

Short communication

## Performance characteristics of Gd-doped barium cerate-based fuel cells

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### Abstract

Results of tests on single element fuel cells incorporating a proton conducting Gd-doped barium cerate solid electrolyte at 700 °C with different anode/cathode combinations are reported. The  $J$ – $V$  and power density characteristics of these cells show that the performance of the fuel cells is strongly dependent on the particular anode/cathode system chosen.  $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$  cathodes gave the best performance regardless of the anode system used. However, the low open circuit voltage of the fuel cells indicated that the electrode/electrolyte interface needs further optimization.

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**Keywords:** Proton conductor; Doped barium cerate; Fuel cell performance; LCFC and LSC cathodes

### 1. Introduction

Fuel cells, in particular polymer electrolyte membrane (PEM) and solid oxide fuel cells (SOFC), are nearing commercialization and as such are receiving significant attention as viable alternatives in transportation and stationary power generation. Fuel cells convert chemical energy directly into electrical energy and their thermodynamic efficiencies are not limited by the Carnot cycle [1–3].  $\text{ZrO}_2$ -based SOFCs have received attention in the past because of the high oxygen ion conductivity of the zirconia electrolyte system. But the high operating temperatures (>1000 °C) required for the zirconia reduce the reliability and operating life of these cells through materials problems. Ceria-based electrolytes are alternatives to  $\text{ZrO}_2$  because of their high oxygen conductivity at 700 °C [4]. These ceria-based electrolytes, however, show considerable electronic conductivity, which is detrimental to long-term fuel cell performance. In addition, these systems are unstable under the hydrogen environment of the anode [5,6]. Oxygen ion conductors, based on a modification of the perovskite, lanthanum gallate, have also been shown to be

potential candidate electrolytes for lower temperature SOFC [7,8].

$\text{SrCeO}_3$ -based oxides were the first class of perovskite materials shown to exhibit proton conductivity at high temperatures in a hydrogen-containing atmosphere [9]. Subsequently,  $\text{BaCeO}_3$ ,  $\text{SrZrO}_3$  and  $\text{BaZrO}_3$  mixed oxides have also been shown to exhibit high protonic conductivity at lower temperatures than pure  $\text{O}^{2-}$  conducting electrolytes, such as lanthanum gallate, making them good candidates for intermediate temperature fuel cell applications [10]. Another advantage of fuel cells utilizing a protonic conducting electrolyte is that they form water at the cathode, unlike SOFCs, hence the fuel at the anode remains pure thus eliminating the need for re-circulation.

A planar anode- or cathode-supported fuel cell is an attractive geometry for integration into a stack configuration. However, this fuel cell architecture requires the use of relatively inexpensive materials for the anode and cathode electrodes to be commercially viable. In this paper, the operation of a fuel cell based on the proton conducting Gd-doped  $\text{BaCeO}_3$  solid electrolyte is reported. The performance of the phase-pure material in a planar type fuel cell configuration with different anode/cathode systems is presented.

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## 2. Experimental

Doped barium cerate ( $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ , BCG) was prepared by conventional solid-state synthesis techniques. Appropriate stoichiometric ratios of oxide powders ( $\text{BaCO}_3$ ,  $\text{CeO}_2$  and  $\text{Gd}_2\text{O}_3$ ) were ground, mixed and then ball milled in isopropyl alcohol for 24 h. Solvents were evaporated and the dried powders were calcined at  $1350^\circ\text{C}$  in air for 10 h. Phase content of the calcined powders and sintered elements was investigated with a Rigaku MINIFLEX XRD system using  $\text{Cu K}\alpha$  radiation. The calcined powder was mixed with a 15% polyvinyl alcohol solution and uniaxially pressed at 65 MPa into approximately 3.175 cm diameter and 2 mm thick pellets. The samples were subsequently isostatically pressed at 216 MPa. The discs were then sintered at various temperatures, ranging from 1500 to  $1650^\circ\text{C}$ , for 10 h and polished to approximately 1 mm thickness.

Planar single cells in two configurations were fabricated for fuel cell evaluation. One structure utilized Engelhard platinum ink A-4338 for the anode and three individual cathode systems: platinum,  $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$  (LCFC) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$  (LSC). The Pt electrodes were air dried and then fired at  $1000^\circ\text{C}$  for 1 h in air, with heating and cooling rates of  $5^\circ\text{C}/\text{min}$ . The LCFC perovskite cathode was prepared as previously described [11,12]. The calcined LCFC powder was ground and mixed with a polyvinyl butyral binder, ethanol, and a polyethylene glycol plasticizer, as described in [11]. The slurry was brushed onto the BCG substrate and sintered at  $1150^\circ\text{C}$  for 2 h with heating and cooling rates of  $5^\circ\text{C}/\text{min}$ . The LSC powder was synthesized through a nitrate route as previously described [13]. LSC calcined powder was ground and mixed with a 15% PVA solution and slurry-coated onto the BCG electrolyte. The

coated disc was fired at  $1150^\circ\text{C}$  for 2 h, with a heating and cooling rate of  $5^\circ\text{C}/\text{min}$ .

