



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 Ω·cm²) [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·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 SiO₂/Si (001) and Al₂O₃ (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[(OC₃H₇)₄], 70 w/w% in propanol and yttrium (III) nitrate hexahydrate (Y(NO₃)₃·6H₂O, 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 H₂O).

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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:H₂O = 1:4:5. The amount of yttrium (III) was equivalent to 8 mol% Y₂O₃ to ZrO₂, 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 SiO₂/Si (001) and single crystal sapphire (10 × 10 × 0.5 mm³, (0001) orientation; CrysTec) substrates were cleaned with a jet of pressurized CO₂ 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 μm², 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 mm².

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 Al₂O₃ 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 Al₂O₃ (5.5 · 10⁻⁶ K⁻¹; from datasheet Crystec GmbH), respectively.

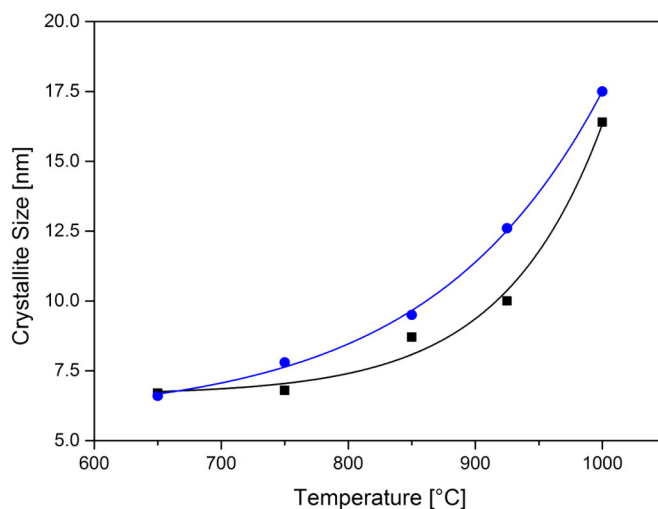


Fig. 1. Crystallite sizes of an 8YSZ thin film after microwave-assisted rapid thermal annealing for 1 h at 650–1000 °C on a SiO₂/Si (black) and Al₂O₃ (blue) substrates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. X-ray reflectivity method

The densification behavior of the 8YSZ thin films was monitored by using a method based on X-ray reflectivity (XRR) [17]. With XRR in general, samples are measured under very low incident beam angles. The material's density is directly related to the critical angle of external reflection, which is ideally marked by a sudden drop of intensity (i.e., step function). For real films, however, the determination of the critical angle is more difficult due to the gradual intensity decrease below the critical angle, rather than a sudden intensity drop. The used method is based on the determination of a so-called *pseudo-critical angle*, defined as the 3rd derivative of the XRR curve versus angle [17]. The measured samples are then compared with a calibration curve, from which the thin film density can be calculated. The calibration curve is based on simulations of the investigated samples (Fig. 2a–b) with manually adjusted densities. For each simulated density, the *pseudo-critical angle* was determined. Fig. 2c shows typical experimental XRR curves for thin films deposited on SiO₂/Si and Al₂O₃ substrates. The *pseudo-critical angle* for both curves was located at $2\theta \sim 0.6^\circ$. Beyond this angle, a rapid intensity drop and Kiessig fringes (i.e., oscillations) were observed [24], which are associated with the interface roughness and film thickness, respectively.

3.3. Thin film densification

The results obtained from analysis using the XRR method are presented in Fig. 3. It clearly illustrates that the thin film densification by rapid thermal annealing proceeded very fast. A maximum density was achieved within 5 min of isothermal heating, irrespective of the annealing temperature. In addition, the choice of substrate had no significant effect on the final density. Maximum densities of approximately 86.3, 91.4, and 95.0% were achieved after annealing at 650, 850, and 1000 °C, respectively. Scanning electron microscopy images showed that the resulting films were crack-free, smooth and consisted of fine grained crystallites (see Fig. 4).

