



A novel approach for substantially improving the sinterability of $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte for fuel cells by impregnating the green membrane with zinc nitrate as a sintering aid

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ABSTRACT

$\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY4) has been widely considered to be a promising electrolyte material for H^+ -SOFC, but it is restricted to commercial applications due to its poor densification behavior. A dense BZCY4 pellet was obtained by sintering at 1250 °C after impregnating the material with a zinc nitrate solution. The dilatometer curves and scanning electron microscopy (SEM) images indicated that the sinterability of the BZCY4 material is effectively improved by impregnating the green membrane with 4 wt% Zn. Moreover, EDX mapping indicated that the Ba, Zr and Ce elements were homogeneously distributed in the BZCY4+4 wt% Zn sample sintered at 1250 °C. In addition, an integrated SOFC employing a BZCY4+4 wt% Zn electrolyte was successfully fabricated without any cracks and delamination by impregnating the BZCY4 electrolyte membrane with zinc nitrate as a sintering aid. This single cell with a 25 mm thick BZCY4+4 wt% Zn electrolyte membrane exhibited power densities as high as 360 and 276 mW cm^{-2} at 700 and 600 °C, respectively. Electrical conductivity measurements demonstrated that the total conductivities of BZCY4+4 wt% Zn were $0.46 \times 10^{-2} \text{ S cm}^{-1}$, $0.56 \times 10^{-2} \text{ S cm}^{-1}$, $0.20 \times 10^{-2} \text{ S cm}^{-1}$ and $0.40 \times 10^{-2} \text{ S cm}^{-1}$ at 600 °C in air, wet air, 10% H_2 -Ar and wet 10% H_2 -Ar, respectively.

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1. Introduction

Since Iwhara et al. first observed proton conductivity in certain perovskite-type oxides with nominal SrCeO_3 composition [1], the interest in such materials for use as SOFC electrolytes has increased. Specifically, this increased interest arose because these oxides form water at the cathode side and have higher proton mobility than oxygen ions. Proton-conducting SOFCs (H^+ -SOFCs) are generally thought to potentially enjoy better performance at lower temperatures and higher cell efficiency than conventional SOFCs with oxygen ion-conducting electrolytes [2]. Due to their high intrinsic proton conductivity and high stability against CO_2 and water vapor chemical degradation, barium yttrium zirconate (BZY)-based perovskite oxides have recently attracted particular attention for their potential use as electrolytes in SOFCs [3–6]. However, BZY-based materials have poor sinterability, and a sintering temperature of 1700 °C or higher is required to achieve sufficient density. Such high sintering temperatures could lead to

the loss of barium via vaporization, thus inevitably affecting the conductivity and stability of the electrolyte [7,8].

$\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY4) derived from BZY-based oxides has been proven to be a promising electrolyte material for H^+ -SOFCs due to its high ionic conductivity and stability against chemical degradation from impurity gases in the atmospheres of fuel cells (CO_2 , H_2O) [9,10]. Anode-supported thin-film electrolyte fuel cell configurations are often applied to achieve high power output at reduced temperatures. Specifically, the anode substrate and the thin-film electrolyte should be co-sintered during the fabrication of this type of cell. Although the sinterability of BZCY4 is better than BZY, a sintering temperature of 1600 °C is still needed to obtain a sufficient density [11]. Such high temperatures, however, could also densify the anode layer and promote a reaction between the anode and electrolyte layers. Sufficient porosity is a prerequisite for fuel cell electrodes to ensure free gas diffusion and prevent serious concentration polarization at high current densities [12]. Furthermore, a sintering temperature that is too high could promote the diffusion of nickel in the anode to the electrolyte layer, which will introduce partial electronic conductivity into the electrolyte layer and decrease the ionic conductivity. Thus, decreasing the sintering temperature of BZCY4 is crucial for its application as an electrolyte for H^+ -SOFCs.

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Currently, considerable research efforts have been focused on the enhanced sinterability of BZY-based electrolytes at reduced temperatures [13]. Liquid phase sintering (LPS) is commonly used for materials that are hard to sinter. LPS is the process of incorporating a sintering additive in the powder that will melt before the matrix phase. This process has three stages: rearrangement of the grains into a more favorable packing conformation driven by the capillary action of the melting liquid, solution-precipitation and final densification of the solid skeletal network. Generally, the major phase should be at least slightly soluble in the liquid phase during the sintering process, and the additive should melt before any major sintering of the solid particulate network occurs to ensure rearrangement of the grains. Among the various sintering aids, ZnO was found to be a promising candidate because it has a relatively low melting point and zinc can partially incorporate itself into the lattice structure of BZY-based materials. To date, a sintering aid has been introduced during the powder preparation stage or homogeneously mixed with the pre-synthesized main phase by ball milling, followed by forming the powder into a ceramic for sintering [14–16]. In the former case, the sintering aid may already promote the sinterability of the powder and thus make the later sintering of the membrane more difficult. Conversely, although mixing the sintering aid with the pre-synthesized main phase was found to effectively improve sintering at a reduced temperature, cracks formed over the membrane in anode-supported, thin-film electrolyte bi-layer cells. This crack formation suggests that the distribution of the sintering aid in the membrane bulk is inhomogeneous, which introduces large internal stresses and thus creates cracks [17].

