



Short communication

A stable and thin $\text{BaCe}_{0.7}\text{Nb}_{0.1}\text{Gd}_{0.2}\text{O}_{3-\delta}$ membrane prepared by simple all-solid-state process for SOFCKui Xie^a, Ruiqiang Yan^b, Xiaoxiang Xu^c, Xingqin Liu^{a,*}, Guangyao Meng^a^a Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China^b Department of Materials Engineering, Taizhou University, Zhejiang 317000, China^c School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK

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ABSTRACT

$\text{BaCe}_{0.7}\text{Nb}_{0.1}\text{Gd}_{0.2}\text{O}_{3-\delta}$ (BCNG) and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ (BCG) were synthesized by solid-state reaction method. The samples obtained were exposed in 3% CO_2 + 3% H_2O + 94% N_2 at 700 °C for 20 h in order to evaluate their chemical stability. It was found that BCNG exhibited adequate chemical stability while BCG decomposed and impurities were observed in the final products. Additionally, the BCNG demonstrated similar behavior as BCG in high-temperature thermal stability and in TEC and displayed a conductivity of 0.0075 S cm^{-1} at 700 °C in humid hydrogen which was slightly lower than BCG (0.0095 S cm^{-1}) at the same conditions. Fuel cells with BCNG as electrolyte were successfully fabricated and the thickness of BCNG layer can be easily adjusted as lower as 10 μm by a simple all-solid-state process. The fuel cells exhibited OCV as high as 1.0 V at 700 °C with maximum output power 340 mW cm^{-2} and interfacial resistance as low as $0.51 \Omega \text{ cm}^2$.

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1. Introduction

Doped perovskite-type barium cerate (BaCeO_3) materials exhibit fairly high proton conductivity at intermediate temperature and was considered as a potential electrolyte for solid oxide fuel cells (SOFCs) [1,2]. Considerable studies have been included in understanding the underlying transport mechanisms and great effort has been devoted into the practical applications of these materials [3–5]. However, it was found that these cerates based electrolytes did not possess a good stability in the presence of H_2O and CO_2 where unfavorable reactions took place with a sharp degradation in fuel cell performance concomitantly [6,7]. Therefore, alternatives with similar conductivity but with higher stability were a continuous incentive for searching and developing appropriate materials.

Although zirconium-based perovskite has been recognized as a potential alternative in replacing cerates due to their stability towards H_2O and CO_2 , their conductivity is usually one order of magnitude lower than cerates. This is attributed to the highly refractory properties of zirconates with low rates of grain growth under typical sintering conditions [6,8]. Although partially replacing cerium with zirconium has been confirmed as an effective way

in improving sintering properties, their conductivity decreases as a compromise [8]. Aiming at this antinomy, much work was reported to improve the sintering by increasing sintering temperature and adding sintering additives [2,6,8,9]. Compared with zirconates, the $\text{Ba}_3\text{CaNb}_2\text{O}_9$ is surprisingly stable reported by Nowick et al. [10]. Thus, it is reasonable to assume that partial replacement of Ce^{4+} by high electronegative Nb^{5+} (dope cerates with Nb_2O_5) can increase the chemical stability.

In this work, BCNG was prepared and the chemical stability, conductivity, thermal stability and thermal expansion were studied. Fuel cell with thin BCNG was fabricated by using an all-solid-state method and was measured from 550 to 700 °C. The interface and short-term performance were also investigated.

