

Short communication

An intermediate temperature direct ammonia fuel cell using a proton conducting electrolyte

N. Maffei^{a,*}, L. Pelletier^b, J.P. Charland^b, A. McFarlan^b

^a *Materials Technology Laboratory, CANMET, Natural Resources Canada, 405 Rochester St., Ottawa, Ont., Canada K1A 0G1*

^b *CANMET Energy Technology Centre, Natural Resources Canada, 1 Haanel Drive, Bells Corners Complex, Ottawa, Ont., Canada K1A 1M1*

Received 16 July 2004; accepted 6 August 2004

Available online 2 October 2004

Abstract

The operation of fuel cells based on proton conducting BaCeO₃ solid electrolyte doubly doped with gadolinium and praseodymium is reported. Fuel cells were operated for up to 96 h with both hydrogen and ammonia individually as fuel. Results show that the performance of the cell is the same irrespective of the fuel used. The only chemical by-products of the ammonia fuel cell are nitrogen and water. The data shows that a fuel cell incorporating a doubly doped proton conducting electrolyte operated on ammonia fuel is a viable alternative to fuel cells utilizing hydrocarbon fuels as sources of hydrogen.

Crown Copyright © 2004 Published by Elsevier B.V. All rights reserved.

Keywords: Ammonia; Proton conductor; Doubly doped barium cerate; Fuel cells

1. Introduction

Increasing greenhouse gas (GHG) emissions worldwide have resulted in a renewed interest in alternative technologies such as fuel cells. Fuel cells are very promising in the transportation and stationary power generation sectors [1–3]. Hydrogen is the preferred fuel for fuel cells because its use ensures zero GHG emissions. However, making the transition to a hydrogen economy poses numerous challenges. In the short to mid term, reforming of hydrocarbons to produce hydrogen will continue in order to meet demand. Also, issues concerning options for hydrogen production, transportation and storage infrastructure are still being resolved [4].

Ammonia, although well known as a feedstock for producing hydrogen, has received relatively little consideration for its use as a direct fuel for fuel cells. It has high hydrogen content, can be stored easily, is widely available and is carbon-free, thereby contributing to reduction of GHG emis-

sions [5,6]. Recently, reports of ammonia as a fuel in intermediate temperature fuel cells have appeared [7,8]. These preliminary reports suggest that ammonia may indeed be a viable fuel, particularly for stationary fuel cell applications.

SrCeO₃-based oxides were the first class of perovskite materials shown to exhibit proton conductivity at high temperatures in a hydrogen-containing atmosphere [9]. Subsequently, BaCeO₃, SrZrO₃ and BaZrO₃ mixed oxides have also shown high protonic conductivity at temperatures lower than those for pure O²⁻ conducting electrolytes, such as lanthanum gallate. This makes 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 recirculation.

In this paper the operation of a fuel cell based on the proton conducting BaCeO₃ solid electrolyte doubly doped with gadolinium and praseodymium is reported. To the best of our knowledge this is the first time that a BaCeO₃ proton conductor has been doubly doped with gadolinium and

* Corresponding author. Tel.: +1 613 992 1391; fax: +1 613 992 9389.
E-mail address: nmaffei@nrcan.gc.ca (N. Maffei).

praseodymium on the B-site of the ABO_3 perovskite structure, although reports of $BaCeO_3$ doubly doped with zirconium and yttrium [10] and zirconium and indium [11] have appeared. The performance characteristics of fuel cells using this electrolyte and utilizing both hydrogen and ammonia (separately) as fuel are presented.

2. Experimental

Barium cerate doped with gadolinium and praseodymium ($BaCe_{0.8}Gd_{0.19}Pr_{0.01}O_{3-\delta}$, BCGP) was prepared by conventional solid-state synthesis techniques. Appropriate stoichiometric ratios of high purity oxide powders ($BaCO_3$, CeO_2 , Gd_2O_3 and Pr_6O_{11}) were ground, mixed and then ball-milled in isopropyl alcohol for 24 h. The dried powders were subsequently calcined at 1350°C in air for 10 h. The calcined powder was mixed with a 15% polyvinyl alcohol solution and uniaxially pressed at 65 MPa into approximately 3 cm diameter and 2 mm thick pellets. The samples were subsequently isostatically pressed at 275 MPa. The discs were then sintered at 1600°C for 10 h and ground and polished to approximately 1.3 mm thickness.

