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Fabrication of yttria-doped barium zirconate electrolyte with sub-micrometer thickness via low temperature viscous flow sintering

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ABSTRACT

Viscous flow sintering strategy has been adopted to obtain dense sub-micrometer thin yttria-doped barium zirconate (BZY) films fabricated via chemical solution deposition method. Viscous flow sintering was carried out at the temperatures between 475 and 575 °C for 24 h to allow densification in amorphous phase so as to avoid coarsening. The sintered films were finally heat treated at 950 °C for 2 h to eliminate the pores generated due to the removal of residual carbon which remains after low temperature viscous flow sintering. Dense, single-phase perovskite BZY films with thickness between 325 and 375 nm were obtained without the presence of barium carbonate, which is a common issue associated with soft chemical synthesis of BZY. In addition to this, this process does not require sintering aid.

1. Introduction

Successful sintering of a ceramic thin film with required properties necessitates the understanding of the sintering process and related phenomena for the particular material. The common sintering related phenomena include solid state sintering, liquid phase sintering and viscous flow sintering. To obtain the required microstructure, combination of sintering phenomena were often adopted.

Sintering involving both liquid and solid materials is categorized as viscous flow sintering which requires a good amount of liquid to facilitate viscous flow of grain-liquid for the densification without changing the grain shape [1]. This sintering method is of great technological importance because of its comparatively lower processing temperature. Commercial products including metals, glass, and ceramics with almost zero porosity are mostly fabricated through viscous flow sintering [2]. Viscous flow sintering is convenient to be combined with chemical solution deposition (CSD) for the fabrication of ceramic thin film since the precursors of CSD process are in the liquid form. The liquid precursors form an amorphous solid layer on the substrate which acts as the visco-elastic material. This visco-elastic film does not introduce significant shrinkage to the film upon sintering. As a consequence, the sintering carried out in the amorphous stage can reduce the chance of thermo-mechanical failure associated with higher temperature solid state sintering due to the mismatch of shrinkages between the substrate and the film. In addition, the requirement of lower sintering temperature brings about many advantages such as suppression of the evaporation of chemical components, wider range of materials selection and lower fabrication cost.

Yttria-doped barium zirconate (BZY) is presently one of the best alternatives to the state-of-the-art oxide ion-conducting electrolyte material of intermediate to low temperature solid oxide fuel cell (operating at ≤750 °C) due to its good compromise between chemical stability in fuel cell environment and optimum protonic conductivity (1×10^{-2} S/cm at 450 °C) [3–5]. BZY shows proton conduction in the environment of hydrogen and/or water vapor with lower activation energy (0.45–0.65 eV) than that of oxygen ionic conductors [3]. One major drawback of using BZY is the high processing temperature required for its sintering at a minimum sintering temperature of 1300 °C [6], which causes several issues such as Ba evaporation, stoichiometric deviation, phase separation and high process cost. Therefore, research on the reduction of the processing temperature of BZY has been active for many years.

The enhancement of conductivity of electrolyte for LTSOFC is another significant part of LTSOFC research. As the thin film electrolyte is quite promising for lowering the operating temperature of SOFC, efforts have been given to find a suitable cost effective fabrication strategy for the thin film electrolyte of LTSOFC. Several thin film fabrication techniques have been adopted to date to reduce the thickness of the electrolyte [7–18]. Among them, vacuum-based techniques such as pulse laser deposition (PLD), atomic layer deposition (ALD), sputtering, etc. have shown a few remarkable progresses [9–15]. However, PLD has been proved to be inefficient to deposit inhomogeneous and non-stoichiometric BZY thin film [19]. On the other hand, conventional powder-based ceramic film fabrication techniques can be more cost-effective, but they require high temperature processing. The major drawback

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associated with high processing temperature leads to Ba evaporation which is the major concern for Ba containing materials; moreover, only micrometer thick film can be produced. As an alternative to those methods, CSD technique along with right sintering strategy has gained momentum for the fabrication of sub-micrometer thin film [18,20,21] due to its simplicity, high yield and cost effectiveness. In this work, a suitable sintering strategy was developed for the fabrication of sub-micrometer thin BZY films for the application as an SOFC electrolyte. The sintering strategy combines a viscous flow sintering below 600 °C and a subsequent solid state sintering at 950 °C. Dense and crack-free BZY films with thickness of 325–375 nm were successfully fabricated following this fabrication technique. The present paper will emphasize the viscous flow sintering strategy whereas the strategy for solution preparation has been described in our recent publication [18].

2. Experimental

2.1. Preparation of solution

Barium acetate (Ba-Ac), zirconium acetate (Zr-Ac), yttrium nitrate (YNO_3), acetylacetone (Acac), polyvinylpyrrolidone (PVP, mol. wt.: 130,000), polyethylene glycol (PEG, M_n 1500), acetic acid, ammonium hydroxide and ethanol (Sigma Aldrich, Singapore) were used to prepare the BYZ solution. First, Ba-Ac powder was dissolved in acetic acid at 110 °C and then cooled down to the room temperature. Next, Zr-Ac, YNO_3, Acac, PVP, and PEG were added to the solution and dissolved with stirring. The pH of the solution was then adjusted to 4 with the addition of ammonium hydroxide. Ethanol was added to improve the wettability of the solution to the silicon substrates, with the ratio of ethanol to acetic acid maintained to 3:5 by volume. The final solution contains 0.625 mol of cations per liter.

