Short communication

An ammonia fuelled SOFC with a $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ thin electrolyte prepared with a suspension spray

Kui Xie, Qianli Ma, Bin Lin, Yinzhu Jiang, Jianfeng Gao, Xingqin Liu *, Guangyao Meng

Department of Material Science and Engineering, University of Science and Technology of China (USTC), Hefei, Anhui 230026, PR China

Abstract

In order to develop a cost effective route to fabricate solid oxide fuel cells (SOFC) with a proton conductive electrolyte, $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ (BCNO) powder was prepared by the modified Pechini method and a suspension of BCNO powder was then deposited as a thin layer by a spray process onto a NiO–BCNO anode. A bi-layer with very dense BCNO electrolyte was obtained by co-sintering at 1400 °C for 5 h. With $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSCO) as the cathode, single cells were assembled and tested with NH_3 and H_2 as fuels and static air as the oxidant. For a commercial liquid ammonia fuel at 700 °C, the OCV and the peak power density of a cell with a 20 μm thick BCNO electrolyte were 0.950 V and 315 mW/cm², respectively. With H_2 fuel as a comparison, the values are correspondingly 0.951 V and 335 mW/cm².
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Keywords: Solid oxide fuel cell; Ammonia fuel; $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$; Proton conductor; Suspension spray

1. Introduction

Solid oxide fuel cells (SOFCs) have gained much attention as advanced power generation devices because of their high energy conversion efficiency, low environmental impact and good fuel flexibility [1]. Current SOFC technology based on oxide ion conductors, such as yittria stabilized zirconia (YSZ) and doped ceria is well established. There are, however, still problems hindering their practical development, such as material incompatibilities and coking within the anode compartment when using hydrocarbon fuels [2].

Perovskite-type doped barium cerate ($BaCeO_3$) materials exhibit fairly high proton conductivity and can be considered to be a possible substitute electrolyte for SOFCs. But $BaCeO_3$ based electrolytes cannot stand use carbon-containing fuels since the produced CO_2 in the anode compartment may react and lead to cell performance degradation. Therefore, an alternative route to promoting the commercialization of SOFCs is to develop a proton conductor electrolyte and try to use carbon-free fuels. Industrially available liquid ammonia is certainly a carbon-free SOFCs fuel with a high content of H_2, and NH_3 can be readily decomposed into $H_2 + N_2$ on the catalysis of nickel-based anode of SOFCs in the ordinary operation temperatures of 500–900 °C.

Our previous attempts have been have described the above idea [3]. SOFCs with $BaCe_{0.9}Gd_{0.1}O_{3-\delta}$ [3] or $BaCe_{0.9}Sm_{0.1}O_{3-\delta}$ [3] as electrolytes and fueled with industrial liquid ammonia showed a high performance in peak power density of 300–500 mW/cm² in the temperature range of 500–700 °C. Obviously, els NH_3 would provide another benefit that it avoids not only the problem of coking but also has no danger of producing CO_2 to react with the doped $BaCeO_3$ based electrolytes. Also, these fuel cells display some unique characteristics, such as OCV values close to theoretically predicted, low electrode polarization and a lower conduction activation energy for the proton conductors, etc. [3].

The electrolytes in the above cells, however, were rather thick (about 50 μm) and was made by co-pressing two kinds of ceramic powders, which is not suitable to fabricate cells with larger area for practical purposes. Thus, it is necessary to develop a cost effective process to prepare thinner electrolyte membrane on porous anode supports, to reach higher performance. In this work, we present the results of SOFCs with a thin proton conductive electrolyte made by a pressurized suspension spray process, which was developed in our laboratory and successfully employed to prepare thin dense YSZ on NiO–YSZ supports [4].

* Corresponding author. Tel.: +86 551 3606249; fax: +86 551 3607627.
E-mail address: xqliu@ustc.edu.cn (X. Liu).

The suspension was prepared with a $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ material that has a relative high conductivity, e.g. 0.084 S/cm at 800 °C [5–7]. The fuel cells were tested at 700 °C with commercial liquefied ammonia and hydrogen as fuels.