2. Experimental

The $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.7}\text{Nb}_{0.1}\text{Gd}_{0.2}\text{O}_{3-\delta}$ were synthesized by solid-state reaction method at 1300 °C for 24 h [6]. XRD (Cu $\text{K}\alpha$, X'Pert Pro, Philips) was performed to detect the phase formations. The obtained powders were exposed in 94% N_2 + 3% CO_2 + 3% H_2O at 700 °C for 20 h and the phase changes were determined with XRD. Green disks (3 mm thick and 15 mm in diameter) were fabricated by pressing the powders under 200 MPa and subsequently sintered at 1550 °C for 5 h. The conductivity was tested in humid hydrogen ($\sim 3\% \text{ H}_2\text{O}$) with an ac impedance method (Chenhua 604C, Shanghai) from 500 to 800 °C. The TEC of sintered disks

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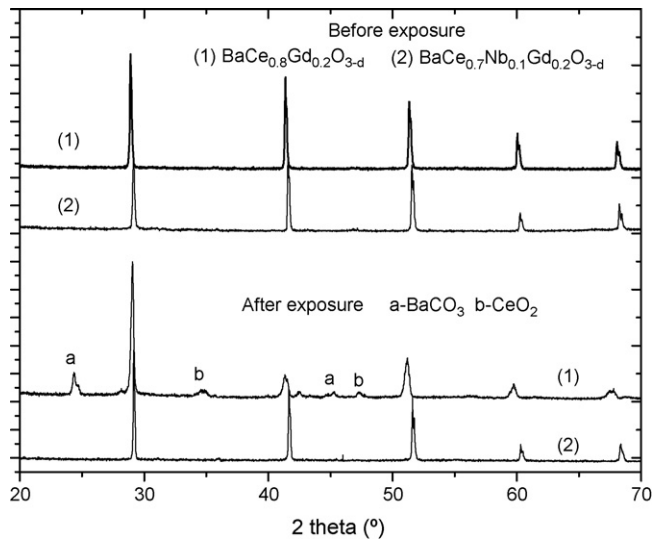


Fig. 1. XRD of $\text{BaCe}_{0.7}\text{Nb}_{0.1}\text{Gd}_{0.2}\text{O}_{3-d}$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-d}$ before and after heating in 3% CO_2 + 3% H_2O + 94% N_2 at 700 °C.

was detected with thermal expansion analyzer (m119973, Beijing). Thermal gravity analysis (TGA) of two powders was carried out in air to 1600 °C ($10^\circ\text{C min}^{-1}$, TGA, HTG-2).

The anode powders were prepared by mixing BaCO_3 , CeO_2 , Nb_2O_5 , Gd_2O_3 , NiO and Starch (BCNG: $\text{NiO}:\text{Starch} = 55:35:10$, in weight ratio) and pressed into anode substrates (3 mm thick and 15 mm in diameter) under 200 MPa. A suspension, prepared by directly ball-milling the mixed powders of BaCO_3 , CeO_2 , Nb_2O_5 and Gd_2O_3 in ethanol for 24 h, was deposited on the anode substrates to form green layers by a suspension spray process [11]. The bi-layers were co-sintered at 1400 °C for 5 h to form half cells. XRD and SEM (JSM-6301F) were employed to analyze and observe the membrane, respectively. $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-d}$ cathode slurry [12] was screen-printed onto the electrolyte surface (0.223 cm^2 in area) and subsequently fired at 950 °C to assemble a single cell. With humid hydrogen (3% H_2O) as fuel (40 ml min^{-1}) and static air as oxidant, cell was tested from 550 to 700 °C in a home-developed testing system. The voltage and current were detected with two digital meters (Model: GDM-8145), and the interface was recorded with an AC impedance method (0.01–100,000 Hz). The short-term performance test was carried out for 20 h. The current density was scanned to evaluate cell performance when the operating voltage was held at 0.50 V.