X-ray diffraction (XRD) patterns of the calcined and sintered samples were collected on a Siemens D500TT automated diffractometer over the angular range $6\text{--}86^\circ 2\theta$ in 2θ steps of 0.02° . The XRD system was operated in the $\theta:\theta$ geometry, employed Cu $K\alpha$ radiation ($\lambda = 1.5405981 \text{ \AA}$), and was equipped with a diffracted-beam graphite monochromator, a scintillation detector and solid-state counting electronics. The generator voltage and current settings were 45 kV and 40 mA, respectively. The slit arrangement for data collection consisted of three 1° beam apertures, one 0.05° detector aperture and one 0.15° diffracted-beam aperture. The JADE[®] version 6.5 XRD pattern processing software was used for determination of the cell parameters. This was done using the total pattern fitting method where the line profile of each Bragg reflection was described through a convolution procedure that yielded accurate peak positions for least squares cell parameter refinement.

Thermogravimetric (TG) studies to determine the stability of the doubly doped barium cerate solid electrolyte in a hydrogen atmosphere were conducted in a Perkin-Elmer TGA7HT analyzer. Calcined powder samples weighing 50 mg were used for these experiments. Runs were made with samples in platinum pans at a heating rate of $30^\circ\text{C min}^{-1}$ to 1000°C with a $40 \text{ cm}^3 \text{ min}^{-1}$ gas flow.

Planar single element fuel cells were fabricated utilizing Engelhard platinum ink A-4338 for the anode and cathode. The Pt electrodes were air dried and then fired at 1000°C for 1 h in air, with heating and cooling rates of 5°C min^{-1} . During fuel cell operation using hydrogen, 100% hydrogen and air, both at a flow rate of $40 \text{ cm}^3 \text{ min}^{-1}$ were supplied at the anode and cathode, respectively. When ammonia was used as fuel the flow to the anode was maintained at $30 \text{ cm}^3 \text{ min}^{-1}$ with air at a flow of $50 \text{ cm}^3 \text{ min}^{-1}$, at the cathode.

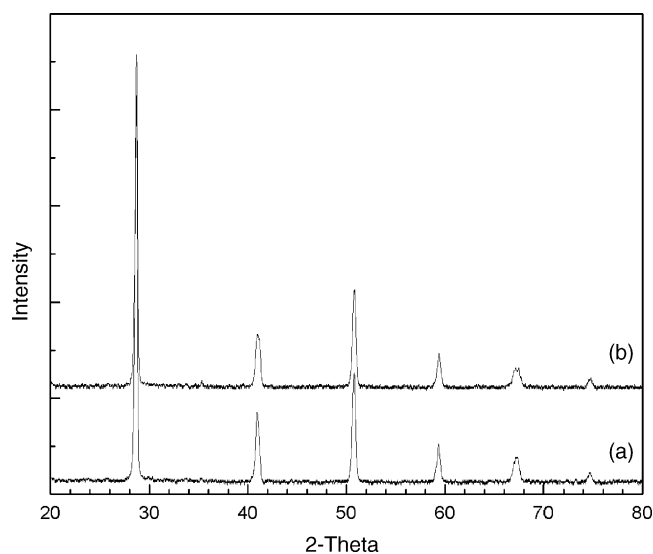


Fig. 1. XRD patterns for doubly doped barium cerate: (a) calcined at 1350°C and (b) sintered at 1600°C . The soak time at temperature was 10 h.

3. Results and discussion

Fig. 1 shows XRD patterns for BCGP samples as a function of processing temperature. Curve (a) shows the XRD pattern for BCGP precursor powder calcined at 1350°C for 10 h. Curve (b) shows the XRD pattern taken on a disc sample sintered at 1600°C , crushed in a mortar and pestle. The two patterns are essentially the same; the flat background scattering and sharp peak profiles indicate good crystallinity. The refined unit cell parameters determined from the XRD data were 0.87663, 0.62555, 0.62213 nm; the space group was orthorhombic $Pm\bar{c}n$.

The results of TG studies done in nitrogen and a 4% H_2 - N_2 gas mixture are shown in Fig. 2. The data shows that BCGP is very stable in both inert and reducing environments; no

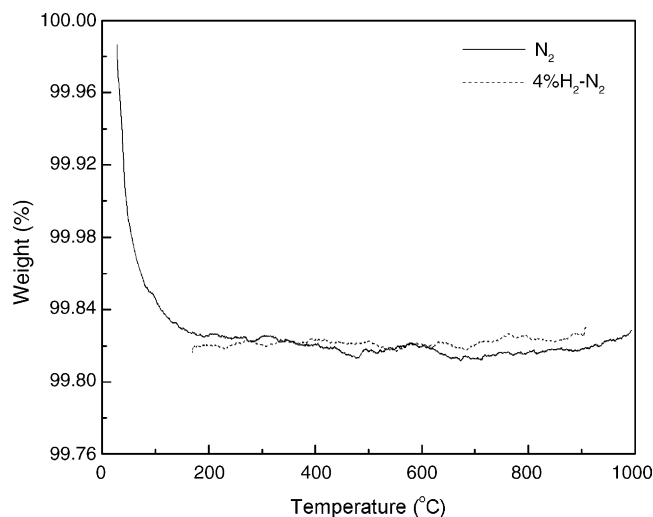


Fig. 2. TG data for Gd-Pr doped barium cerate in N_2 and 4% H_2 - N_2 gas mixture to 1000°C , at a heating rate of $30^\circ\text{C min}^{-1}$.

significant weight change is observed, the total weight loss percentage is less than 0.2%.