2.2. Fabrication of BZY films

The fabrication of BZY films was executed by three steps of heat treatment, as summarized in Fig. 1a. The first step involved deposition of the chemical solution of BZY precursors solution on (100) silicon substrates by spin coating at 3000 rpm for 30 s, followed by a baking step at 300 °C for 10 min (step I) to remove some of the organics and to dry the films. This step (deposition-coating-baking) was repeated for 4 cycles to establish the desirable film thickness.

The second step (step II) was to perform the viscous flow sintering at four selected temperatures of 475, 525, 575 and 750 °C for separate films, with the holding time varying from 4 to 24 h. The optimized holding time was selected through the observation of the change in microstructure of the film sintered at 475 °C with holding duration.

The third step (step III) was to complete the crystallization and densification of BZY films by solid state sintering at 950 °C for 2 h, which was selected based on our previous result [22].

2.3. Characterization of BZY solution and sintered BZY films

X-ray diffraction (XRD, PANalytical Empyrean system) patterns of the films were recorded with CuKα (λ = 1.54 Å) radiation with the step size of 0.01° within diffraction angle (2θ) of 20 to 60°. The XRD patterns were analyzed using JCPDS data file.

The microstructures of the films were observed under field emission scanning electron microscope (FESEM, JEOL JSM-7600 F), coupled with energy dispersive X-ray spectroscopy (EDS) for stoichiometric analysis.

X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi) was carried out to qualitatively identify the presence of $BaCO_3$, where the instrument is capable of detecting 0.1 at.% of impurity. The spectra were obtained with AlK_α X-ray source with 1483 eV excitation energy under 300 W and 15 kV. The vacuum was maintained at 5×10^{-10} mbar.

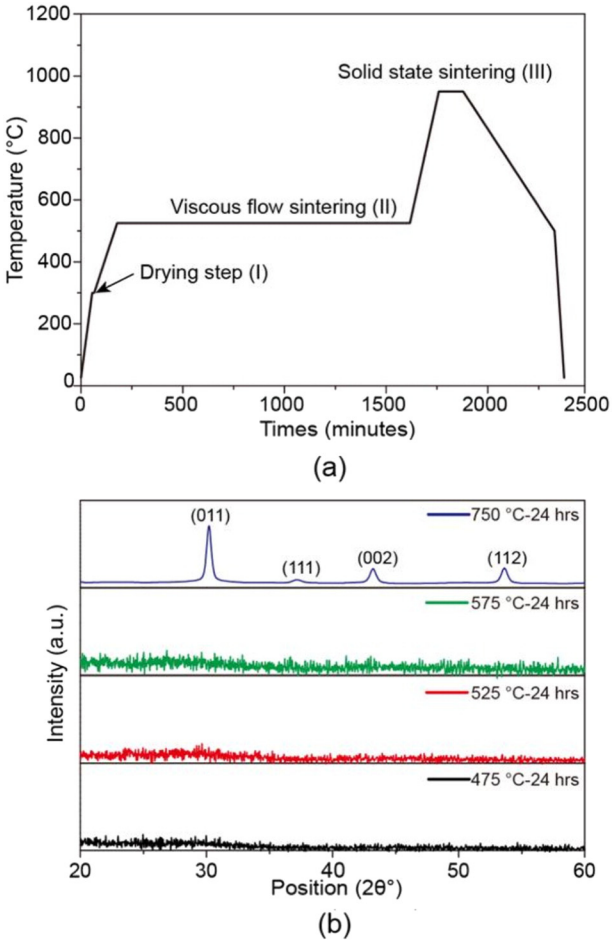

Fig. 1. (a) Sintering schedule and (b) XRD profile.

3. Result and discussion

3.1. Selection of temperature for viscous flow sintering

Since the crystallization temperature for BYZ is around 700 °C [18], the selection of temperature for viscous flow sintering was kept below 600 °C. Fig. 1b shows XRD profile of BZY films after the viscous flow sintering at 475, 525, 575, and 750 °C for 24 h. The higher temperature of 750 °C was purposefully chosen to compare the densification in crystalline stage with the films sintered in the amorphous stage. As shown in Fig. 1b, the films remained amorphous from 475 to 575 °C, while the film became crystalline at 750 °C.

3.2. Microstructural development

The microstructural development of the BZY films after each segment of the heat treatment described in Fig. 1a was observed under FESEM to select the most appropriate temperature range for viscous flow sintering.

3.2.1. After the first step of baking at 300 °C

Fig. 2a shows the microstructure of a BZY film after 4 cycles of spin-coating and baking at 300 °C (stage I in Fig. 1a). The film shows uniform granular structure with a few pores, which could have been generated due to the evaporation of water and organics during baking. No crack was observed on the entire surface of the film.

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