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Short communication

Prontonic ceramic membrane fuel cells with layered $GdBaCo_2O_{5+x}$ cathode prepared by gel-casting and suspension spray

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Abstract

In order to develop a simple and cost-effective route to fabricate protonic ceramic membrane fuel cells (PCMFCs) with layered $GdBaCo_2O_{5+x}$ (GBCO) cathode, a dense $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) electrolyte was fabricated on a porous anode by gel-casting and suspension spray. The porous NiO–$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (NiO–BZCY7) anode was directly prepared from metal oxide (NiO, $BaCO_3$, ZrO_2, CeO_2 and Y_2O_3) by a simple gel-casting process. A suspension of $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ powders synthesized by gel-casting was then employed to deposit $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) thin layer by pressurized spray process on NiO–BZCY7 anode. The bi-layer with 10 μm dense BZCY7 electrolyte was obtained by co-sintering at 1400 °C for 5 h. With layered GBCO cathode synthesized by gel-casting on the bi-layer, single cells were assembled and tested with H_2 as fuel and the static air as oxidant. An open-circuit potential of 0.98 V, a maximum power density of 266 mW cm^{-2}, and a low polarization resistance of the electrodes of 0.16 Ω cm^2 was achieved at 700 °C.

Keywords: Solid oxide fuel cells; $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$; $GdBaCo_2O_{5+x}$; Gel-casting; Suspension spray

1. Introduction

The development of solid oxide fuel cells (SOFCs) has reached its new stage characterized with thin electrolytes on porous electrode support, in which the most important fabrication techniques developed are almost all concerned with inorganic membranes, and so can be named as ceramic membrane fuel cells (CMFCs). Protonic ceramic membrane fuel cells (PCMFCs) based on proton electrolytes may exhibit more advantages than CMFCs bases on oxygen-ion electrolytes in many respects, such as energy efficiency and avoiding carbon deposit [1].

There is now considerable interest in proton-conducting oxide electrolytes for PCMFCs. Many perovskite-type oxides show high proton conductivity in a reducing atmosphere. One of the major challenges for this type of proton conductor is a proper compromise between conductivity and chemical stability. Zuo et al. [2] reported a new composition, $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) that exhibited both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel-cell operation. BZCY7, at temperatures below 550 °C, displayed the highest ionic conductivity of all known electrolyte materials for SOFC applications. The electrolytes in the above cells, however, were rather thick (about 65 μm) and were made by co-pressing two kinds of ceramic powders, which is not suitable to fabricate cells with larger area for practical purpose. Thus, it is necessary to develop a simple and cost-effective route to fabricate PCMFCs with thinner electrolyte membrane on porous anode support, in order to reach higher performance. In this work, the porous NiO–$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (NiO–BZCY7) anode was directly prepared from metal oxide by a simple gel-casting process. Recently, gel-casting has gained attention as a new method in the preparation of electrode powders and electrode-supported

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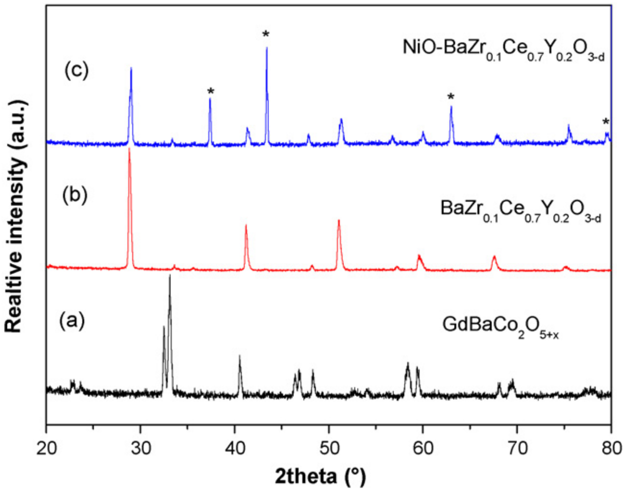

Fig. 1. XRD patterns for (a) the layered $GdBaCo_2O_{5+x}$ powders, the bi-layer of (b) BZCY7 membrane and (c) NiO–BZCY7 anode substrate. Asterisk (*): NiO.

substrates for SOFCs [3,4]. Then the 10 μm dense BZCY7 electrolyte was fabricated on the anode support by a pressurized suspension spray process which was developed in our laboratory [5].

