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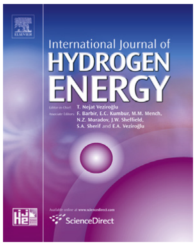

Novel doped barium cerate–carbonate composite electrolyte material for low temperature solid oxide fuel cells

Yuanfei Hei [a], *Jianbing Huang* [a,*], *Cheng Wang* [b,*], *Zongqiang Mao* [b]

[a] *International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xianning West Road No. 28, Xi'an 710049, PR China*
[b] *Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China*

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ABSTRACT

A composite of a perovskite oxide proton conductor ($BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$, BCZ10Y20) and alkali carbonates ($2Li_2CO_3$:$1Na_2CO_3$, LNC) is investigated with respect to its morphology, conductivity and fuel cell performance. The morphology shows that the presence of carbonate phase improves the densification of oxide matrix. The conductivity is measured by AC impedance in air, nitrogen, wet nitrogen, hydrogen, and wet hydrogen, respectively. A sharp increase of the conductivity at certain temperature is seen, which relates to the superionic phase transition at the interface phases between oxide and carbonates. Single cell with the composite electrolyte is fabricated by dry-pressing technique, using nickel oxide as anode and lithiated nickel oxide as cathode, respectively. The cell shows a maximum power density of 957 mW cm^{-2} at 600 °C with hydrogen as the fuel and oxygen as the oxidant. The remarkable proton conductivity and excellent cell performance make this kind of composite material a good candidate electrolyte for low temperature solid oxide fuel cells (SOFCs).

Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising power-generation technologies due to their high energy conversion efficiency, fuel flexibility and reduced pollution [1]. Although some SOFC systems are available for residential and business power generation, the high operating temperature of 800–1000 °C leads to prohibitive system costs, high degradation rates and slow startup times, seriously impeding the widespread practical implementation of the technology [2]. In the last decades, attempts have been made to reduce the operating temperature of SOFCs to intermediate temperature ranges (600–800 °C) and even to low temperature ranges (300–600 °C) [3]. At low operating temperature small-scale applications and even portable devices can be achieved, which opens more opportunities for SOFCs.

One crucial issue to develop low temperature SOFCs is minimizing the ohmic resistance of ceramic electrolyte at low operating temperatures. Reducing the electrolyte thickness and using alternative electrolyte materials with high ionic conductivity are two common strategies [4,5]. Oxide proton conductors are

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[*] *Corresponding authors.*
E-mail addresses: huangjb@mail.xjtu.edu.cn (J. Huang), wangcheng@mail.tsinghua.edu.cn (C. Wang).

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promising candidates as electrolytes for low-temperature SOFCs because of their low activation energy for proton conduction. In particular, perovskite-type oxides based on $BaCeO_3$ and doped with some trivalent cations exhibit high protonic conductivity in a humidified H_2 containing atmosphere at temperatures >300 °C, but the chemical stability in an atmosphere containing CO_2 and H_2O is inadequate for fuel cell applications [6]. Considerable research efforts have focused on tailoring the phase stability and conductivity of such oxide proton conductors for SOFC via doping [7–10]. The replacement of Ce by Zr into the barium cerate can form a solid solution that exhibits both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation. However, a reduction of conductivity along with the Zr-doping increase has been found in the barium cerate–zirconate solid solutions due to its relatively poor sinterability.

In order to enhance the ionic conductivity of single phase oxide electrolytes, Bin Zhu [11] proposed the cerium oxide based two-phase composite electrolyte materials with greatly enhanced ionic conductivity and excellent cell performance in fuel cell operation for the first time. Since then, these composite materials attract more and more attention for low temperature SOFC application. Among these composite electrolyte materials, doped cerium oxide-carbonate composites have been widely studied. Jianbing Huang et al. [12,13], Andreas Bod'en et al. [14], Jing Di et al. [15] have conducted many studies on samarium doped ceria (SDC)-carbonate composite electrolyte materials. However, there is still no convincing and satisfactory explanation for the proton conduction mechanism in these composite materials due to their complex components.

