DEVELOPMENT OF METALLIC SUBSTRATE SUPPORTED THIN-FILM SOFC BY APPLYING PLASMA SPRAY TECHNIQUES

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ABSTRACT
A novel concept for a metallic substrate supported thin-film SOFC to be operated at a reduced operating temperature of 700 – 800 °C has been developed by applying an advanced vacuum plasma spray process. This fabrication process enables the deposition of thin and dense electrolyte layers of about 30 – 50 μm in thickness as well as of controlled porosity electrodes in only one consecutive process step. The state of development of plasma sprayed thin-film cells is presented. The electrochemical characterization of the cells revealed a high electrochemical cell performance using H₂ and air as the operating gases of 300 – 400 mW/cm² at a reduced operating temperature of 750 – 800 °C.

INTRODUCTION
A common objective in current SOFC development work throughout the world is lowering the operating temperature of solid oxide fuel cells to below 800 °C. At these reduced temperatures lower stresses during thermal recycling and improved long-term stability of SOFC stacks is to be expected. Furthermore, intermediate SOFC operating temperatures in the range 600 – 800 °C result in reduced production costs of SOFC systems due to the possible use of lower cost materials particularly for containment. A fundamental precondition for SOFC operation at an intermediate temperature is given by minimized ohmic losses in the electrolyte which principally can be realized in two ways: either through the use of alternative electrolyte materials to the conventionally used yttria-stabilized zirconia (YSZ) having enhanced ionic conductivity such as e. g. doped ceria (1) and doped lanthanum gallates (2,3) or novel thin-film concepts when using zirconia as the electrolyte material.

Several processing techniques such as screen-printing (4), slip casting (5), tape calendaring (6), colloidal deposition (7), sol-gel deposition (8), PVD techniques (9) and reactive magnetron sputtering (10) have been applied to deposit thin-film electrolytes onto various substrates. The vacuum plasma spray technique (VPS) which has been further developed and adapted to the specific requirements of SOFC fabrication at the DLR Stuttgart (11) has the potential to not only fabricate thin electrolytes but also the entire membrane-electrode assembly (MEA) in one consecutive spray process. Based on this technology thin-film cells of a metallic substrate supported planar SOFC concept have been developed (12). The utilization of plasma torches with specially developed Laval-like nozzles enables the consecutive deposition of thin and dense electrolyte layers as
well as of controlled porous electrodes. In the present paper the DLR spray concept for planar SOFC, the structural characterization and the electrochemical performance of plasma sprayed thin-film cells are presented.

THE DLR SPRAY CONCEPT

The principle of the DLR spray concept for a metallic substrate supported thin-film SOFC is demonstrated by the scheme shown in Fig. 1. In this planar SOFC design the electrolyte layer needs no longer to be the mechanically supporting component thus enabling a significantly reduced electrolyte thickness compared to conventional self-supporting SOFC cells. The spray process requires a substrate to be coated for which in this case an open porous metallic structure such as a porous plate or a felt of about 1 mm thickness is used. Onto this substrate which serves as a fuel gas distributor to the anode, the electrolyte and the cathode layer, each of about 30 – 50 µm in thickness, are consecutively deposited by the VPS process in only one process step. In order to provide a low ohmic contact to the bipolar plate a porous and ductile contact layer is also needed. For the bipolar plate facing the cathode side of the MEA a protective coating has been developed at the DLR (13). The substrate supported MEA is fitted into a recess within the bipolar plate and sealed by a glass sealant layer as it is shown in Fig. 1b.

Figure 1. Principle of the SOFC design according to the DLR spray concept: overview (a) and detailed view (b)
EXPERIMENTAL

The VPS technique and the equipment used at the DLR Stuttgart have been described in detail elsewhere (14). Therefore, only some special features of the DLR installation that are essential for the manufacture of SOFC components are emphasized. Novel plasma torches with Laval-like nozzle contours for supersonic plasma jet velocities of up to 2000 – 3000 m/s have been developed resulting in enhanced spray particle velocities of up to 800 – 900 m/s and improved spray conditions in order to achieve thin but very dense electrolyte layers. The internal powder injection by several integrated powder injection ports at different positions along the nozzle allows the spraying of very different materials simultaneously, thus enabling complex coatings such as graded cermet layers exhibiting a desired material and porosity profile. Controlled porosity electrode layers can be obtained by carefully adjusting the torch nozzle, the powder injection (internally or externally), the grain size fraction of the spray powder and the spray parameters. An electrical heating device which has been developed for operation in vacuum conditions is applied to heat up the substrates prior to coating in order to diminish the thermal gradients during deposition. More details on the plasma spray process applied for the fabrication of SOFC components are given in (15).

The metallic substrates used for the spray process consisted either of porous plates made of the chromium-based alloy CrFe5Y2O31 as it is used for metallic bipolar plates (Plansee, Reutte, Austria) or of nickel or steel felts (Medicoat, Mägenwil, Switzerland and GKN Sinter Metal Filters, Radevormwald, Germany, respectively).

