Short communication

Novel structured gadolinium doped ceria based electrolytes for intermediate temperature solid oxide fuel cells

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ARTICLE INFO

ABSTRACT

Novel three-layered intermediate temperature solid oxide fuel cell (SOFC) electrolytes based on gadolinium doped ceria (GDC) are developed to suppress the electronic conductivity of GDC, to improve the mechanical properties of the cell and to minimize power loss due to mixed conductive nature of GDC. Three different electrolytes are fabricated by sandwiching thin YSZ, ScSZ and ScCeSZ between two relatively thick GDC layers. An electrolyte composed of pure GDC is also manufactured for comparison. NiO/GDC and LSCF/GDC electrodes are then coated on the electrolytes by a screen printing route. SEM results show that it is possible to obtain dense and crack free thin layers of YSZ, ScSZ and ScCeSZ between two GDC layers without delamination. Performance measurements indicate that interlayered thin electrolytes act as an electronic conduction barrier and improve open circuit voltages (OCVs) of GDC based cells.

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1. Introduction

Gadolinium doped ceria (GDC) has been regarded as a promising electrolyte material candidate for intermediate temperature SOFCs ($\sim$500–650 °C) due to its high ionic conductivity [1–3]. However, cerium ions are reduced from Ce^{4+} to Ce^{3+} showing an electronic conductivity at reducing conditions occurring in a SOFC environment [4–6]. The volume difference of these two oxidation states usually results in severe structural and mechanical problems such as micro-crack and delamination at low oxygen partial pressure atmospheres [7–9]. Thus, the cell exhibits low mechanical strength, low OCV and power loss due to short circuiting the cell.

In the literature, the most common way to avoid the reduction of ceria and thus avoid the electronic conductivity as well as to have high mechanical strength is to employ a composite electrolyte material by the addition of some oxide powders as electron-trapping inclusions to ceria/doped ceria powders. Al_2O_3 (alumina) is the most frequent oxide in this aspect. Zhang et al. [10] developed GDC/Al_2O_3 composite electrolyte at various compositions. A remarkable improvement in mechanical properties such as microhardness and fracture toughness was reported. However, the addition of alumina adversely affected the conductivity. In particular, fast decrease in the grain boundary conductivity was observed

at higher alumina contents which were attributed to the formation of $GdAlO_3$. Chockalingam et al. [11] applied manganese/cobalt doped alumina as the electron-trapping nano inclusion to GDC. Although the electrical conductivity measurements showed that no electronic conductivity resulting from Ce^{4+} to Ce^{3+} conversion was detected, the conductivity of the nano-composite sample was very low (10^{-2} to 10^{-3} S cm^{-1} at 800 °C) due to the insulating effect of 50 wt.% alumina addition. Similar results were also concluded in the relevant literature [12–14].

Another approach is coating the ceria based electrolytes with zirconia/doped zirconia based ones. Virkar [15] provided a theoretical study for a two layered solid electrolyte composed of ceria with a thin layer of zirconia on the fuel side. It was suggested that it would be better to use coated electrolyte instead of zirconia based electrolytes. Atkinson and Selcuk [16] produced bilayer laminated electrolyte composite of 180 μm thick GDC and 5 μm thick YSZ. The bilayer electrolytes were found stronger than the single GDC electrolyte by a factor between 1.75 and 4.6. Yahiro et al. [17] fabricated ceria–yttria composite electrolytes coated with YSZ (yttria stabilized zirconia) on the fuel side. The coated electrolyte was found to be very conductive and unreduced in the operating conditions. However, the cell composite of coated electrolyte produced only 20 mW cm^{-2} peak power density at 600 °C operation temperature and the reported open circuit potentials are lower than the theoretical value indicating that only fuel side coating of the electrolyte may not be adequate to suppress the reduction of ceria. In a similar study, Jang et al. [18] fabricated an alternative electrolyte by

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coating fuel side of GDC with 2 μm thick YSZ by dip-drawing technique. Pure GDC electrolyte was also fabricated for comparison. Although, the coating of the YSZ layer on GDC improves OCV, the coated and uncoated samples showed still very low OCVs (0.670 V and 0.725 V at 900 °C, respectively) compared to pure YSZ electrolyte.

