



Short communication

Micro-solid oxide fuel cells using free-standing 3 mol.% yttria-stabilised-tetragonal-zirconia-polycrystal electrolyte foils

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ABSTRACT

Ultrathin 3 mol.% yttria-stabilised-tetragonal-zirconia-polycrystal (Y-TZP) foils with thicknesses of 1–10 μm are fabricated by a new wet-chemical processing route. The foils are free-standing, semi-transparent and flexible. The in-plane electrical conductivity of the Y-TZP foil is 0.03 S m^{-1} at 500°C . Cross-plane impedance measurements with sputtered Pt electrodes yield two arcs, of which the high-frequency arc is attributed to the ohmic resistance of the electrolyte and the low-frequency arc to the electrode–electrolyte interface. A symmetrical micro-solid oxide fuel cell (SOFC) is designed using this ultrathin free-standing Y-TZP foil as the electrolyte and sputtered Pt electrodes. An open-circuit voltage of 0.98 V and a maximum power density of 12 mW cm^{-2} are measured at 500°C . These results prove the feasibility of this approach to the fabrication of miniaturised planar SOFCs without the need for microfabrication.

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1. Introduction

Solid oxide fuel cells (SOFCs) are intended for stationary and mobile applications and can be designed with a planar or tubular geometry [1]. For distributed power generation in the kilowatt to megawatt range, the SOFCs are operated at elevated temperatures between 650°C and 1000°C to ensure a high ionic conductance of the electrolyte. In planar designs, the electrolyte is a ceramic tape with a thickness of several hundred microns or a thick film of 5–20 μm in the case of anode-supported cells [2]. In tubular designs, the SOFC is electrode-supported with an electrolyte film that is several tens of microns thick. More recently, SOFCs were proposed for portable applications in the watt to kilowatt range, such as leisure cogeneration systems, hybrid electric vehicles and portable devices [3]. Very new research focuses on the development of miniaturised SOFCs, so-called micro-SOFCs, for powering small portable devices in the milliwatt to watt range [4]. Micro-tubular SOFCs consist of millimetre to centimetre long tubes with a diameter down to 100 μm which are bundled together into a stack and can deliver up to 1.1 W cm^{-2} at 600°C [5–8]. This tubular configuration is highly suitable for short start-up times, and thermal stresses can be minimised. However, problems related to the interconnects and the current collection of micro-SOFC tubes assembled in a stack remain to be solved [5]. Planar micro-SOFCs follow a chip-based approach and are fab-

ricated by micro-electro-mechanical-system (MEMS) techniques which involve processing-intensive, time-consuming and expensive microfabrication steps [4,9–17]. The micro-SOFC membrane consists of a cathode and an anode separated by a dense oxygen-ion conducting electrolyte with a total thickness of $\sim 1 \mu\text{m}$. Different microfabricated planar micro-SOFC membrane designs are discussed in the literature [9–17]. However, all designs require a micromachinable substrate, and often only small electrochemically active areas per substrate area can be achieved due to the mechanical stability of the membrane and the anisotropic etching angle of 54.7° in the case of silicon wafers [15]. The resulting free-standing thin-film membranes are rather fragile and are subject to differential stresses between the substrate and the deposited films when heated to the micro-SOFC operation temperature [13]. The thermomechanical stability of the membrane is, however, essential to ensure reliable operation during the thermal cycling of the micro-SOFC.

In this paper, we present a new planar micro-SOFC fabrication approach that does not involve any microfabrication steps but uses ultrathin 1–10 μm thin 3 mol.% yttria-stabilised-tetragonal-zirconia-polycrystal (Y-TZP) free-standing foils fabricated by wet-chemical processing. It should be noted that even though thin films are thinner with typical thicknesses up to several hundred nanometres, we are reporting on foils which better compare to ceramic tapes. Typical tapes are in the range of a few tens to several hundred micrometres and are thus much thicker. Y-TZP was chosen, as it has an increased fracture toughness compared to 8 mol.% yttria-fully-stabilised-zirconia (8YSZ) [18]. However, this foil fabrication route is, in principle, also applicable to 8YSZ. As the ohmic

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resistance of these micrometer-thick Y-TZP foils is expected to be only marginally larger than that of the 8YSZ thin-film electrolytes of several hundred nanometres thickness, a SOFC comprising the Y-TZP foil as the electrolyte can be operated in a similar temperature range as typical micro-SOFC membranes. Furthermore, the wafer stack and packaging will only be slightly larger than those for MEMS-based micro-SOFCs.

