Mechanical properties and electrochemical characterisation of extruded doped cerium oxide for use as an electrolyte for solid oxide fuel cells

Oliver Bellon [a], Nigel M. Sammes [a, *], John Staniforth [b]

[a] *Department of Technology, The University of Waikato, Private Bag 3105, Hamilton, New Zealand*
[b] *The Birchall Centre for Materials Science, Keele University, Keele, Staffs, ST5 5BG, UK*

Abstract

Doped cerium oxide is a promising electrolyte for use in a medium-temperature solid oxide fuel cell (SOFC), due to its high ionic conductivity at low temperatures. A colloidal processing route has been undertaken to prepare slurries from very fine doped-cerium oxide. The dried slurry is extruded into rods and tubes and the room temperature modulus of rupture is then measured. It is shown that the material could attain a modulus in excess of 220 MPa for $(CeO_2)_{0.8}(GdO_{1.5})_{0.2}$, which is considerably greater than values obtained using traditional routes. A preliminary investigation is made of the electrochemical properties of single cells fabricated from the extruded doped-ceria tubes. At 600°C, a maximum power output of approximately 38 mW cm^{-2} is realised. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Solid oxide fuel cells (SOFCs) are all-ceramic electrochemical reactors, which have the capability of converting most oxidizable gases directly into electricity. The work to date on SOFC stacks has concentrated on three main designs, viz., the tubular design, the planar design, and the monolithic design. The traditional electrolyte material is based on yttria-stabilised zirconia, and the system for all three designs must typically be operated at 950 to 1000°C, due to the relatively high resistivity of the electrolyte at lower temperatures. Lowering the temperature, however, to between 600 and 800°C has a number of potential benefits, including, for example, cheaper materials, lower degradation problems, less thermal mismatch, and closer temperature match for internal reformation possibilities [1–3].

Recently [4], a novel tubular SOFC design, based on small, shock-resistant, yttria stabilized zirconia (YSZ) tubes, was developed and allowed for very rapid heating and cooling (a matter of a few seconds, compared with traditional planar and tubular designs, which require several hours). A recent publication [5] has shown that YSZ-based SOFC cells, fabricated using the design described in [4], can produce an output of approximately 0.16 W cm^{-2} at 900°C. The aim of the research report here is to investigate the possibility of fabricating a SOFC based on this design, but using an electrolyte material that can operate at lower temperatures.

$(CeO_2)_{1-x}(GdO_{1.5})_x$ is a very promising material for use as an electrolyte in these so-called 'medium-temperature' SOFCs, because of its high ionic conductivity between 500 and 700°C. $(CeO_2)_{0.8}(GdO_{1.5})_{0.2}$, for example, has been examined in great detail by a number of authors [6–8], and has been shown to have an ionic conductivity of about 0.1 to 0.2 S cm^{-1} at 800 to 850°C. There are, however, a number of potential problems with using a doped-ceria electrolyte. Work to-date has shown that the mechanical strength of the material is relatively low when fabricated using traditional routes [9]; a value for the room temperature modulus of rupture of 143 MPa has been reported for $(CeO_2)_{0.8}(GdO_{1.5})_{0.2}$.

Recent studies on zirconia [4,10] have shown that a colloidal suspension technique used to process zirconia slurries, which can then be fabricated into extruded rods and tubes, can improve the material strength by a factor of two or more.

* Corresponding author. Tel.: +64-7-838-4065; Fax: +64-7-838-4219; E-mail: n.sammes@waikato.ac.nz

This paper, therefore, describes how the properties of doped-ceria can be improved using the colloidal suspension technique in order to acquire the physical and mechanical characteristics required by an SOFC electrolyte. The study also provides some preliminary data on the electrochemical performance of cells fabricated from the ceria-based electrolyte material.

2. Experimental

2.1. Powder preparation

$(CeO)_{20.8}(GdO_{1.5})_{0.2}$ powder (CGO) was obtained from Nextech Materials, USA. The powder had been prepared via the hydrothermal synthesis route, described below. It should be noted that the powder synthesis route is proprietary and, hence, not all the details can be given. The process, however, involves the following steps:

(i) co-precipitation of an intimately mixed cerium-gadolinium hydroxide gel;

(ii) hydrothermal treatment at modest temperatures and pressures;

(iii) washing of the reacted product to remove residual salts, followed by drying.

The particle size of the powders was then analysed using a Malvern Instruments Mastersizer E laser diffraction system, with a MS17 sampler.

