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Influence of anode pore forming additives on the densification of supported $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ electrolyte membranes based on a solid state reaction

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Abstract

We describe a solid state reaction for the preparation of both NiO–$BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ anode substrates and $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY10) electrolyte membranes on porous NiO–BCTY10 anode substrates. The amounts of the pore forming additive in the substrates showed a significant influence on the densification of the BCTY10 membranes. After sintering at 1450 °C for 5 h, the BCTY10 membrane on a NiO–BCTY10 anode containing 30 wt.% starch achieved a high density and showed adequate chemical stability against H_2O and CO_2. The chemical stability of BCTY10 was even better than that of $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$. With a mixture of $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BZCY7) and $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) as a cathode, a single fuel cell with 12 μm thick BCTY10 electrolyte generated maximum power densities of 142, 93, 29 mW/cm^2 at 700, 600 and 500 °C, respectively. The electrolyte resistance and interfacial polarization resistance of the cell under open circuit conditions were also investigated.
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Keywords: Sintering; Solid state reaction; Fuel cell; Membranes; Pore forming additive

1. Introduction

Ceramic proton conductors have received much attention from the solid oxide fuel cell (SOFC) community because proton-conducting SOFCs would permit a reduction of the working temperature to the range 500–700 °C.[1–5] In addition, unlike conventional SOFCs with YSZ electrolyte, no circulation of fuel gas is necessary for proton-conducting SOFCs, as water is produced at the cathode side. Among these ceramic proton conductors, considerable attention has been paid to ABO_3-type perovskites, particularly rare earth doped $BaCeO_3$ materials, which exhibit the highest protonic conductivities. Various processing techniques have been used for producing the doped $BaCeO_3$ thin film electrolytes in order to reduce the electrolyte resistance and improve cell performance, such as suspension spray,[6] co-pressing,[7] spin coating[8] and screen printing.[9] The majority has been proved to be suitable for laboratory demonstration but may present difficulties for mass production because the doped $BaCeO_3$ powders are usually needed to be prepared by a wet chemical route. This wet chemical process has complicated processing steps and high processing costs though ceramic powder prepared by a wet chemical process has better sintering activity. In addition, the solid state reaction has the advantages of simple processing steps and lower costs, which can fit the requirements for commercialization. However, the powders prepared by solid state reaction show lower sintering activity due to the high calcination temperatures used. In recent studies, an in situ solid state reaction method has been successfully used to prepare dense ceramic membranes on porous substrates.[6,10–13] However, ceramic powders with high sintering activity (powders prepared through a wet chemical route[6] or nano-sized ceramic powders[12]) are usually required to prepare the anode substrate, in order to maintain high sintering activity for the substrate. This can still hinder the commercialization of proton-conducting SOFCs because of the relatively high processing costs. Recently, Meulenberg et al.[11] have successfully used conventional techniques and materials to prepare proton-conducting electrolytes on standard anodes, which shed light on the manufacture of

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SOFCs. As for mass production, it is necessary to find a simple route for preparing SOFCs based solely on a solid state reaction.

Another challenge for rare earth doped $BaCeO_3$ materials is the poor chemical stability of $BaCeO_3$, which makes them inadequate for fuel cell applications.[14] In order to solve this problem, much attention has been paid to the preparation of chemically stable ceramic proton conductors. The most widely used approach is the partial replacement of Ce by Zr at the cost of reducing the protonic conductivity, in order to seek a proper compromise between the conductivity and chemical stability.[14] However, some investigations show that only $BaCeO_3$-based materials with high doping concentrations of Zr can produce adequate chemical stability against H_2O and CO_2.[14,15] In addition, the high sintering temperature for the Zr-doped $BaCeO_3$ materials is another challenge for their practical use. Therefore, it is necessary to find alternative strategies for improving the chemical stability of $BaCeO_3$. In our previous research,[16] we have found that doping with a small amount of Ta can greatly increase the stability of the $BaCeO_3$-based material. However, a wet chemical route for preparing the fuel cell is necessary, which may not fit the requirement of mass production. Furthermore, no direct comparison between the chemical stability of the commonly used Zr-doped $BaCeO_3$ and the Ta-doped $BaCeO_3$ has been made.

In this study, the stable $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY10) electrolyte membranes have been successfully fabricated on porous NiO–BCTY10 anode substrates using a solid state reaction. We aim to study the influence of the amounts of the anode pore forming additive on the densification of the anode-supported BCTY10 membranes as well as the electrochemical properties of the BCTY10-based fuel cell.