The other configuration utilized a NiO–BCG cermet anode and the following cathode systems: Pt, LCFC and LSC. The NiO–BCG cermet powders were prepared by conventional solid-state synthesis techniques. To ensure that the anode cermet was sufficiently conductive, the composition was chosen so that the volume percent of Ni in the anode cermet was 60%. Appropriate stoichiometric ratios of oxide powders (NiO and BCG) were ground, mixed and then ball milled in isopropyl alcohol for 24 h. Solvents were evaporated and the dried powders were calcined at  $1400^\circ\text{C}$  in air for 5 h. The calcined NiO–BCG cermet powder was ground and mixed with a 15% PVA solution and slurry-coated onto the BCG electrolyte. The coated disc was fired at  $1400^\circ\text{C}$  for 2 h, with a heating and cooling rate of  $5^\circ\text{C}/\text{min}$ .

During fuel cell operation, a 4%  $\text{H}_2$  in Ar gas mixture at a flow of  $500\text{ cm}^3/\text{min}$  was supplied at the anode while a flow of compressed air at  $100\text{ cm}^3/\text{min}$  was maintained at the cathode. The gas flow to the NiO–BCG cermet anode was introduced at  $300^\circ\text{C}$  to ensure that the NiO got reduced to Ni metal by the time the cell operating temperature of  $700^\circ\text{C}$  was reached. Platinum mesh was placed on top of the anode and cathode to act as current collectors.

## 3. Results and discussion

Fig. 1 shows XRD patterns for BCG samples as a function of processing temperature. Curve (a) shows the XRD pattern for BCG precursor powder calcined at  $1350^\circ\text{C}$  for 10 h. The XRD trace indicates that BCG is formed at  $1350^\circ\text{C}$ , although the presence of a minor amount of secondary phase is

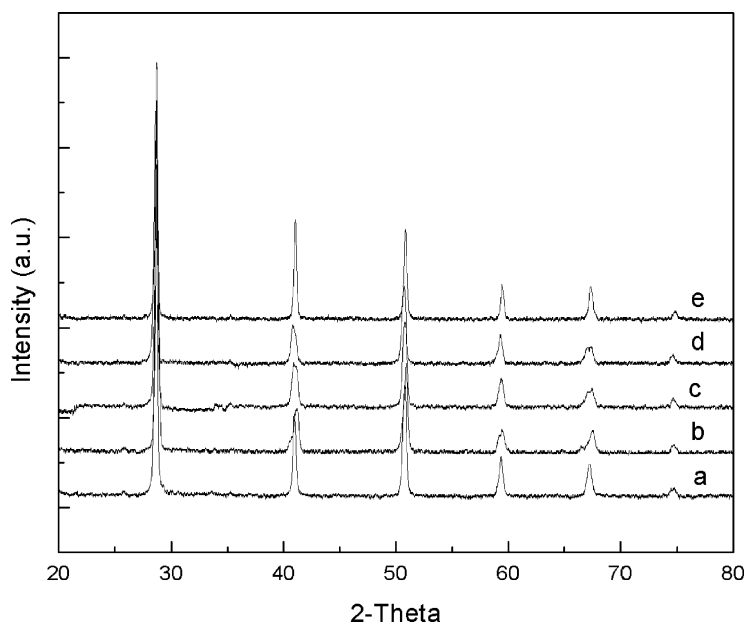


Fig. 1. XRD patterns for BCG processed at various temperatures: (a) calcined at  $1350^\circ\text{C}$ ; (b) sintered at  $1500^\circ\text{C}$ ; (c) sintered at  $1550^\circ\text{C}$ ; (d) sintered at  $1600^\circ\text{C}$  and (e) sintered at  $1650^\circ\text{C}$ . The soak time at temperature was 10 h.

also present. Discs sintered at higher temperatures 1500 °C (b), 1550 °C (c), 1600 °C (d) and 1650 °C (e) were crushed in a mortar and pestle and XRD was taken on the crushed powders. The XRD data shows that the patterns are essentially all the same irrespective of sintering temperature. The sharpness of the peaks does however increase with sintering temperature. This increase in peak sharpness is associated with increase in particle size of the grains within the powders. The XRD patterns indicate that the samples sintered at 1600 and 1650 °C did not have any secondary phases, detectable by XRD, while samples sintered at lower temper-

atures had minor amounts of secondary phases. The BCG XRD patterns obtained in this study are similar to those previously reported. However, samples in that study had to be sintered at 1650 °C in order to obtain phase pure materials [14]. The density of all samples sintered from 1500 to 1650 °C was in excess of 90% of the theoretical value.