Perovskite oxide proton conductor ($BaCeO_3$, $BaZrO_3$)-carbonate composite electrolyte materials have not been extensively studied as compared with cerium oxide-carbonate composite electrolyte materials. Until now, only the electrical conductivity of some composite electrolyte materials [16,17] at low temperatures has been investigated but the fuel cell performance operating below 600 °C has never been reported. Unlike cerium oxide-carbonate composites, the matrix phase in these composites is a proton conductor instead of an oxygen–ion conductor. The added carbonate phase can create a lot of two-phase interfaces with the matrix phase which benefit the proton conduction at low temperatures. Thus, these composites are potential proton-conducting electrolyte materials for fuel cell application. It will be very convenient to verify the proton conduction mechanism in these composite materials.

In this study, we use the same strategy to prepare a dense composite electrolyte by adding $Li_2CO_3–Na_2CO_3$ binary carbonates into $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BCZ10Y20) matrix. This kind of two-phase composite is expected to be a pure proton conductor in hydrogen–oxygen fuel cell operation. Here, we report the results of preparation, densification and characterization of the composite electrolyte.

Experimental

Preparation of BCZ10Y20-LNC composite

Preparation of BCZ10Y20 powder: BCZ10Y20 was prepared by a homogeneous precipitation method. Stoichiometric $Ba(NO_3)_2$, $Ce(NO_3)_3 \cdot 6H_2O$, $Zr(NO_3)_4 \cdot 4H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were mixed and dissolved in deionized water. A certain quality of urea was added with the molar ratio of metal to urea = 1:20. The mixed solution was homogenized by continuous stirring. The solution was heated at 85 °C until it became a paste. The paste was dried in an oven at 120 °C overnight. Then the dried paste was sintered in air at 1000 °C for 4 h to obtain BCZ10Y20 powder.

The BCZ10Y20 powder was mixed with 20 wt% binary alkali carbonates ($2Li_2CO_3$:$1Na_2CO_3$, LNC). The mixtures were ground thoroughly and then heated at 680 °C for 1 h in air. The resultants were taken out directly from the furnace to room temperature and ground again to obtain BCZ10Y20-LNC composite electrolytes.

Characteristics of composite electrolytes

The BCZ10Y20 and BCZ10Y20-LNC composite were cold-pressed uniaxially at 300 MPa to form cylindrical pellets of 13 mm in diameter and about 1 mm in thickness. Then the green pellets were sintered at 1450 °C for 4 h and 600 °C for 1 h, respectively. Silver electrodes were subsequently prepared by painting silver paste onto both sides of the pellets. The phase structure was detected by the X-ray powder diffraction (XRD, D8 ADVANCE, Bruker AXS Corp.Germany) at room temperature using Cu K_α radiation. The morphology of powders and microstructure of the sintered pellets were obtained by scanning electron microscopes (SEM, JSM-4500 and JSM-6301F, JEOL Ltd., Japan). Electrical conductivities of the electrolyte pellets in different atmospheres were measured by AC impedance spectroscopy, using IM6eX electrochemical workstations produced by Zahner. The impedance data were taken over a temperature range from 400 °C to 600 °C and a frequency range of 0.1 MHz–100 mHz with an excitation voltage of 10 mV.

Fabrication and testing of single cell

The single cells were fabricated using a dry-pressing process. The composite anode was the mixture of NiO (50 vol.%) and composite electrolyte (50 vol.%). The cathode powder was composed of lithiated NiO (50 vol.%) mixed with composite electrolyte (50 vol.%). The anode, electrolyte and cathode were uniaxially pressed into a pellet at a pressure of 300 MPa and then sintered at 600 °C for 30 min in air. The size of the pellets had diameter of 13 mm and thickness of 1.3 mm, including 0.4 mm thick electrolyte. The effective working area is 0.5 cm^2. Two pieces of nickel foams were placed on both sides of the holder as current collectors. Then silver glue was applied as the sealant. The single cells were tested between 400 °C and 600 °C. Hydrogen and oxygen were used as the fuel and the oxidant, respectively.

Results and discussion

Structure and morphology of composite material

XRD patterns of BCZ10Y20 and BCZ10Y20-20 wt% LNC composite are shown in Fig. 1. Only diffractions for $BaCeO_3$ phase are found in the as-prepared BCZ10Y20 sample. It indicates that pure BCZ10Y20 powders are prepared successfully after calcining at 1000 °C for 4 h. The composite sample shows the

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