

Short communication

# An ammonia fuel cell using a mixed ionic and electronic conducting electrolyte

N. Maffei<sup>a,\*</sup>, L. Pelletier<sup>b</sup>, J.P. Charland<sup>b</sup>, A. McFarlan<sup>b</sup>

<sup>a</sup> *Materials Technology Laboratory, CANMET, Natural Resources Canada, 3484 Limebank Road, Ottawa, Ontario, Canada K1A 0E4*

<sup>b</sup> *Natural Resources Canada, CANMET Energy Technology Centre, 1 Haanel Drive, Bells Corners Complex, Ottawa, Ontario, Canada K1A 1M1*

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## Abstract

The performance characteristics of fuel cells based on proton conducting BaCeO<sub>3</sub> solid electrolyte doped with europium is reported. Fuel cells were operated for up to 200 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 open circuit voltage of the cells was lower than the theoretically expected value due to the presence of significant electronic conduction. Nevertheless, the data show that a fuel cell incorporating a europium doped barium cerate electrolyte operated on ammonia fuel is a viable alternative to fuel cells utilizing hydrocarbon fuels as sources of hydrogen.

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## 1. Introduction

Concerns about climate change and ever increasing greenhouse gas emissions (GHG) have renewed interest in alternative energy production technologies such as fuel cells. Fuel cells convert chemical energy directly into electrical energy and their thermodynamic efficiencies are not limited by the Carnot cycle. Worldwide, intensive research and development efforts are underway to evaluate their use in the transportation and stationary power generation sectors [1–3]. Ideally, hydrogen is the preferred fuel for fuel cells because its use ensures zero GHG emissions. However, the transition to a hydrogen economy cannot occur until numerous technical challenges such as hydrogen production, transportation and storage infrastructure are resolved [4].

Ammonia has high hydrogen content, can be stored easily, is widely available and is carbon-free, thereby contributing to reduction of GHG emissions [5,6]. Recently, reports of ammonia as a fuel in intermediate temperature fuel cells have appeared [7,8]. These reports clearly show that ammonia is a viable fuel, particularly for stationary fuel cell applications.

SrCeO<sub>3</sub>-based oxides were the first class of perovskite materials shown to exhibit proton conductivity at high temperatures in a hydrogen-containing atmosphere [9]. Subsequently, BaCeO<sub>3</sub>, SrZrO<sub>3</sub> and BaZrO<sub>3</sub> mixed oxides have also shown high protonic conductivity at temperatures lower than those for pure O<sup>2-</sup> 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 a mixed protonic and electronic conducting europium doped barium cerate (BaCe<sub>0.85</sub>Eu<sub>0.15</sub>O<sub>3</sub>, BCE) solid electrolyte is reported. The objective of this research was to investigate whether BCE based fuel cells might provide superior performance to those based on gadolinium doped barium cerate (BCG). BCE was previously studied for potential application as a hydrogen pump [11]. The hydrogen permeation data showed that BCE was capable of pumping significantly more hydrogen than BCG. The performance characteristics of electrolyte supported monolithic fuel cells using BCE electrolyte and utilizing both hydrogen and ammonia (separately) as fuel are presented.

\* Corresponding author. Tel.: +1 613 946 9806; fax: +1 613 946 4341.  
E-mail address: [nmaffei@NRCCan.gc.ca](mailto:nmaffei@NRCCan.gc.ca) (N. Maffei).

## 2. Experimental

BCE powders were prepared by conventional solid-state synthesis techniques. Appropriate stoichiometric ratios of high purity oxide powders ( $\text{BaCO}_3$ ,  $\text{CeO}_2$  and  $\text{Eu}_2\text{O}_3$ ) were ball milled in isopropyl alcohol for 24 h. The dried powders were subsequently calcined at  $1350^\circ\text{C}$  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  $1550^\circ\text{C}$  in air for 10 h and ground and polished to approximately 1 mm thickness.

X-ray diffraction (XRD) patterns of the sintered samples were collected on a Siemens D500TT automated diffractometer over the angular range  $5\text{--}95^\circ 2\theta$  in steps of  $0.02^\circ$ . The XRD system was operated in the  $\theta:\theta$  geometry, employed  $\text{Cu } K_\alpha$  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  $1^\circ$  beam apertures, one  $0.05^\circ$  detector aperture and one  $0.15^\circ$  diffracted-beam aperture. The JADE<sup>®</sup> 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.