In order to achieve a film density of ca. 95% using a conventional oven, a dwell time of 12 h at 1000 °C (heating/cooling rates 5 °C min⁻¹) was necessary. Naturally, such a long time at elevated temperature increases the susceptibility of Si to diffuse into the thin film,

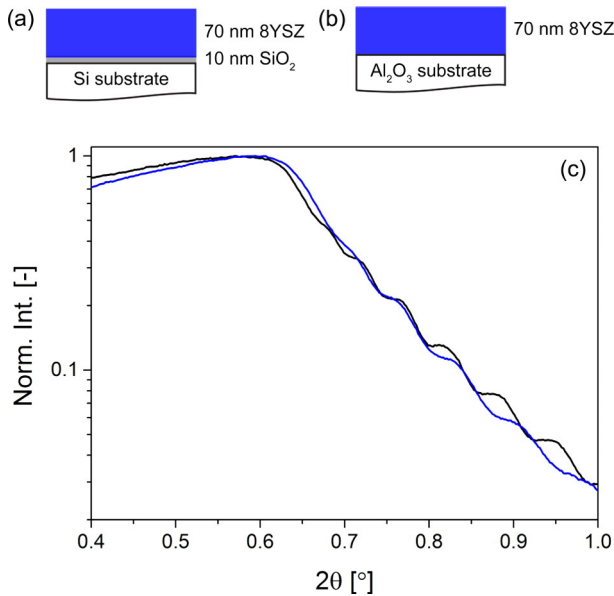


Fig. 2. Schematic representation of the investigated system: a 70 nm 8YSZ film on (a) 10 nm SiO₂/Si (001); and (b) Al₂O₃ (0001). (c) Typical X-ray reflectivity curves of thin films annealed for 1 h at 1000 °C on SiO₂/Si (black) and Al₂O₃ (blue), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

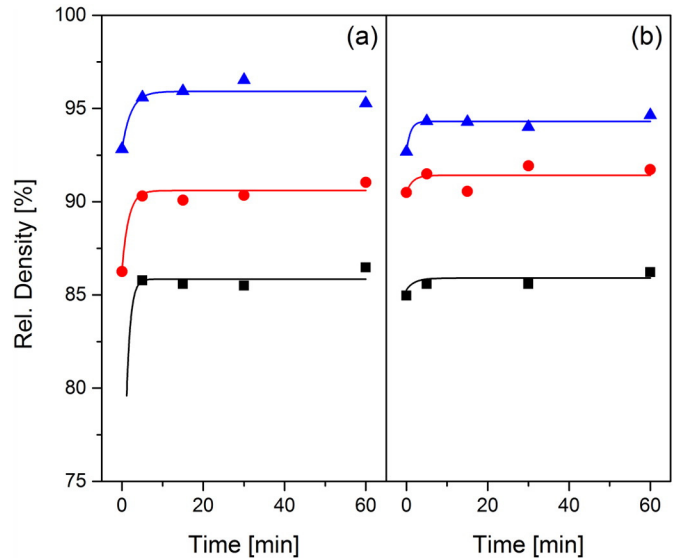


Fig. 3. Densification behavior of 8YSZ films on (a) Al₂O₃ (0001) and (b) SiO₂/Si (001) substrates at 650 °C (black), 850 °C (red), and 1000 °C (blue), respectively. The absolute measurement error is ~1%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