2. Experiments

The $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ (BCNO) powder was synthesized by a modified Pechini method [8]. In this process, $Ba(C_2H_3O_2)_2$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Nd(NO_3)_3$ at the stoichiometric ratio of BCNO were dissolved in water. Citric acid, which was used as complexation/polymerization agent, was then added with a citric/metal mole ratio set at 1.2:1. This solution was stirred on a heating plate until it changed into a brown foam and finally ignited. The obtained brown ash was subsequently calcined at 1200 °C for 3 h to get a fine BCNO powder.

The well-mixed powder of fine BCNO and a commercial NiO powder in a weight ratio of 35:65 was pressed into disks of 15 mm in diameter and 0.65 mm in thickness under 200 MPa, and subsequently fired at 1000 °C for 2 h as the anode support.

The BCNO powder was dispersed into ethanol by ball-milled for 24 h to form a suspension with 10 wt.% of BCNO. The BCNO suspension was sprayed on the anode support, which was heated on a heating plate during the spraying process. The suspension was fluidized by an airflow and the droplets were deposited on the heated anode substrate to form a green electrolyte layer. Then the bi-layer of green electrolyte and anode support were co-fired at 1400 °C for 5 h. A scanning electron microscope (SEM, JSM-6301F) was employed to observe the surface and fracture morphology of the sintered bi-layers.

For cell preparation, a graded cathode slurry made of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSCO) and BCNO powder was applied to the electrolyte surface by printing and then firing at 1050 °C for 3 h. In order to evaluate the performance of the cells, Ag paste current collectors were applied onto both electrodes followed by calcination at 600 °C for 30 min.

The cells were tested at 700 °C. Both liquid ammonia and hydrogen were used as fuels and static air as oxidant. The flow rate of the fuel gas was about 40 ml/min. The cell voltages and output current of the cells were measured with digital multi-meters (CDM-8145). A scanning electron microscope was used to observe the microstructure of the cells after testing.

3. Results and discussion

XRD spectra (Fig. 1) of the as-prepared BCNO powders showed that there were only peaks corresponding to $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$, indicating a single phase without formation of a impurity phase. Fig. 2 is a SEM photo of surface morphology of a sintered bi-layer of BCNO electrolyte on anode. It can be seen that the BCNO membrane is completely dense and the grains are quite uniform in the size of 5–10 μm. There is no obvious pores and cracks on the surface. A few needle-like particles on the sample surface may be dust or something un-identified but unlikely any impurity phase formed from BCNO decomposition. The result demonstrates that the pressurized suspension spray process followed by a heat treatment at a quite low temper-
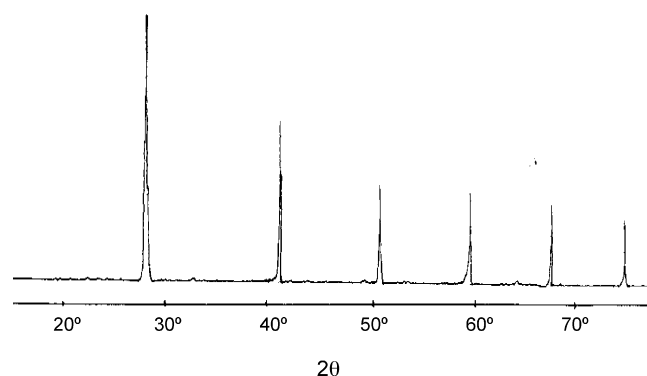

Fig. 1. The XRD spectra of BCNO powders.

ature (1400 °C) to fabricate dense BCNO electrolyte membrane on porous anode support was successful.