A planar fuel cell incorporating a single BCGP monolithic solid electrolyte element with porous platinum electrodes operated continuously, with the fuel alternating between hydrogen and ammonia, for 96 h did not show any deterioration in performance. First, the cell was run with hydrogen as fuel for 48 h, then hydrogen was stopped and ammonia was introduced to the anode. The fuel cell was then operated continuously for another 24 h under ammonia flow. The ammonia flow to the anode was then stopped and 100% hydrogen was reintroduced and the fuel cell was operated for an additional 24 h. The measured J - V data of the fuel cell are shown in Fig. 3a. The linear J - V data indicate little if any polarization at the electrodes. These data also indicate that the potential drop of the device was mostly due to the IR drop across the electrolyte. The open circuit voltage (OCV), however, is less than the theoretically expected value. The power density data for this cell are shown in Fig. 3b. The results clearly show that the performance of the cell is stable over the entire duration of operation. The relatively low values for current and power densities are a consequence of the relatively thick BCGP solid electrolyte elements, approximately 1.3 mm.

The J - V and power density data collected after operation in ammonia for 24 h, Fig. 3a and b, respectively, show that

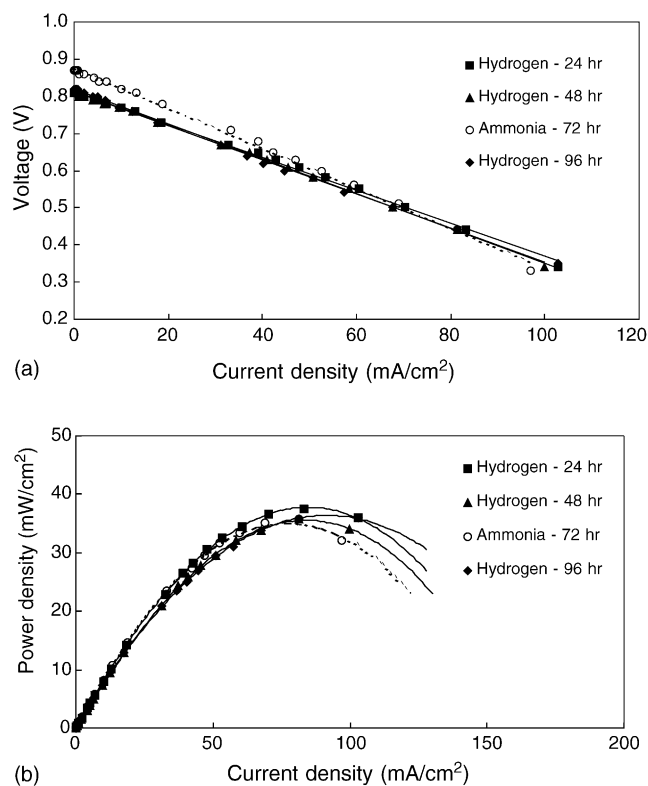


Fig. 3. (a) J - V data for a planar fuel cell incorporating a single Gd-Pr doped barium cerate monolithic solid electrolyte element, approximately 1.3 mm thick, porous platinum electrodes in hydrogen and ammonia. The operating temperature was 700 °C. (b) Power density data for the single planar fuel cell shown in (a).

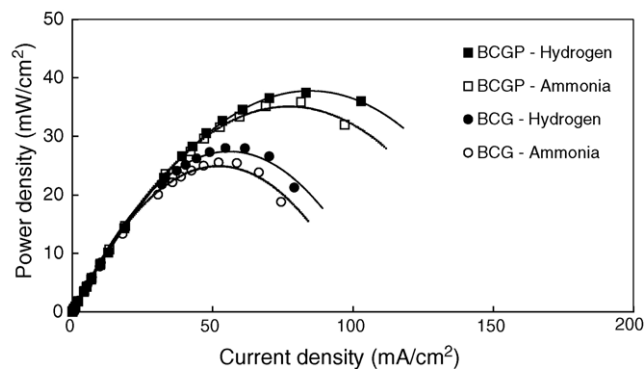


Fig. 4. Power density data for BCG and BCGP planar fuel cells in hydrogen and ammonia. The operating temperature was 700 °C.

the performance of the fuel cell in ammonia is stable over the duration of operation and comparable to operation under 100% hydrogen. The J - V and power density data taken 24 h after the reintroduction of hydrogen clearly show that the performance of the fuel cell is similar to that prior to the operation under ammonia.