2. Experimental

The NiO–BCTY10 anode substrates were prepared by directly mixing the metal oxides (NiO, $BaCO_3$, CeO_2, Y_2O_3 and Ta_2O_5) in appropriate proportions to make sure that the BCTY10 composition was $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ and the weight ratio of BCTY10:NiO was 4:6. Different amounts of starch (10, 20 and 30 wt.%) were added as the pore former. The mixed powders were pressed under a pressure of 200 MPa into disks 15 mm in diameter and 0.8 mm thick. These as-prepared green anode substrates containing different amounts of pore forming additive were stored ready for use. For comparison, another anode substrate containing the BCTY10 powder synthesized by a conventional solid state reaction process was prepared. In the conventional solid state reaction process, appropriate amounts of $BaCO_3$, CeO_2, Y_2O_3 and Ta_2O_5 were mixed and ball-milled in alcohol for 24 h. The mixture was then dried and calcined at 950, 1200 and 1400 °C for 5 h with intermittent grinding in an agate mortar. 30 wt.% starch was added as the pore former in this anode.

The BCTY10 membranes were fabricated on the anode substrates by an in situ reaction. The starting materials $BaCO_3$, CeO_2, Y_2O_3 and Ta_2O_5 were mixed in the molar ratio 1:0.7:0.1:0.05 and dispersed into ethanol by ball-milling for 24 h to form a suspension. The well-mixed suspension was directly deposited on the anode substrate by a suspension spray method. The suspension was fluidized by a flow of air and sprayed on to the anode substrates, which rested on a heating plate during this process. Then the bi-layers of green electrolyte and anode were co-fired at 1450 °C in air for 5 h. A mixture of $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BZCY7) and $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) was printed on the dense anode-supported BCTY10 membrane electrolyte and then fired at 1000 °C for 3 h to form a porous cathode. The electrode active area was 0.237 cm^2. Pt paste was applied to the electrode as a current collector.

Powder X-ray diffraction measurements were made using a Philips X'Pert Pro Super diffractometer with Cu Kα radiation. The shrinkage behaviors of the green anode substrates from room temperature to 1450 °C were measured with a thermal expansion analyzer (DIL 402C, NETZSCH). Electrochemical measurements on the fuel cell were performed in an Al_2O_3 test housing placed inside a furnace. Humidified hydrogen (∼3% H_2O) was fed to the anode chamber at a flow rate of 25 mL/min while the cathode was exposed to atmospheric air. The anode side was sealed with Ag paste. Fuel cell performance was measured with a DC Electronic Load apparatus (ITech Electronics model IT8511). Resistances of the cell under open circuit conditions were measured at different temperatures by an impedance analyzer (CHI604C, Chenhua Inc., Shanghai). A 5 mV A.C. signal was applied and the frequency was swept from 100 KHz to 0.1 Hz. A scanning electron microscope (SEM, JEOL JSM-6700F) was used to observe the fracture morphologies of the BCTY10 membranes and the tested cell.

3. Results and discussion

We know that the high shrinkage of an anode substrate can promote the densification of a supported electrolyte membrane during the co-firing process. Fig. 1 shows the shrinkage behavior of the anode substrates containing different amounts of pore forming additive. With increasing amount of starch, the shrinkage of the anode substrate became greater. The anode substrate containing 30% starch shows the highest shrinkage after sinter-

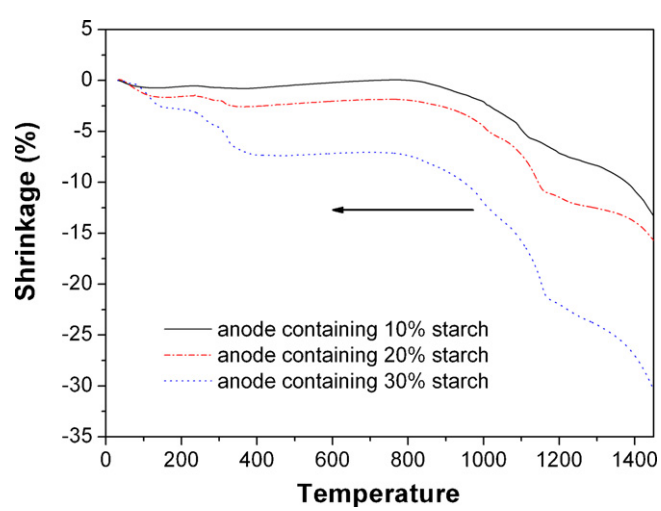

Fig. 1. Shrinkage of green anode substrates containing different amounts of starch.