2.2. Slurry preparation

The slurries were obtained by milling the CGO powder with a surfactant (Hypermer KD1, ICI Americas) and solvent (acetone) in a roller mill for 4 to 12 h, and then adding a binder (Polyvinyl-butyral (PVB), Aldrich Chemicals, Milwaukee, USA)) and a plasticiser (Octanol-1, BDH Laboratory Supplies, Poole, UK, 99%), and milled for a further 12 to 24 h. Previous work has shown [9] that ceria based powders calcined at approximately 500 to 600°C produced higher strength after sintering. Nevertheless, trials either with powders heat-treated at 1000°C or with as-received powders were also conducted.

The slurries were consequently tape cast on to an acetate sheet. The thickness of the material was limited as much as possible in order to reduce the drying time. Periods of 2 to 10 min were required to allow the tape-cast slurry to obtain a plastic consistency. The green tape was then manually pressed into a homogeneous bulk.

2.3. Extrusion

The extrusion device was designed in-house, and consisted of two different dies so that both rods and tubes could be extruded. The diameters of the green extruded samples were 1 mm (rods) and 2.5 mm (tubes); the thickness of the tube walls was 0.3 mm.

The extrusion was carried out by means of a Lloyds LR 100 K tensile tester equipped with a 100 kN load cell at a crosshead speed of 3 mm per min. Typically, 1 to 15 kN was required to extrude the samples; the load depended on the stiffness of the material.

After extrusion, the samples were dried in air for at least 24 h to allow the solvent to evaporate fully from the green extrudate.

2.4. Sintering

Initially, rods were sintered at 1600°C for 4 h in between two thin 8-mol% YSZ (8YSZ) plates. These plates were used in order to avoid bending of the samples during shrinkage on sintering. Considering that the small dimensions of the samples would allow easier sintering, this temperature was later reduced to between 1500 and 1300°C for the tubes. In all cases, dwell times of 2 and 10 h were examined.

The burn-out of the additives was included in the sintering programme up to 550°C, a slow heating rate of 0.5°C per min was used, followed by a rate of 2°C per min up to the sintering temperature (1300 to 1600°C). The cooling rate was kept at 3°C per min.

2.5. Mechanical testing

Sintered rods were mechanically tested (modulus of rupture) using a 3-point bend technique on an INSTRON 4204 using a 10 N load cell. The room-temperature modulus of rupture was measured to compare the behaviour of the material with literature results, in order to confirm the improvement with respect to conventional preparation routes.

The percentage theoretical density of the sintered samples was measured using the standard Archimedes method and the theoretical density (%) calculated from XRD data.

Microstructural examination was undertaken by means of a Hitachi S4000 scanning electron microscope.

2.6. Cell fabrication

Electrochemical measurements were undertaken on doped-ceria tubes, which had an outside diameter and thickness of approximately 2.5 mm and 150 μm, respectively. The full experimental details of the cell fabrication are described elsewhere [5], but some of the major details are described below. A commercial $La_{0.82}Sr_{0.18}MnO_3$ (LSM) cathode (LSM 82X96019-2, Merck) was applied on the outside of the tube and an Ni/YSZ ceramic metal composite anode on the inside. The cathode consisted of two layers, viz., an electrochemical contacting layer (first layer) and an outer layer. The contacting layer was applied by brush using an ink made up of the commercial LSM mixed with 10-mol% YSZ, 1,1,1-trichloroethane, and glycerol trioleate. The ink was then dried at 1400°C for 0.5 h.

The LSM outer layer was prepared from LSM, acetone and KD1 (Zeneca). This was applied over the top of the first layer and again dried in an oven at 1400°C for 0.5 h.

The anode was deposited on to the entire inside length of the tubular cells by drawing anode ink (containing a mixture of pre-calcined YSZ, NiO, glycerol trioleate, 1,1,1-trichloroethane, methanol, and PVB) up through a cell using a syringe. An anode coating of ~ 40 μm was achieved. After the anodes and cathodes were applied, the cells were fired using a ramp rate of 1°C per min to 500°C (no dwell), 5°C per min to 1300°C (dwell 1 h), and then 10°C per min to room temperature.

The cells were placed in a purpose-built furnace and attached to a gas line, which was connected to a dual supply of H_2 and N_2. The current–voltage characteristics ($I–V$) of the cells were then measured using a passive potentiostat in air at 600 to 900°C, and a H_2 flow rate of 10 to 25 cm^3 per min.