The power density data for planar single element fuel cells incorporating barium cerate doped with gadolinium (BCG) [7] and BCGP solid electrolytes, approximately 1.3 mm thick, are shown in Fig. 4 for comparison. The performance characteristics of BCGP fuel cells, using either hydrogen or ammonia as fuel, are significantly better than fuel cells incorporating a monolithic BCG solid electrolyte element [7].

The power density data, close to the peak power point, as a function of operating time is shown in Fig. 5. The figure presents data for operation under both hydrogen and ammonia. The performance of the fuel cell is stable for the relatively long periods of time the cell was run, irrespective of the fuel. The data also show that no detectable deterioration in performance occurs as a result of operation in ammonia and that the fuel to the anode can be cycled between hydrogen and ammonia without any decrease in power. Similar data have been reported for fuel cells using an oxygen ion conducting electrolyte and ammonia as fuel [8]. The significant difference is that the use of a proton conducting solid electrolyte precludes the formation of any NO_x species

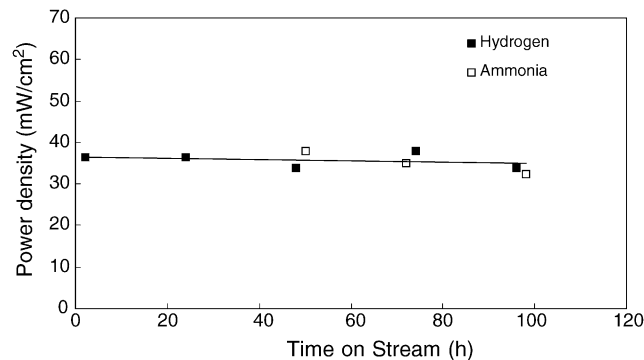


Fig. 5. Power density data in hydrogen and ammonia as a function of operating time. The operating temperature was 700 °C.

at the anode. Gas chromatographic analysis indicated that the only chemical by-products of the fuel cell using ammonia as fuel were nitrogen at the anode and water at the cathode.

4. Summary

The performance of single element fuel cells using a proton conducting BCG solid electrolyte doubly doped with gadolinium and praseodymium at 700 °C is reported. The *J–V* and power density data indicate that cells using this electrolyte are stable for up to 96 h, using either 100% hydrogen or ammonia as fuel. The use of ammonia does not affect the performance of the fuel cell, thus showing its viability as a source of hydrogen in the application. A direct ammonia fuel cell using a proton-conducting electrolyte thus should offer cost and environmental benefits over fuel cells using hydrocarbons as hydrogen source. Nitrogen and water are the only chemical by-products in the ammonia fuel cell, which makes it environmentally benign. Future work will be directed at fabricating anode-supported fuel cell elements utilizing cermet anodes to improve performance characteristics, as well as lowering the cost of the fuel cell.

Acknowledgment

The authors wish to acknowledge funding for this project from the Office of Energy Research and Development (OERD) at Natural Resources Canada.

References

- [1] Q. Minh, *J. Am. Ceram. Soc.* 76 (1993) 563.
- [2] K. Kinoshita, E.J. Cairns, *Encyclopedia Chem. Technol.* 11 (1994) 1098.
- [3] K. Ushiba, *Chem. Tech.* (1984) 300.
- [4] D. Simbeck, E. Chang, US Department of Energy, NREL/SR-540-32525, 2002.
- [5] S.E. Gay, M. Eshani, *Fuel Cells: Technology, Alternative Fuels and Fuel Processing*, SAE International, Warrendale, PA, 2003.
- [6] J. Rothstein, *Int. J. Hydrogen Energ.* 20 (1995) 283.
- [7] A. McFarlan, L. Pelletier, N. Maffei, *J. Electrochem. Soc.* 151 (2004) A930–A932.
- [8] A. Wojcik, H. Middleton, I. Damopoulos, J. Van herle, *J. Power Sources* 118 (2003) 342.
- [9] H. Iwahara, T. Esaka, H. Uchida, N. Maeda, *Solid State Ionics* 3/4 (1981) 359.
- [10] K. Katahira, Y. Kohchi, T. Shimura, H. Iwahara, *Solid State Ionics* 138 (2000) 91.
- [11] T. Shimada, C. Wen, N. Taniguchi, J. Otomo, H. Takahashi, *J. Power Sources* 131 (2004) 289.