sprayed GDC was fabricated by injecting the material into the plasma flow (Speed: Mach 2 and central temperature: 16,500 °C) with the help of mixture of inert gasses, i.e. argon and helium in an Ar:He ratio of 9 : 1 by the non-transfer arc and fused momentarily to inject the completely fused powdered plasma-spray materials in high speed to form the films. With the help of this technique, GDC film with a thickness of ~2 mm was fabricated. The effect of fed powder particle size and distance between injecting gun and substrate on the adhesion strength and microstructure was also studied.

To perform a comparative study, standard GDC powder (Fuel cell materials, United States) was studied as a reference. In this regard, the powder was molded into a disc and cold iso-statically pressed (CIP) at a pressure of 1500 MPa for 15 min. It was further sintered at 1600 °C for 12 h in air atmosphere with heating and cooling rate of 5 °C/min.

Characterizations

The crystalline phases developed in synthesized and

reference GDC powders after calcination were studied by powder X-ray diffraction (XRD) technique using a D/MAX Ultima III diffractometer (Rigaku Corporation, Tokyo, Japan) coupled with Cu $K\alpha$ radiation (λ) 1.54056 Å. Data was collected in a range of 2θ from 10° to 80° at a scanning rate of 2 °/min. Microstructural and morphological developments were studied using field-emission scanning electron microscopy (FE-SEM) over a Hitachi High-Tech S-4700 scanning electron microscope (Minato-ku, Tokyo, Japan). The samples were coated with gold by sputter coating instrument prior to SEM analysis. Particle size distribution of the synthesized powder was studied by a Beckman coulter LS 13-320 particle size analyzer (Beckman Coulter Inc., United States) having particle size analysis range of 0 to 2000 μm . The strength of adhesion between plasma-sprayed GDC film and the alumina substrate was studied using a PosiTest AT-A pull-off adhesion tester (DeFelsko Corporation, United States). The density of plasma-sprayed and reference GDC was measured using Archimedes principle. Atomic force microscopy (AFM) experiments were performed on a Park XE-100 Atomic Force Microscope (Park Systems, South Korea) to obtain a topographic image of the surface structure of plasma-sprayed GDC. For the electrochemical characterization, Dc 4-probe measurements were performed on a Keithly Series 2200 (Tektronix Inc., United States) USB/GPIB programmable DC power supply.

Results and Discussion

Physical properties

Figs. 1(a,b) shows the XRD pattern of synthesized and reference GDC powder calcined at 1300 °C, respectively. As per the data profile matching, it is observed that the diffraction peaks correspond to the cubic fluorite lattice (space group no. 225 Fm3m) for compound cerium oxide. Identical diffraction peaks corresponding to (111), (200), (220), (311), (222), (400), (331) and (420) crystal planes of CeO_2 are observed in both of the GDCs (JCPDS Card No. 75-0161). None of the extra peaks are observed in the XRD which eliminate the possibility of the presence of any impure secondary phase formation.

Figs. 2(a,b) shows FE-SEM images of the synthesized and reference GDC powder. In Fig. 2(a), spherical agglomerates are observed consisting fine primary particles of synthesized GDC. The particle size of these agglomerates calculated from SEM is in a wide range of 8–40 μm with a mean of $\sim 20 \pm 0.1 \mu\text{m}$ which is in good agreement with the mean size of 23.56 μm obtained by particle size analyser shown in Fig. 3. This wide range of particle size may have come as a result of synthesis process and may lead to differential film properties after plasma spray deposition. In Fig. 2(b), extremely fine particles without agglomeration are observed for reference GDC powder having a mean