In this study, a novel structured electrolyte is developed by placing different thin electrolyte layers as an electronic conduction barrier between two thick GDC layers to suppress the electronic conduction as well as to enhance the mechanical strength of GDC for intermediate temperature SOFCs without compromising the ionic conductivity of GDC. The effects of the barrier layers on the open circuit voltage and performance of a cell are also investigated.

2. Experimental

2.1. Electrolyte fabrication

GDC ($Gd_{0.10}Ce_{0.90}O_{2-\delta}$) powders are purchased from Nextech Materials. Then, a tape casting slurry of GDC is prepared by ball milling for around 24 h with an organic dispersant, plasticizer and binder with proper ratios. Then the GDC slurry is tape casted with a blade gap of 200 μm. Similarly, YSZ (($Y_2O_3)_{0.08}(ZrO_2)_{0.92}$), ScSZ (($ZrO_2)_{0.90}(Sc_2O_3)_{0.10}$) and ScCeSZ (($Sc_2O_3)_{0.1}(CeO_2)_{0.01}(ZrO_2)_{0.89}$) (Nextech Materials) slurries are prepared and tape casted. The blade gap is kept as 50 μm to obtain thin YSZ, ScSZ and ScCeSZ electrolyte layers, since they all have lower ionic conductivity than that of GDC at intermediate temperature range. After drying for 30 min in air atmosphere, the thicknesses of the green tapes are measured as 40 μm and 15 μm for GDC and thin electrolytes, respectively.

Then 5 tapes of GDC–1 tape of YSZ–5 tapes of GDC electrolyte (GDC–YSZ–GDC: Sample A) are stacked together. Similarly, Sample B (GDC–ScSZ–GDC) and Sample C (GDC–ScCeSZ–GDC) are prepared. A schematic diagram for the fabricated electrolyte structure is given in Fig. 1. For comparison, ten layered pure GDC (Sample D)
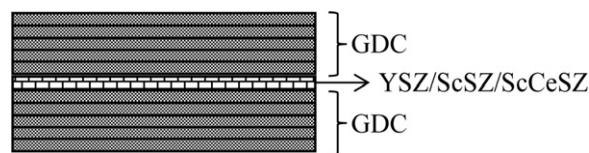

Fig. 1. Block diagram of the electrolytes fabricated.

electrolyte is also fabricated. The electrolytes are then laminated isostatically under 30 MPa pressure for 30 min. The laminates are then cut by a laser cutter to produce 60 mm diameter electrolyte discs. GDC discs are then co-sintered at 1450 °C for 4 h to obtain fully dense electrolytes. The final diameter of the electrolytes is measured as 45 mm.

2.2. Cell preparation and testing

NiO–GDC (60–40 wt.%) anode material are mixed with ethyl cellulose and terpineol at a proper ratio (50 wt.% of solid loading) to prepare the anode screen printing paste. The paste is then screen printed on the one side of Sample A with 30 mm diameter and sintered at 1250 °C for 2 h. Similarly, LSCF (($La_{0.60}Sr_{0.40})(Co_{0.20}Fe_{0.80})O_{3-\delta}$)–GDC (50–50 wt.%) cathode powders (Nextech Materials) are mixed with ethyl cellulose and terpineol at a similar ratio to prepare the cathode screen printing ink. The ink is then coated on the other surface of Sample A with again 30 mm in diameter and sintered at 975 °C for 2 h to obtain Cell A. Cells B–D are fabricated similarly by coating electrodes of the corresponding electrolyte structures of Samples B–D.