In this study, we reported a novel approach for the introduction of a sintering aid that significantly improved the sintering behavior of BZCY4 membranes at reduced temperatures. BZCY4 green membranes were synthesized and impregnated with zinc nitrate, which served as a precursor for the ZnO sintering aid. The results demonstrated that the BZCY4 membranes could be well-densified at 1250 °C with a small amount of ZnO (4 wt%). The obtained thin-film electrolyte fuel cells were further studied by *I*–*V* polarization and showed good performance.

2. Experimental section

2.1. Materials processing

The $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY4) powders were synthesized using an EDTA-citrate-complexing sol-gel process. All starting

materials used in this study were of analytical reagent grade. The precursor powders were prepared by adding stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_4 \cdot 5 \text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ to deionized water containing the proper amount of EDTA and citric acid, which served as the complexing agents. The molar ratio of total metal ions to EDTA and citric acid was set at 1:1:2, and the pH value of the solution was adjusted to approximately 6 by using $\text{NH}_3 \cdot \text{H}_2\text{O}$. After heating the solution to evaporate the water, a transparent purple gel was obtained, which was then pretreated at 240 °C to form a solid precursor. The precursor powders were subsequently calcined at 1000 °C for 5 h to obtain a single crystalline phase. The $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) cathode was also prepared by the same method. The zinc nitrate, which served as the sintering aid, was dissolved in ethanol to produce a 0.08 mol L⁻¹ solution.

2.2. Impregnating the green pellets

The BZCY4 compact green pellets were fabricated by uniaxially pressing the appropriate amount of BZCY4 powders at 300 MPa for 1 min in a stainless steel die with a diameter of 15 mm. While heating the pellets to 50 °C, a proper amount of the zinc nitrate alcohol solution was gradually impregnated into the BZCY4 green pellet porous scaffold with a microliter syringe to precisely control the amount of Zn^{2+} . Two different BZCY4+xZn ($x=2.4 \text{ wt}\%$ or 4 wt%) materials were fabricated with this method. After drying in the oven at 80 °C for 30 min, the impregnated BZCY4 green pellets were sintered at 1250 °C, 1350 °C or 1450 °C for 5 h. The procedure used for impregnating the green membrane electrolytes of SOFCs is shown in Fig. 1. Anode powders were produced by mixing 40 wt % BZCY4 powder and 60 wt% commercial NiO (Chengdu Shudu Nano-Science Co., Ltd.) using high-energy ball milling (Pulverisette 6) and ethanol as a solvent. Polyvinyl butyral (PVB, molecular weight 30,000–45,000) was also added to the anode mixture during the ball milling process to create pores. First, the appropriate amount of anode powder was dry-pressed into a disk-shaped anode substrate with a hydraulic pressure of 150 MPa using a stainless steel die. Subsequently, the BZCY4 green electrolyte membrane was dry-pressed onto the NiO–BZCY4 anode substrate, and the thickness of the layer was controlled by fixing the amount of powder used. After the dual-layer green pellets were heated to 80 °C in air, the Zn sintering aid was introduced into the porous green electrolyte membrane by impregnating the BZCY4 scaffold with the zinc nitrate alcohol solution. To prevent

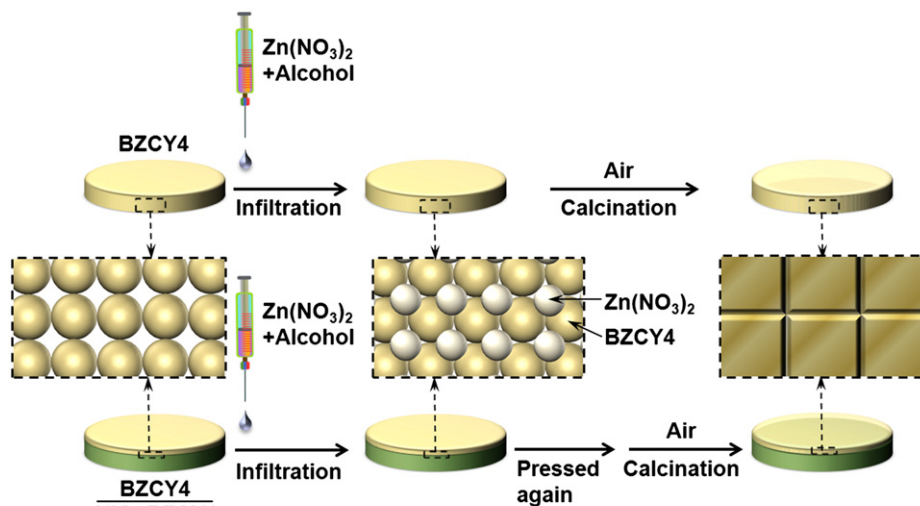


Fig. 1. The experiment schematic diagram for impregnating BZCY4 green membranes with zinc nitrate.

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