Journal of Applied Electrochemistry **32**: 871–874, 2002.

Electrochemical characterization of vacuum plasma sprayed thin-film solid oxide fuel cells (SOFC) for reduced operating temperatures[☆]

M. LANG*, T. FRANCO, G. SCHILLER and N. WAGNER*
Deutsches Zentrum für Luft und Raumfahrt (DLR), Institut für Technische Thermodynamik, Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany
*(*author for correspondence, emails: norbert.wagner@dlr.de or michael.lang@dlr.de)*

Received 22 June 2001; accepted in revised form 19 March 2002

Key words: current–voltage behaviour, electrochemical impedance spectroscopy (EIS), solid oxide fuel cells (SOFC), vacuum plasma spraying (VPS)

Abstract

This paper focuses on the electrochemical characterization, such as current–voltage measurements, impedance spectroscopy and long-term operation of completely plasma-sprayed SOFC assemblies for a planar metallic substrate-supported thin film concept. The influence of the variation in operating conditions is presented. To determine the different resistances in the cells, the measured impedance spectra were fitted to an equivalent circuit. This enables further improvement of the electrochemical performance of the cells and allows the assembling of high performance SOFC stacks.

1. The DLR plasma pray SOFC concept

Solid oxide fuel cells (SOFCs) convert the chemical energy of fuel gases (H_2, CO, CH_4 and other hydrocarbons) by reaction with oxygen into electrical power. SOFCs are operated at temperatures of about 900 °C. The cell consists of a porous (La, Sr)MnO_3 (LSM) cathode, a gas tight oxygen ion conductive yttria- or scandia-stabilized ZrO_2 (YSZ, ScSZ) electrolyte and a porous ZrO_2/Ni anode (Figure 1). At the cathode the oxygen is reduced to O^{2-} ions which are conducted through the ZrO_2 electrolyte and combine with the H_2 at the anode to produce water. In comparison to power generation by means of combustion processes, the electrochemical oxidation of the fuel gases in an SOFC leads to higher overall efficiencies with very low harmful emissions [1].

To increase the long-term stability of SOFC stacks the operating temperature of the cells has to be reduced to about 700–800 °C. This leads to a decrease in detrimental material diffusion and evaporation processes in the cells and promises reduced material costs for interconnects and peripheral high-temperature components. For the reduction of the operating temperature it is necessary to decrease the overall thickness of the SOFC and particularly of the electrolyte [2].

A novel concept for a metallic substrate-supported thin-film SOFC (Figure 1) has been developed at DLR Stuttgart. In the DLR concept, the entire cells are deposited onto a porous metallic substrate by an integrated multistep vacuum plasma spray process [3]. Its characteristic properties such as short process time, high material deposition rate and the ability to be transferred to an automated production line promise a fast and cost-effective fabrication of cells with large active cell areas. Because of this substrate support the electrolyte layer may have a significantly reduced thickness of only 20–30 μm, resulting in a thin-film cell with a total thickness of less than 100–120 μm.

2. Cell fabrication by vacuum plasma spraying

The plasma spraying process is based on the generation of a plasma jet consisting of Ar which is ionized by a high current discharge in the plasma torch. Powder which is injected into the plasma is accelerated and melted in the fast plasma jet. The coating is formed by solidification and flattening of the fast particles at impact on the substrate.

Different porous metallic substrates (e.g., porous felts, plates and foam), were used for the fabrication of the SOFCs [4]. Both YSZ (ZrO_2–8 mol% Y_2O_3) and ScSZ (ZrO_2–10 mol% Sc_2O_3) powders are used for the electrolyte layer and are combined with NiO in the case of the anode and with $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$ in the case of the cathode. The particle size of the powders used is in the range 5–40 μm.

Figure 2 shows the cross section of a completely plasma sprayed SOFC consisting of a NiO + YSZ

[☆] This paper was initially presented at the 5th International Symposium on Electrochemical Impedance Spectroscopy at Marilleva, Trento, Italy, June 2001.

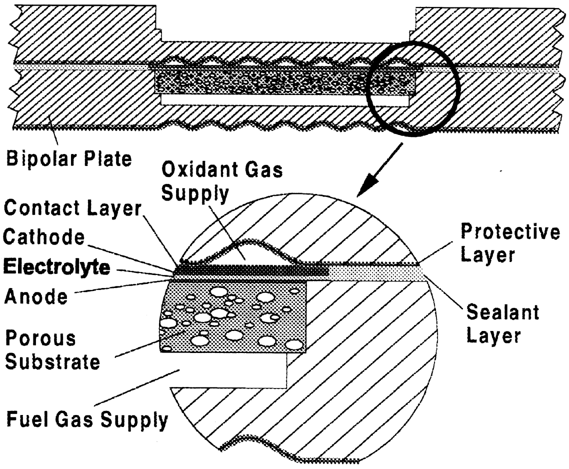

Fig. 1. Principle of SOFC design according to the DLR spray concept.