Single cells having 7 cm² active area are placed between two stainless steel interconnectors for the performance tests. Ag paste is applied as a current collector and Pt wire as lead. *I–V* tests are conducted with a fuel cell test station (Arbin Instruments FCTS, TX, USA) which has a temperature controlled furnace with a push rod pressing capability to improve the contact for better current
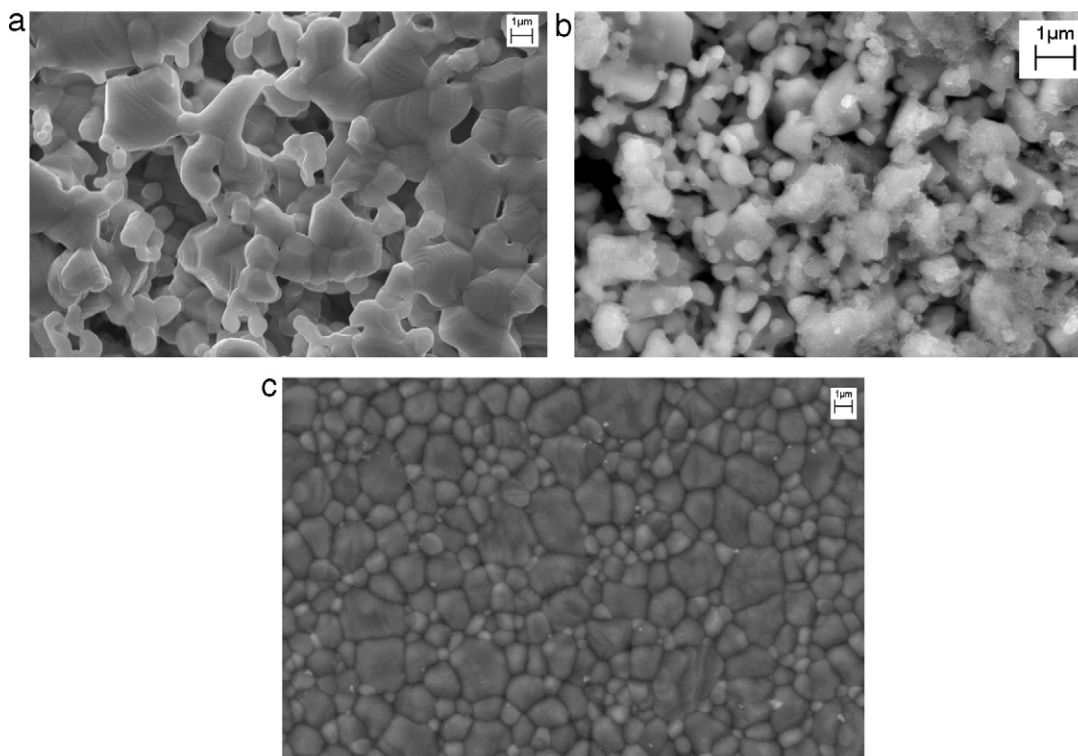

