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Rapid densification of sol–gel derived yttria-stabilized zirconia thin films

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ABSTRACT

A method based on X-ray reflectivity was used to study the densification behavior of 8 mol% yttria-stabilized zirconia for use in solid oxide fuel cells. Sol–gel derived thin electrolyte films were prepared via spin coating. Subsequent microwave-assisted rapid thermal annealing at 650–1000 °C resulted in crack-free 70 nm thin films. A maximum density of approximately 95% was achieved within 5 min at 1000 °C. X-ray photoelectron spectroscopy depth analysis on the thin films showed that the shorter annealing times, as opposed to conventional heating, resulted in lower Si concentrations at the top surface and at the substrate interface.

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1. Introduction

Yttria-stabilized zirconia (YSZ) is one of the most commonly used electrolyte materials in solid oxide fuel cells (SOFC). Due to the thermal activation of ionic conduction through the electrolyte membrane, fuel cells mostly operate at high temperatures (800–1000 °C). The high operational temperatures result in long start-up times, high material costs, and material degradation, which contribute to a reduced life time of the cell.

A reduction of the operating temperature to intermediate temperatures (400–700 °C) would enable the use of cheaper materials (e.g., stainless steel supports), and concurrently reduce the thermal stresses in the system [1]. A major problem, however, is that the reduced temperature leads to an increased Ohmic resistance in the electrolyte membrane, and thus to a reduction of the overall ionic conductivity. This can be compensated by decreasing the electrolyte film thickness. It has been shown that a decrease of film thickness from 15 μm to 500 nm for a 10 mol% YSZ electrolyte allowed for the reduction of the operational temperature from 700 to 525 °C (for an area-specific resistance of 0.15 $\Omega \cdot cm^2$) [2]. Thin electrolyte films are currently prepared using a wide array of deposition techniques, like e.g., pulsed laser deposition (PLD) [3,4], spin coating [5], spray casting [6], and sputtering techniques [7].

The fabrication of micro-SOFCs based on thin film electrolytes for portable power generation has received considerable attention due to their high power output, exceeding 200 $mW \cdot cm^{-2}$ at temperatures <600 °C [8–10]. Micro-electro mechanical systems (MEMS) technology based on Si supports and back-etching procedures is often employed for their fabrication [7,9,11,12]. However, the use of Si in the fabrication procedure may lead to the formation of undesirable glassy siliceous phases [13–15]. These phases segregate at the grain boundaries and severely impede the ionic conduction through the electrolyte [16]. The high temperatures necessary to form dense membranes may thus be problematic due to the high mobility of Si. Consequently, fast densification may be an advantageous approach to achieve high density, while impeding the Si mobility.

Here, we describe the densification behavior of 8 mol% YSZ thin films on SiO_2/Si (001) and Al_2O_3 (0001) single crystalline substrates by microwave-assisted rapid thermal annealing (RTA) and conventional heating. The thin film density was determined by using X-ray reflectivity (XRR) method described earlier [17]. Thin films with a density of approximately 95% were obtained within 5 min at 1000 °C when RTA was employed. The short times at high temperatures, resulted in less siliceous phases in the thin films compared to films annealed by conventional heating. In addition, the usefulness of the XRR method for thin film density determination is illustrated in the presented densification study.

2. Experimental section

2.1. Chemicals and materials

Zirconium (IV) *n*-propoxide ($Zr[(OC_3H_7)]_4$), 70 w/w% in propanol and yttrium (III) nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$, purity 99.9%) were purchased from Alfa Aesar GmbH. Glacial acetic acid (99.8%), 2-methoxyethanol (99.3%) and 1-propanol (99.9%) were acquired from Sigma-Aldrich. All chemicals were used as-received from the suppliers without any further purification. Due to its high reactivity, zirconium (IV) *n*-propoxide was stored and handled in a water-free environment (<0.1 ppm H_2O).

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2.2. Sol–gel precursor preparation

A 1.0 mol·dm^{-3} solution of zirconium (IV) *n*-propoxide in 2-methoxyethanol was made in a glove box and stirred for 24 h under nitrogen atmosphere. After addition of glacial acetic acid, the reactants were allowed to mix for 5 min; subsequently, an yttrium (III) nitrate hexahydrate solution in 1-propanol was added. The sol was hydrolyzed by addition of water, and further diluted with 2-methoxyethanol to a final concentration [Zr] = 0.6 mol·dm^{-3}. The sol was prepared at room temperature, with final molar ratios of Zr:HAc:H_2O = 1:4:5. The amount of yttrium (III) was equivalent to 8 mol% Y_2O_3 to ZrO_2, i.e., to form 8YSZ. More details on the sol–gel precursor solution preparation can be found elsewhere [18].

2.3. Substrate preparation

Prior to thin film deposition, 10 nm thermally oxidized SiO_2/Si (001) and single crystal sapphire (10 × 10 × 0.5 mm^3, (0001) orientation; CrysTec) substrates were cleaned with a jet of pressurized CO_2 on a hot plate at 250 °C and subsequently treated with oxygen plasma (Harrick Plasma, Ithaca, USA) operating at 24 W for 150 s to remove organic residues attached to the surface. The substrates were used directly after this surface treatment.