3. Results and discussion

3.1. Powder analysis

The particle size of the powder examined in this study is given in Table 1. It is quite apparent that the GCO powder has a relatively small particle size distribution; more than 90% of the volume of the particles is below 10 μm. Although the particle-size analysis seems to indicate that the powders do have some large agglomerates, S.E.M. analysis (Fig. 1) shows a very fine distribution. It is, therefore, apparent that the particle-size analyser cannot differentiate between hard and soft (easily broken down in the milling stage) agglomerates; the latter is present in this powder. The high surface area of the GCO powder (126 m^2 g^{-1}) also implies that the powder easily forms soft agglomerates.

3.2. Slurry formation

The slurries prepared from the as-received powder (GCO) required a large percentage of additive to achieve a workable consistency. The powder volume in the final slurry was below 25 vol.%, which led to a high shrinkage during firing and, therefore, less homogeneity in the final sample. The high shrinkage also limited the size control of the sample. The slurry of the as-received powder, once tape-cast on to an acetate sheet, dried almost immediately
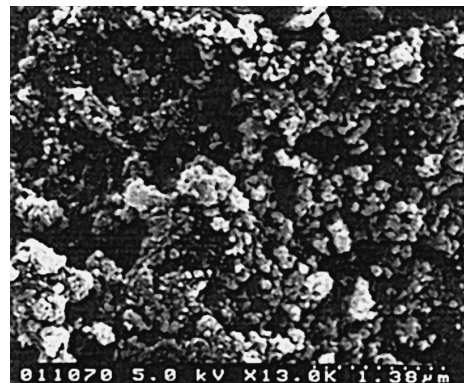

Fig. 1. Scanning electron micrograph of CGO powder used in this study.

to form a plastic, extrudable mass. Timing of the drying process was very critical, however, and thus, the as-received powder was disregarded due to difficulty in controlling the drying time.

Accordingly, slurries were prepared from powders that had been heat-treated at 550 and 1000°C (labeled GCO5.5 and GCO10, respectively). The slurries obtained from the GCO10 powder were much easier to handle. Drying times achieved with this powder were sufficient to be controlled, and the paste maintained a plastic consistency for a longer period of time, compared with the as-received GCO powder. The dough which was produced was sufficiently soft to be extruded at low load pressures, and the solid content (the powder content) reached up to 50 vol.%. The shrinkage during sintering was limited, which also allowed reasonable size control. The major problem with the GCO10 samples, as shown in Table 2 below, was that the powder produced materials with high porosity (low density), and thus low strength. Hence, samples were examined, which had been heat-treated at 550°C (COM5.5). These contained lower solids content (between 30 and 45 vol.%) and most slurries prepared from this powder dried out after 2 to 3 min.

3.3. Extrusion

Depending on the stiffness of the dough, the load pressure required for extruding the rods and tubes varied between 500 N and 12 kN. It was observed that as the extrusion pressure was reduced, it was more likely that the sample would be straight; which was related to the ease of flow through the die. Stiffer doughs will encounter more friction on the walls of the die, although some of the better rods were produced at the higher extrusion pressures. Further work is required to determine the effect of viscosity of the dough in relation to its ease of extrusion. Soya-oil was also used as a lubricant and helped the flow of the dough through the die by limiting this friction.

All the samples were dried for at least a further 24 h in air. In order to keep the rods and tubes straight during the

Table 1
Particle size of the base powder

	10th percentile (μm)	50th percentile (μm)	90th percentile (μm)
GCO	0.45	8.97	39.28

Table 2
Modulus of rupture and percentage theoretical density of samples as a function of sintering time and temperature

Sample	Sintering temperature (°C)	Sintering time (h)	Percentage theoretical density (%)	Modulus of rupture (MPa)
GCO10 (rod)	1600	4	87	172 ± 41
GCO10 (rod)	1600	2	80	110 ± 25
GCO5.5 (rod)	1300	2	90	155 ± 22
GCO5.5 (rod)	1400	10	90	161 ± 24
GCO5.5 (rod)	1500	2	91	179 ± 37
GCO5.5 (rod)	1500	10	90	177 ± 45
GCO5.5 (rod)	1600	10	94	210 ± 65
GCO5.5 (rod)	1400	2	79	182 ± 20
GCO5.5 (rod)	1400	10	89	177 ± 22
GCO5.5 (rod)	1500	2	91	204 ± 18
GCO5.5 (rod)	1500	10	85	185 ± 42
GCO5.5 (rod)	1600	10	94	222 ± 55
GCO5.5 (tube)	1400	10	96	–
GCO5.5 (tube)	1500	2	86	–
GCO5.5 (tube)	1500	10	90	–
GCO5.5 (tube)	1600	10	93	–
GCO5.5 (tube)	1400	10	88	–
GCO5.5 (tube)	1500	10	92	–
GCO5.5 (tube)	1300	2	77	–

drying stage, a small load was applied and this also allowed evaporation of the solvent to occur.