anode, a YSZ electrolyte and a LSM + YSZ cathode, which were consecutively sprayed onto a porous Ni felt. The plasma sprayed YSZ electrolyte exhibits a dense lamellar microstructure, whereas the anode has a fine open porosity of 21 vol % after the reduction of the NiO with H_2 to pure Ni. The overall porosity of the LSM + YSZ cathode reaches only about 10 vol % with relatively coarse pores. Recent developments aim at improving the cathode microstructure by using LSM powders which contain pore formers. For the stack design the scale up of square-shaped cells up to a final size of 20 × 20 cm is required and is currently under development.

3. Electrochemical characterization

Figure 3 shows the electrochemical performance of a plasma sprayed thin-film cell (12 cm^2 area) containing a NiO + ScSZ anode, a ScSZ electrolyte and a LSM + ScSZ cathode as a function of temperature. At 900 °C power densities in the range of 800 mW cm^{-2} with ScSZ containing cells and of 600 mW cm^{-2} with YSZ containing cells are achieved at 0.7 V when operated with hydrogen and air. At reduced operating temperatures down to 750 °C the power densities decrease to approximately 300 mW cm^{-2} with ScSZ containing cells and 200 mW cm^{-2}, with YSZ containing cells, respectively.

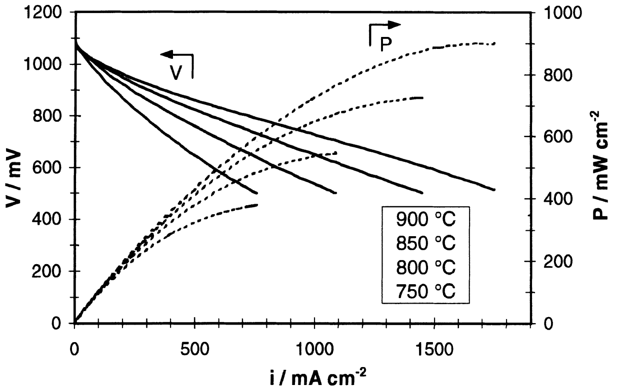

Fig. 3. I/V behaviour of a plasma sprayed SOFC at different temperatures (active area 12 cm^2; operating gases: 0.9 SLPM H_2, 1.5 SLPM air).

Figure 4 shows the corresponding impedance spectra (Bode plot) of the SOFC at different temperatures and at a current density of 200 mA cm^{-2}. The impedances R_{HF} at high frequencies of about 100 kHz increase from 6 mΩ to 10 mΩ when the temperature is reduced from 900 °C to 750 °C. Four point ionic conductivity measurements, which were performed at the plasma sprayed

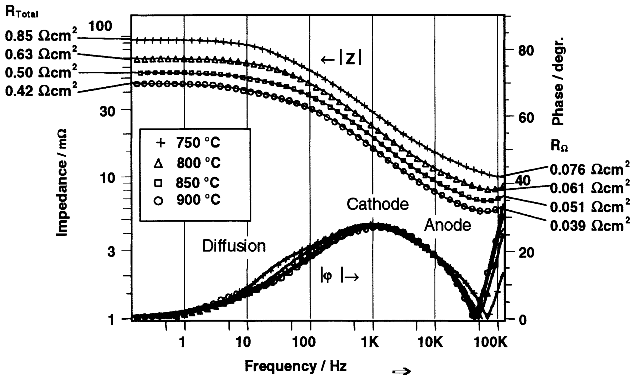

Fig. 4. Impedance spectra of a plasma sprayed SOFC at different temperatures (200 mA cm^{-2}; operating gases 0.9 H_2 SLPM, 1.5 SLPM air).

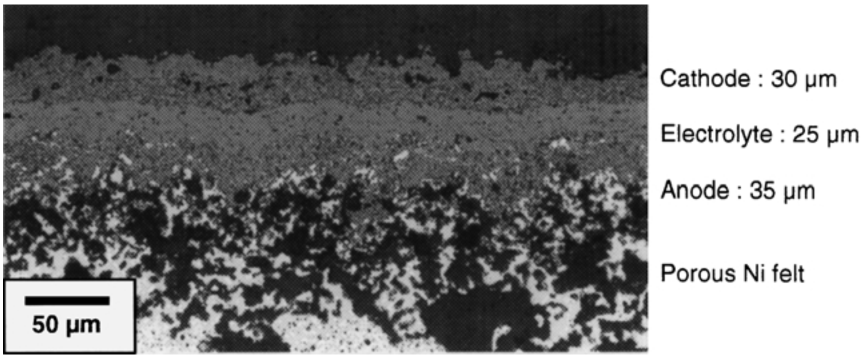

Fig. 2. Cross section of a vacuum plasma sprayed SOFC.

electrolyte layers, have shown that R_{HF} corresponds to the ohmic resistance (R_{Ω}) of the ScSZ electrolyte layer [5]. These values are very low due to the thin plasma sprayed electrolyte layer of approximately 40 μm. The corresponding ohmic area specific resistances change from 0.039 Ω cm^2 at 900 °C to 0.076 Ω cm^2 at 750 °C. Moreover, the spectra show low area specific total impedances (R_{TOTAL}) in the low frequency range from 0.42 Ω cm^2 at 900 °C to 0.85 Ω cm^2 at 750 °C.