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  $1000^\circ\text{C}$  for 1 h in air, with heating and cooling rates of  $5^\circ\text{C min}^{-1}$ . During fuel cell operation a gas flow of  $50 \text{ cm}^3 \text{ min}^{-1}$  of hydrogen or ammonia was supplied at the anode while  $50 \text{ cm}^3 \text{ min}^{-1}$  of air was maintained at the cathode. The fuel cell was heated to  $700^\circ\text{C}$  at a ramp of  $3^\circ\text{C min}^{-1}$ .

## 3. Results and discussion

Fig. 1 shows an XRD pattern for a BCE sample sintered at  $1550^\circ\text{C}$ , crushed in a mortar and pestle. The flat background

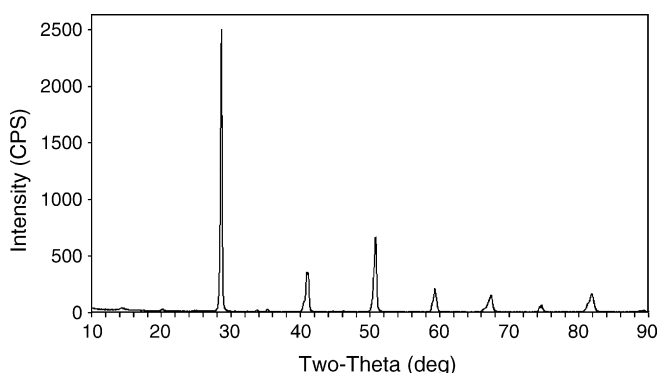


Fig. 1. XRD pattern for BCE sintered at  $1550^\circ\text{C}$ . The soak time at temperature was 10 h.

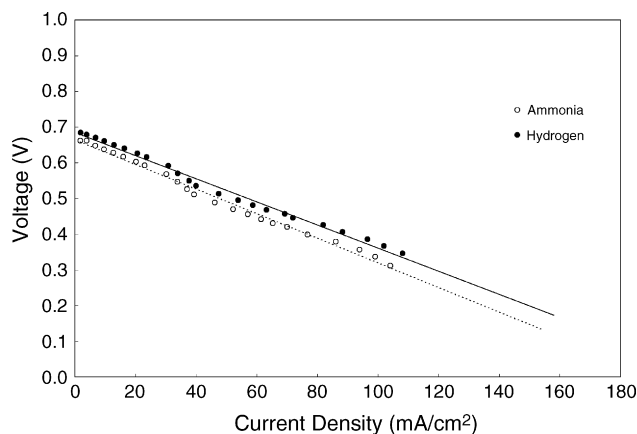


Fig. 2.  $J$ - $V$  data for BCE, the data were collected in both hydrogen and ammonia at  $700^\circ\text{C}$ .

scattering and sharp peak profiles indicate good crystallinity, no secondary phases were detected. The refined unit cell parameters determined from the XRD data were 0.876433, 0.622266, 0.624952 nm; the space group was orthorhombic  $Pm\bar{c}n$ .

Fig. 2 shows  $J$ - $V$  data for a BCE monolithic fuel cell with porous platinum electrodes collected in hydrogen and ammonia at  $700^\circ\text{C}$ . 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 low OCV indicates the presence of significant electronic conduction [12]. The cell voltage, at a given current, was only slightly lower when the fuel cell was operated using ammonia compared to pure hydrogen. The power density data for this cell are shown in Fig. 3. The maximum power density values are slightly less in ammonia as compared to hydrogen. This behaviour can be attributed to the lower partial pressure of hydrogen due to the presence of nitrogen [7]. 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 BCE solid electrolyte elements, approximately 1 mm. The power density data for BCE based

