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Magnetron sputtered gadolinia-doped ceria diffusion barriers for metal-supported solid oxide fuel cells

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HIGHLIGHTS

- Sputtered gadolinia-doped ceria barriers implemented in metal-based SOFCs.
- Sr diffusion along column boundaries in the barrier layer is observed.
- Tuning deposition parameters makes 0.6 μm GDC effectively stop Sr diffusion.
- Area specific resistance of 0.34 Ω cm^2 is achieved for cells operating at 650 °C.

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ABSTRACT

Gadolinia-doped ceria (GDC) thin films are deposited by reactive magnetron sputtering in an industrial-scale setup and implemented as barrier layers between the cathode and electrolyte in metal-based solid oxide fuel cells consisting of a metal support, an electrolyte of ZrO_2 co-doped with Sc_2O_3 and Y_2O_3 (ScYSZ) and a Sr-doped lanthanum cobalt oxide cathode. In order to optimize the deposition of GDC to obtain high electrochemical performance of the cells, the influence of film thickness and adatom mobility is studied. The adatom mobility is varied by tuning the deposition temperature and substrate bias voltage.

A GDC layer thickness of 0.6 μm is found to effectively block Sr diffusion when bias voltage and deposition temperature is tuned to promote dense coatings. The adatom mobility has a large influence on the film density. Low temperature and bias voltage result in underdense column boundaries which function as channels for Sr to diffuse to the GDC–ScYSZ interface. By tuning deposition temperature, bias voltage and film thickness area specific resistances down to 0.34 Ω cm^2 are achieved at cell tests performed at an operating temperature of 650 °C.

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1. Introduction

At intermediate temperatures, metal-supported solid oxide fuel cells (SOFCs) designs are of interest as an alternative to ceramic supported cells in view of their low materials cost and high robustness, which is advantageous both in the production line and in applications such as auxiliary power units [1]. During fabrication of metal-supported cells, care must be taken to avoid corrosion of the steel components. This involves processing at lower temperatures or in reducing atmospheres. Therefore traditional cathodes developed for ceramic cells, such as (La,Sr)$MnO_{3-\delta}$ (LSM) and (La,Sr)(Co,Fe)$O_{3-\delta}$ (LSCF), cannot be transferred directly to metal-supported cells, as these cathodes requires sintering in air at 1000–1200 °C to achieve good adhesion of the cathode [1].

(La,Sr)$CoO_{3-\delta}$ (LSC) is another cathode material which has been found to be suitable for metal-supported cells as it sinters readily at temperatures below 900 °C and has a good electrochemical performance at intermediate temperatures [2,3]. However, LSC is incompatible with yttria-stabilized zirconia (YSZ) traditionally used for SOFC electrolytes, as strontium from the cathode reacts with zirconium from the electrolyte to form $SrZrO_3$ which has a low ionic

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conductivity [4–6] and therefore a detrimental effect on cell performance. This reaction is known to take place during sintering at temperatures above 1000 °C [7] but has also been observed at intermediate temperatures down to 650 °C [5,8]. To avoid this reaction a gadolinia-doped ceria (GDC) barrier can be applied between electrolyte and cathode. Several studies have shown the suitability of GDC as a barrier for Sr diffusion [3,9–11]. GDC can be applied by screen printing, spraying, or tape casting followed by sintering at temperatures above 1200 °C. In itself GDC is an excellent ionic conductor but at these temperatures a solid solution of YSZ and GDC is formed which has significantly lower oxide ion conductivity than the pure form of both compounds [7,12,13]. Alternatively the GDC barrier can be applied by physical vapor deposition (PVD) techniques such as pulsed laser ablation [7], electron beam evaporation [14], or magnetron sputtering [3,11,15,16]. GDC barriers prepared by PVD techniques stops Sr diffusion better than barriers prepared by wet ceramic techniques. This may be due to higher density of such layers [3,11], which can be achieved at lower temperatures. Low-temperature deposition is particularly important for metal-supported cells, which cannot withstand as high temperatures as ceramic cells. When depositing on metal-supported cells it is reasonable to set 400 °C as the upper limit deposition temperature as the oxygen present for the reactive deposition process may oxidize the metal-support at elevated temperatures which reduces cell performance. When synthesizing GDC coatings for ceramic SOFCs high deposition temperatures are often used to grow coatings sufficiently dense to prevent Sr diffusion [11,17]. In a recent study, we showed using a model system that the main route for Sr diffusion in sputtered GDC films are along underdense column boundaries which can be densified and/or limited by increasing the adatom mobility [18]. Besides the deposition temperature, other ways to increase adatom mobility includes increasing the ionization degree of the plasma and applying a substrate bias. Especially the combination of elevated temperatures and the application of substrate bias have been found to be an effective method to tune the microstructure when depositing GDC for ceramic-supported SOFC [16].

