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A novel anode supported $BaCe_{0.4}Zr_{0.3}Sn_{0.1}Y_{0.2}O_{3-\delta}$ electrolyte membrane for proton conducting solid oxide fuel cells

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ABSTRACT

A novel $BaCe_{0.4}Zr_{0.3}\,Sn_{0.1}Y_{0.2}O_{3-\delta}$ (BSY) electrolyte membrane with thickness of 20 μm was fabricated on NiO-based anode substrate via a one-step all-solid-state method followed by a co-sintering at 1450 °C for 5 h. Chemical stability test demonstrated that BSY electrolyte showed adequate chemical stability against CO_2 and H_2O at intermediate temperature. Besides, the doping of Sn also enhanced the conductivity in humidified hydrogen. With $Nd_{0.7}Sr_{0.3}MnO_{3-\sigma}$ cathode and hydrogen fuel, the fuel cell generated maximum output of 320, 185 and 105 mW cm^{-2} at 700, 650 and 600 °C, respectively. The interfacial resistance of the fuel cell was studied under open circuit conditions and the short-term cell performance also confirmed the stability of BSY electrolyte membrane.

1. Introduction

Solid oxide fuel cells (SOFCs) have been extensively studied as advanced power generation devices because of their high energy conversion efficiency, low environment impact, and good fuel flexibility [1–3]. Up to date, considerable efforts have been made to reduce the high SOFC operation temperature either by developing novel electrolyte with high ionic conductivity or by reducing the electrolyte thickness [4]. Since Iwahara et al. in 1980's found some perovskite oxides (such as doped $BaCeO_3$) that show excellent proton conductivity at intermediate temperature, proton conducting ceramic oxides had developed into the promising electrolyte candidate for intermediate temperature SOFC because of their high proton conductivity and low activation energy compared with conventional oxide-ion conductor (such as YSZ) [5]. Acceptor-doped $BaCeO_3$ shows the highest conductivity among all the ceramic proton conductors, however, they have been found to be instable in the presence of CO_2 and H_2O where unfavorable reactions take place and lead to a degradation in the fuel cell performance [6,7]. It seems that the high conductivity and high chemical stability are antagonistic, as studied by Kreuer [8] and Norby [9]. Much work has been reported to improve the chemical stability of cerates by partially replacing cerium with zirconium [10–12]. This method is at the cost of poor sintering at typical sintering temperatures because of the refractory properties of zirconates, which is crucial to thin membrane fabrication technology at low temperatures. In order to improve sintering, a lot of investigations have been devoted by adding transition metal oxide to improve the sintering of the solid solution of cerates and zirconates under typical sintering conditions [13–15].

Up to now, alternative with similar conductivity and adequate stability is still a continuous incentive for searching and developing appropriate proton conducting electrolytes. In the process of searching for stable proton conducting electrolytes, Kreuer and his co-workers found that some mixed pervoskite-type oxides, such as doped $Ba_2Sn_2O_6$, display surprising stability against CO_2 and H_2O as well as promising proton conductivity [16]. Thus, it is reasonable to make a reasonable assumption that partial replacement of Ce with Sn can increase the chemical stability. On the other hand, SnO_2 with a low melting point is expected to form liquid phase to promote sintering. In this study, we present a new strategy of partially substituting Zr and Sn for Ce to increase the chemical stability. Half cells with $BaCe_{0.4}Zr_{0.3}Sn_{0.1}Y_{0.2}O_{3-\delta}$ (BSY) electrolyte membranes on NiO-based anodes were fabricated by a one-step all-solid-state method. And the electrochemical characterizations of the BSY-based fuel cell were performed.

2. Experimental

$BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ (BZY) and $BaCe_{0.4}Zr_{0.3}Sn_{0.1}Y_{0.2}O_{3-\delta}$ (BSY) samples for chemical stability test were synthesized by solid-state reaction method [12]. In the process, $BaCO_3$, CeO_2, ZrO_2, SnO_2 and Y_2O_3 were ball-milled and then fired at 1200 °C for 10 h. X-ray powder diffractions (XRD, Cu Kα, X′Pert Pro, Philips) were used for the phase identifications. The two fresh powders were exposed