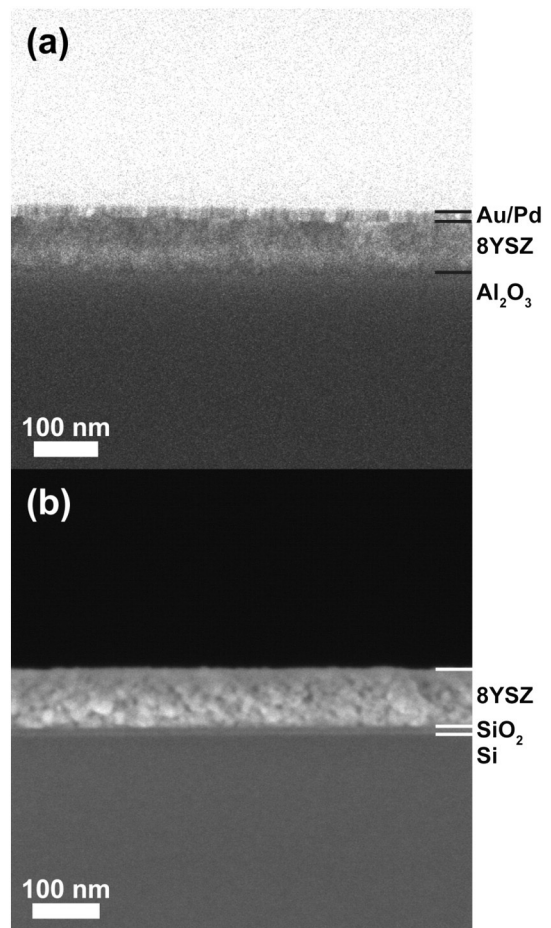


Fig. 4. Scanning electron microscopy cross-sections of 8YSZ films annealed for 1 h at 1000 °C in a microwave oven on (a) Al₂O₃ (0001) and (b) SiO₂/Si (001) substrates, respectively. For better imaging stability, sample (a) was tilted and a ~15 nm Au/Pd layer was deposited on top of the 8YSZ film.

and segregate at the GBs. Furthermore, the average crystallite sizes after conventional heat treatment were approximately 2 times larger than after RTA.

3.4. Thin film chemistry

X-ray photoelectron spectroscopy was used to investigate the composition of the surface and bulk region of the thin films. Segregation of Y and Si species in YSZ electrolytes is a well-known problem. The lowering of the interfacial energy is the driving force of segregation, and results in the tendency to transport the segregated species from the bulk to the surface [25]. Theunissen et al. showed with Auger electron spectroscopy (AES) that independent of the bulk Y concentration, the surface layer (2–4 nm) consisted up to 36 at.% Y [13]. De Ridder et al. used low-energy ion scattering (LEIS) and observed concentrations in a 5 Å top-layer ranging from 36 to 60 at.% Y for 3YSZ and 10YSZ, respectively [14]. Secondary ion mass spectroscopy (SIMS) experiments between 800 and 1400 °C showed that at 1000 °C, the highest Y enrichment was found, irrespective of oxidizing or reducing atmosphere [25]. It was postulated that the effect of temperature on segregation results from a competition between thermodynamic and kinetic factors.

Fig. 5 shows the depth profiles of thin film (on SiO₂/Si substrates) annealed in a microwave and a conventional oven. Both samples show different Y segregation behavior at the top surface (<8 nm) of the thin films. Although the film annealed using a conventional oven showed a Y enrichment of approximately 13 at.%, a Y depletion of 10–30 at.% was observed for the MW annealed sample. The degree of enrichment or depletion is determined by comparing the [Y] / ([Zr] + [Y]) ratio of measured samples with what is theoretically expected for the 8YSZ composition. The Y depletion is most likely related to the thermal shock of the RTA method due to non-equilibrium segregation. As a result, different concentration gradients in the film may be expected

