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Fabrication of scandium stabilized zirconia thin film by electrostatic spray deposition technique for solid oxide fuel cell electrolyte

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ABSTRACT

A cost-effective and promising simple deposition method, electrostatic spray deposition (ESD), was used to fabricate dense scandium stabilized zirconia (ScSZ) thin films. The effect of solvent mixtures on their surface morphology was investigated. The films deposited using a mixed ethanol-butyl carbitol solvent with high boiling point showed higher smoothness compared with those deposited using ethanol and a mixture of ethanol and ethylene glycol, respectively. Single-phase ScSZ dense films were formed within 2 h at a low deposition temperature of 450 °C. Analysis of as heat-treated films using scanning electron microscope and atomic force microscope also indicated the formation of the uniform, smooth and dense thin films even at a low densification temperature. Furthermore, the ScSZ film deposited under the optimal condition showed the maximum in electrical conductivity of approximately 0.33 S cm^{-1} at a low operating temperature of 800 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) have been considered as a highly efficient electric power energy source due to their environmentally friendly processes. However, the high operating temperature of SOFCs has a significant influence on the constraint of material systems and maintenance costs. Hence, the trend in the reduction of operating temperature is of great interest in SOFC development. The lower operating temperature has several advantages, such as shorter start-up time, longer stack lifetime and possibility to use metallic alloy interconnects between the individual cells instead of expensive ceramic materials. Typically, there are two approaches to reduce the operating temperature: the decrease in electrolyte thickness and the use of alternative electrolyte materials with higher ionic conductivity [1]. The required properties for SOFC electrolyte are high oxygen ion conductivity and dense structure to achieve greater movement of oxygen ion from cathode to anode and to suppress the diffusion of oxidant and fuel from electrode into electrolyte. The metal oxide materials, in general, are used as the electrolyte for SOFCs, such as yttria stabilized zirconia and rare earth doped ceria [2,3] which have the fluorite crystal structure. Scandium stabilized zirconia (ScSZ) electrolyte was employed in the present work as a solid electrolyte due to its high oxygen ion conductivity at the intermediate temperature range [4]. In another approach, a variety of fabrication techniques, such as screen-printing, sol–gel, tape casting and dry pressing, have been widely used to prepare films in both laboratory and industrial practices. To achieve a better control of the film quality, other techniques including electrochemical vapor deposition [5], plasma spray [6], metal-organic chemical vapor deposition [7] and flame assisted vapor deposition [8] are presently available for the fabrication of SOFC components. However, these methods generally require special raw materials and targets, sophisticated equipment and well-controlled atmosphere. Furthermore, the films fabricated by some of these techniques require post-deposition heat treatment which is costly and time consuming. Compared with other techniques, electrostatic spray deposition (ESD) is a simple setup, with relatively high film growth rate, non-vacuum deposition conditions and a well-controlled structure and composition [9–11].

In spite of enormous literature reported for the preparation of ScSZ thin films by different techniques, attempts are still being made to improve their electrical conductivity at lower operating temperature. With very few studies on the part of EDS of ScSZ thin films, the fabrication of dense and crack-free ScSZ thin films at low densification temperature was investigated. The present work is focused on the effect of solvent mixtures in the precursor solution on the morphological properties of ESD-deposited ScSZ films to achieve dense and crack-free thin films with high electrical conductivity at operating temperatures lower than those previously reported.

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2. Experimental details

10ScSZ (90 mol% ZrO_2–10 mol% Sc_2O_3) thin films were deposited on a stainless steel substrate through a vertical ESD setup used in our previous works [11–13]. Precursor solutions were prepared by dissolving zirconyl nitrate hydrate (~27% (Zr, gravimetric), Fluka) and scandium nitrate hydrate (99.9%, Aldrich Chemical) in different three solvents: ethanol (95%, commercial grade, boiling point of 78 °C), mixed solvent of ethanol and butyl carbitol (99%, Carlo Erba, boiling point of 230 °C) in the ratio of 80:20 (defined as Et/Bu) and mixed solvent of ethanol and ethylene glycol (99.5%, Carlo Erba, boiling point of 198 °C) in the ratio of 80:20 (defined as Et/EG). The butyl carbitol and ethylene glycol were used for the mixed solvent systems because their high boiling point is suitable for the control of film deposition at lower evaporation rate. Their total concentration was fixed at 0.01 M. The obtained precursor solution was pumped through the nozzle at a flow rate of 0.84 ml h^{-1}. The applied voltage, deposition time and nozzle-to-substrate distance were controlled at 15 kV, 2 h and 13 cm, respectively. The suitable deposition temperature of different solvent systems for the ScSZ films was determined by thermogravimetric analysis (Perkin Elmer, TGA7) under air atmosphere. The TGA result of all precursor solutions showed major weight losses below 400 °C, which corresponded to the evaporation of solvent and water and the decomposition of organic components and nitrate in the precursor solution. The spraying temperature was thus controlled at 450 °C.

The phase composition and crystal structure of the as-deposited and annealed films were characterized by X-ray diffraction (XRD) with an automated (Bruker D8 advance) diffractometer equipped with Cu$K\alpha$ radiation source. The film morphology and composition were examined by a scanning electron microscope (SEM; Model S3400N, Hitachi) coupled with energy dispersive X-ray (EDX) analyzer. The film roughness was measured by an atomic force microscope (AFM; Model SPA 400, Seiko) in dynamic force mode. Additionally, the effect of temperature on the crystallinity of ScSZ films was investigated. Therefore, the as-sprayed films were annealed at 700 °C for 2 h in air. The electrical conductivity of the annealed films was measured by direct current four point probe technique under oxygen gas using a Keithley 6517 A.