Another advantage of the Y-TZP foil is the possibility of integrating electrode materials that require annealing temperatures of above 600 °C to obtain the desired microstructural and electrochemical properties. Since the Y-TZP foils are sintered at 1350 °C, these electrolyte foils can be annealed at high temperatures for electrode preparation without any degradation. This is not possible for thin-film yttria-stabilised-zirconia electrolytes in microfabricated micro-SOFCs in which crystallisation, grain growth and the micromachinable substrate (e.g. silicon wafer) have to be taken into consideration, since the thin film electrolytes were processed at low temperatures and will change when annealed at higher temperatures for electrode fabrication.

In the first part of this paper, the fabrication and microstructural characteristics of the Y-TZP foil are described. Then, the electrical and electrochemical properties of the Y-TZP foil are investigated and a symmetrical micro-SOFC based on these Y-TZP electrolyte foils is demonstrated.

2. Experimental

The 12 vol.% Y-TZP powder suspension (3 mol.% yttria-stabilised-tetragonal-zirconia TZ-3Y-E, Tosoh, Japan) with 5 wt.% steric stabiliser sorbitan monooleate (Span80, Fluka, Switzerland) in toluene (Fluka, Switzerland) is ball-milled with 2 mm TZP milling balls for 4 days [19]. The Y-TZP foil is fabricated by off-centred spin-coating (custom-made device, 500 rpm, +100 rpm s⁻¹ acceleration, 180 s) of the Y-TZP powder suspension onto a flat-pressed graphite foil substrate (5 cm × 5 cm, Sigraflex® TH, SGL Group, Germany) as described in [19]. The 5 cm × 5 cm green film is sintered in air up to 1350 °C for 2 h (heating and cooling rates of 15 °C min⁻¹ and 5 °C min⁻¹, respectively), whereby the graphite foil is burnt off and free-standing 4 cm × 4 cm ultrathin Y-TZP foils with a thickness of 1–10 µm are formed. Further processing details can be found in Ref. [19].

The thickness of the Y-TZP foils was determined both gravimetrically (using the foil area and a density of 6.2 g cm⁻³ for Y-TZP) and from cross-sectional scanning electron microscopy images (SEM, Leo 1530, Carl Zeiss SMT).

The in-plane electrical properties of a 6.8 µm thick Y-TZP foil (1 cm × 3 cm) were measured using a four-point setup [20]. The Y-TZP foil was placed on a sapphire single crystal substrate (Stettler Sapphire AG, Switzerland), and four Pt electrodes (thickness of ~150 nm) were sputtered onto the foil through a shadow mask (SCD 050 Sputter Coater, Bal-Tec, 40 mA, 0.05 mbar, 120 s). On each sputtered Pt stripe, a flat-pressed Pt wire (125 µm diameter) covered with Pt paste (C3605P, Heraeus GmbH, Germany) was placed on the Y-TZP foil and glued to the sapphire substrate with two bonds of ceramic binder (Firag Ebmatingen, Switzerland). The four-point electrical d.c. conductivity measurements were performed using a digital multimeter (197 A, Keithley Instruments, USA). All the conductivity experiments were performed in air as a function of temperature (250–1000 °C) with heating and cooling rates of 3 °C min⁻¹.