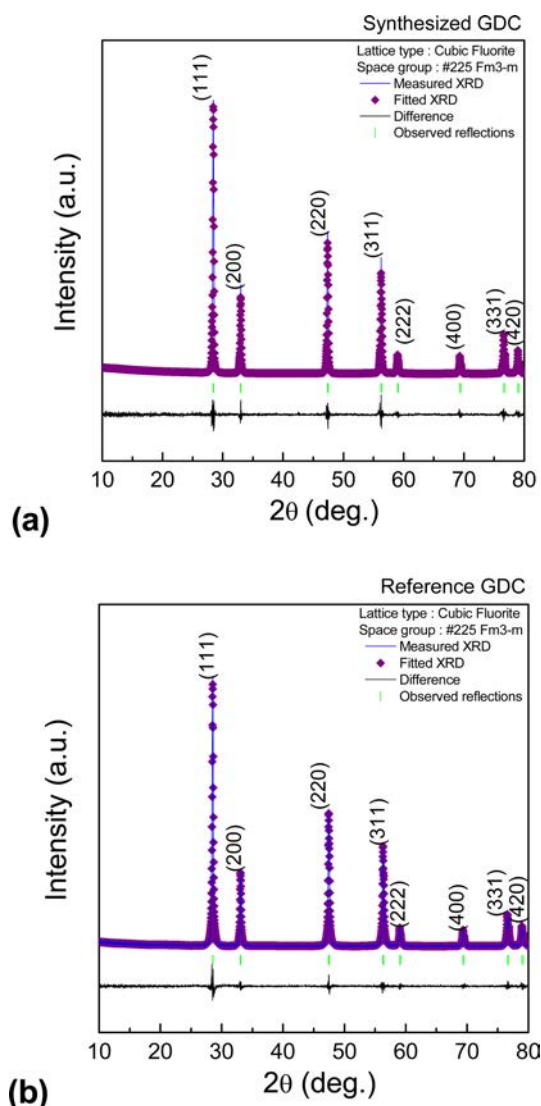


Fig. 1. XRD patterns for synthesized (a) and reference (b) GDC powder.

particle size of $\sim 0.21 \pm 0.1 \mu\text{m}$. The FE-SEM experiments were also performed for the CIP-sintered reference and plasma-sprayed GDC to study the microstructural and morphological developments in the samples and results are shown in Fig. 2(c & d). In Fig. 2(c), it is observed that the plasma-sprayed films have a microstructure comprising columnar grains stacked together vertically. The similar microstructure was also observed in our previous study of plasma-sprayed YSZ [18]. However, the size of the GDC columnar grains is considerably small having height and width in a range of 1–2 μm and 0.2–1 μm , respectively. Multiple rows of columnar grains are stacked together throughout the film but a well-visible cleavage and thick grain boundary lie between them which may increase the porosity of the film which may further contribute to the degradation of the mechanical strength and electrical conductivities of these films. Fig. 2(d) represents the FE-SEM image of the cold isostatic pressed reference sample sintered at

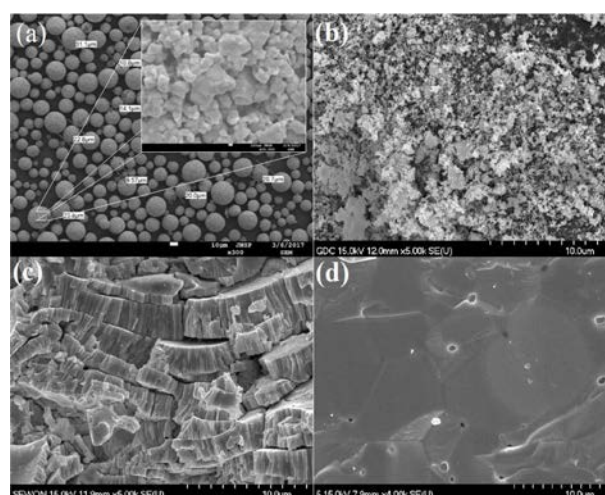


Fig. 2. FE-SEM images of the (a) synthesized powder, (b) reference powder, (c) plasma-sprayed and (d) CIP-sintered GDC.