The development of proper cathode materials for protonic ceramic membrane fuel cells (PCMFCs) in order to improve materials compatibility and reduce costs remains a challenge. Many simple perovskite-type mixed ionic–electronic conductors such as doped $LaCoO_3$ [6], $BaCoO_3$ [7] or $LaFeO_3$ [8] have been extensively studied as possible cathodes, however not much attention has been paid to the perovskite related structures such as the double or layered perovskites. Recently Tarancón et al. [9,10] have shown the potential of layered $GdBaCo_2O_{5+x}$ (GBCO) for cathode application and evaluated the performance of this material working as a cathode in SOFCs based on oxide ion conductors (YSZ). However, to our knowledge, the performance of GBCO cathodes as a part of protonic ceramic membrane fuel cells (PCMFCs) has not been reported to date. In this work, the layered GBCO synthesized by gel-casting were employed as a new PCMFCs cathode.

2. Experimental

The NiO–BZCY7 anode support was directly prepared using a gel-casting method with metal oxide (NiO, $BaCO_3$, ZrO_2, CeO_2 and Y_2O_3) precursors in a certain proportion to make sure that the BZCY7 composition was $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ and the weight ratio of NiO:BZCY7 was 6:4. The precursors were mixed with organic monomer (mixture of acrylamide (AM) and *N*,*N*-methylenebis-acrylamide (MBAM), AM:MBAM = 5:1) in an aqueous solution. The resulting slurry with the initiator ammonium bisulphate ($(NH_4)_2S_2O_8$) was poured into a mould, and subsequently heated in an oven at 80 °C for 1 h. The gel was cut into discs, followed by drying at 80 °C for 24 h. The as-prepared green anode-substrates were stored ready for use.

A suspension of $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ powders synthesized by gel-casting was then employed to deposit BZCY7 thin layer by pressurized spray process on NiO–BZCY7 anode. The BZCY7 powders were dispersed into ethanol by ball-milling for 24 h to form a suspension with 10 wt% of BZCY7. 10 wt% triethanolamine as dispersant, 5 wt% dibutyl phthalate (DBP) and 5 wt% polyethylene glycol as plasticizer, and 5 wt% polyvinyl butyral (PVB) as binder were added, respectively. The obtained suspension was sprayed on the anode support which was heated on a heating plate during the spraying process. The bi-layer of green electrolyte and anode support were then co-fired at 1400 °C for 5 h. Layered $GdBaCo_2O_{5+x}$ powder was synthesized by an aqueous gel-casting method using Gd_2O_3, $BaCO_3$, and Co_3O_4 as precursors, followed by calcinations at 1100 °C for 10 h. The GBCO slurry was applied to the electrolyte by printing and then fired at 975 °C for 3 h to form a porous cathode.

The phase identification of the sintered anode–electrolyte bilayer and prepared cathode powders was studied with the powder X-ray diffraction by Cu Kα radiation (D/Max-gA, Japan). Single cells were tested from 550 °C to 700 °C in a home-developed cell-testing system with humidified hydrogen (∼3% H_2O) as fuel and the static air as oxidant, respectively. The flow rate of fuel gas was about 40 ml min^{-1}. The cell voltages and output current of the cells were measured with digital multi-meters (GDM-8145). AC impedance spectroscopy (Chi604c, Shanghai