3.4. Sintering

The rods were sintered at temperatures ranging from 1300 to 1600°C, as described above. The effect of heating rate on the samples did not appear to be a factor in the

final properties of the material (up to certain limits), and, thus, the heating and cooling rates were kept constant.

The density of the samples sintered at 1600°C reached 95% of theoretical (see Table 2, which shows the effect of sample preparation on the density and modulus of rupture of the final materials), while the density of the rods fired at lower temperatures (1300 to 1500°C) was much lower (90% in most cases).
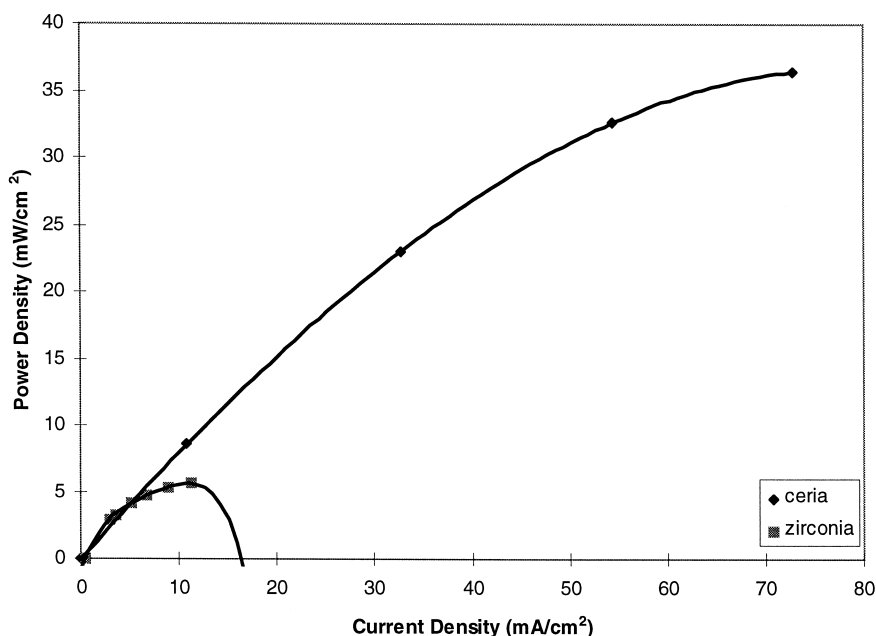

Fig. 2. Power output for extruded doped-ceria (ceria) and extruded doped-zirconia (zirconia) based-single cell SOFCs (600°C and 10 ml per min H_2 fuel throughput).

Table 3
Maximum power density and maximum efficiency of extruded doped-ceria and doped-zirconia SOFC single-cells

	Maximum power density	Cell efficiency
CeO$_2$-based cell	38.3 mW cm^{-2} at 600°C	7.9% at 600°C
	Hydrogen throughput: 10 ml per min	Hydrogen throughput: 2.5 ml per min
ZrO$_2$-based cell	74 mW cm^{-2} at 900°C	30.3% at 900°C
	Hydrogen throughput: 25 ml per min	Hydrogen throughput: 2.5 ml per min

Preliminary results on the fabrication of the tubes are also included in Table 2. Tubes were successfully sintered at 1300°C for 2 h. At high sintering temperatures, however, the mechanical integrity of the ceramic was reduced, and the thin walls (less than 200 μm) collapsed under the load of the top zirconia sheet. Thus, the tubes prepared at temperatures above 1300°C were sintered without the use of the top zirconia sheet. Relative densities of over 90% of theoretical were achieved in most cases. No mechanical measurements were performed on the tubes.

3.5. Mechanical properties

Table 2 also lists the modulus of rupture of the various heat-treated powder samples sintered at different temperatures and for different times. Each value represents the mean for at least 20 samples.

