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Solid State Ionics 177 (2006) 2075–2079
SOLID STATE IONICS
www.elsevier.com/locate/ssi

Spray pyrolysis of electrolyte interlayers for vacuum plasma-sprayed SOFC

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Received 21 July 2005; received in revised form 25 June 2006; accepted 25 June 2006

Abstract

The effects of gadolinia-doped ceria (CGO, $Ce_{0.8}Gd_{0.2}O_{1.9-x}$) and yttria-doped zirconia (8YSZ, $Zr_{0.92}Y_{0.08}O_{2-x}$) interlayers prepared by spray pyrolysis between vacuum plasma-sprayed 8YSZ electrolytes (8YSZ–VPS) and screen-printed $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ cathodes (LSM) on the power output of solid oxide fuel cells (SOFC) are investigated. Amorphous thin films are deposited and then converted to nanocrystalline electrolyte–cathode interlayers during the first heat-up cycle of a SOFC to the operating temperature. CGO thin films between the YSZ plasma-sprayed electrolyte and the LSM cathode increased the power output by more than 20% compared to cells without interlayers, whereas YSZ films degraded the power output of cells. It is assumed that CGO improves the charge transfer at the electrolyte–cathode interface and that the CGO layer prevents the formation of undesirable insulation of La-zirconate at the interface 8YSZ/LSM.

Keywords: SOFC; Electrolyte; Spray pyrolysis; Vacuum plasma spray; Thin film; Ceria

1. Introduction

One main cause for the degradation of SOFC during operation was identified to be the formation of high ohmic-resistant $La_2Zr_2O_7$ and $SrZrO_3$ between 8 mol% doped yttria stabilized zirconia (8YSZ) electrolytes and La-based cathodes [1]. These phases are highly insulating and lead to degradation of fuel cell power output. On the other hand, it is known that ceria solid solutions are chemically compatible with $(La_{0.8}Sr_{0.2})x_{0.98}MnO_3$ or even less stable with La-perovskites such as $La(Sr)CoO_3$ [2], as they are in thermodynamic equilibrium with the ceria electrolyte.

In this study spray pyrolysis gadolinia-doped ceria (CGO) thin films are integrated at the cathode–electrolyte interface between YSZ and LSM in order to avoid the formation of La-zirconates. The power output of such cells is compared to those with 8YSZ interlayers prepared also by spray pyrolysis. Further, gas tightness experiments elucidate whether spray pyrolysis thin films are suitable to improve the gas tightness of vacuum plasma-sprayed ceramics.

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doi:10.1016/j.ssi.2006.06.033

2. Experimental

2.1. Fuel cell preparation

Circular solid oxide fuel cells (SOFCs) of 40 mm diameter were produced on metallic substrates by vacuum plasma spraying the NiO/YSZ anode and YSZ electrolyte (DLR, for plasma spraying details see [3,4]). A CGO and alternatively a 8YSZ interlayer was then prepared on the 8YSZ electrolyte by spray pyrolysis [5] and a cathode (LSM) by screen printing techniques. Due to pronounced metal substrate oxidation during plasma spraying at oxygen partial pressures up to 210 hPa, not every state-of-the-art metal substrate, i.e. nickel, is suitable. Thus, ferritic steel, which, under oxidized conditions, shows a low thermal expansion mismatch with respect to the ceramic fuel cell components, was chosen.

The anode and the electrolyte were produced by vacuum plasma spray technique from NiO (BECON, Switzerland) and 8 mol% doped yttria stabilized zirconia (8YSZ) (Medicoat, Switzerland) powders. In case of the anode a 3:5 volume ratio NiO and 8YSZ was used (210 hPa, 34 kW), whereas the electrolyte was sprayed from pure 8YSZ powder (100 hPa, 34 kW).