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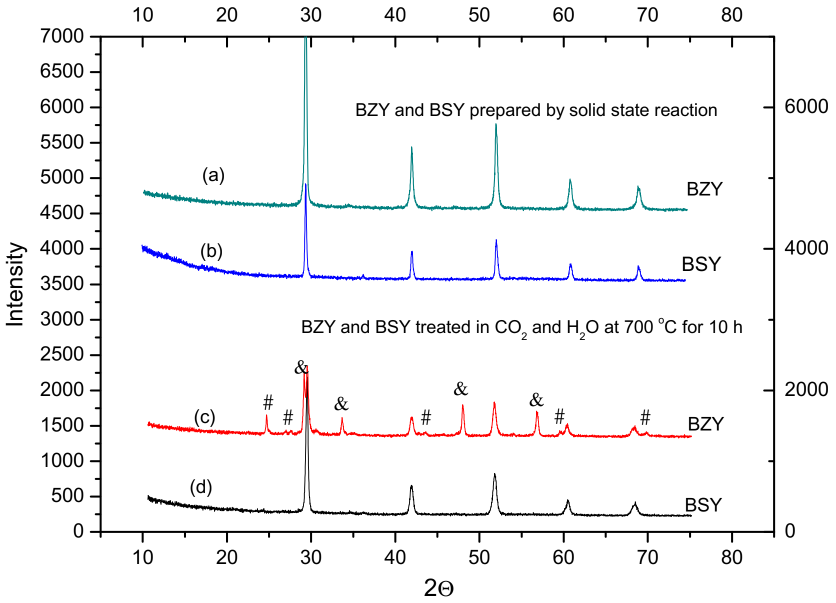

Fig. 1. XRD of $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ (BZY) and $BaCe_{0.4}Zr_{0.3}Sn_{0.1}Y_{0.2}O_{3-\delta}$ (BSY) (a) and (b) are BZY and BSY prepared by solid state reaction method; (b) and (d) are the two samples after being treated in $CO_2 + H_2O$ at 700 °C; in (c), $BaCO_3$ and CeO_2 are symbolized with # and &, respectively.

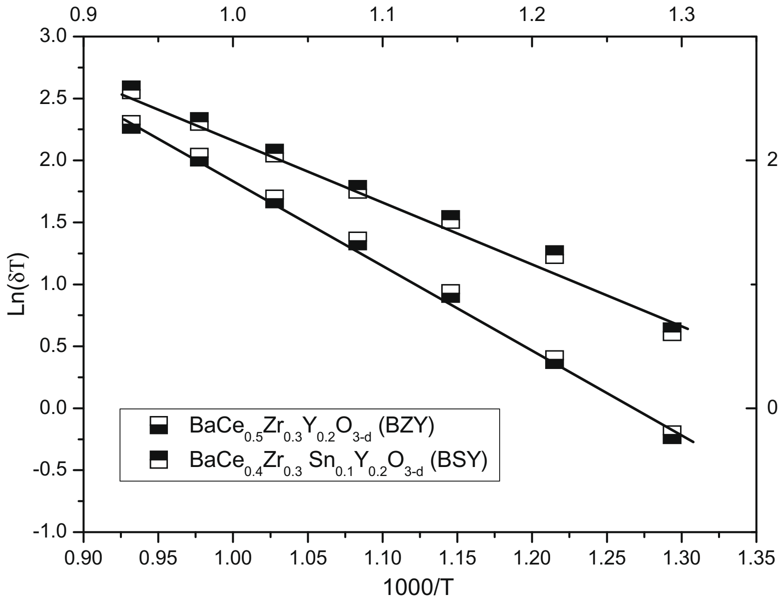

Fig. 2. Conductivity of $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ (BZY) and $BaCe_{0.4}Zr_{0.3}\ Sn_{0.1}Y_{0.2}O_{3-\delta}$ (BSY) in humidified hydrogen from 600 °C to 800 °C.

in mixed atmosphere (3% CO_2 + 3% H_2O + 94% Ar) at 700 °C for 24 h. After that, XRD was performed to detect the phase changes. Then another two fresh BZY and BSY powders were pressed into disks followed by sintering at 1450 °C for 5 h, respectively. The conductivity of the two disks in ~3% H_2O + 97% H_2 was tested with AC impedance.

Fuel cell with BSY as electrolyte was fabricated as follows. BSY-1, NiO and starch in weight ratio of BSY:NiO:starch = 30:55:15 were mixed and pressed into disks (2 mm in thickness and 15 mm in diameter) and then stored for future use as anode substrates. In this process, the BSY-1 corresponds to the precursors as follows: $BaCO_3$, CeO_2, Y_2O_3, ZrO_2 and SnO_2. In the mean time, $BaCO_3$, CeO_2, Y_2O_3, ZrO_2 and SnO_2 at the stoichiometric ratio of BSY were ball-milled in ethanol for 24 h to form a stable suspension. This suspension was homogeneously sprayed onto the anode supports to form green bi-layers by spray coating [17]. After co-sintering at 1450 °C for 5 h, half cells were successfully assembled. The electrolyte of one half-cell was polished with sand paper and then etched at 1000 °C for 30 min. A scanning electronic microscope (SEM, model KYKY 1010B) was employed to observe the surface of BSY electrolyte. At the same time, one of the stored anode supports was sintered at 1450 °C for 5 h to get a ceramic disk and subsequently reduced in pure hydrogen at 700 °C to get a porous anode. The porosity of this reduced anode was determined with Archimedes method. With $Nd_{0.7}Sr_{0.3}MnO_{3-\sigma}$ cathode (0.223 cm^2 in area), a single cell was assembled and measured from 600 °C to 700 °C while the interfacial resistances were evaluated by AC impedance (0.01–100,000 Hz) under open circuit conditions.