[25]. Prolonged heating for 1 h at 1000 °C in a microwave oven, however, resulted in a Y enrichment of 13 at.%, equal to the film annealed using a conventional oven (data not shown). Although the Y concentration is fairly constant throughout both films, differences in Si concentrations at the top surface and substrate interface were observed. Samples annealed for 12 h at 1000 °C showed a Si concentration of ca. 4.1 at.% at the top surface, compared to no Si for the sample annealed in the microwave oven. In the interior of both films, the Si concentration remained <0.5 at.%. This is consistent with the values found by Scherrer and co-workers [16]. They found a surface and bulk concentration of approximately 9 and 1.1 at.%, respectively, for thin films deposited on SiO₂ single crystal substrates, after annealing for 20 h at 1000 °C. Near the film-substrate interface, significant differences in Si concentrations were observed between the two heating protocols. Especially for the conventionally heat treated sample, the Si concentration increased rapidly at approximately 15 nm distance from the substrate interface. For a fast annealed sample, the increase was only observed at ca. 5 nm from the substrate.

The effect of RTA on the surface and bulk composition of an 8YSZ film deposited on Al₂O₃ is presented in Fig. 6. The major advantage of using sapphire substrates is that Si diffusion does not play a role in the densification and film composition. No Si was found at the surface, and the film interior showed an average Si concentration of <0.3 at.%. The minor impurities may arise from impurities from the used chemicals. The Y enrichment at the surface was reduced to ~5 at.%.

To summarize, the results show that the rapid thermal annealing can be effectively used to obtain dense electrolyte films within several minutes. Faster annealing seems to reduce the degree of Si diffusion, and may allow for improved fabrication of micro-SOFCs based on MEMS technology. Two-step sintering techniques may be explored to further exploit the difference between grain boundary diffusion and migration [26].

4. Conclusions

A method for the density determination of sol-gel derived 8YSZ thin films was used to study the densification behavior on various substrates. Microwave-assisted rapid thermal annealing was employed to form dense films in the temperature range of 650 to 1000 °C. A maximum relative density of approximately 95% was reached after annealing for 1 h at 1000 °C. However, no significant densification was observed after 5 min. The shorter annealing times at high temperature, as opposed to long conventional heating procedures, resulted in lower Si concentrations at the top surface of the films and at the substrate interface.

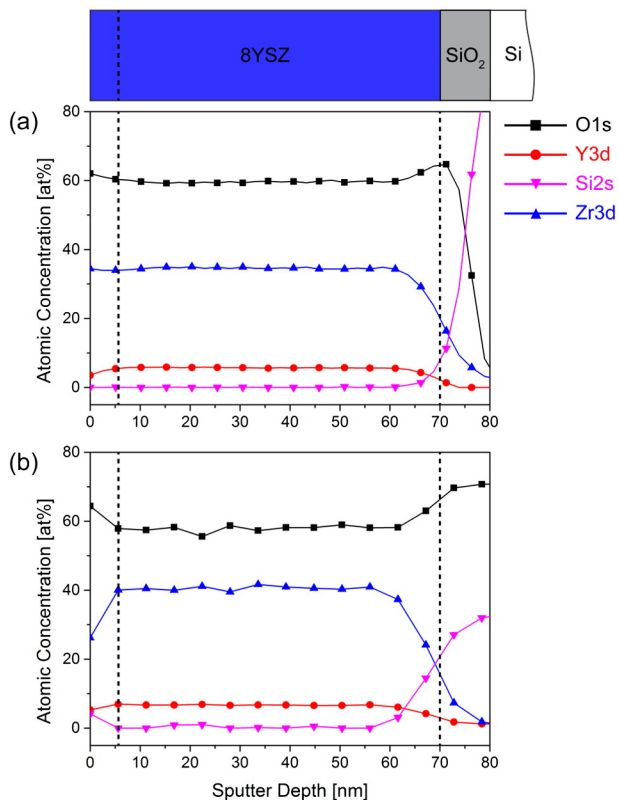


Fig. 5. Elemental depth profile from XPS for a 70 nm 8YSZ thin film on a SiO₂/Si (001) substrate, annealed in (a) microwave oven for 5 min at 1000 °C; and (b) conventional oven for 12 h at 1000 °C.

