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Spray pyrolysis of doped-ceria barrier layers for solid oxide fuel cells

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ABSTRACT

Gadolinium doped ceria ($Ce_{0.8}Gd_{0.2}O_{2-x}$-CGO) layer fabricated by spray pyrolysis is investigated as the diffusion barrier for solid oxide fuel cell. It is deposited between the $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ cathode and the yttria stabilized zirconia electrolyte to mitigate harmful interdiffusion of elements. The parameters of the fabrication process are linked to the measured area specific resistances of the symmetrical cells and the efficiency of the fuel cells. Results show, that application of 800 nm thick barrier effectively hinder negative reactions, while 400 nm thick layer is sufficient to prevent degradation of the Ohmic resistance.

1. Introduction

Widespread market introduction of solid oxide fuel cell (SOFC) technology requires a significant reduction of the fabrication costs. To achieve this goal the development is driven to operate fuel cells at temperatures below 800 °C [1,2]. These fuel cells are usually anode supported cells with cathode made of the (La,Sr)(Co,Fe)$O_{3-\delta}$ (LSCF) perovskite family [3,4]. Due to LSCF high mixed ionic and electronic conductivity and excellent catalytic activity, the cathode overpotential is significantly reduced in comparison to the outdated (La,Sr)$MnO_{3-\delta}$ (LSM) cathode material [5]. However, a major disadvantage to the use LSCF as a SOFC cathode is its chemical reaction with the 8 mol% yttria-stabilized zirconia (YSZ, $Zr_{0.84}Y_{0.16}O_{2-x}$) electrolyte. It leads to the formation of two insulating phases: $La_2Zr_2O_7$ and $SrZrO_3$ [6,7]. These phases contribute to an increase of the Ohmic and polarization loss, which leads to the decrease of the overall performance of the cell [8]. The same insulating phase formation was reported also for the $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) cathode [9–12]. A diffusion barrier interlayer is thus necessary at the cathode/electrolyte interface to prevent cations diffusion during the cell sintering and operation. An ideal diffusion barrier should be thin, dense and fabricated by a fast, cost-efficient, and up-scalable process.

Promising results have been obtained when the perovskite cathodes and the YSZ electrolyte have been separated by a gadolinium doped ceria (CGO, $Ce_{0.8}Gd_{0.2}O_{2-x}$) thin films. Fuel cells including the CGO buffer layer with the LSCF cathode have shown better electrochemical performance and long term stability [13]. CGO exhibit high oxide ion conductivity, inertness towards both LSCF and YSZ as well as chemical stability under intermediate temperature solid oxide fuel cell operating conditions [14].

Formation of resistive $SrZrO_3$ phase seems to occur primarily during high temperature cathode synthesis step, where Sr^{2+} can diffuse through the barrier layer [15]. Low porosity of the barrier layer plays a major role in blocking Sr diffusion. It has been shown that a relatively porous barrier layer prepared by screen printing and high temperature sintering had inferior properties in comparison to barrier layer prepared by magnetron sputtering [16]. Nevertheless, the CGO buffer layer is frequently fabricated by a screen printing technology, since it is a conventional and cost effective thick ceramic layer deposition technique. In this case the sintering temperatures above 1200 °C are required in order to provide sufficient densification and adhesion of the CGO layer to the electrolyte. However, even the sintering temperature close to 1300 °C may result in the porosity of the screen-printed barrier layers of 25–30% [17]. What is more, at these temperatures a solid solution CGO_x:$YSZ_{(1-x)}$ is formed, which leads to a significant decrease in the ionic conductivity and thus may result in an increased cell resistance. An alternative production method is to use vacuum deposition techniques such as Chemical Vapor Deposition (CVD) [18], Physical Vapor Deposition (PVD) [19], Magnetron Sputtering [20] and Pulsed Laser Deposition (PLD) [14]. These methods may provide very thin and practically ideal CGO barrier layers. However, for SOFC application scalability and cost-effectiveness of these techniques are questionable.