In this work, the influence of substrate bias voltage, film thickness, and deposition temperature on reactively sputtered GDC barriers for metal-supported cells are investigated. The purpose of the study is twofold. First, we demonstrate how deposition of GDC can be tuned to form effective diffusion barriers to metal-supported cells. Furthermore, we prove the Sr diffusion mechanism to be as previously demonstrated in a model system [18].

2. Experimental details

GDC ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$) coatings were deposited by reactive pulsed magnetron sputtering using a CC800/9 SinOx industrial batch coater from CemeCon AG. Two metallic Ce–Gd targets (90:10 at.%) with purity 99.9% and size 88 × 500 mm^2 were sputtered in mixed Ar/O_2 atmosphere. The purity of the applied gasses were 99.999%. The coatings were grown on 20 × 20 mm^2 metal-supported half cells mounted on a stage carrying out a two-fold planetary rotation during deposition. The half cells consisted of a metal support and a ScYSZ (ZrO_2 co-doped with Sc_2O_3 and Y_2O_3) electrolyte. Before starting the deposition the chamber was pumped down to a base pressure below 1 mPa and the substrates were heated to a temperature slightly higher than the deposition temperature of either 300 °C or 400 °C. The total pressure was 0.4 Pa during deposition. A pulsed DC power supply (Advanced Energy, Pinnacle II) delivered 2 kW to each sputtering target with a repetition frequency of 50 kHz and a duty cycle of 50%. Before the deposition series, the voltage hysteresis loop for the system was determined. The films were deposited operating in the transition region between the metallic and poisoned state of the targets in order to obtain both high deposition rate and stoichiometric films. In order to run the system in the transition region, the cathode current was used as an oxygen partial-pressure feedback signal for controlling the reactive sputtering process. A pulsed DC bias with a frequency of 350 kHz and a reverse time of 1 μs was applied to the mounting stage/samples and used to vary the kinetic energy of ions bombarding the growing film. In order to study the influence of deposition parameters on the ability of the GDC barrier coatings to prevent Sr diffusion, three sets of depositions were performed where the substrate bias voltage, deposition temperature, and film thickness were varied, respectively.

The metal-supported half cells used in this work were fabricated by tape casting of the metal-support (a 22% Cr-based stainless steel alloy), the cermet backbone and the ScYSZ electrolyte followed by co-sintering in a reducing H_2/Ar atmosphere under proprietary conditions above 1000 °C. The active fuel cell anode was formed by infiltrating the porous metal-support and cermet with the electrocatalytic active $Ce_{0.8}Gd_{0.2}O_{1.9}$ and Ni. The fabrication procedure and infiltration route of the metal-supported half-cells is described in detail elsewhere [19]. After deposition of the GDC barrier coating on the ScYSZ electrolyte layer, cathodes with a composition of 50 vol.% GDC–50 vol.% LSC $(La_{0.6}Sr_{0.4})_{0.99}CoO_{3-\delta}$ were printed with an area of 0.5 cm^2. The cathode layer was fired in situ in air flow during the cell test start-up at a maximum temperature of 800 °C.

The cells were tested in a set-up also described in Ref. [3]. Platinum meshes placed in parallel with the cell were used to contact the cell to the set-up, and the fuel and oxidant gas was supplied to the cell via alumina tubes perpendicular to the cell active area. Polarization curves were collected at 650 °C, with fuel consisting of 4 vol.% H_2O–96 vol.% H_2 on the anode side, and air or O_2 on the cathode side, and using flows of 100 ml min^{-1} (equivalent to 6 L h^{-1}).

Scanning electron microscopy (SEM, Nova 600 nanoSEM from FEI) was performed on cross-sections of the samples in order to determine the thickness and morphology of the GDC barrier. In order to prepare the samples for SEM they were either vacuum embedded in Epofix (Struers, Denmark), and polished to 1 μm or simply broken into two pieces. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX) were performed on film cross-sections using a Tecnai G2 TF 20 U-Twin 200 kV FEGTEM from FEI. Cross-section samples were prepared by mechanically polishing down to a thickness of approximately 55 μm followed by ion milling using Precision Ion Polishing System (PIPS; Gatan) operated at 5 keV and 5° incident angle with argon ions and a final polishing step at 2 keV for 10 min. X-ray diffraction (XRD) measurements in the θ–2θ geometry were carried out with a Bruker D8 Discover diffractometer using CuKα radiation. Single-line profile analysis was performed with the TOPAS 2.1 [20] software using a pseudo-Voigt peak profile [21]. The size of the coherently diffracting domains, which was used as a measure for the average grain size, and the microstrain were determined from the integral breadths of the Lorentzian and Gaussian constituents of the pseudo-Voigt function, respectively.

A few as-deposited GDC barriers were annealed in a tube furnace (Heraeus, Ro 4/25) in an Ar atmosphere in order to study effect of elevated temperatures on the film microstructure.

3. Results and discussion

3.1. Influence of adatom mobility on the GDC barrier

In order to study the effect of adatom mobility on the ability of the GDC barrier to prevent Sr diffusion, two series of depositions were carried out where either the substrate bias or the deposition

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