The  $J$ - $V$  characteristics of planar fuel cells incorporating a single BCG monolithic solid electrolyte element, approximately 1 mm thick, with porous platinum anodes are shown in Fig. 2a. The acronym P1 indicates a cell with a Pt anode and a Pt cathode, P2 a cell with a Pt anode and a LSC

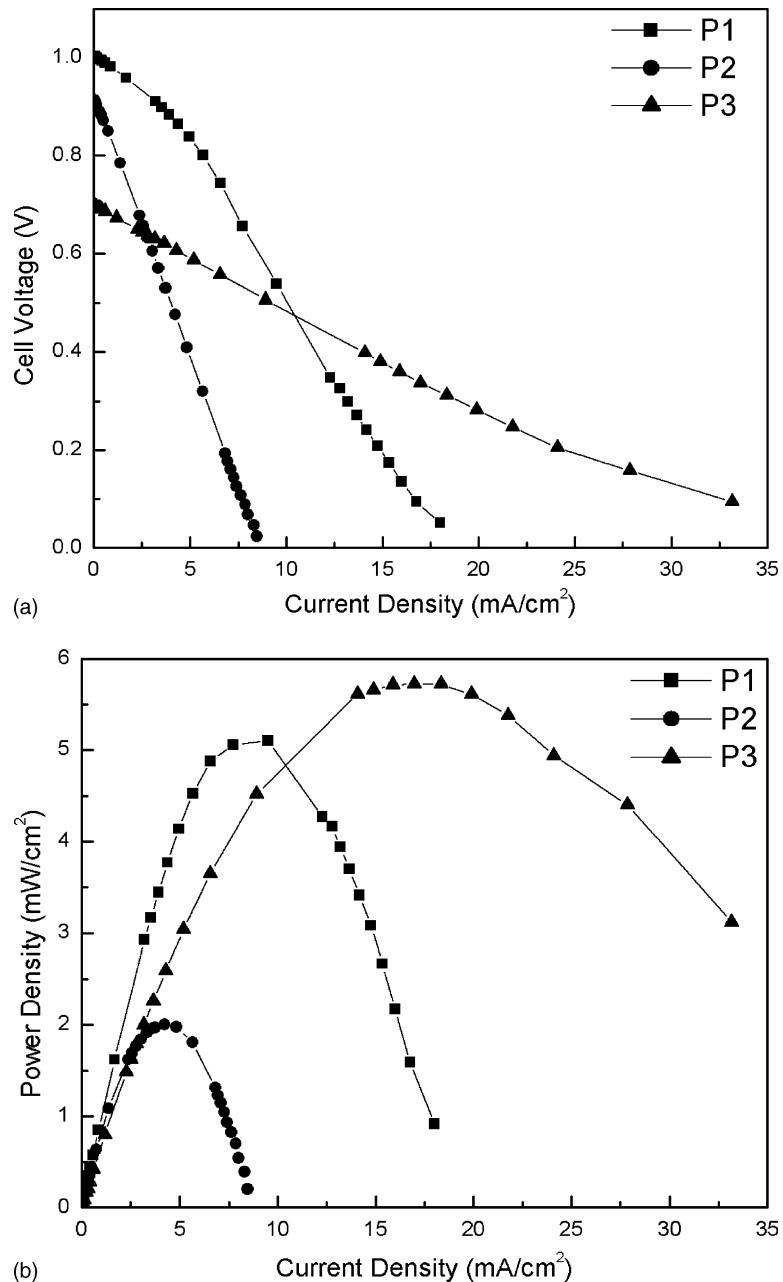


Fig. 2. (a)  $J$ - $V$  data for planar fuel cells incorporating a single BCG monolithic solid electrolyte element, approximately 1 mm thick, with porous platinum anodes. The acronym P1 indicates a cell with a Pt/BCG/Pt electrode structure, P2 a cell with Pt/BCG/LSC electrodes and P3 a cell with Pt/BCG/LCFC electrodes. (b) Power density data for the single planar fuel cells shown in (a).

cathode and P3 a cell with a Pt anode and a LCFC cathode. The cells were operated continuously for 24 h. The non-linear  $J$ - $V$  data for cell P1 indicates the presence of significant polarization at the electrode/electrolyte interface. The oxidizing conditions present at the cathode tend to affect the platinum electrode detrimentally, after long periods of fuel cell operation in this system. In addition, the high cost of platinum is a disadvantage for its use in commercial fuel cells.