To correlate the measured impedances with the different electrochemical processes in the SOFC, the cells were examined at different operating conditions, For example, temperature, flow rate and process gas composition, gas humidity and current load. Moreover, the thickness of the electrolyte layer and shape of the gas supply channels were varied.

Figure 5 shows the impedance spectra of the plasma sprayed SOFC at 900 °C with H_2 and air, H_2 and O_2 and humidified H_2 and air as operating gases. The ohmic resistance of the ScSZ electrolyte R_{Ω} at high frequencies of about 100 kHz is independent of the gases used and remains constant at 6 mΩ. This result is in accordance with theory because the ionic conductivity of ceramics is not a function of the operating gases.

With H_2 and air, the cell reaches a high overall impedance in the low frequency range of about 73 mΩ. The change of the H_2 through humidified H_2 (H_2 + H_2O) leads to a decrease in the phase shift mainly in the low frequency range and to a reduction of the cell impedance to about 51 mΩ, mainly in the low frequency range. Additional measurements between 750 °C and 900 °C and with different shaped gas channels have shown only a very weak dependence of the low frequency phase shift and impedance on the temperature but a strong dependence on the fuel gas distribution on the anode side. This leads to the conclusion that the corresponding impedance detected in the low frequency range can be attributed to a diffusion process, such as the diffusion of H_2 and H_2O produced at the anode side [6, 7].

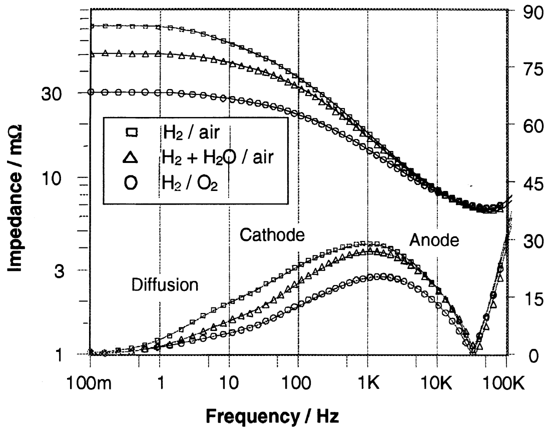

Fig. 5. Impedance spectra of a plasma sprayed SOFC operated at 900 °C with different process gases to OCV.

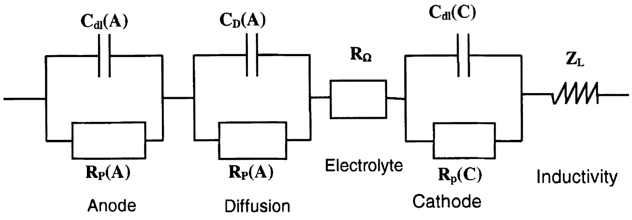

Fig. 6. Equivalent circuit of a SOFC.

Replacement of air by oxygen leads to a decrease in the phase shift mainly in the middle frequency range and to a low overall cell impedance of about 30 mΩ (Figure 5). The increase in current load and temperature from 750 °C to 900 °C produces a decrease in the high and the middle frequency impedance. Therefore, the polarization resistances at the anode R_P(A) is related to the high frequency range and the polarization resistance of the cathode R_P(C) contributes to the impedance mainly in the middle frequency range.

To determine the individual resistances in the cells, the measured spectra were fitted to an equivalent circuit (Figure 6) which contains three RC terms, for example the polarization of the anode and the cathode and the diffusion process. These RC terms are connected in series with the ohmic resistance of the electrolyte. The impedance of the current collector wires is taken into account by the inductive element Z_L.

Figure 7 shows the calculated area specific resistances and their relative contribution to the overall cell impedances at a current density of 200 mA cm^{-2} in the temperature range 750–900 °C. The thin plasma sprayed ScSZ electrolyte contributes very little to the overall resistance. The relative losses are around 7% in the whole temperature range. The porous anode also has low area specific resistances which increase slightly from 3% at 900 °C to 4% at 750 °C. The diffusion resistance R(Diffusion) increases from about 0.06 Ω cm^2 at 900 °C (15%) to approximately 0.21 Ω cm^2 (24%) at 750 °C. The highest losses are caused by the polarization resistance of the cathode, which are in the range of 0.3 (900 °C) to 0.6 Ω cm^2 (750 °C).