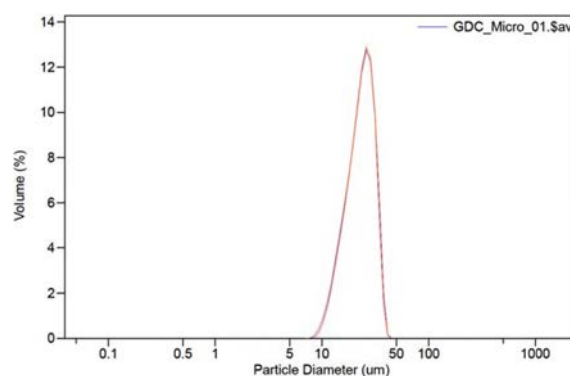


Fig. 3. Particle size distribution of GDC powder.

1600 °C. It is observed that the sample has a very uniform microstructure comprising integral large grains (5–10 μm). Thin grain boundaries, low porosity with negligible intergranular spaces are observed. This type of highly dense microstructure may give rise to the mechanical strength as well as the electrical conductivity of the material.

The density measurements were done by Archimedes principle method. It was found that CIP-sintered reference GDC has a maximum density of $99.9 \pm 0.1\%$ whereas plasma-sprayed GDC has a density of $95 \pm 0.1\%$. The similar density was observed for plasma-sprayed YSZ as well [18]. This density loss with the comparison to reference GDC can be attributed to the difference in the preparation technique and the microstructural distinctions observed through FE-SEM.

The effect of feed particle size and distance between substrate and gun nozzle, on the microstructure of the plasma-sprayed GDC, was also examined. Fig. 4 shows the cross-sectional images of the plasma-sprayed GDC. It has been observed that the wide range of particle size observed in Fig. 3, has led to some significantly differential microstructural developments. The films prepared from the powder having particle size $\leq 32 \mu\text{m}$

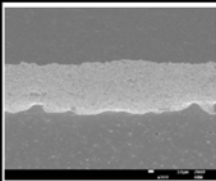
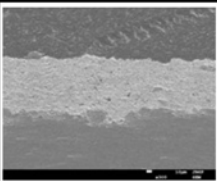
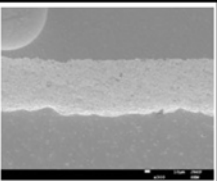
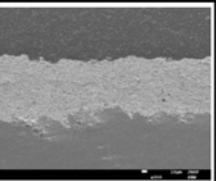
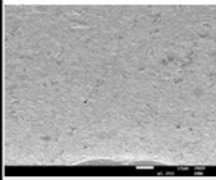
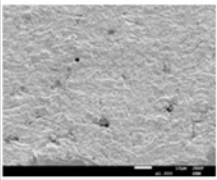
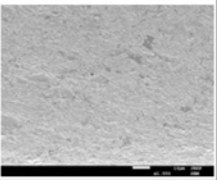
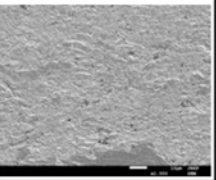
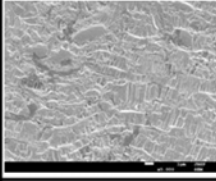
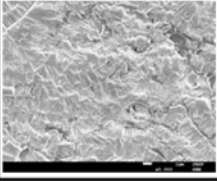
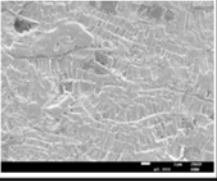
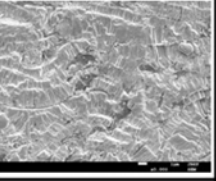
Gun distance : 100 mm		Gun distance : 120 mm	
Particle size: $\leq 32 \mu\text{m}$	Particle size: $32 \sim 53 \mu\text{m}$	Particle size: $\leq 32 \mu\text{m}$	Particle size: $32 \sim 53 \mu\text{m}$
			
			
			
Adhesion strength: 1.32 MPa	Adhesion strength: 1.19 MPa	Adhesion strength: 1.43 MPa	Adhesion strength: 1.33 MPa

Fig. 4. Cross-sectional FE-SEM images of the plasma-sprayed GDC with the variation of feed particle size and distance between the substrate and gun nozzle along with the corresponding adhesion strengths.