Fig. 3 presents the I–V data of a cell for both hydrogen and ammonia as fuels at 700 °C. The almost linear I–V curve implies little electrode polarization. And also, we can deduce that the voltage drop of the cell is mostly from the IR fall across the BCNO electrolyte because of both anode and cathode materials exhibiting a much higher conductivity than BCNO. The open circuit voltage (OCVs) was 0.950 V in hydrogen and 0.951 V in ammonia at 700 °C, the value is quite close to that obtained for the cells with $BaCe_{0.9}Gd_{0.1}O_{3-\delta}$ (0.975 V) [3]. Obviously, the OCVs were a bit lower than the theoretical value (about 1.17 V at 700 °C) and attributed to the electronic conduction of $BaCeO_3$ based electrolyte materials to some extent at the relative high temperatures [9]. But the close OCV values in the two cases, however, was not consistent to their difference in H_2 content for the two fuels as we may expect the complete decomposition of NH_3 at 700 °C. Also, the maximum power density of the cell was 335 and 315 mW/cm^2, respectively, for hydrogen fuel and ammonia fuels. The small difference is not expected, either. As seen from Fig. 3 the slopes of the V–I curves are slightly different for the two cells, indicating a different total resistance of the cell with the two fuels. From the slopes, the total resistances
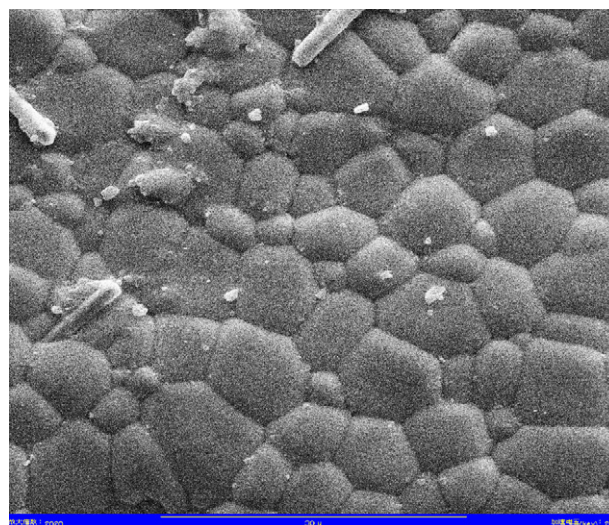

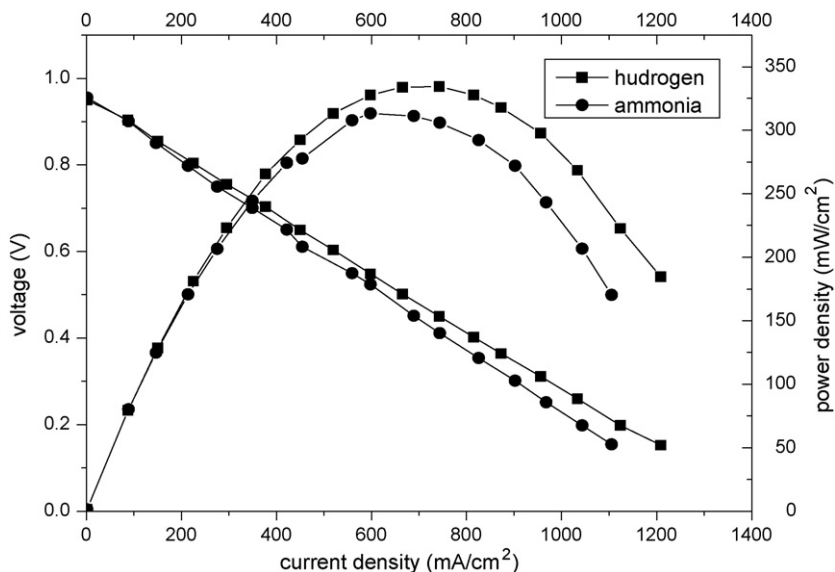Fig. 2. The surface of electrolyte after being fired at 1400 °C for 5 h.

Fig. 3. Performance of cell with hydrogen and ammonia at 700 °C.

were calculated by linear fitting to be 0.672 and 0.728 Ω/cm^2 in H_2 and NH_3 fuels, respectively. Assuming the cell resistance mostly comes from the electrolyte the conductivity of BCNO are 0.00298 S/cm for H_2 cell and 0.00275 S/cm for NH_3 cell if the BCNO layer thickness is taken as 20 µm as seen from Fig. 4. The values are about 30 times smaller than that mentioned above (0.084 S/cm), which seems incredible.