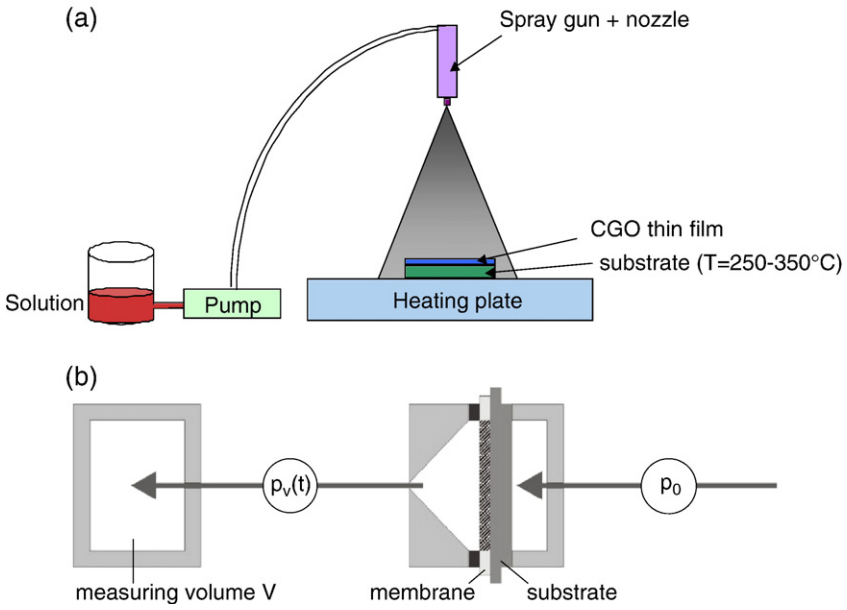

Fig. 1. Principle of (a) the spray pyrolysis process and (b) the gas tightness experiments.

Spray pyrolysis thin films were deposited on the vacuum plasma-sprayed 8YSZ electrolytes. The appropriate settings of spray parameters have been optimized for the deposition of 20 mol% gadolinia-doped ceria (CGO) [6] and 8 mol% yttria stabilized ZrO_2 8YSZ [7] on the 8YSZ–VPS electrolyte. In airblast spray pyrolysis a precursor solution is atomized to droplets by air undergoing pyrolytic decomposition once hitting a heated substrate. Thereby, amorphous metal oxide films form, which can be crystallized by secondary annealing to nanocrystalline microstructures. The CGO spray pyrolysis precursor solutions were made of 0.02 mol/l gadolinium chloride (Alfa Aesar, 99.9% purity) and 0.08 mol/l cerium nitrate (Alfa Aesar, 99% purity) dissolved in 33:33:33 vol.% ethanol, diethylene glycol monobuthyl ether and methoxy propanol (all solvents from Fluka Chemie, >99% purity). The 8YSZ spray pyrolysis precursor solutions were made of 0.008 mol/l yttrium chloride (Aldrich Chemicals, 99% purity) and 0.092 mol/l zirconium acetylacetonate (Fluka, 98% purity) dissolved in 50:50 vol.% of ethanol and diethylene glycol monobuthyl ether (all solvents from Fluka Chemie, >99% purity). The spray gun (Compact 2000 KM, Bölhoff Verfahrenstechnik, Germany) was operated in all experiments at 1 bar air pressure. Temperature, flow rate and deposition time were experimentally investigated. Fig. 1a shows the principle of spray pyrolysis.

For the here used solvents and salts a substrate temperature of 300–330 °C resulted in crack-free thin films. If higher substrate temperatures were chosen, the solvents dry already before reaching the 8YSZ substrate and mostly nano-powder is deposited. In this case, no thin film can be formed. At deposition temperatures below 300–330 °C dense thin films form, but those remain in a wet stage, as the solvents have not completely evaporated. This leads to a pronounced crack-formation of the thin films once annealed after spray pyrolysis deposition.

Flow rates of 30.4 ml/h of solvent and 1 to 3 h deposition time resulted in 100 to 300 nm CGO film thicknesses. Fig. 2 displays the microstructure of a dense and crack-free CGO thin