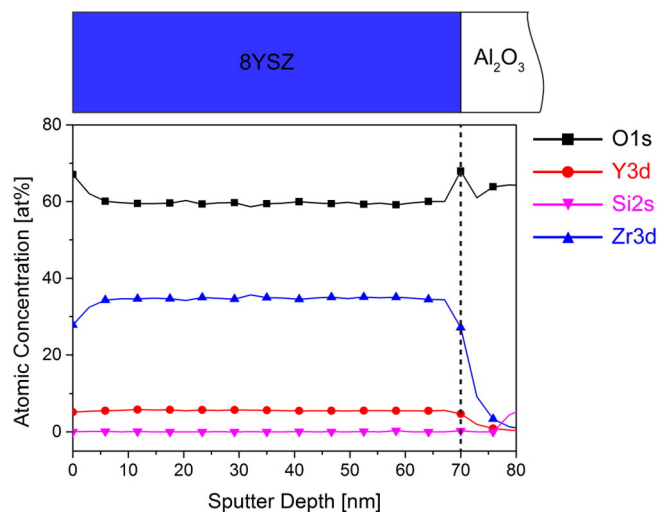


Fig. 6. Elemental depth profile from XPS for a 70 nm 8YSZ thin film on an Al₂O₃ (0001) substrate, annealed in a microwave oven for 5 min at 1000 °C.

Ceramics with 95% relative density typically have only isolated porosity left, and are impermeable to gases, which is a sufficient requirement for SOFC electrolytes. Rapid thermal annealing in combination with sol–gel derived electrolyte thin films may thus prove to be a good alternative for Si-based micro-SOFC devices.