As is observed from Table 2, the values vary quite significantly with the different sintering regimes. All samples with lower than 90% theoretical density can be considered too porous for SOFC applications, as gas leakage can occur. Modulus of rupture values of the samples, which have low theoretical densities reach a maximum of 180 MPa at room temperature (which is likely to drop to below 100 MPa at typical SOFC operating temperatures). Thus, the results appear to indicate that a sintering temperature of at least 1400°C for a dwell time of 10 h is necessary in order to achieve the required density and improved mechanical strength of a material if it is to be used as a SOFC electrolyte (typical running temperatures of the ceria-based electrolyte are expected to be between 600 and 800°C). Ceramics prepared with lower strength are likely to fail under repeated thermal shock and, to a lesser extent, mechanical stresses. Samples sintered at 1600°C for 10 h, for example, attained modulus of rupture values in excess of 220 MPa. Although this result is not two-to-three times that observed for samples fabricated using traditional routes (143 MPa [9]), the value is still considerably higher. Thus, further work is needed to optimize the fabrication route, although this work shows the great potential of this particular fabrication method for producing high-strength, ceramic electrolyte materials.

3.6. Electrochemical measurements

A plot is given in Fig. 2 of the power output as a function of current, at 600°C, for a single SOFC cell with an extruded $(CeO_2)_{0.8}(GdO_{1.5})_{0.2}$ electrolyte material. It is apparent that the power output, for this particular cell, is approximately 38 mW cm^{-2}. For comparison, a zirconia-based cell of the same dimensions was also examined, as described by Hatchwell et al. [5]. The ceria-based cell out-performed the zirconia based cell; the latter reached a powder output of ~ 6 mW cm^{-2} at the same temperature, and under the same conditions. As the temperature was increased to 700°C, the ceria-based cell started to short, due to an increase in the electrical conductivity of CeO$_2$ at this temperature (Ce^{4+} is reduced to Ce^{3+}), and thus became unworkable. It should be noted that the long-term stability of the cell was not examined in this work, but future work will examine this problem.

Table 3 provides a comparison of the maximum power output for ceria-based cells (at 600°C) and zirconia-based cells (at 900°C), under specified conditions. It can be concluded that the ceria-based electrolyte, fabricated using the extrusion technique, does have reasonable potential in a medium-temperature SOFC. Although the power output is quite low, the electrodes used in this system have not been optimized for the lower temperatures, and are the same as those used in traditional SOFCs at usual temperatures.

4. Conclusions

The extruding of doped ceria is shown to be feasible. Beginning with very fine powders, the use of a colloidal suspension technique allows the fabrication of homogeneous slurries, which dry quickly and can be formed easily. A sufficiently high sintering temperature is required in order to produce tubes with good densities. Although a gain in strength of the Gd$_2$O$_3$ doped CeO$_2$ ceramic is desirable to obtain a good reliability, tubular electrolytes for fuel cells can be processed using this technique, similar to the technique used for stabilized zirconia. This research shows that doped-ceria, fabricated using an extrusion technique, is a suitable electrolyte for medium-temperature SOFC applications. A power density of about 36 mW cm^{-2} at 600°C was realized, which, although quite low, may be optimized by the correct selection of electrode materials.

Acknowledgements

References

[1] H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1.

[2] K Zheng, B.C.H. Steele, M Sahibzada, I.S. Metcalfe, Solid State Ionics, 86–88, 1996, p. 1241.

[3] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563.

[4] K. Kendall, M. Prica, in: U. Bossel (Ed.), First European Solid Oxide Fuel Cell Forum, Lucerne, Switzerland, 3–7 October, 1994, p. 163.

[5] C. Hatchwell, N.M. Sammes, K. Kendall, J. Power Sources, Vol. 70/1.

[6] G.M. Christie, F.P.F. Van Berkel, Solid State Ionics 83 (1996) 17.

[7] N.M. Sammes, Z. Cai, G.A. Tompsett, in: U. Stimming, S.C. Singhal, H. Tagawa, W. Lehnert (Eds.), Solid Oxide Fuel Cells, Vol. V, The Electrochem. Soc., Pennington, NJ, 1997, p. 1105.

[8] H. Yahiro, Y. Baba, K. Eguchi, H. Arai, J. Electrochem. Soc. 135 (1988) 2077.

[9] N.M. Sammes, Y. Zhang, G. Tompsett, A. Cartner, R. Torrens, Denki Kagaku 64 (1996) 674.

[10] I.P. Kilbride, J. Power Sources 61 (1996) 167.