LSC has high electronic conductivity and oxygen activity [15] and is considered a promising cathode material for

fuel cells not utilizing a zirconia electrolyte. The linear  $J$ - $V$  behaviour for cell P2 suggests little, if any, polarization of the electrodes. The open circuit voltage (OCV), however, is less than the theoretically expected value. The initial OCV for this cell was approximately 1 V but the data clearly indicates a decrease in OCV after approximately 24 h. The reasons for the decrease in OCV are not known. The appearance of the cathode after the testing period did not indicate any deterioration.

LCFC is an inexpensive alternative for the cathode and like LSC, possesses a perovskite structure. This material

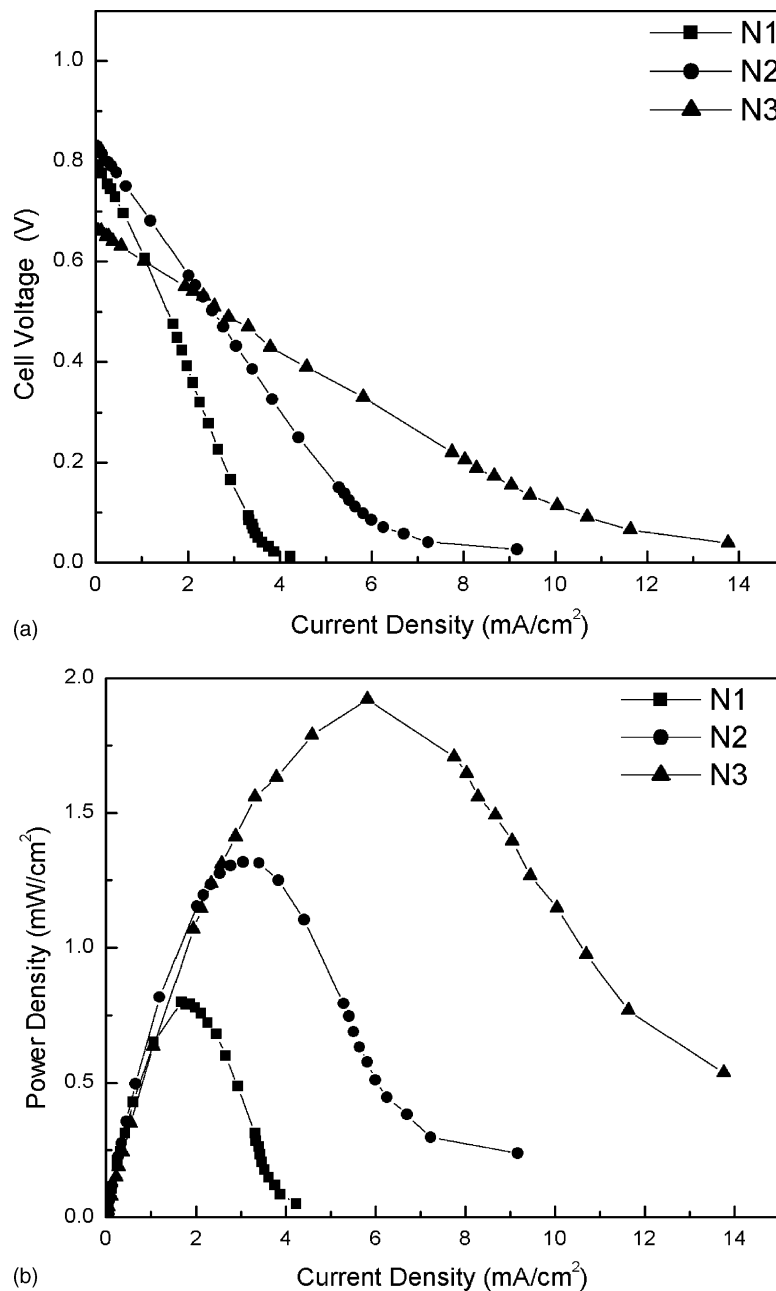


Fig. 3. (a)  $J$ - $V$  data for planar fuel cells incorporating a single BCG monolithic solid electrolyte element, approximately 1 mm thick, with NiO-BCG cermet anodes. The acronym N1 indicates a cell with a NiO-BCG/BCG/Pt electrode structure, N2 a cell with NiO-BCG/BCG/LSC electrodes and N3 a cell with NiO-BCG/BCG/LCFC electrodes. (b) Power density data for the single planar fuel cells shown in (a).

