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Short communication

Gas-tight yttria-doped barium zirconate thin film electrolyte via chemical solution deposition technique

Mridula Biswas, Hanlin Xie, Jong Dae Baek, Pei-Chen Su*

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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ABSTRACT

A 500 nm thick yttria-doped barium zirconate (BZY) proton conducting electrolyte film, fabricated via a low-cost and high-throughput chemical solution deposition (CSD) technique, was sintered at a remarkably low temperature of 1000 °C, which is much lower than the typical solid state sintering temperature of minimum 1300 °C. Therefore, the detrimental issues, commonly encountered in solid state sintering, such as barium evaporation and phase separation, were not observed. Gas-tightness of the BZY film was confirmed by 8 h of stable open circuit voltage (OCV) at 1.08 V from a button fuel cell with NiO-BZY anode substrate and LSCF cathode. The application of the film is aimed at the electrolytes of intermediate to low temperature solid oxide fuel cells (SOFCs).

1. Introduction

Solid oxide fuel cells (SOFCs) have been demonstrated as efficient energy conversion devices. The issue pertaining to the commercialization of SOFCs is the high cost associated with high operating temperature, which puts stringent limitation on the selection of materials [1]. The present research focus of SOFCs is on reducing the operating temperature to intermediate to low temperature range (750–300 °C) [2–10]. For low to intermediate temperature SOFCs, yttria-doped barium zirconate (BZY) is the state-of-the-art benchmark material among the proton-conducting perovskite electrolytes. BZY has superior chemical stability in fuel cell environment and has higher ionic conductivity [11] than that of standard oxygen ion-conducting electrolytes such as yttria-stabilized zirconia (YSZ) for high temperature SOFCs. Moreover, decreasing BZY electrolyte thickness is expected to further enhance conductivity, leading to higher cell performance. The thicknesses of Ba containing protonic ceramic electrolyte films fabricated by conventional powder-based sintering process are usually in the micrometer range [12,13]. For sub-micrometer thick BZY films, only vacuum-based thin film deposition methods such as sputtering, pulsed-laser deposition (PLD), and atomic layer deposition (ALD), have been demonstrated [2,5–7,9,10,14,15]. These methods require sophisticated equipment and clean environment to obtain high quality electrolyte, and therefore the process scalability is limited.

Chemical solution deposition (CSD) technique can be the best alternative for the fabrication of sub-micrometer thin BZY film electrolytes for its simplicity, scalability and cost effectiveness [16]. The major advantage of CSD, compared to other conventional film fabrication methods [12,13], is the capability of sintering ceramic materials at low temperature. Particularly, for the processing of Ba containing materials, the low sintering temperature can effectively maintain the stoichiometry of the material by suppressing Ba evaporation, which is a common issue in conventional solid state sintering at high temperatures. As Ba-containing electrolyte materials are highly covalent-bonded, solid state sintering of BZY requires high process temperatures (typically 1300 °C or above) [17–19]. Decreasing the sintering temperature will result in grain growth, but the densification of the electrolyte cannot be achieved. Therefore, a common practice is to add sintering aids such as ZnO, NiO, BaO-CuO eutectic melt, etc., to improve the densification of the electrolyte [17–19].

CSD technique helps in lowering the sintering temperature of ceramic film as the precursors of CSD technique contains 'OH' and 'OR' groups which forms metal-oxide framework via hydrolysis-polycondensation reaction and delays crystallization until higher temperature. The delayed crystallization facilitates densification process at lower temperature in the disordered state (amorphous state) of the film prior to the attainment of its ordered and stable crystalline state. Therefore, not only the CSD method but also the sintering schedule plays important role in lowering the sintering temperature.

This work demonstrates the successful fabrication of BZY electrolyte thin film with sub-micrometer thickness on the BZY-NiO

* Corresponding author.
E-mail address: peichensu@ntu.edu.sg (P.-C. Su).

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anode substrate at a remarkably low temperature of 1000 °C. The CSD method modified with the dispersed BZY nanoparticles and with a carefully controlled sintering schedule effectively eliminates the drying and constraint sintering cracks of the thin film. The entire process does not require addition of any sintering aid, which often results in second phase formation. This modified method is capable of producing crack-free, polycrystalline, single phase and stoichiometric BZY thin film at a low temperature of 1000 °C. The gas-tightness of the film was verified through the open circuit voltage (OCV) experiment on a button fuel cell, which is the first successful electrochemical measurement reported for submicrometer thin BZY electrolyte fabricated by CSD process.

2. Experimental

2.1. Preparation of solution

The chemical solution of BZY film was prepared by dissolving barium acetate (Ba-ac), zirconium acetate (Zr-ac), yttrium nitrate (YNO_3), acetylacetone (Acac), polyvinylpyrrolidone (PVP, m.wt.: 130,000), and polyethylene glycol (PEG) (Sigma Aldrich, Singapore) in a common solvent of acetic acid. Firstly, Ba-ac was dissolved in acetic acid at 110 °C. After the solution was cooled down to room temperature, Zr-ac, Acac, YNO_3, PVP and PEG were added to Ba-ac solution. Ethanol was added to improve the wettability of the solution to the anode substrate; the ratio of ethanol to acetic acid was 3:5 by volume. The solution had the strength of 0.6 M.