has resulted in an even microstructure comprising close packing of columnar grains with small intergranular spaces and low porosity. In comparison to this, the films prepared from the powder having the larger particle size ($32\text{--}53 \mu\text{m}$) has resulted in an uneven microstructure comprising slightly larger columnar grains stacked together loosely leading to larger intergranular spaces and porosity. A well visible cleavage is also observed between the rows of columnar grains. Concerning the effects of the distance between substrate and gun nozzle; it is observed that the sample prepared with a distance of 120 mm has resulted in better uniformity in the microstructure in comparison to the sample prepared through 100 mm distance. Moreover, the sample prepared through the feed powder having particle size $\leq 32 \mu\text{m}$ and the distance between the substrate and gun nozzle of 120 mm has resulted in the most optimum microstructure consisting uniform grain growth provided by low porosity and small intergranular spaces.

The strength of adhesion between film and substrate is very important property in thin film technology because usually, the thin films are so weak that these must be supported by more substantial substrates and the degree to which the film can share the strength of the substrate depends upon the adhesion between the two. It also plays a major role in governing kinetics of the growth and structure of the films leading to differential durability and surface chemistry of the film. Therefore, to measure the strength of adhesion between

plasma-sprayed GDC film and alumina substrate, the pull-off adhesion test was performed. Upon completion of a pull-off test, the dolly and coated surface are examined. In addition to pull-off force, the nature of the fracture is also recorded. It was observed that the fracture occurred in this test is a cohesive fracture which occurs with-in the coating layer. Based upon the force applied to pull-off the dolly, adhesion strength is given in Fig. 4 for each sample prepared by the variation of particle size and distance between the substrate and gun nozzle. The sample prepared from a distance of 150 mm resulted in low adhesion strength of 0.5 MPa, therefore it was not further used. Moreover, the sample prepared through the feed powder having particle size under $\sim 32 \mu\text{m}$ and the distance between substrate and gun nozzle of 120 mm has resulted in the maximum adhesion strength of $\sim 1.43 \text{ MPa}$. The possible reason behind this comparative high strength comes from the uniform columnar grain growth. The low porosity and small intergranular spaces in the sample have resulted in a dense microstructure which further contributed to rising in the mechanical strength of the material.

A traditional fuel cell is typically constructed by a three-layer structure; i.e. anode–electrolyte–cathode. The porous anode and cathode are separated by an electrolyte that is composed of a dense material which provides selective ion conduction. The interface between these electrodes and electrolyte plays a highly important role, not just in term of electrochemical properties, but also in terms of the mechanical properties. Thus, it becomes

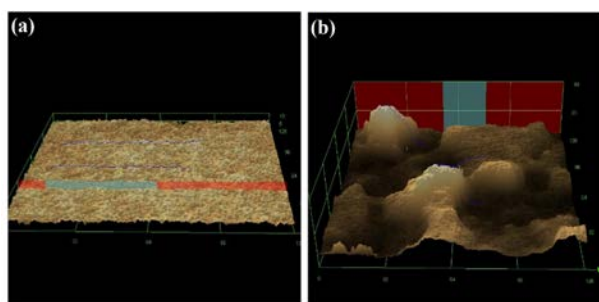


Fig. 5. Topographical 3D image of the (a) alumina substrate and (b) plasma-sprayed GDC by AFM analysis.

necessary to examine the surface structure of plasma-sprayed GDC for appraising its quality to be used as an electrolyte material. In this regard, atomic force microscopy (AFM) analysis was carried out. The topographical image of the plasma-sprayed GDC along with the alumina substrate is shown in Fig. 5(a,b). The experiment was operated in non-contact AFM mode in which the tip of the cantilever does not contact the sample surface. The micro and nano-scale features of the film can be observed with a maximum height of $\sim 4.1 \mu\text{m}$. Based upon the observations, two types of the hypothesis can be considered to explain the effect of this surface structure in the application for the fuel cell. First, that the surface roughness and cavities can actually be helpful in providing better mechanical adhesion at the interface between electrode and electrolyte. This could be beneficial in obtaining better life cycle from the fuel cell. On the other hand; these surface roughness and unevenness may also lead to maximize the contact area between the electrode and electrolyte at certain sites which could result in reduction of the charge transport resistance. So, further schematic studies need to be carried out to understand the optimum surface structure required for this purpose.