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References

- [1] J.W. Fergus, Electrolytes for solid oxide fuel cells, *J. Power Sources* 162 (2006) 30–40.
- [2] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, *Nature* 414 (2001) 345–352.
- [3] X. Chen, N.J. Wu, L. Smith, A. Ignatiev, Thin-film heterostructure solid oxide fuel cells, *Appl. Phys. Lett.* 84 (2004) 2700–2702.
- [4] H.S. Noh, H. Lee, B.K. Kim, H.W. Lee, J.H. Lee, J.W. Son, Microstructural factors of electrodes affecting the performance of anode-supported thin film yttria-stabilized zirconia electrolyte (~1 μm) solid oxide fuel cells, *J. Power Sources* 196 (2011) 7169–7174.
- [5] K. Chen, Z. Lü, N. Ai, X. Huang, Y. Zhang, X. Xin, R. Zhu, W. Su, Development of yttria-stabilized zirconia thin films via slurry spin coating for intermediate-to-low temperature solid oxide fuel cells, *J. Power Sources* 160 (2006) 436–438.
- [6] P. Charpentier, P. Fragnaud, D.M. Schleich, E. Gehain, Preparation of thin film SOFCs working at reduced temperature, *Solid State Ionics* 135 (2000) 373–380.
- [7] H. Huang, M. Nakamura, P. Su, R. Fasching, Y. Saito, F.B. Prinz, High-performance ultrathin solid oxide fuel cells for low-temperature operation, *J. Electrochem. Soc.* 154 (2007) B20–B24.
- [8] Z. Shao, S.M. Haile, J. Ahn, P.D. Ronney, Z. Zhan, S.A. Barnett, A thermally self-sustained micro solid-oxide fuel-cell stack with high power density, *Nature* 435 (2005) 795–798.
- [9] M. Tsuchiya, B.K. Lai, S. Ramanathan, Scalable nanostructured membranes for solid-oxide fuel cells, *Nat. Nanotechnol.* 6 (2011) 282–286.
- [10] U.P. Muecke, D. Beckel, A. Bernard, A. Bieberle-Hütter, S. Graf, A. Infortuna, P. Müller, J.L.M. Rupp, J. Schneider, L.J. Gauckler, Micro solid oxide fuel cells on glass ceramic substrates, *Adv. Funct. Mater.* 18 (2008) 3158–3168.
- [11] P.C. Su, F.B. Prinz, Nanoscale membrane electrolyte array for solid oxide fuel cells, *Electrochem. Commun.* 16 (2012) 77–79.
- [12] A. Evans, A. Bieberle-Hütter, J.L.M. Rupp, L.J. Gauckler, Review on microfabricated micro-solid oxide fuel cell membranes, *J. Power Sources* 194 (2009) 119–129.
- [13] G.S.A.M. Theunissen, A.J.A. Winnubst, A.J. Burggraaf, Segregation aspects in the ZrO₂–Y₂O₃ ceramic system, *J. Mater. Sci. Lett.* 8 (1989) 55–57.
- [14] M. De Ridder, R.G. Van Welzenis, A.W.D. Van Der Gon, H.H. Brongersma, S. Wulff, W.F. Chu, W. Weppner, Subsurface segregation of yttria in yttria stabilized zirconia, *J. Appl. Phys.* 92 (2002) 3056–3064.
- [15] K.V. Hansen, K. Norrman, M. Mogensen, TOF-SIMS studies of yttria-stabilised zirconia, *Surf. Interface Anal.* 38 (2006) 911–916.
- [16] B. Scherrer, A. Rossi, J. Martynczuk, M.D. Rossell, A. Bieberle-Hütter, J.L.M. Rupp, R. Erni, L.J. Gauckler, Impact of substrate material and annealing conditions on the microstructure and chemistry of yttria-stabilized-zirconia thin films, *J. Power Sources* 196 (2011) 7372–7382.
- [17] S.A. Veldhuis, P. Brinks, T.M. Stawski, O.F. Göbel, J.E. Ten Elshof, A facile method for the density determination of ceramic thin films using X-ray reflectivity, *J. Sol–Gel Sci. Technol.* 71 (2014) 118–128.
- [18] S.A. Veldhuis, A. George, M. Nijland, J.E. ten Elshof, Concentration dependence on the shape and size of sol–gel-derived yttria-stabilized zirconia ceramic features by soft lithographic patterning, *Langmuir* 28 (2012) 15111–15117.
- [19] J. Zhao, Y. Ikuhara, T. Sakuma, Grain growth of silica-added zirconia annealed in the cubic/tetragonal two-phase region, *J. Am. Ceram. Soc.* 81 (1998) 2087–2092.
- [20] M. Aoki, Y.M. Chiang, I. Kosacki, L.J.R. Lee, H. Tuller, Y. Liu, Solute segregation and grain-boundary impedance in high-purity stabilized zirconia, *J. Am. Ceram. Soc.* 79 (1996) 1169–1180.
- [21] A. Bernasik, K. Kowalski, A. Sadowski, Surface segregation in yttria-stabilized zirconia by means of angle resolved X-ray photoelectron spectroscopy, *J. Phys. Chem. Solids* 63 (2002) 233–239.
- [22] H. Hayashi, T. Saitou, N. Maruyama, H. Inaba, K. Kawamura, M. Mori, Thermal expansion coefficient of yttria stabilized zirconia for various yttria contents, *Solid State Ionics* 176 (2005) 613–619.
- [23] P. Becker, P. Scyfried, H. Siebert, The lattice parameter of highly pure silicon single crystals, *Z. Phys. B: Condens. Matter* 48 (1982) 17–21.
- [24] H. Kiessig, Interferenz von Röntgenstrahlen an dünnen Schichten, *Ann. Phys.* 402 (1931) 769–788.
- [25] M.A. Idris, T. Bak, S. Li, J. Nowotny, Effect of segregation on surface and near-surface chemistry of yttria-stabilized zirconia, *J. Phys. Chem. C* 116 (2012) 10950–10958.
- [26] I.W. Chen, X.H. Wang, Sintering dense nanocrystalline ceramics without final-stage grain growth, *Nature* 404 (2000) 168–171.