These high values of 65–75% of the total cell losses are caused by the low porosity of the cathode layer. It is

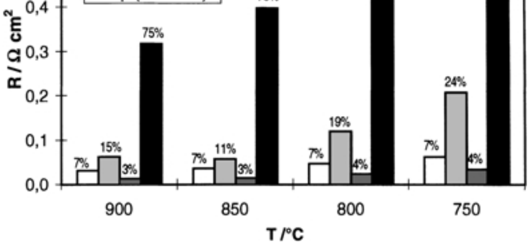

Fig. 7. Impedance values of a plasma sprayed SOFC at different temperatures (OCV; 0.9 SLPM H_2, 1.5 SLPM air).

expected that these values will be reduced by the optimization of the cathode's microstructure.

4. Long-term operation

First long-term measurement at 200 mA cm^{-2} and 900 °C with H_2 and O_2 as operating gases were performed. Figure 8 shows that during the 2500 h of operation the degradation of the cell performance was in the region of 1% per 1000 h.

To evaluate the mechanisms for this decrease in cell voltage, impedance spectra of the SOFC were measured at 900 °C as a function of time. Figure 9 shows a strong increase in the overall cell impedance from 60 mΩ after 2 h to approx. 120 mΩ after 1990 h of operation. The corresponding enhancement of the phase shift appears mainly in the high frequency range. This can be interpreted by a strong increase in the polarization resistance of the YSZ + Ni anode which may be caused by the reduction of electrochemical active area due to diffusion of the Ni phase. According to this, the evaluation of the microstructure of the anode has shown coarsening of the Ni particles and an increase in pore size. Further improvement of long-term stability can be achieved by lowering the operating temperature to below 800 °C and by reducing the Ni content in the anode.

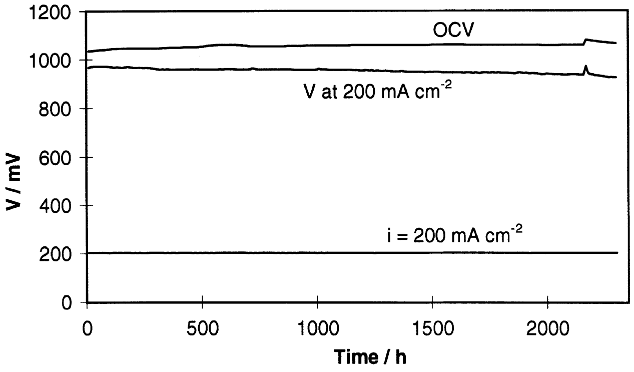

Fig. 8. Long-term measurement of a plasma sprayed SOFC at 900 °C operated with H_2 and oxygen.

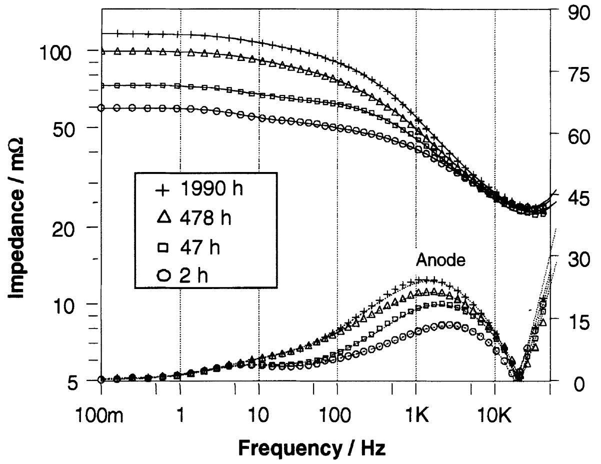

Fig. 9. Impedance spectra of a plasma sprayed SOFC operated at 900 °C as a function time at OCV.

5. Conclusion

Metallic substrate-supported thin-film solid oxide fuel cells were fabricated by using an advanced plasma spray technique according to a novel 'spray concept'. The current–voltage behaviour of the entirely plasma sprayed cells of laboratory scale show promising high electrochemical performance in the temperature range 750–900 °C. Electrochemical impedance spectroscopy is an important tool for evaluation of the individual impedances in the SOFC assembly. The plasma sprayed electrolyte and anode layers contribute very little to the overall losses in the cells whereas the highest losses occur through polarization resistance of the cathode. The degradation of the performance during the long-term operation of the cells at 900 °C is mainly caused by increase in polarization resistance of the anode. Therefore, further development activities aim at the improvement of the cathode and the anode microstructure, scale-up of the cells up to 20 cm × 20 cm and assembling of stacks.

Acknowledgement

The development of the 'spray concept' for thin-film SOFC is financially supported by the German Federal Ministry of Economics and Technology (BMWi) which is gratefully acknowledged.

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