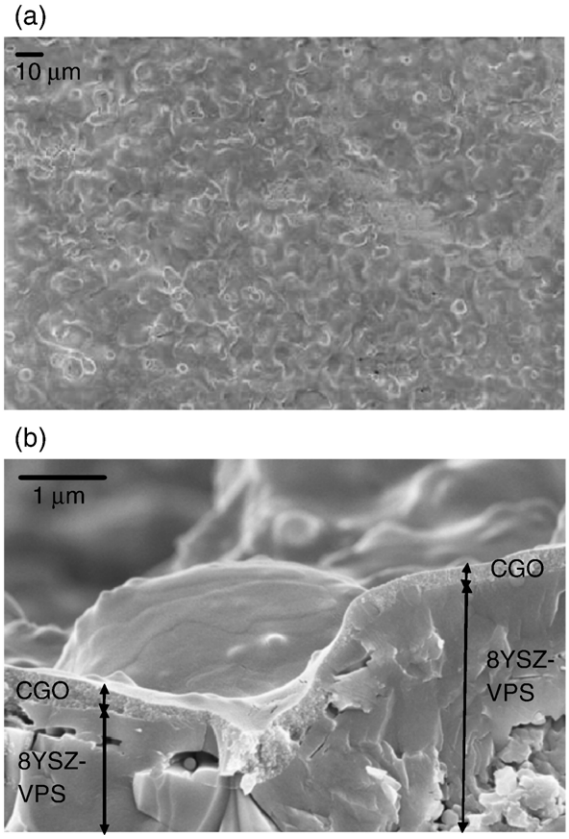

Fig. 2. SEM microstructures of CGO spray pyrolysis thin film on 8YSZ VPS electrolyte: (a) in-plane and (b) cross-sectional view. The film was previously annealed at 780 °C for 2 h (3 °C/min).

film on a 8YSZ–VPS substrate after annealing at 780 °C (for 2 h, 3 °C/min) in an in-plane (Fig. 2a) and cross-sectional view (Fig. 2b). It can be noticed, that although a very rough substrate is present the thin film covers the substrate completely. At higher magnification even the nanocrystalline microstructure of the CGO thin film can be observed. Due to the thermal expansion mismatches between metal substrate and ceramic components weights of 800 g on the SOFC multilayers were placed during annealing process to avoid bending of the cells. Cathodes of $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ (LSM) were applied by screen printing on either the spray pyrolysis thin film interlayer or directly on the 8YSZ–VPS electrolyte.

2.2. Spray pyrolysis interlayer characterization

The spray pyrolysis thin film interlayer microstructure was investigated by SEM (Zeiss LEO 982, and LEO 1530, Germany).

Spray pyrolysis gas tightness experiments were conducted on half cells containing a ferritic steel substrate and a NiO–8YSZ–VPS anode with a 8YSZ–VPS electrolyte. Half cells with and without spray pyrolysis prepared CGO or 8YSZ interlayers were tested. The test set-up of the measurement is shown in Fig. 1b. A negative pressure of 700 hPa is generated in the test volume V by a vacuum pump. Due to this underpressure, an airflow is forced through the membrane in case it shows open porosity. The ambient pressure p_0 and the time response of the pressure in the measured volume $pV(t)$ is registered. From these measured quantity the gas leakage rate of a fuel cell or a half fuel cell can be calculated [8].

2.3. Electrochemical characterization of SOFC

The electrochemical characterization has been carried out at temperatures from 850 to 650 °C. For the measurements an atmosphere of 50 vol.% H_2/50 vol.% N_2 (80 sccm/cm^2) as fuel (dry) and 160 sccm/cm^2 air as oxidant was chosen.

The impedance measurements were performed with a Zahner Electrochemical Workstation IM6 in a frequency range of 0.1 Hz to 1 MHz. The polarisation and ohmic resistances were extracted from the spectra using the SIM module of the Zahner Thales package.

3. Results and discussion

3.1. Effects of spray pyrolysis electrolyte interlayers on gas permeability

To evaluate the gas permeability of the half cells of metallic substrate, VPS anode and VPS electrolytes the gas leakage rate (GLR) improvement being the ratio of gas flow before and after applying a thin film was determined. Moreover, the effect of multiple spray pyrolysis layer depositions on the GLR was studied also. After each deposition of a layer, an annealing at 780 °C (for 2 h at a heating rate of 3 °C/min) was applied. The results of the gas leakage rates are shown in Table 1. All cells with CGO and YSZ thin film layers showed improved gas tightness by a factor of 2 to 6. The gas tightness was improved with increasing number of thin film layers and was independent of the material's composition e.g. whether it was YSZ or CGO. The highest gas tightness was obtained by applying two thin film layers of 8YSZ (thickness of thin films is not constant due to solvent composition and spray parameters).