Fig. 4 shows the cross-section view of the cell, Ni-BCNO/BCNO/LSC-BCNO after testing. As can be seen, the BCNO electrolyte is about 20 µm in thickness, quite dense and adhered very well to the layers of anode and cathode. A higher power density should be expected than the values mentioned above and those reported by et al. [3], because of the thin electrolyte and cathode layers. The reason may mainly come from
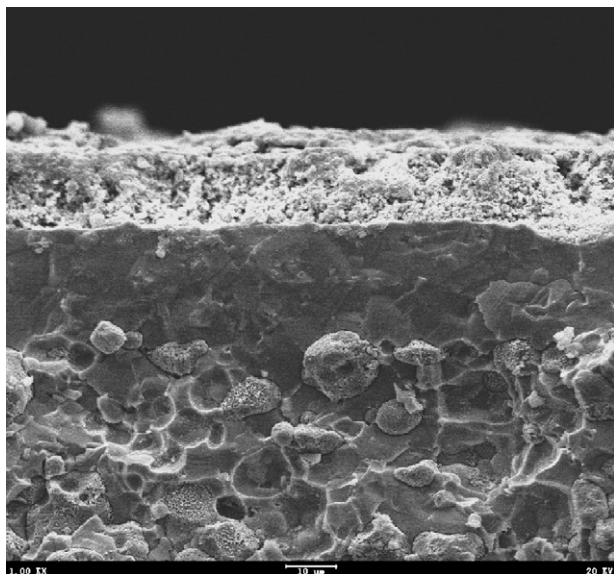
the anode layer. As we can see from Fig. 4, the anode layer was rather dense instead of porous, indicating incomplete reduction of the NiO into metal Ni. The dense layer of BCNO + NiO would have a rather large thickness and a much poorer conductivity compared with the BCNO electrolyte layer. Therefore, the cell exhibited a very high resistance and thus a rather low output power density. It is also understandable that only protons in the NH_3 case (not N_2) can reach the interface between the electrolyte and the anode, so that the cell OCV is close to that for a H_2 cell. As far as the larger slope of the *V–I* curve and thus higher resistance in the NH_3 cell it may attribute to the lower temperature due to the endothermic reaction of NH_3 decomposition.

In order to check if the CO_2 in the environment air which was employed as oxidant may be harmful to the cell performance, the cell with BCNO electrolyte was tested with H_2 fuel at 700 °C at an operating voltage of 0.802 V and current density about 0.220 A/cm^2. After 1000 min, the voltage and the current density were 0.799 V and 0.210 A/cm^2, respectively, showing no obvious degradation. Of course such a short term testing cannot certify the cell is stable, the work to search proton conductors more stable in CO_2 ambient is on-going.

4. Conclusions

The proton conductor, Ni–$BaCe_{0.9}Nd_{0.1}O_{3-\delta}$ (BCNO), with a pure perovskite phase was synthesized by a modified Pechini method. A BCNO powder suspension was prepared and employed to make a thin layer on a porous anode of BCNO + NiO using a pressurized suspension spray process followed by firing at 1400 °C for 5 h. The thin BCNO membrane was very dense and uniform, indicating the success of such a cost effective process in cell preparation.

A mixture of BCNO + LSCO as the cathode was applied onto the bi-layer to assemble cells and Ag paste used as the current

Fig. 4. Cross-section of cell after testing.

collector. The cell was tested in H_2 and NH_3 fuels. The cells showed a high OCV value (0.951 V), lower electrode polarization and a high peak power density, of 335 and 315 mW/cm^2, respectively, for H_2 and NH_3 fuels.

It was found that although the cell structure was successful with a thin BCNO electrolyte and cathode of only about 20 μm in thickness, the anode which consisted of NiO + BCNO, was not completely reduced to Ni + BCNO which may explain the lower cell performance than expected.

Acknowledgements

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