3. Results and discussions

X-ray diffraction (XRD) patterns before and after exposure in 94% N_2 + 3% CO_2 + 3% H_2O 700 °C for 20 h were shown in Fig. 1. It can be noticed that for BCNG, XRD patterns remain almost unchanged and exhibit only sharp intense peaks which could be indexed as orthorhombic symmetry. However, for BCG, after being exposed in 94% N_2 + 3% CO_2 + 3% H_2O 700 °C for 20 h, additional peaks corresponding to BaCeO_3 and CeO_2 were observed, indicating partial decomposition took place during the exposure process. This phenomenon evidently suggests that BCNG demonstrates a better chemical stability compared with BCG in the presence of CO_2 and H_2O which are typical products if carbon hydrates were utilized as fuels in fuel cells. This relatively high chemical stability of BCNG might be ascribed to the higher electronegativity of Nb^{5+} which enhances the acidity of BCNG and stabilizes the oxides against carbonation correspondingly [3,5]. Thermogravimetric analysis (TGA) shows similar weight loss behaviors for BCNG and BCG from 20 to

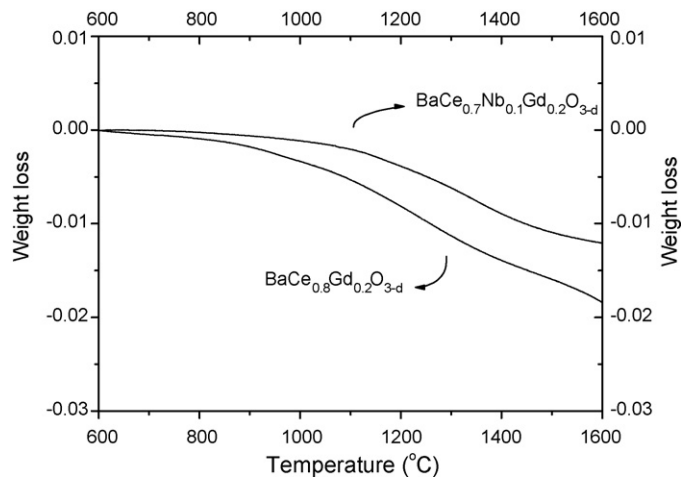


Fig. 2. TGA of $\text{BaCe}_{0.7}\text{Nb}_{0.1}\text{Gd}_{0.2}\text{O}_{3-d}$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-d}$ from 20 to 1600 °C in air.

1600 °C in air (Fig. 2) where slow weight loss occurs at 1000 °C and could be attributed to the escape of oxygen from oxides. However, it can be noticed that BCNG present less weight loss than BCG during the whole temperature range implying a higher thermal stability.

The tested TEC of BCNG is $10.1 \times 10^{-6}\text{ K}^{-1}$, quite close to $9.8 \times 10^{-6}\text{ K}^{-1}$ for BCG from 20 to 1000 °C, which proves that the improvement of chemical stability does not result in obvious changes in TEC. It is well known that the doped- BaCeO_3 generally conducts oxygen, proton and electron but predominantly conducts proton as function of the partial water pressure [4,5]. The conductivity of two samples is compared in Fig. 3. The BCNG exhibits lower conductivity than BCG at corresponding temperatures and show 0.007 S cm^{-1} at 700 °C, lower than 0.009 S cm^{-1} for BCG, but generally consistent with that of Zr-replaced BaCeO_3 reported by Zhong [9]. The doping of Nb is expected to increase oxides acidity and decreases the stability of free $[\text{HO}^\bullet]$ defect as proton charge carrier in lattice, which could easily result in a decline in conductivity [5]. Additionally, the Nb^{5+} doped may lead to a decrease of oxygen vacancy created by the substitution of Gd^{3+} for Ce^{4+} , which may concurrently result in a conductivity drop. The defect reactions may be written as following:

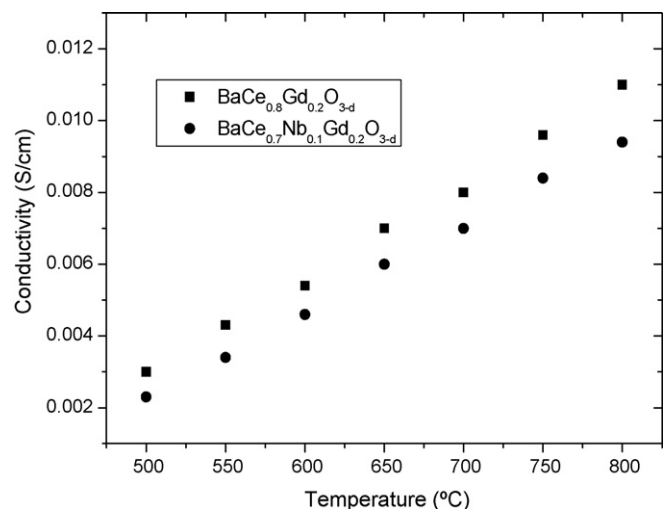


Fig. 3. Conductivity of $\text{BaCe}_{0.7}\text{Nb}_{0.1}\text{Gd}_{0.2}\text{O}_{3-d}$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-d}$ in humid hydrogen from 500 to 800 °C

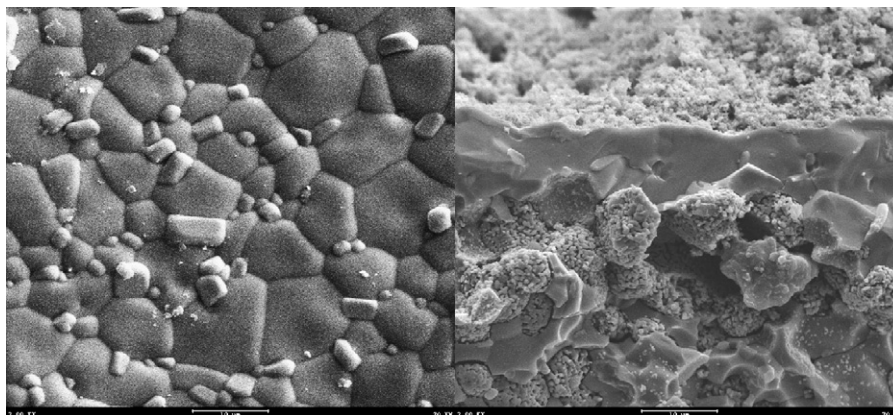


Fig. 4. Microstructures of thin membrane sintered at 1400 °C for 5 h.



Up to now, it is still a challenge to prepare fuel cell by a cost-effective and efficient technology. In this work, we develop an all-solid-state process, which is possible to further simplify the cell preparation. As shown in Fig. 4, the 10 μm thick membrane with grain size of 2–6 μm is pretty dense and in a single phase according to XRD. In Fig. 5, the OCVs respectively reach 1.0 V at 700 °C, 1.015 V at 650 °C, 1.024 V at 600 °C and 1.03 V at 550 °C, very close to theoretical values and generally consistent to that of the cell with $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$ (50 μm) reported by Ma et al. [13]. The small electronic conduction of cerates may result in the OCV drop at high temperature [14]. The maximum outputs reach 340 mW cm^{-2} at 700 °C, 280 mW cm^{-2} at 650 °C, 220 mW cm^{-2} at 600 °C and 110 mW cm^{-2} at 550 °C, respectively, generally consistent with that of the cell prepared by dry-pressing [8]. Although the conductivity of BCNG is lower than $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$, the thickness of BCNG is just one fifth of $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$, indicating the reduction of electrolyte thickness could easily improve cell performance. As shown in Fig. 6, the interfacial resistances were 0.51 Ωcm^2 at 700 °C, 0.66 Ωcm^2 at 650 °C, 0.89 Ωcm^2 at 600 °C and 1.59 Ωcm^2 at 550 °C, respectively. They mainly dominate the fuel cell performance, especially at low temperatures. So it may be assumed that the improvement of interface could further increase the cell performance. The calculated conductivity of BCNG is 0.0035 S cm^{-1} at 700 °C, just 50% of the tested values (0.007 S cm^{-1}). In deed, the atmosphere for BCNG membrane in SOFC is quite different from the one for sintered BCNG disk. The conductivity of sintered disk is