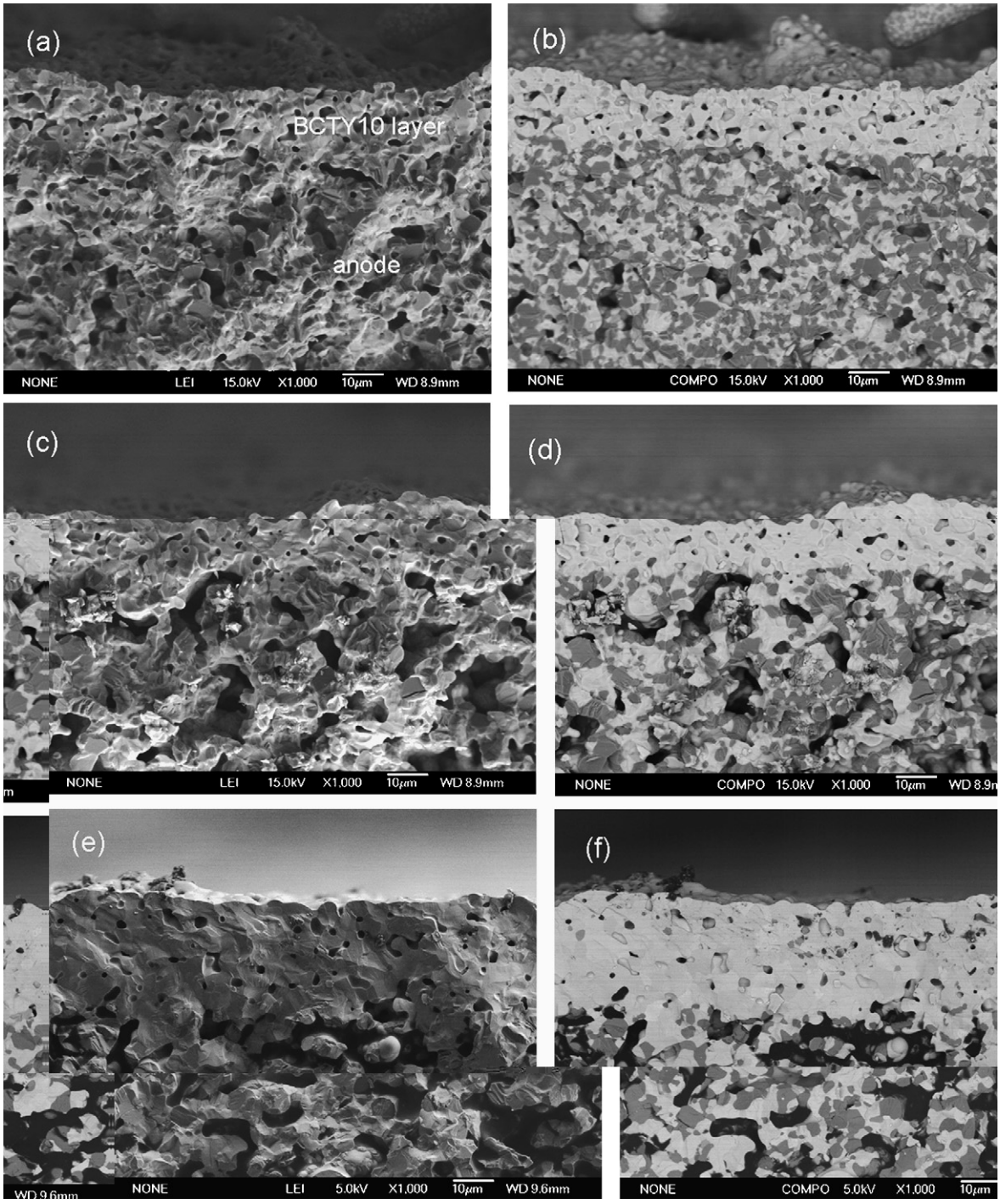

Fig. 2. Fracture surface of the half-cell based on a BCTY10 electrolyte membrane after sintering at 1450 °C. Secondary electron images of BCTY10 membranes on the anode substrates containing different amounts of starch (a) 10 wt.%, (c) 20 wt.% and (e) 30 wt.%. Backscattered electron images of the corresponding areas for (b) 10 wt.% starch containing anode, (d) 20 wt.% starch containing anode and (f) 30 wt.% starch containing anode.

ing at 1450 °C (∼32.4%), which is beneficial to the densification of the membrane on this anode.

Fig. 2 presents cross-sectional views of the membranes prepared on the anode substrates containing different amounts of starch after sintering at 1450 °C for 5 h. Fig. 2(a), (c) and (e) are the secondary electron images of the fracture morphologies of the membranes on the anode substrates containing 10, 20 and 30 wt.% starch, respectively. Fig. 2(b), (d) and (f) are the backscattered electron images of the corresponding areas of Fig. 2(a), (c) and (e), respectively. There is only one phase in the thin membranes as well as a good distribution of two phases in the anode substrates, implying that the pure phase ceramic membranes have been fabricated on the anode substrates. Furthermore, we can see from the SEM images that the membranes become denser with increasing amount of pore forming additive in the anode substrates. When 30 wt.% pore forming additive