In contrast to the vacuum deposition techniques, there are alternative technologies which are cost effective, scalable and enable fabrication of dense and homogeneous layers without requiring high temperature sintering step. These include spray pyrolysis [21,22],

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electrostatic spray pyrolysis [13], spin coating [14,23] and flame spray deposition [24]. In the case of these technologies the formation of a solid solution of CGO and YSZ might be avoided due to significantly lowered sintering temperature than in the case of the screen printing.

It was demonstrated [25,26], that ceria barrier layer fabricated by a PVD deposition method allowed to reach high power (>1 W cm^{-2}) of anode supported SOFCs at 600 °C. Cell with a PVD processed barrier layer had a 1 μm thin and dense barrier which resulted in lower Ohmic and polarization losses. This clearly shows the importance of the barrier layer and the process by which it is manufactured.

CGO layers fabricated by spray pyrolysis, studied in this work, were investigated before mostly for the purpose of the electrolyte fabrication for SOFCs [27–34]. In this paper sprayed gadolinium doped ceria is investigated as the interlayer between the YSZ electrolyte and the $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ cathode, which should prevent formation of disadvantageous phases between the electrolyte and the cathode. Still, in the case of the dense films fabricated by low temperature technologies, the effect of CGO layer thickness on the electrical/electrochemical properties of electrolyte-interlayer-cathode structures needs to be evaluated. Only recently, this problem was investigated for the films deposited by the DC magnetron sputtering [35]. In the case of the spray pyrolized interlayers, the effect of mesoporous film thickness was only lately investigated [36]. As literature reports show, reactivity between the cathode material and the YSZ electrolyte and barrier layer depends significantly on the specific cathode material, buffer layer preparation method, its thickness, cell processing etc. [37–42].

In this paper, CGO layers with different thicknesses were produced and evaluated as a diffusion barrier between the YSZ electrolyte and the $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ cathode. Impedance spectroscopy measurements were performed on symmetrical cells. Additionally, interlayers were studied in anode supported fuel cells.

2. Experimental

For symmetrical cells evaluation, the CGO layers were deposited on the YSZ substrates. To prepare dense yttria stabilized zirconia substrates, an YSZ powder (Tosoh Corporation) was uniaxially pressed under a pressure of 45 MPa and sintered for 2 h in air at 1400 °C. The obtained samples were in the shape of disks, 12.6 mm in diameter and ~0.8 mm thick.

Thin $Ce_{0.8}Gd_{0.2}O_{2-x}$ films were deposited using spray pyrolysis method. The precursor solution was prepared using $Ce(NO_3)_3 \times 6H_2O$ (Sigma-Aldrich, 99%) and $Gd(NO_3)_3 \times 6H_2O$ (Sigma-Aldrich, 99.9%) dissolved in water and mixed with ethylene glycol and tetraethylene glycol (Sigma-Aldrich, 99%). Total concentration of salts was fixed at 0.05 mol/l. The solution was sprayed on the substrates heated to temperatures between 350 °C–450 °C on a hotplate. Additional thermocouple located next to the substrate was used during the deposition process to control the surface temperature. The distance between the substrate and the nozzle during the deposition was fixed at 330 mm. The solution flow rate was controlled by nozzle opening and varied between 3 ml/h and 6 ml/h, which corresponded to layers growth rate from 300 nm/h to 600 nm/h, respectively. The 400 nm, 800 nm and 1200 nm thick layers were deposited and annealed at 900 °C before further evaluation. The layers thicker than 400 nm, were deposited with multiple steps, first the 400 nm CGO film was sprayed and annealed at 900 °C and then this procedure was repeated until the required thickness was obtained (leading to 400 nm (1×), 800 nm (2×) and 1200 nm (3×) films). This multi–step process enables deposition of thicker layers without cracks induced by strains during sintering and subsequent shrinkage of CGO film. This phenomenon is pronounced in the case of spray-pyrolysis since the layer is initially amorphous and might contain some organic residues [28,43].