2.4. Thin film preparation

Thin films were prepared by spin-coating the sol–gel precursor using a Laurell spin-coater (Model WS-400B-6NPP/LITE/AS/OND). Substrates were held in place using a vacuum stage and the deposition chamber was continuously purged with dry nitrogen gas. All films were obtained by rotating the samples for 40 s at 3000 rpm. Directly after thin film deposition, the samples were placed on a hot plate at 150 °C, on which they were allowed to dry for 1 h. Subsequently, the samples were annealed for 1 h in a pre-heated microwave oven (MW; MultiFAST, Milestone, Sorisole, Italy) or 12 h in a conventional oven at temperatures ranging from 650–1000 °C.

2.5. Thin film characterization

X-ray powder diffraction (X'Pert Pro MRD, PANalytical, Almelo, The Netherlands) was used to confirm the formation of the YSZ phase. An X-ray diffractogram of the crystalline YSZ phase can be found in [18]. Atomic force microscopy (AFM; Dimension Icon, Bruker Nano, Santa Barbara, CA, USA) was used to determine the surface roughness of the thin films. Per sample, the RMS surface roughness was determined on three different locations with an area of 5 × 5 μm^2, using the Gwyddion software package (version 2.25).

2.5.1. Density determination

The thin film density was determined using a recently developed method based on X-ray reflectivity [17]. X-ray reflectivity measurements were carried out using an X'Pert Pro MRD diffractometer (PANalytical, Almelo, The Netherlands). Samples were scanned under very low incident angles using Cu Kα irradiation (λ = 1.5418 nm), from 2θ = 0.4–1.0° (step sizes of 0.002°; 1.5 s per step; 1/16° slits) with an acceleration voltage and current of 45 kV and 40 mA, respectively.

2.5.2. X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) was used to determine the atomic concentration of Si in thin films annealed using rapid thermal annealing and conventional heating. Spectra were acquired using a Quantera SXM scanning probe XPS (Physical Electronics) with a monochromatic Al Kα X-ray at 1486.6 eV. The data were further analyzed using the PHI Multipak (version 9.4.0.7) software package. A depth profile was created by sputtering with an Ar ion beam at 3 kV in an area of 3 × 3 mm^2.

3. Results and discussion

One of the main requirements for electrolyte membranes in fuel cells applications is a high film density (i.e., gas impermeable). Knowledge of the grain growth, thin film density, and the densification behavior will enable optimized processing conditions, in which e.g., the times at high temperatures can be minimized. This is especially important for the fabrication of micro-SOFCS and the integration in Si-based MEMS technology. Due to the high mobility of Si, fast densification is necessary to limit the segregation in the electrolyte's grain boundaries.

3.1. Crystallite growth

Samples were annealed for t = 0, 5, 15, 30 and 60 min in a pre-heated microwave oven at temperatures ranging from 650 to 1000 °C. In the case of 0 s the sample was only heated to the desired temperature and then cooled. After the heat treatment, the crystallite sizes were determined by analyzing the XRD peak broadening of the (111) peak of YSZ using Scherrer's equation, see Fig. 1. The figure shows that irrespective of the substrate's choice, the crystallites grew from approximately 6.6 to 17 nm after annealing at 650 and 1000 °C, respectively. Scherrer et al. found significantly different crystallite sizes for samples deposited on Al_2O_3 and Si substrates [16]. After annealing for 20 h at 1000 °C, the average crystallite sizes were approximately 130 and 48 nm, respectively. Silicon is known to impede the grain growth of YSZ even in very low concentrations [19,20], due to segregation in the grain boundaries (GB) and the subsequent reduction of GB mobility. Segregation of Si was already observed after heat treatment for 5 h at 800 °C [21]. However, due to the different heating profiles (i.e., thermal shock) and the annealing temperatures of our samples, strain from the substrate played a more important role. Instead, crystallite growth may be inhibited due to compressive strain exerted by the substrate, since the thermal expansion coefficient of 8YSZ (10.8 · 10^{-6} K^{-1}) [22] is significantly higher than that of Si (2.6 · 10^{-6} K^{-1}) [23] and Al_2O_3 (5.5 · 10^{-6} K^{-1}; from datasheet Crystec GmbH), respectively.

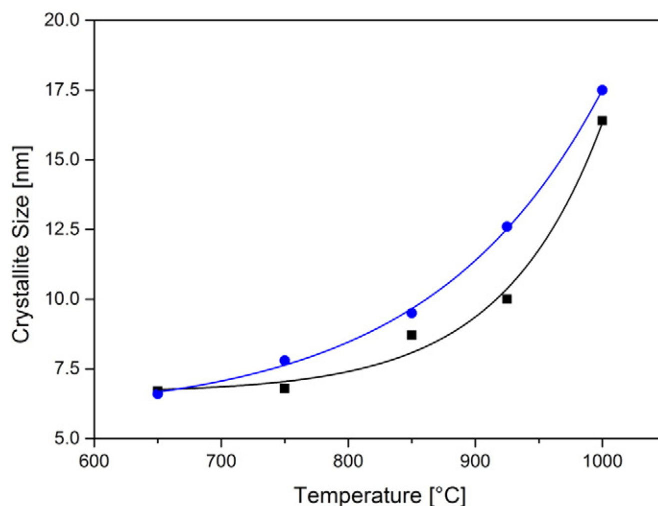

Fig. 1. Crystallite sizes of an 8YSZ thin film after microwave-assisted rapid thermal annealing for 1 h at 650–1000 °C on a SiO_2/Si (black) and Al_2O_3 (blue) substrates.

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