Fig. 2. SEM images of Cell D: (a) anode, (b) cathode and (c) electrolyte surface.
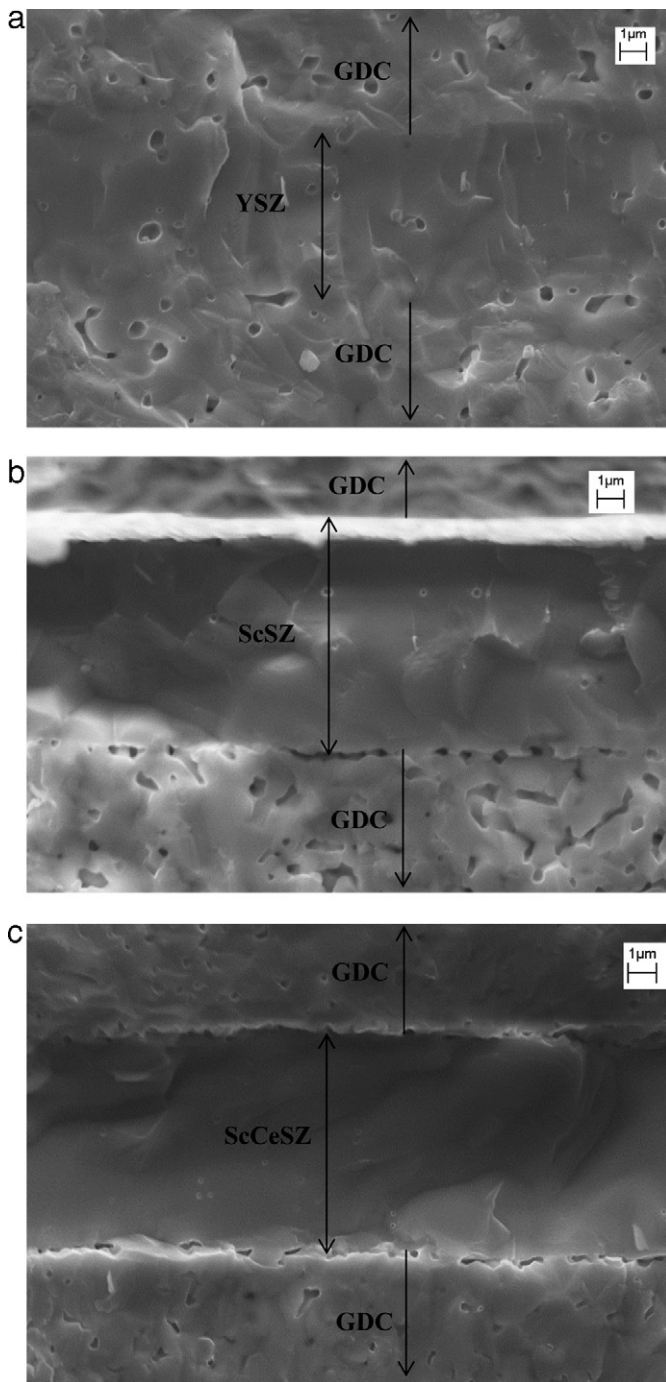
Fig. 3. Electrolyte cross-sections of Cell A (a), Cell B (b) and Cell C (c).

Fig. 4. OCV comparison of Cells A–D.

Fig. 5. Power curves of Cells A–D at 650 °C operation temperature.

collection. The cell performances are measured from 550 °C and 650 °C with hydrogen as a fuel and air as an oxidant whereas micro-structural investigation is conducted with a scanning electron microscope (SEM, Carl Zeiss Evo 40, London, England).

3. Results and discussion

3.1. Microstructure

Fig. 2 shows the surface microstructure of pure GDC electrolyte based cell. It is seen that the electrodes have typical porous structure to allow g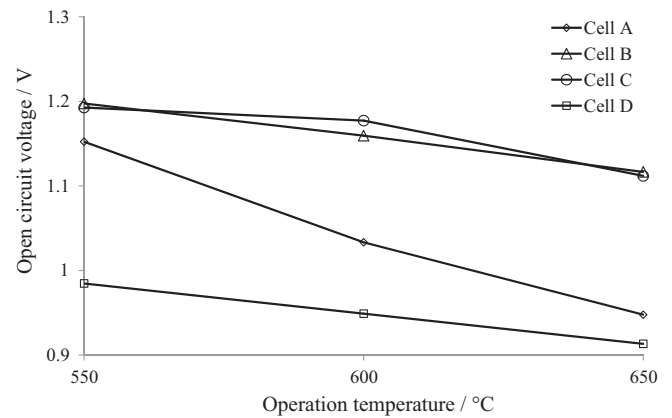as flow. The electrolyte, on the other hand, seems to be fully dense and crack free. The grain sizes of the electrolyte are varying between 1 μm and 3 μm.
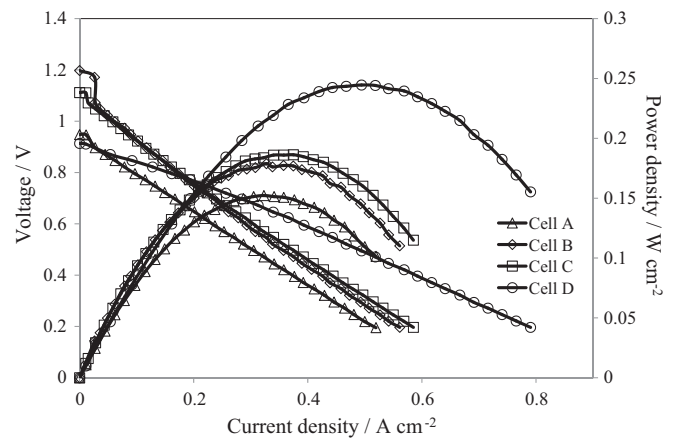
Cross-sectional images of electrolytes captured from Cells A–C are given in Fig. 3. Fig. 3a shows the YSZ interlayered GDC electrolyte structure. It is seen that dense YSZ layer is successfully fabricated between two GDC layers. Neither delamination nor crack is visible. Similar characteristics can be seen from Fig. 3b and c for ScSZ and ScCeSZ interlayered electrolytes, respectively. All thin electrolyte layers are well bonded to upper and lower GDC layers and seen to be fully dense and crack free. However, YSZ and GDC layers in Cell A are seen to be well adhered compared to those of Cells B and C. This may be due to the formation of a secondary phase between YSZ and GDC as pointed out in previous studies. Tsoga et al. [19–21] found that, YSZ and GDC diffuse each other and react during the sintering process leading to the formation of $Ce_{0.37}Zr_{0.38}Gd_{0.18}Y_{0.07}O_{1.87}$ at the YSZ/GDC interfaces.