In order to study the properties of the buffer layer, both symmetrical cells and anode supported fuel cells were prepared. Symmetrical cells were prepared without the CGO layer or by spraying 400 nm, 800 nm, 1200 nm thick CGO film on both sides of the YSZ substrate. $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ electrodes (electrode area of 0.38 cm^2, 100 μm thickness) were brush painted and sintered at 1100 °C. The current collectors were in the form of platinum layers, which were brush painted on top of the LSF electrode using ESL 5554 (ElectroScience Laboratories, USA) paste and sintered at 900 °C. Fuel cell samples were prepared using commercial 0.5 in. diameter YSZ/Ni-YSZ half-cells with the YSZ thickness of 4.5 μm (ECN/InDec, Petten). Fuel cells without and with 400 nm and 800 nm thick CGO layer were evaluated. The LSF cathode layer was brush-painted in the shape of a circle with diameter of 5 mm and sintered at 1100 °C for 2 h. The cathode and anode current collector was deposited using the silver paste (DuPont 4922 N, USA) sintered in situ. As the result, the highest processing temperature of CGO/LSF layers for all samples was 1100 °C.

The film morphology and cross-sections of the samples were investigated by Schottky field emission scanning electron microscopy (SEM) (FEI Quanta FEG 250) with ET secondary electron detector. Beam accelerating voltage was kept at 30 kV. For elemental analysis, the Energy Dispersive X-ray Spectroscopy (EDS) was performed by the EDAX Genesis APEX 2i with the Apollo SDD spectrometer having 100 nm resolution on fuel cells after electrical evaluation. Electrochemical impedance spectroscopy measurements on the symmetrical cells were performed using the Solartron SI 1260 Frequency Response Analyzer coupled with the Solartron SI 1287 potentiostat/galvanostat in a two-electrode configuration. Measurements were performed on the unbiased cells in the frequency range from 1 MHz to 0.1 Hz with an excitation voltage of 20 mV and in the temperature range of 600 °C–800 °C. The impedance spectra obtained on the symmetrical structures were analyzed using ADIS (analysis of the differences in impedance spectra). In ADIS, derivatives of real parts of impedances with respect to frequency are calculated. Then, the derivative of the sample with CGO layers is subtracted from the derivative of the sample without CGO layer (reference) and the resulted dependence (ADIS) as a function of frequency is plotted. The details of ADIS analysis method are described in [44]. For characterization of the fuel cells, they were mounted to the alumina tube based measuring setup and were sealed with the ESL 4905 (ElectroScience Laboratories) glass sealant. The fuel cell was fueled by hydrogen with 3% of steam (flow rate of 100 cm^3/min) and air as an oxidant. The current-voltage measurements were performed using Solartron SI 1287 potentiostat/galvanostat in a four-electrode configuration. The impedance spectra have been collected at OCV at 800 °C.

3. Results

At the initial stage of this study, the selected parameters of the CGO precursor deposition process were optimized in order to obtain high quality, crack free and visibly dense CGO layers. Fig. 1a, b & c shows SEM micrographs of the CGO film surface sprayed onto YSZ substrates heated to 350 °C, 410 °C and 450 °C, respectively. Based on micrographs it can be noticed that the substrate temperature is one of the critical parameters in the spray pyrolysis method. If temperature is too low (350 °C) precursor does not form continuous layer (63% of surface was covered by cracks). If the temperature is too high (450 °C) the layer is heavily cracked (44% of cracks). It has been shown that the optimum temperature of the substrate during the spraying process should be close to 410 °C (36% of cracks). Another important parameter is the solution flow rate. Maximum solution flow rate which allows obtaining a uniform layer is 3 ml/h (2% of cracks), as shown in Fig. 2. Deposition with flow rate of 4 ml/h and 6 ml/h resulted in crack formation because liquid phase from precursor solution did not have enough time to evaporate, decompose and form a high quality coating (19% and 24% of cracks, respectively). Flow rate of 3 ml/h corresponds to the layer growth rate of 300 nm/h. It was also observed that the quality of the resulting layer is influenced by the layer thickness. Fig. 3a, b & c shows the surface SEM images of the 400 nm, 800 nm and 1200 nm thick CGO film sprayed on YSZ, respectively. One can notice that it was not