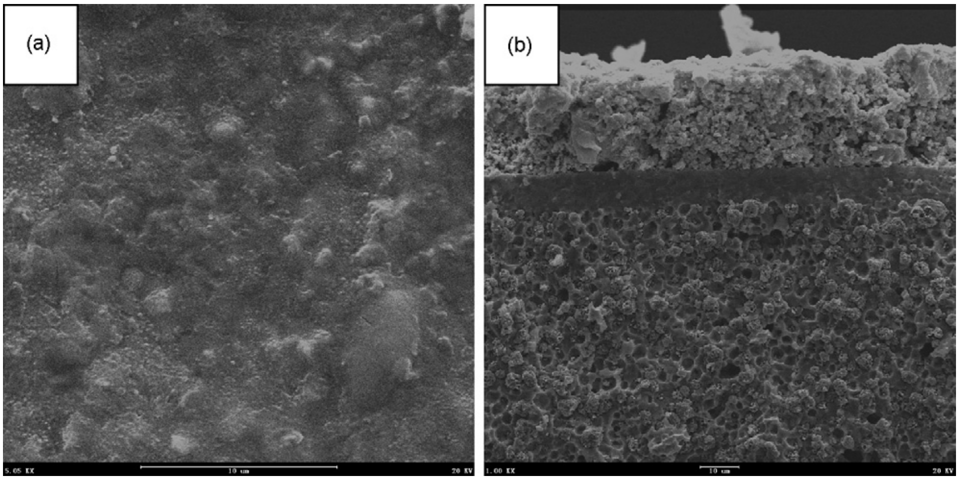

Fig. 2. SEM micrographs of cell after testing: (a) the surface of electrolyte and (b) the cross-section of cell with a 10 μm-thick BZCY7 membrane.

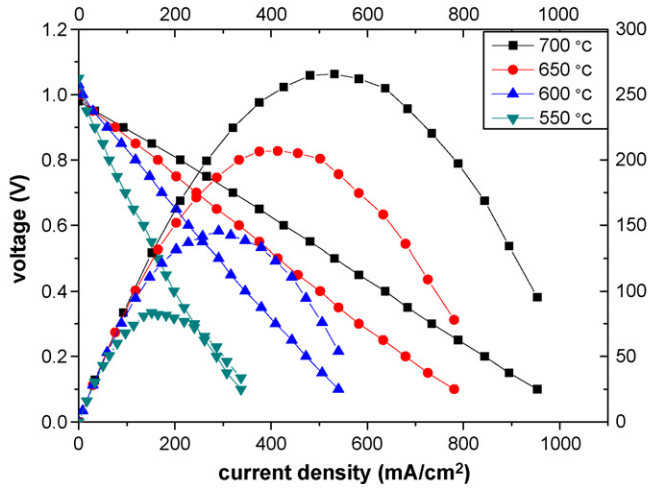

Fig. 3. Performance of the as-prepared cell with hydrogen at different temperatures.

Chenhua) was performed on the cell under open-current conditions from 550 °C to 700 °C. A scanning electron microscope (SEM) was used to observe the microstructure of the cells after testing.

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of $GdBaCo_2O_{5+x}$ exhibits a layered perovskite phase structure [11]. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at 1400 °C for 5 h. It could be clearly seen that there were only peaks corresponding to $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) in electrolyte membrane (Fig. 1(b)) and to NiO and BZCY7 in the anode substrate (Fig. 1(c)), which gave no evidence for the formation of other substance.

Fig. 2(a) is the SEM image of surface morphology of the as-prepared tri-layer cell of BZCY7 electrolyte on the porous anode support after testing. It can be seen that the BZCY7 membrane is completely dense. There is no obvious pores and cracks on the surface. From the cross-section view of the spray BZCY7 membrane (Fig. 2(b)), it is found that the BZCY7 membrane is only about 10 μm thick.

Fig. 3 presents the *I–V* and *I–P* characteristics of the as-prepared cell, the SEM image of which is shown in Fig. 2. 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 IR fall across the BZCY7 electrolyte because of both anode and cathode materials exhibiting much higher conductivity than electrolyte materials. The open-circuit voltages (OCV) of 0.98 V at 700 °C, 1.00 V at 650 °C, 1.03 V at 600 °C and 1.05 V at 550 °C indicate that the electrolyte membrane is sufficiently dense. Peak power densities were 266, 207, 146, and 84 mW cm^{-2} at 700, 650, 600, and 550 °C, respectively. From the slopes the total resistances were calculated by linear fitting to be 0.93, 1.16, 1.71 and 2.79 Ω cm^2 at 700, 650, 600, and 550 °C, respectively. Assuming the cell resistance mostly comes from the electrolyte the conductivity of BZCY7 (10 μm) are 0.00108, 0.00086, 0.00058, and 0.00036 S cm^{-1} at 700, 650, 600, and 550 °C, respectively. The values are about 30 times smaller than that mentioned above (∼0.03 S cm^{-1} at 700 °C), which seems incredible.