3.2. Single cell characteristics

The effects of the interlayer on OCVs are shown in Fig. 4. OCV values of Cells A–D are compared in the figure. Results showed that OCV values of Cells A–C which have doped zirconia interlayer are close to theoretical value and higher than that of Cell D which has no doped zirconia interlayer indicating thin electrolyte layers act as an electronic conduction barrier as expected. However, OCV values of Cell A are found to be lower than those for Cells B and C. This can be attributed to the lower ionic conductivity of the secondary phase ($Ce_{0.37}Zr_{0.38}Gd_{0.18}Y_{0.07}O_{1.87}$) formed at YSZ/GDC interfaces which exhibits an ionic conductivity by two orders of magnitude

lower than that of YSZ [20,21]. Another possible explanation for lower OCV values of Cell A may be relatively low ionic conductivity of YSZ at intermediate temperature range considered in this study.

Fig. 5 shows performance characteristics of Cells A–D at 650 °C operation temperature. Although Cells A–C exhibited higher OCV values than that of Cell D, they all provided lower power densities than Cell D. This behavior is reasonable and can be attributed to lower ionic conductivities of YSZ, ScSZ and ScCeSZ compared to that of GDC at intermediate temperatures. Among Cells A–C, the highest power is obtained from Cell C which possesses GDC–ScCeSZ–GDC electrolyte structure. Cell C provides $186\,mW\,cm^{-2}$ peak power density which is 25% lower than obtained from pure GDC based cell. This amount of reduction in power is acceptable when the stability and long term operation without degradation are the issue.

4. Conclusion

Novel three layered GDC–YSZ–GDC, GDC–ScSZ–GDC and GDC–ScCeSZ–GDC composite electrolytes are successfully fabricated to suppress the electronic conductivity of pure GDC and to prevent cells from power loss or mechanical failure. Measurements showed that the cells having doped zirconia interlayer exhibit substantially higher OCVs indicating that thin layers of YSZ, ScSZ and ScCeSZ behave as an electronic conduction barrier. Performance results showed that especially thin ScCeSZ interlayered electrolyte can be employed instead of pure GDC electrolyte with sacrificing only 25% power. Further improvement in the performance can be achieved by optimizing the microstructure and fabrication parameters of the anode and the cathode layers. The results are

considered to be significant for manufacturing SOFC system below 650 °C which is not possible with doped zirconia electrolytes. At such lower temperatures, it is possible to use cheaper interconnect materials and substantially reduce the cost and startup/shut down times of a SOFC system.

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