CURRENT STATUS OF METALLIC SUBSTRATE SUPPORTED THIN-FILM SOFC AT DLR STUTTGART

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ABSTRACT

The planar metallic substrate supported thin-film SOFC concept developed at DLR Stuttgart on the basis of advanced plasma spray technology ("spray concept") enables the fabrication of complete cells with a size of up to 20 x 20 cm². The electrode layers and the thin electrolyte with a total thickness of the MEA structure of less than 100 - 120 μm are consecutively deposited onto a porous metallic substrate in a single time- and cost-effective spray procedure. The thin-film cells show high electrochemical performance at reduced operating temperature in the temperature range 750 - 800 °C. The present paper describes the current status of the DLR spray concept including fabrication technology and scale-up aspects, recent developments with materials and components and electrochemical performance of plasma sprayed thin-film SOFC.

INTRODUCTION

Second-generation planar solid oxide fuel cells to be operated at an intermediate temperature regime below 800 °C are currently under development at various research groups. Such a lower operating temperature promises reduced material costs for interconnects and peripheral high-temperature components as well as a longer lifetime of SOFC stacks. The move from self-supporting electrolyte to thin-film concepts requiring a supported cell technology is a commonly applied approach in this respect, mostly on the basis of anode-supported cell structures (1-5). At DLR Stuttgart (German Aerospace Center) a novel planar concept ("spray concept") for a metallic substrate supported thin-film SOFC based on advanced vacuum plasma spray technology (VPS) as manufacturing process has been developed (6,7). The plasma spray technique which has been further developed at DLR is applied to fabricate the entire membrane-electrode assembly (MEA) in a single consecutive fast spray process avoiding any time-consuming sintering steps. 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. The principle and design of the...
substrate supported DLR spray concept is schematically shown in Fig. 1 and has been described in detail previously (8).

![Diagram of SOFC design according to DLR spray concept]

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

The mechanical strength of the thin-film cell is provided by an open porous metallic substrate which also serves as a fuel gas distributor. The anode, electrolyte and cathode layers are consecutively deposited by the VPS process in a single procedure onto this substrate. 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. A stack concept based on plasma sprayed cells has been designed and the adequate stack technology in order to build and test stacks in the power range of 1 - 5 kW is currently being developed.

CELL FABRICATION BY VACUUM PLASMA SPRAYING

The plasma spray technology and the special VPS installation which is used at DLR for the fabrication of SOFC components has been described in previous publications (8,9). Some special features of the equipment used that are essential for SOFC application include novel high-velocity DC plasma torches with Laval-like nozzle contours to be operated at supersonic conditions, internal powder injection through different injection ports along the torch nozzles, a robot-controlled torch manipulation and the additional utilization of radio-frequency (RF) plasma technology.

The spray powders used for the deposition of the different layers of the MEA are summarized in Table 1. Both YSZ and ScSZ powders are used for the electrolyte layer and both are combined with NiO in the case of the anode and with LSM in the case of the cathode.
Table 1: Powders used for cell fabrication

| Powder                          | NiO | ZrO$_2$ 7 mol% Y$_2$O$_3$ | ZrO$_2$ 10 mol% Sc$_2$O$_3$ | (La$_{0.8}$Sr$_{0.2}$)$_{0.98}$MnO$_3$ |
|--------------------------------|-----|---------------------------|----------------------------|--------------------------------------|
| Short name                     | NiO | YSZ                       | ScSZ                       | LSM                                  |
| Morphology                     | sintered, crushed | sintered, crushed        | sintered, crushed           | sintered, spherical                  |
| Size distribution              | 10 - 25 µm | 5 - 25 µm                 | 2 - 35 µm                  | 20 - 40 µm                           |
| Supplier                       | Cerac, USA | Medicoat, Switzerland | Siemens, Kerafol, Germany | EMPA, Switzerland                    |

In order to determine the optimum spray conditions to achieve the desired microstructures the spray parameters of the different powders were optimized by means of laser Doppler anemometry (LDA) measurements. Applying optimized process parameters entirely plasma sprayed cells of different sizes have been fabricated in a consecutive spray process. Fig. 2 shows an optical micrograph of the metallographic cross-section of a thin-film cell consisting of a 35 µm thick NiO/YSZ anode, a 25 µm thick electrolyte and a 30 µm thick cathode deposited onto a porous metallic felt structure.