has been shown to have good surface exchange coefficients and exchange current densities [16]. The  $J$ - $V$  characteristics for a cell utilizing a LCFC cathode, P3, are also shown in Fig. 2a. The linear  $J$ - $V$  behaviour suggests little, if any, polarization of the electrodes. The data does, however, indicate some non-linear behaviour at higher current densities. The OCV for P3 is even lower than those observed for cells P1 and P2, again the initial OCV for this cell was approximately 1 V. Nevertheless, this cell's performance was superior to cells P1 and P2, at least in terms of the current densities obtained in the cells. The data suggest that the LCFC electrode is a viable cathode material for fuel cells incorporating BCG solid electrolyte elements. BCG has been shown to become a mixed ionic conductor under fuel cell conditions [17], this could in part be responsible for the decrease in OCV observed for cells P2 and P3. Although, if this were the case it is unclear why cell P1 did not show similar behaviour. The performance characteristics of these cells, however, indicate a degradation of the electrode/electrolyte interfacial region, which is dependent on both time and electrode material.

The power density data for these cells are shown in Fig. 2b. The results clearly show that the performance of cell P3 is superior to the other cells. The relatively low values for current and power densities are a consequence of the relatively thick BCG solid electrolyte elements, approximately 1 mm. The performance of cell P2 is inferior to the other cells but still has reasonable power output. The data suggest that a cathode supported fuel cell using either LCFC or LSC can be fabricated.

The  $J$ - $V$  characteristics of planar fuel cells incorporating a single BCG monolithic solid electrolyte element, approximately 1 mm thick, with NiO-BCG cermet anodes are shown in Fig. 3a. The acronym N1 indicates a cell with a NiO-BCG anode and a Pt cathode, N2 a cell with a NiO-BCG anode and a LSC cathode and N3 a cell with a NiO-BCG anode and a LCFC cathode. The cells were operated continuously for 24 h. The linear behaviour of the  $J$ - $V$  data suggests very little polarization of the fuel cell structure, at least for low current densities. The  $J$ - $V$  behaviour for all the cells indicates some polarization effects at high current flows. The OCV for all three cells is significantly less than the expected theoretical value. The initial OCV for these cells is approximately 0.95 V but the data clearly indicates a decrease in OCV after approximately 24 h. The decrease in OCV may be due, in part, to the reported BCG mixed conduction under fuel cell conditions [17]. However, a previous study using a thin BCG layer on a NiO-BCG anode found that diffusion of Ni into the BCG electrolyte resulted in a decrease in OCV [18]. The fact that the OCV of the fuel cells studied seems to be dependent on both anode and cathode materials suggests that the lower OCV is a consequence of the electrode/electrolyte interfacial characteristics. Although, diffusion of Ni or the mixed conduction of BCG under fuel cell conditions may also contribute, in part, to the observed lower OCV values. Clearly,

further optimization of the electrode/electrolyte interface is required.

The power density data for these cells is given in Fig. 3b. The data suggest that LCFC is the most appropriate cathode material to be used with a NiO-BCG cermet anode. The data also suggest that the performance of cells incorporating a Ni-based anode is inferior to that of cells with a Pt-based anode. However, no attempt was made in this study to optimize the NiO-BCG anode morphology or the anode/electrolyte interface. The data do suggest, however, that cheaper alternative materials show good fuel cell performance characteristics. Future work will investigate the performance characteristics of anode- and cathode-supported fuel cells incorporating the electrode materials studied in this work.

#### 4. Summary

The fuel cell performance of two different anode systems using single element proton conducting BCG solid electrolyte with different cathode combinations at 700 °C is reported. The  $J$ - $V$  and power density data indicate that the LCFC cathode material showed the best performance characteristics of the systems studied. Fuel cells incorporating a Pt anode perform better than fuel cells with a NiO-BCG anode, although the affects of morphology and other characteristics needs further investigation to optimize the NiO-BCG anode. The data suggest that both the cathode- and anode/electrolyte interface needs further optimization. The data also indicate that anode- and/or cathode-supported planar fuel cells are feasible with the electrode systems presently studied. This cell architecture would allow the thickness of the BCG electrolyte to be decreased thereby improving the performance characteristics, as well as lowering the cost of the fuel cell.

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