Table 1
Gas tightness of the cells

Cell number	Number of applied spray pyrolysis thin films and sprayed material	Thermal treatment/ condition when measured	GLR improvement
26R01	1×CGO	Direct after spray pyrolysis layer applied	1.79
26R02	1×CGO	No thermal pretreatment	1.25
26R05	None	No thermal pretreatment	1.00
PX281	3×CGO	Direct after spray pyrolysis layer applied	3.78
PX300	None	No thermal pretreatment	1.00
PX303	2×8YSZ	Direct after spray pyrolysis layer applied	6.79

The GLR (gas leakage rate) improvement is the ratio of gas flow before and after applying a thin film.

3.2. Electrical performance of cells with spray pyrolysis of electrolyte interlayers

The current–voltage characteristics of cells with and without thin film interlayers are shown in Fig. 3. Fig. 3a shows the current–voltage characteristics of the cells with and without CGO spray pyrolysis interlayer thin films. The reference cell was not supplied with a CGO interlayer for comparison. The SOFC without CGO spray pyrolysis interlayer shows the highest losses which we attribute to a hindered charge transfer process. In Table 2 the cell performances at 0.7 V are compared.

The power output of the cells was increased by more than 20% (at a current density of 200 mA/cm^2, see Fig. 3b) or more than 40% (at a potential of 0.7V) in case of CGO interlayers on 8YSZ–VPS electrolytes compared to the SOFC without spray pyrolysis interlayer. The improved cell performance seems not much affected by the thermal treatment of the CGO spray pyrolysis thin film. Reasons for the improved cell performance can be: Hindered La-zirconate formation due to the CGO interlayer and/or the improved gas tightness of the cells due to the thin film interlayers. To elucidate this point further, experiments have been conducted on the long term current–voltage characteristics of SOFCs with CGO and YSZ interlayer thin films. Fig. 3b shows current–voltage characteristics of the cells without interlayer, with a CGO interlayer and with a 8YSZ interlayer. The cell with the CGO interlayer shows a smaller loss compared to the cell without any interlayer. The highest losses were exhibited in the cell with the 8YSZ interlayer. The current–voltage characteristics of the cells with and without a CGO interlayer remain stable within 120 h. However, the cell with the 8YSZ interlayer shows a large degradation with time. From literature it is known, that La-zirconates hinder the charge transfer acting as an insulator at the cathode–electrolyte