![Fig. 2: Metallographic cross-section of entirely plasma sprayed thin-film cell](image)

**RECENT DEVELOPMENTS IN MATERIALS AND COMPONENTS**

**Substrate**

Metallic substrates to support thin-film cells exhibit high mechanical strength and excellent electrical conductivity. Further requirements which have to be met by candidate materials are a sufficient gas permeability, an adapted thermal expansion behavior with respect to the MEA layers and adequate oxidation stability at SOFC operating conditions. Various metals and alloys shaped as porous plates as well as felt or gauze structures (Table 2) have been investigated and tested for SOFC application.
Table 2: Materials studied for use as substrate for SOFC cells

| Substrate  | Material                  | Thickness [mm] | Porosity [Vol.%] | Supplier               |
|------------|---------------------------|----------------|------------------|------------------------|
| Cr-ODS     | Cr-5%Fe-1%Y₂O₃ plate      | ~1.0           | ~35              | Plansee, Austria       |
| Ni felt    | Ni felt                   | ~2.0           | ~80              | Medicoat, Switzerland  |
| Sika-R20-AS| Fe-18%Cr-12%Ni-2%Mo plate  | ~2.0           | ~45              | GKN, Germany           |
| Hastalloy  X| Ni-22%Cr-19%Fe-9%Mo felt  | ~1.0           | ~80              | Technetics, FL, USA    |
| Bekipor ST | Fe-18%Cr-14%Ni-3%Mo felt  | ~0.5           | ~80              | Bekaert, Belgium       |

Both chromium- and nickel-based alloys (Cr-ODS, Hastalloy X) and stainless steel plates and felts (Sika-R20-AS, Bekipor ST) show adequate behavior in terms of porosity (35 - 80 vol. %) thermal expansion and electrical conductivity (see Fig. 3). But in most cases poor oxidation stability particularly at annealing at 900 °C (for 50 hours) in Ar-5% H₂ atmosphere with different amounts of water steam between 2 and 50 % was observed. The most promising material studied with regard to the above mentioned criteria turned out to be a nickel felt which in particular showed excellent oxidation stability in all relevant gas atmospheres. A problem could possibly arise with this material with large cell areas above 10 x 10 cm² because of the mismatch of the thermal expansion coefficients (YSZ: 10.5 \( \cdot 10^6 \) K⁻¹, Ni: 16.0 \( \cdot 10^6 \) K⁻¹). But on the other hand, the inherent flexibility of the felt structure is able to compensate this mismatch to a certain extent. It is expected that crack-free deposition of MEA layers onto large Ni felts is strongly dependent on the manner how to fix the felt on the interconnect in order to provide favorable conditions.

![Electrical conductivity of different porous metallic substrates](image.png)

Fig. 3: Electrical conductivity of different porous metallic substrates in Ar-5% H₂-2 % H₂O atmosphere at 900 °C as a function of time
Cathode

The porosity of the electrodes can be controlled with plasma spraying by proper selec­tion of the process parameters such as predominantly the powder grain size fraction, the torch power, the tank pressure and the spray distance. Due to the subsequent reduction of NiO to Ni during operation of the cells the anode’s porosity is further increased to a sufficient extent of more than 20 vol. % including many small pores while the lack of this “pore forming process” leads to a significantly lower overall porosity in the cathode layers. Impedance spectroscopy measurements revealed that the by far highest contribution to the cell’s polarization resistance is from the cathode, resulting from its limited porosity. Therefore, strong effort is made on the improvement of the cathode’s pore structure. Two approaches are pursued in this respect, namely the use of pore formers during spraying and subsequent removal and the in situ synthesis of cathode coatings by applying radio-frequency (RF) plasma technology.