The electrochemical characterisation of a 6.7 µm Y-TZP foil electrolyte was carried out by impedance spectroscopy cross-plane measurements. The 1 cm × 1 cm Y-TZP foil was placed on a sapphire single crystal substrate (Stettler Sapphire AG, Switzerland) which had a thin Pt layer sputtered through a 1 cm × 1 cm shadow mask

(SCD 050 Sputter Coater, Bal-Tec, 40 mA, 0.05 mbar, 240 s) and was covered with Pt paste. The top electrode was achieved by brushing Pt paste (C3605P, Heraeus GmbH, Germany) onto a flat-pressed Pt-mesh current collector (52 mesh, Alfa Aesar, Germany) which was carefully placed onto the Y-TZP foil and attached with ceramic glue. The impedance data was recorded between 250 °C and 750 °C in steps of 50 °C with heating and cooling rates of 3 °C min⁻¹ using an IM6 workstation (Zahner Elektrik, Germany) in a frequency range of 1 Hz to 4 MHz with an a.c. excitation amplitude of 100 mV. All the measurements were performed in air without a bias. The impedance data from the second thermal cycle was used for the evaluation in order to avoid any effects from burning off the Pt paste during the first heating. The impedance data was analysed and fitted using the ZView software (version 3.2c, Scribner Associates, USA).

For the micro-SOFC testing, the 4 cm × 4 cm Y-TZP foil was cut down to 2 cm × 2 cm in order to remove the wrinkled parts on the edge and to use only the middle part which was almost flat. 80 nm Pt electrodes with a diameter of 1 cm were sputtered (PVD Products, USA, 100 W, 75 mTorr Ar, 246 s) onto a 3.0 µm thick 2 cm × 2 cm Y-TZP foil electrolyte. This micro-SOFC was then carefully placed between two 2 cm × 2 cm Foturan® glass ceramic wafers, with a 0.5 cm hole in the bottom piece and a 1 cm hole in the top piece. The Foturan® wafer pieces were etched according to the procedure described in [21]. The micro-SOFC was clamped between two aluminium oxide spacer rings covered with ceramic paper (Fiberfrax FT1, Unifrax, USA) for sealing.

Electrochemical testing was carried out between 250 °C and 550 °C, under air (cathode) and ~3 vol.% humidified N₂:H₂ 4:1 (anode). All gas flows (60–500 sccm) were controlled by mass flow controllers (El-Flow, Bronkhorst, Switzerland). The heating and cooling rates were 1 °C min⁻¹. Current collection was performed via flat-pressed 80 µm Pt wires. Electrochemical impedance spectra and current–voltage curves were recorded with an IM6 workstation (Zahner Elektrik, Germany) at the open-circuit voltage (OCV).

3. Results and discussion

The recently developed fabrication technique from our laboratory for the preparation of free-standing ceramic foils was used to make thin 3 mol.% Y-TZP foils [19]. The off-centred spin-coating of the powder suspension onto the 5 cm × 5 cm graphite foil substrates ensured that the resulting green films had a homogeneous thickness. After sintering, the Y-TZP foils have dimensions of 4 cm × 4 cm and a thickness of between 1 µm and 10 µm (Fig. 1). The foils are semi-transparent, very flexible, and slightly wrinkled due to the three-dimensional shrinking of the green film during sintering [19]. The foils are easy-to-handle with tweezers as shown in [19] and have an increased mechanical stability compared to the thin-film electrolytes typically used in micro-SOFCs. The SEM cross-sectional image of a 3 µm thin Y-TZP foil sintered at 1350 °C reveals a dense microstructure with round grains of about 300 nm (Fig. 1(b)). Larger grains are related to small chunks originating from the TZP milling balls used for processing of the powder suspension. No thickness gradient within the Y-TZP foils was observed in the cross-sectional SEM images, and the surface roughness is negligible compared to the thickness of the Y-TZP foil.

The electrical characterisation of an Y-TZP foil with a thickness of 6.8 µm was carried out by four-point d.c. in-plane conductivity measurements on a sapphire single crystal (Fig. 2(a)). The Arrhenius-type diagram of the conductivity vs. the inverse temperature is shown in Fig. 2(b). The conductivity of the 3 mol.% Y-TZP foil is 0.03 S m⁻¹ at 500 °C. From a linear fit of the data, an activation energy of 1.01 ± 0.03 eV was obtained. These data are in good

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