Electrical properties

In a solid oxide fuel cell system, GDC based electrolyte membrane typically provides the path for oxygen ion conduction from cathode to anode. In this regard; conductivity measurements for the plasma-sprayed GDC must be done and studies must be taken to understand the phenomenon involved. The direct current (dc) conductivity measurement provides the overall conductivity behaviour of the material. DC conductivity was measured using the 4-probe measurement equipment. 4-probe measurement is considered to be more reliable as it offers minimum polarization potential unlikely 2-probe measurements. The extremely low partial pressure of oxygen was obtained by maintaining the mixture of CO & CO₂ whereas relatively higher partial pressure of oxygen was obtained by maintaining the mixture of N₂ & O₂. Rectangular samples were used for dc conductivity measurements. The current was provided from external

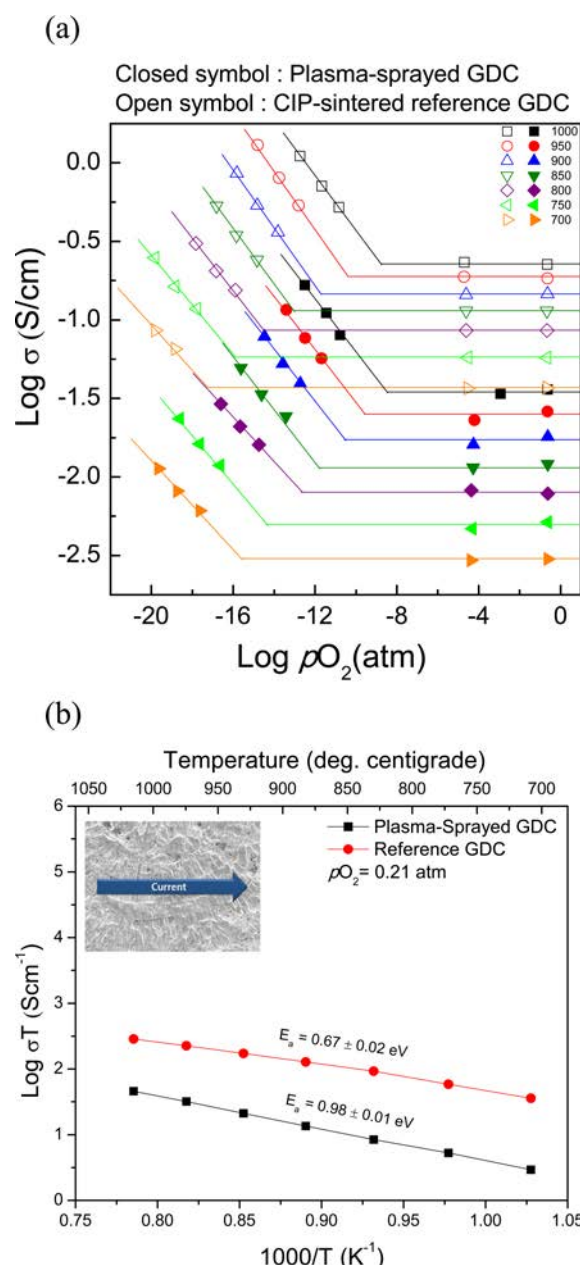


Fig. 6. (a). Variation of dc conductivity of samples as a function of partial pressure of oxygen ($p\text{O}_2$) at different operating temperature, (b). Arrhenius plot of dc conductivities for plasma-sprayed GDC and reference GDC.

electrodes and voltage was measured through internal electrodes.