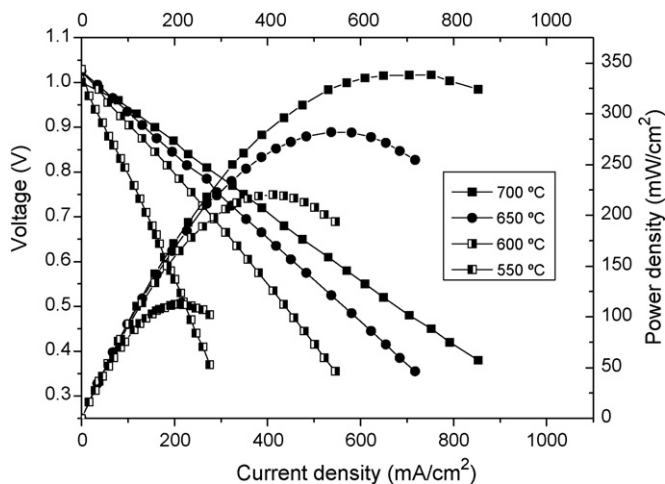


Fig. 5. Performance of cell from 550 to 700 °C.

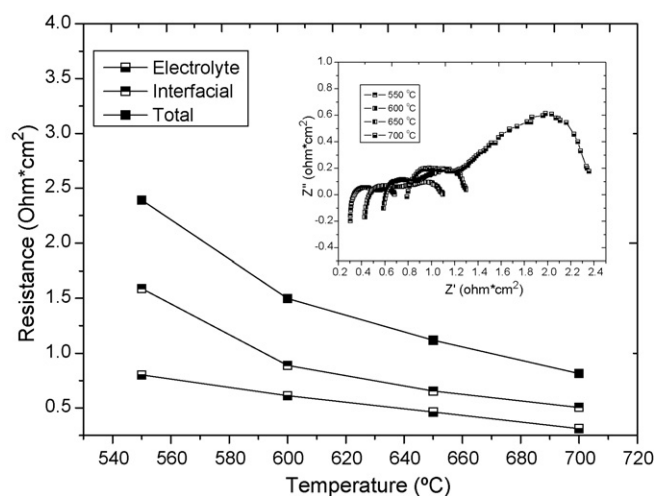


Fig. 6. Impedance of fuel cell from 550 to 700 °C.

tested in humid hydrogen, while two sides of the BCNG membrane contact oxidation atmosphere in cathode and reducing atmosphere in anode, respectively, which makes the conduction mechanism quite complex.

In order to check whether the CO_2 and H_2O in air are detrimental to the cell performance, the cell was tested at 500 °C for 20 h. The current density was scanned to evaluate cell performance when the operating voltage was held at 0.50 V. It was found that current density did not degrade but slightly increased during the operation time, which could be attributed to the slow balance established during fuel cell operations. Generally, such a short-term test cannot guarantee the stability on a long time basis therefore the work to prove the stability of fuel cell in atmosphere containing CO_2 and H_2O is still on-going.

4. Conclusions

$\text{BaCe}_{0.7}\text{Nb}_{0.1}\text{Gd}_{0.2}\text{O}_{3-\delta}$ (BCNG), $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ (BCG) were successively synthesized by solid-state reaction method at 1300 °C for 24 h. It was found that BCNG demonstrated higher stability in the presence of CO_2 and H_2O as was compared with BCG and exhibited a better thermal stability and similar TEC behavior to BCG. The conductivity of BCNG is 0.007 S cm^{-1} at 700 °C in humid hydrogen which is slightly lower than that of BCG (0.009 S cm^{-1}) under the same conditions. Fuel cells using BCNG as electrolyte were successively fabricated by a simple all-solid-state process and the thickness of the electrolyte can be decreased as low as 10 μm on anode

support at 1400 °C. Single cell with $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ cathode and humid hydrogen as fuel exhibited a high performance at 700 °C which implies promising applications in various areas. In conclusion, BCNG brings on good composition for chemical stability, thermal stability, thermal expansion coefficient and conductivity.

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