3. Results and discussion

SEM micrographs of the as-deposited ScSZ films at 450 °C and post-deposition heat-treated films at 700 °C using various solvents are shown in Fig. 1. The dense microstructures with crack-free surface were achieved for all solvents even at a low deposition temperature of 450 °C. Similar results have been obtained in our previous studies for the deposition of dense samarium doped ceria under low temperature conditions [11]. Nevertheless, the films prepared using ethanol and Et/EG solvents showed more spherical agglomerates on the surface compared with those prepared using Et/Bu solvent. This may be explained in that the charged droplets were atomized under the electric field onto the heated substrate, leading to the formation of film due to the evaporation of the solvent and the decomposition of the precursor solution. The evaporation of the solvent during spraying before landing occurred incompletely, leading to a spreading of the charged droplets before solidification. In the precursor solution containing lower boiling point solvent, the droplets are drier before arriving at the substrate surface, resulting in the powder-like agglomerates of tiny particles emerging from the dense underlayer

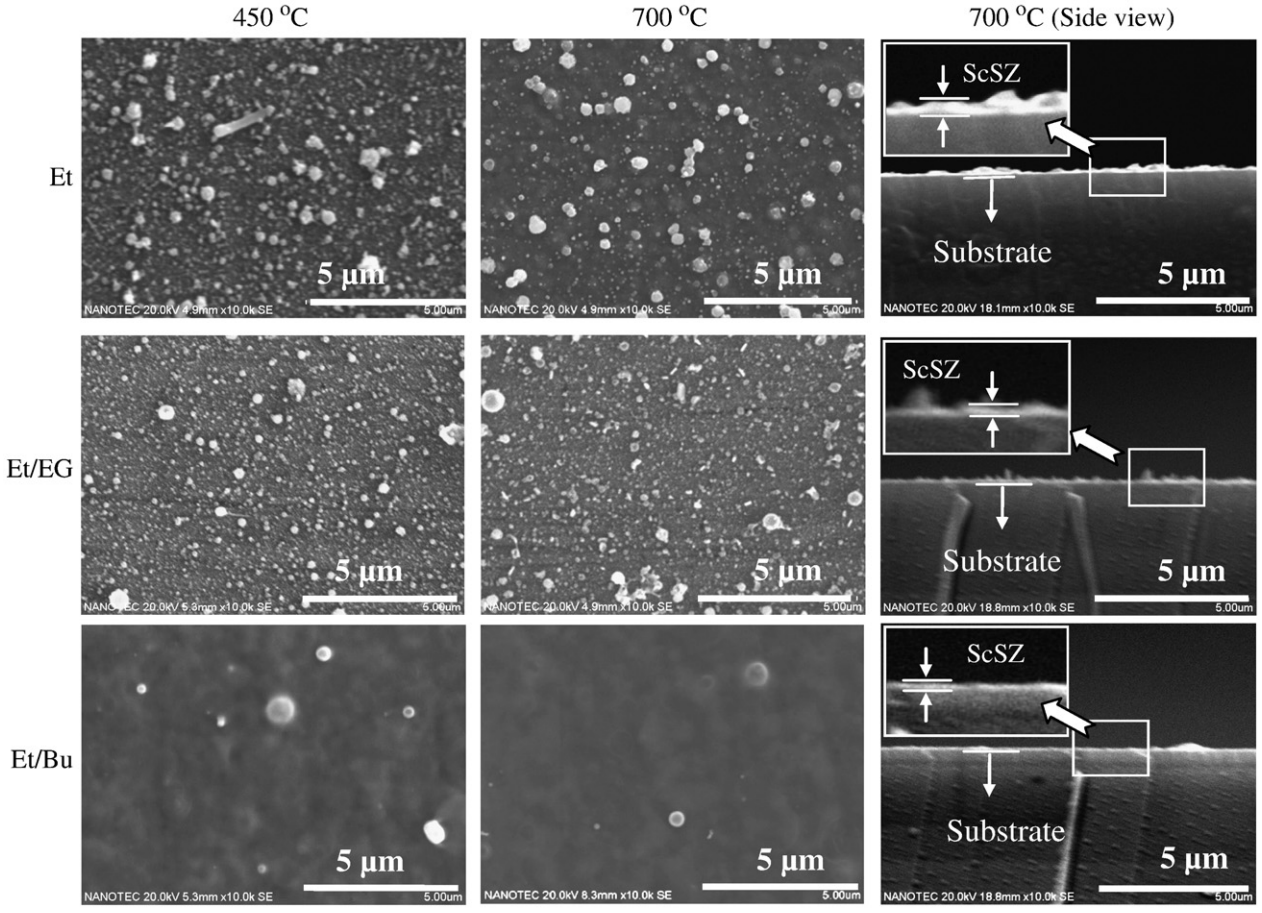

Fig. 1. Top-view SEM images of as-deposited ScSZ coating deposited at 450 °C and heat-treated ScSZ films at 700 °C and cross-sectional SEM images of heat-treated ScSZ films at 700 °C using different solvents.