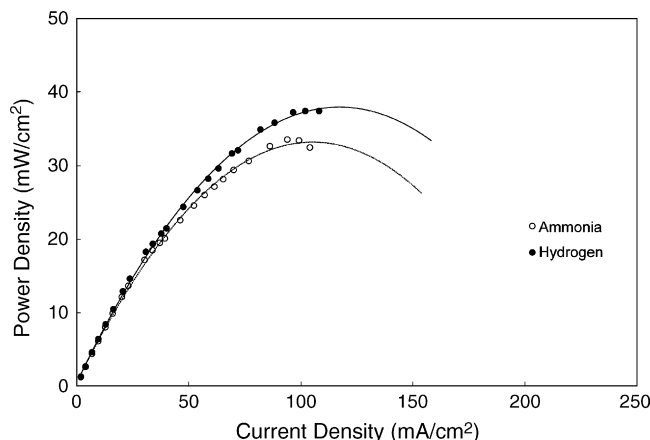


Fig. 3. Power density data for BCE, the data were collected in both hydrogen and ammonia at  $700^\circ\text{C}$ .

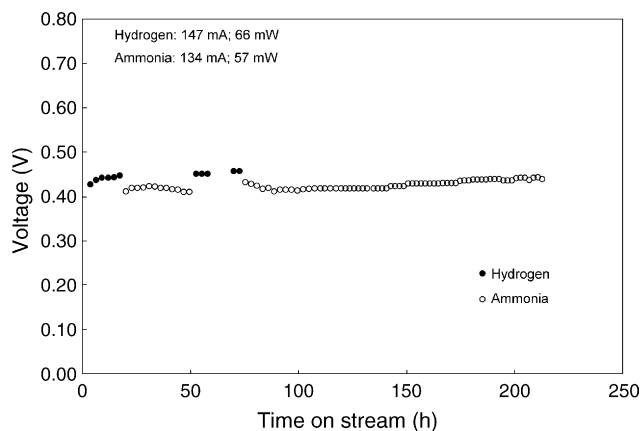


Fig. 4. Voltage vs. time data for a BCE fuel cell operated both in hydrogen and ammonia at 700 °C.

fuel cells are slightly higher than those for gadolinium doped barium cerate fuel cells [13].

Fig. 4 shows the voltage versus time data, close to the peak power point, the data were collected at 700 °C. The fuel was switched between hydrogen and ammonia without significant degradation in performance. The stability of the data over extended periods of time (greater than 200 h) show that BCE is a viable electrolyte material for both a hydrogen and ammonia fuel cell. The power density data, close to the peak power point, as a function of operating time for a monolithic BCE fuel cell operated at 700 °C in ammonia is shown in Fig. 5. The data show

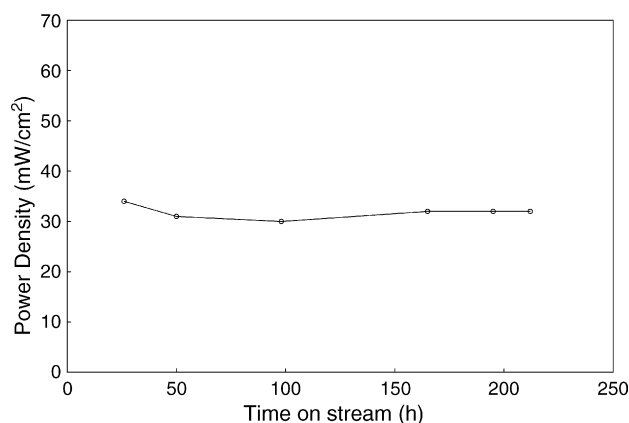


Fig. 5. Power density vs. time data for a BCE fuel cell operated at 700 °C in ammonia.

that the power output of the fuel cell is stable for extended periods of time. The data also show that no detectable deterioration in performance occurs as a result of operation in ammonia.

#### 4. Summary

The performance characteristics of intermediate temperature single element fuel cells using a proton and electron conducting BCE solid electrolyte at 700 °C are reported. The  $J$ - $V$  and power density data indicate that cells using this electrolyte are stable for extended periods of time, using either 100% hydrogen or ammonia as fuel. The use of ammonia as fuel did not degrade the performance of the fuel cell. A direct ammonia fuel cell offers cost and environmental benefits over fuel cells using hydrocarbons as hydrogen source. Future work will be directed at improving the performance characteristics of the BCE electrolyte.

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