To control the shrinkage and prevent crack in BZY film on BZY-NiO anode after sintering, BZY nanoparticles were dispersed into the solution. The BZY powder was obtained via calcining a part of the above solution at 800 °C. The calcined BZY powder was ball milled with 42 wt.% of PVP (m. wt.: 10,000) [20] for 24 h to minimize the agglomerate size, where PVP plays the role of dispersant for the milled agglomerates. The milled agglomerates of the average size range of 0.5–1.5 μm, as 10 wt.% of BZY within the solution, were then added to the chemical solution and further reduced to the size below 150 nm using an ultrasonic probe for 30 min for better dispersion.

2.2. Fabrication of BZY films

The solution with the dispersed BZY nanoparticles was deposited on both Si_3N_4 passivated Si and polished BZY-NiO anode substrates by spin coating at a spinning rate of 4000 rpm for 20 s. After coating, the films were baked in oven at 300 °C for 10 min to remove a part of the organics for the spin-coating of the subsequent layers. Repetitions of spin-coating and oven baking were performed for 4 cycles to obtain a film of around 500 nm thickness after sintering. The baked films were then sintered at several different temperatures from 600 to 1000 °C for 2 h for densification and further characterizations.

2.3. Characterizations of solution and BZY films

The stability of the solution over time was confirmed with Fourier transformed infrared (FTIR) spectroscopy between the wave number range of 4000–500 cm^{-1} at room temperature. To verify the crystalline phases of BZY films sintered at various temperatures between 600–1000 °C, X-ray diffraction (XRD, PANalytical Empyrean system) pattern was recorded with CuKα (λ = 1.54 Å) radiation with the step size of 0.01°. The XRD data of BZY electrolyte with micrometer-sized grains was chosen as reference for the estimation of peak broadening. Approximate crystallite size was determined using Scherrer equation [21]. The microstructures of the BZY films and the agglomerate size of externally added powder were observed under field emission scanning electron microscope (FESEM, JEOL JSM-7600 F, operating voltage 15 kV), combined with energy dispersive X-ray spectroscopy (EDX) 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 atomic percent of impurity.

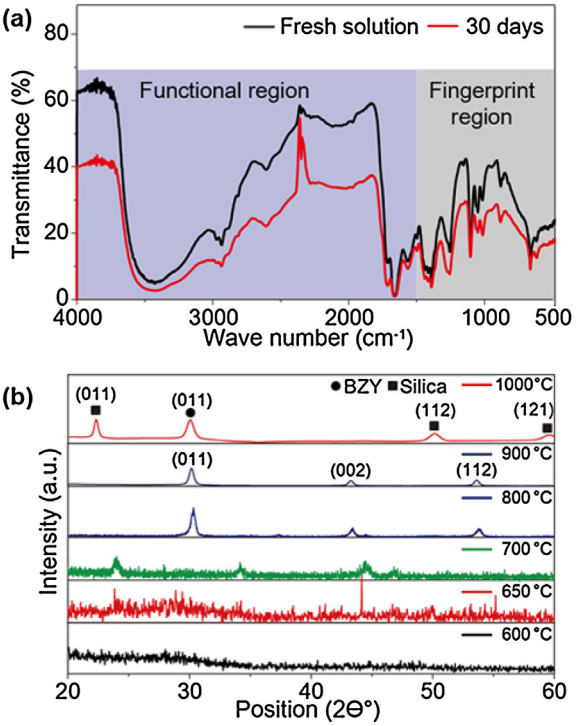

Fig. 1. (a) FTIR spectra showing the stability of the formulated BZY solution over time. (b) Crystallinity development of sintered BZY films with temperature.

2.4. Electrochemical study

A button cell was fabricated by spin-coating BZY nanoparticle-dispersed solution onto a sintered BZY-NiO anode substrate, followed by sintering of the electrolyte film at 1000 °C. The cathode was printed by brush painting of the lanthanum strontium cobalt ferrite (LSCF) over 1 cm^2 of area on BZY electrolyte and sintered at 800 °C. The OCV of the button cell was recorded at 450 °C using an electrochemical potentiostat (Autolab PGSTAT302) with pure hydrogen and air supplied as fuel and oxidant, respectively. In-situ reduction of the anode was carried out overnight at 400 °C in pure hydrogen before OCV was recorded.

3. Results and discussion

3.1. Stability of solution

Fig. 1a shows the FTIR spectra of both the fresh solution and the solution aged for one month. Two spectra overlap each other. The functional group region shows that both the solutions have same functional groups, while the overlapped fingerprint region demonstrates no distortion in metal-oxygen coordination within one month of time. The chemical property of the solution was stable for month. However, solution showed sedimentation of particles after a few days. Therefore, the solution was always ultrasonicated before each use. The heat generated due to ultrasonication did not change the chemical properties of the solution.

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