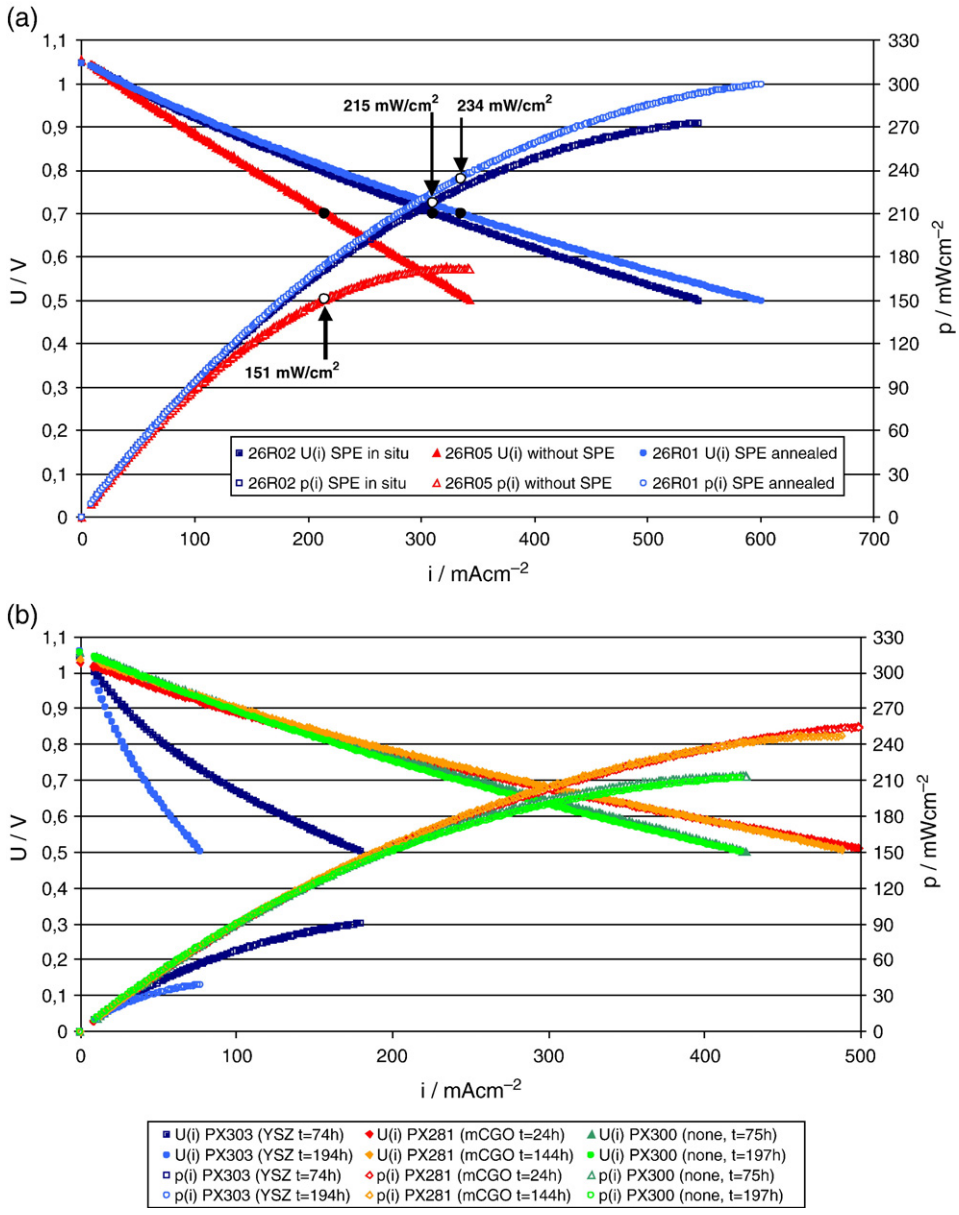

Fig. 3. Current/voltage characteristics: (a) effect of CGO interlayer at the cathode–electrolyte interface: 26R01 with prior annealed CGO thin interlayer before SOFC testing, 26R02 with in situ annealed CGO interlayer during SOFC testing and 26R05 without spray pyrolysis thin film. (b) Long-term degradation (given in hours) of SOFC containing CGO and 8YSZ spray pyrolysis interlayers at the cathode–electrolyte interface: PX281 with CGO interlayer, PX300 without interlayer and PX303 with YSZ interlayer.

interface (i.e. LSM and 8YSZ) [9]. It can be speculated that once the 8YSZ is present in the form of nanocrystalline thin films with small grains in the order of 10 to 20 nm surface and volume diffusion for the formation of La-zirconates are enhanced. This may explain the fast degradation of the cell with the 8YSZ nano-crystalline interlayer. The cell with the thin CGO interlayer shows almost no degradation. This is in accordance with literature where stable electrochemical interfaces for perovskite cathodes with CGO electrolytes were reported [2].

Table 2
Influence of thermal treatment of a CGO interlayer on cell performance at 0.7 V

Cell number	Spray pyrolysis interlayer material	Thermal treatment	Performance at 0.7 V (mW/cm^2)
26R01	CGO	780 °C for 2 h after spray pyrolysis before SOFC testing	234
26R02	CGO	In situ annealing during first SOFC heat up cycle to 800 °C	215
26R05	None	None	151

4. Conclusions

The reproducible deposition of dense and crack free CGO and 8YSZ spray pyrolysis interlayers at the cathode (LSM)–electrolyte (8YSZ–VPS) interface is possible. Furthermore, spray pyrolysis is a suitable process to improve the gas tightness of VPS ceramics.

The polarisation resistance between 8YSZ–VPS electrolyte and LSM screen printed cathode can be reduced by a CGO spray pyrolysis interlayer, as the formation of La-zirconates is avoided, leading to a high fuel cell power output. In addition, the long-term stability of LSM/8YSZ interfaces can be improved with a CGO thin interlayer due to the thermodynamic stability of CGO with perovskites.

Acknowledgments

The production of the VPS layers and the electrochemical characterization of the cells examined in this study were performed at the German Aerospace Center (DLR), Institute of Technical Thermodynamics, in Stuttgart, Germany. The support from the SOFC Crew and the VPS Crew is gratefully acknowledged.

The authors thank Christian Zink (Swiss Federal Institute of Technology, ETH Zurich, Switzerland) for his help in the experimental investigation of the spray pyrolysis thin film parameters on 8YSZ–VPS electrolytes.

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