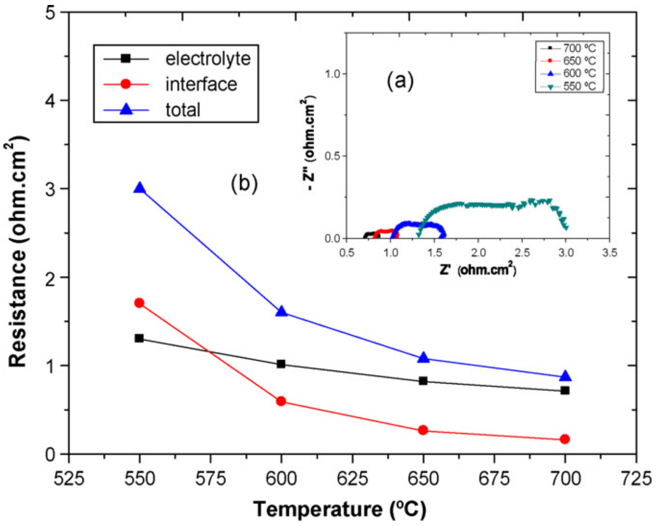

Fig. 4. (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures.

Fig. 2(b) shows the cross-section view of the cell, Ni–BZCY7/BZCY7/GBCO after testing. As can be seen, the BZCY7 electrolyte is about 10 μm in thickness, quite dense and adhered very well to the layers of anode and cathode. It surely should be expected to get a higher power density than the values mentioned above and that reported by Zuo et al. [2], as here we have pretty thin electrolyte and cathode layers. The reason may mainly come from the anode layer. As we can see from Fig. 2(b), the anode layer was rather dense instead of porous, indicating incomplete reduction of the NiO into metal Ni. The dense layer of BZCY7 + NiO would have rather large thickness and much poorer conductivity compared with BZCY7 electrolyte layer. Therefore, the cell exhibited a very high resistance and thus rather low output power density.

In order to evaluate the performance of layered $GdBaCo_2O_{5+x}$ working as a cathode in a PCMFC, the impedance spectra of the as-prepared cells under open-current conditions at different temperatures as shown in Fig. 4(a). In these spectra, the intercept with the real axis at low frequencies represents the total resistance of the cell and the value of the intercept at high frequency is the electrolyte resistance, while the difference of the two values corresponds to the sum of the resistance of the two interfaces: the cathode–electrolyte interface and the anode–electrolyte interface. As expected, the increase of the measurement temperature resulted in a significant reduction of the interfacial resistances, typically from 1.7 Ω cm^2 at 550 °C to 0.16 Ω cm^2 at 700 °C. The results indicated that the layered GBCO cathode is a good candidate for operation at or below 700 °C. Further, Fig. 4(b) shows that the cell performance is influenced by the interfacial resistances, especially at temperatures below 550 °C, where the cell performance is essentially determined by the interfacial resistances.

At 550 °C, the polarization resistance of the electrodes is about 1.7 Ω cm^2 whereas the resistance of the electrolyte is only about 1.3 Ω cm^2. So we can deduce that development of proper cathode materials is a grand challenge for developing the low-temperature PCMFCs.

4. Conclusions

In order to develop a simple and cost-effective route to fabricate protonic ceramic membrane fuel cells (PCMFCs) with layered $GdBaCo_2O_{5+x}$ cathode, a dense $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) electrolyte was fabricated on a porous anode by gel-casting and suspension spray. A laboratory-sized tri-layer cell of NiO–BZCY7/BZCY7 (10 μm)/GBCO, not yet optimized for performance, was operated from 550 °C to 700 °C fed with humidified H_2 (~3% H_2O). An open-circuit potential of 0.98 V and a maximum power density of 266 mW cm^{-2} was achieved at 700 °C. The polarization resistance of the electrodes was as low as 0.16 Ω cm^2 at 700 °C. These results have indicated that the layered GBCO cathode is a good candidate for operation at or below 700 °C, and that gel-casting and suspension spray is a simple and potentially commercial prospective route for preparing the key components of SOFCs.

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