For the deposition of the different MEA layers specially adapted spray powders are used for the powder feedstock. For the electrolyte layer both YSZ (ZrO2-8 vol. % Y2O3) with a grain size ~22 μm (Medicoat, Mägenwil, Switzerland) and scandia-stabilized zirconia ScSZ ((Zr0.78Sc0.2Al0.018)O2-x) with a grain size ~20 μm (Siemens, Munich, Germany) were applied. The same YSZ and ScSZ powders were also used for the cermet anode and the mixed cathode layers. For the cermet anode NiO powder (~25 μm, Cerac, Milwaukee, USA) was separately fed to the plasma torch and mixed with the zirconia powder whereas for the mixed cathodes non-stoichiometric LSM with a composition (La0.8Sr0.2)0.99MnO3~40 μm, EMPA, Dübendorf, Switzerland) was used together with the YSZ or ScSZ powders.

The plasma sprayed layers were characterized by optical (OM) and scanning electron microscopy (SEM), by energy dispersive X-ray microanalysis (SEM/EDX) and by X-ray diffraction (XRD). The porosity was determined by using image analysis (Kontron Electronics KS 300, Munich, Germany) and mercury intrusion porosimetry. The electrochemical characterization of the plasma sprayed cells included I-V-measurements, impedance spectroscopy and 4-point electrical conductivity measurements.
RESULTS AND DISCUSSION

Development and Structural Characterization of Plasma Sprayed Cells

The process parameters for the single layers of the MEA were first elaborated separately and based on these parameters the multilayer MEA structure was then deposited onto various porous metallic substrates in a consecutive spray process.

Dense and gastight electrolyte layers of high melting YSZ and ScSZ, even with a thickness in the range of only 30 - 50 μm, are obtained by taking advantage of the DLR high-velocity torches with controlled expansion of the plasma providing enhanced kinetic energy and improved melting conditions for the spray particles. For the electrode layers, however, porous layers with extended three-phase boundaries are required. The layer porosity can be controlled with plasma spraying by the proper selection of the torch nozzle, the powder grain size fraction, the location of the powder injection and the spray parameters. Options to produce porous coatings include the reduction of the torch power, the reduction of the jet and particle velocity by raising the tank pressure and the increase of the spray distance between torch and substrate.

The plasma spray parameters for the different layers were optimized by means of Laser Doppler Anemometry (LDA) measurements in order to determine optimum melting conditions for the different powders for achieving the desired microstructures. The metallographic cross-section of an entirely plasma sprayed thin-film cell is shown in Fig. 2.

![Figure 2. Optical micrograph of a metallographic cross-section of an entirely plasma sprayed thin-film cell](image-url)
For an optimum cermet anode layer the zirconia and the NiO powders were injected separately into the plasma which means the internal injection of YSZ or ScSZ and the external injection of NiO. At the SOFC operating temperature the NiO is then completely reduced by hydrogen to pure Ni. A mixed or graded microstructure for the cathode was also prepared by the internal injection of zirconia and the external injection of LSM. The layer porosity measured by image analysis and mercury intrusion porosimetry is in the range of 1 vol.% for the electrolyte and of 15 - 20 vol.% for the electrodes. The cells prepared for the electrochemical characterization are circular with an area of 5 cm² but the fabrication process can be scaled up to produce cells with an area of up to 1000 cm².

**Electrochemical Performance of Plasma Sprayed Cells**

In order to evaluate the electrochemical performance of entirely plasma sprayed cells I-V-characteristics and impedance spectroscopy measurements were performed in the temperature range 750 - 900 °C. The I-V-characteristics of a plasma sprayed cell using YSZ for the electrolyte and as an addition to the anode and the mixed cathode are shown in Figs. 3 and 4. At 900 °C power densities of 970 mW/cm² at a voltage of 0.7 V for H₂ and O₂ as the operating gases and 740 mW/cm² for H₂ /air were measured (Fig. 3).

![Graph](image)

**Figure 3.** Performance of a VPS thin-film cell (YSZ/Ni anode, YSZ electrolyte, YSZ/LSM cathode) at 900 °C and H₂/O₂ and H₂/air as the operating gases

The temperature dependence of the electrochemical performance of the cell operated with H₂/air can be seen from Fig. 4. The power density at a voltage of 0.7 V decreases from 740 mW/cm² at 900 °C to 520 mW/cm² at 850 °C, 360 mW/cm² at 800 °C and 240 mW/cm² at 750 °C. The voltage losses of the different cell components were determined by impedance spectroscopy measurements. The Bode diagram (Fig. 5) measured at a current density of 200 mA/cm² shows low ohmic impedances R₀ in the high frequency
Figure 4. Performance of a VPS thin-film cell (YSZ/Ni anode, YSZ electrolyte, YSZ/LSM cathode) with H₂/air as the operating gases in dependence of temperature.