Fig. 6(a) shows the variation of dc conductivity of samples as a function of partial pressure of oxygen ($p\text{O}_2$) at different operating temperature. It is observed that the total conductivities of the plasma-sprayed GDC are less than the reference GDC at all operating temperatures. The conductivities of entire samples are independent of the partial pressure of oxygen. This independence indicates that the conduction mechanism is dominated by the pure ionic conductivity of oxygen ion in low oxygen partial pressure with negligible

electronic conduction. However, in highly reducing conditions, the conductivity of GDC is dependent upon the oxygen partial pressure and it is decreasing as per the increase in pO_2 . It suggests that the conduction mechanism in highly reducing conditions is dominated by electronic conductivity. Such n-type semiconducting behaviour under highly reducing conditions is well known for GDC material because of the reduction of Ce^{4+} into Ce^{3+} ion [19]. It is also observed that the lower electrolytic boundary for plasma-sprayed GDC is similar to CIP-sintered reference sample and it shifts to lower pO_2 as temperature decreases. Thus, the difference in the total conductivity is attributed to the difference in the absolute value of conductivity of the materials. Moreover, the conductivity behaviour observed with respect to the variation of measurement temperature and partial pressure of oxygen for both of the sample suggests that the conduction mechanisms in the plasma-sprayed GDC are similar to that of the reference GDC even though they possess different morphologies.

Fig. 6(b) represents the Arrhenius plot of dc conductivities for plasma-sprayed GDC and reference GDC. Experiment was performed in between the temperature range of 700 to 1000 °C at atmospheric oxygen partial pressure. It is observed that the conductivities of entire GDC increase in accordance to the increase in operating temperature. It suggests that the entire GDC follows Arrhenius equation as with increasing the temperature, increase in the conductivity comes from the increased pre-exponential factor. Plasma-sprayed GDC has shown conductivity of 3.60×10^{-2} – $2.94 \times 10^{-3} \text{ Scm}^{-1}$ in comparison to 2.25×10^{-1} – $3.66 \times 10^{-2} \text{ Scm}^{-1}$ for the reference GDC in a temperature range of 700–1000 °C. At all operating temperatures, conductivity for plasma-sprayed GDC is observed to be less than that of the reference sample. It suggests that the conductivity trend in both the GDCs are significantly different. By definition, the conductivity depends upon two factors, i.e. Activation energy (E_a) and Pre-exponential factor (A or Z). In our case, the activation energy (E_a) calculated from the Arrhenius plot is $0.98 \pm 0.01 \text{ eV}$ and $0.67 \pm 0.02 \text{ eV}$ for plasma-sprayed and reference GDC, respectively. It is clearly observed that the conductivity differences observed in the Arrhenius plot have origin from the differences in activation energies. The possible reason behind the significant increase in the activation energy lies in the microstructural distinction between plasma-sprayed and reference GDC. As observed in the FE-SEM analysis, the plasma-sprayed GDC has larger intergranular spaces and thick grain boundaries which generally result in contributing, higher activation energies compared to the bulk [20–23]. Thus, the conductivity of plasma-sprayed GDC is lower than the reference GDC. However, by optimizing the plasma-spraying parameters and GDC powder, it is expected to obtain a homogenous microstructure leading to increased conductivity.

Conclusions

Gadolinium-doped ceria was successfully prepared by the thermal (plasma) spray technique. The prepared film was characterized for its physical and electrical properties. The conductivity mechanism in plasma-sprayed GDC was confirmed to be dominated by oxygen ion conductivity independent of oxygen partial pressure in oxidizing conditions, however; in highly reducing conditions, electronic conductivity was observed. The plasma-sprayed and CIP-sintered GDC have shown the maximum conductivity of 3.60×10^{-2} and $2.25 \times 10^{-1} \text{ Scm}^{-1}$, respectively at 1000 °C in $pO_2 = 0.21$ atm atmosphere. It is concluded that by optimizing the experimental parameters, the plasma-spray technique can be considered as a reliable method for the preparation of GDC electrolyte for fuel cell application.

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