Figure 5. Bode plot of a VPS thin-film cell (YSZ/Ni anode, YSZ electrolyte, YSZ/LSM cathode) with H₂/air as the operating gases at 200 mA/cm² current density in dependence of temperature.
range and also low total impedances $R_{\text{total}}$ in the low frequency range. The ohmic area specific resistances (ASR) change from 0.11 $\Omega \text{cm}^2$ at 900 °C to 0.24 $\Omega \text{cm}^2$ at 750 °C and the total ASR from 0.44 $\Omega \text{cm}^2$ (900 °C) to 1.14 $\Omega \text{cm}^2$ (750 °C). The ASR of the different cell components and their percentage of the overall cell resistance calculated from the fit of the spectra which were performed at varying conditions is depicted in Fig. 6 for the temperature range 750 – 900 °C.

![Figure 6. Area specific resistances of the components of a VPS thin-film cell (YSZ/Ni anode, YSZ electrolyte, YSZ/LSM cathode) with H$_2$/air as the operating gases at 200 mA/cm$^2$ current density as a function of temperature](image)

From the variation of the operating conditions three frequency dependent processes could be determined: The polarization resistance at the anode $R_{\text{ct(A)}}$ appears in the high frequency range and the polarization resistance at the cathode $R_{\text{ct(C)}}$ in the middle frequency region. In the low frequency range the binary diffusion of H$_2$ and H$_2$O is taken into consideration by the Nemst-term $R_{\text{N}}$. The relative losses at the YSZ electrolyte decreases from 25 % at 900 °C to 21 % at 750 °C. The resistances at the plasma sprayed anode and the losses due to Nemst-diffusion are in the range 5-14 %. These values are nearly temperature independent. A strong increase of the cathode’s polarization resistance with decreasing operating temperature can be observed. In order to further enhance the performance of the cells it is therefore necessary to improve the microstructure of the cathode and to use higher ion-conducting electrolyte materials, such as e.g. ScSZ.

In Fig. 7 the I-V behaviour of a sprayed cell using ScSZ for the electrolyte and as an addition for the anode and the mixed cathode is shown. The power density at a voltage of 0.7 V is about 1250 mW/cm$^2$ at 900 °C for H$_2$/O$_2$ operation and 750 mW/cm$^2$ for operation with H$_2$/air. The reduction of the power density with decreasing operating tempera-
Figure 7. Performance of a VPS thin-film cell (ScSZ/Ni anode, ScSZ electrolyte, ScSZ/LSM cathode) at 900 °C and H₂/O₂ and H₂/air as the operating gases.

Figure 8. Performance of a VPS thin-film cell (ScSZ/Ni anode, ScSZ electrolyte, ScSZ/LSM cathode) with H₂/air as the operating gases as a function of temperature.
tures can be seen from Fig. 8 for H$_2$ and air as operating gases for the temperature range 750 – 900 °C. At 750 and 800 °C reasonably high power densities of 280 mW/cm$^2$ and 410 mW/cm$^2$ respectively were achieved with ScSZ containing plasma sprayed cells. Impedance spectroscopy measurements performed at a current density of 200 mA/cm$^2$ (Fig. 9) revealed further reduced ohmic area specific resistances (0.04 – 0.06 Ωcm$^2$) resulting in also very low total ASR values between 0.42 Ωcm$^2$ at 900 °C and 0.91 Ωcm$^2$ at 750 °C.

![Bode plot of a VPS thin-film cell](image)

**Figure 9.** Bode plot of a VPS thin-film cell (ScSZ/Ni anode, ScSZ electrolyte, ScSZ/LSM cathode) with H$_2$/air as the operating gases at 200 mA/cm$^2$ current density as a function of temperature.

The area specific resistances of the components of this cell type evaluated from impedance spectra are summarized in Fig. 10 for the temperature range 750 – 900 °C. It is shown that ScSZ is an effective material in order to reduce the ohmic resistance of the cell. The relative losses are in the range of 9 % at 900 °C and of only 7 % at 750 °C. The polarization resistance of the sprayed ScSZ+NiO - anode is very low, whereas the polarization resistance of the cathode gives the highest contribution.
CONCLUSION

The concept of a metallic substrate supported thin-film SOFC and the fabrication of the cells by a vacuum plasma spray process adapted to the specific task has been demonstrated. The electrochemical characterization of the plasma sprayed cells revealed good electrochemical cell performance with power densities of 300 – 400 mW/cm² at reduced operating temperatures of 750 – 800 °C. The further development work will focus on further improving the layers’ microstructures and thus the electrochemical performance and on scaling up the cells to a size of 250 x 250 mm². Stacks with several cells of this size will be assembled and investigated in short-term and long-term operation in order to obtain stack performance and durability results.

The vacuum plasma spray technology has a high potential to be a mass production process. Within a multi-chamber installation using several plasma torches for each layer thin-film cells might be manufactured continuously in only one consecutive process. Cost estimations for such a process revealed a significant cost reduction for the production of thin-film cells in the range of less than $150/kW.
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