A promising method to improve porosity of plasma sprayed layers is the addition of particles such as carbon species to the powder feedstock which act as pore formers and to remove these species after spraying by annealing in air (10). A first attempt to apply this method for SOFC cathodes was carried out by using LSM powders containing carbon particles with different grain sizes. The powders prepared by spray drying of aqueous slurry mixtures at EMPA, Dübendorf (Switzerland), consist of a 1:1 mixture of LSM powder as used for VPS cathode fabrication which was ground to a size fraction between 1 μm and 6 μm and carbon particles of different grade with grain sizes between 0.3 and 12 μm resulting in agglomerated spheres with a grain size of 21 μm < d_{50} < 37 μm. Fig. 4a shows the typical morphology of the LSM/carbon powder used.

![Fig. 4a: Morphology of LSM/carbon powder agglomerates](image1)

![Fig. 4b: Plasma sprayed cathode layer using LSM/carbon powder after annealing in oxygen at 900 °C](image2)
These powders were successfully plasma sprayed followed by annealing in oxygen at 900 °C to burn out residual carbon and to form porous LSM layers. The microstructure of the resulting layers (Fig. 4b) shows significantly enhanced porosity of about 30 vol. %. Quantitative image analysis has shown a fine pore size distribution in the range of 0.1 - 10 μm. In comparison the layers originating from pure LSM powder feedstock revealed a porosity of only 10 vol. % with a coarser pore size distribution. The development of improved cathodes by using pore formers is continued.

Radio-frequency inductively coupled plasma with its intrinsic properties such as the slow but large volume plasma jet resulting in a long residence time of species in the plasma and the electrodeless plasma generation which enables operation under a wide range of conditions including oxidizing atmosphere offers favorable properties for plasma chemical reactions by using liquid precursors such as suspensions or solutions. With the so-called Thermal Plasma Chemical Vapor Deposition (TPCVD) process using aqueous solutions of nitrates and acetates which are fed and directly gas atomized into the plasma through an atomization probe it is possible to synthesize and directly deposit perovskite-type cathode layers onto a substrate (11). As the perovskite phase is formed with this process from the vapor phase and subsequent condensation the deposited layer exhibits columnar crystal growth resulting in a microstructure with high open porosity. Fig. 5 shows a SEM image of a fracture section of a TPCVD perovskite coating with the composition La_{x}Sr_{y}MnO_{3} having high open porosity in perpendicular direction to the substrate and hence giving good chances to overcome the problem of limited cathode porosity.

![Fig. 5: SEM image of a fracture section of TPCVD perovskite coating](image-url)
**Contact layer between cathode and interconnector**

In usual planar stack assembly the interconnector is contacted with the cathode at temperatures above 800 °C. At this temperatures the ductility of the contact layer (for instance lanthanum strontium manganese cobaltite) has to be sufficiently high. It has been seen from experiments that the contact layer should be ductile up to 30 % of its original thickness. There are different procedures to prepare the electrically conducting and ductile contact layer. With wet powder spraying (WPS) a sprayed suspension is used for the contact layer whereas with the screen printing technique a paste is applied. In both cases the dried contact layer has a green density of 2.9 to 3.9 g/cm³.

Experiments have shown that the printed layers are not ductile up to 1000 °C with a load of 400 p/cm² while the WPS layers are ductile at temperatures of 200 to 300 °C at the same load due to the burn out of the organic binder. These values differ significantly from the desired ones. At 850 °C sintering of the powder starts leading to a solidification of the structure. From this reason the required ductility of the contact layer can not be achieved above 850 °C. SEM micrographs show that only 30 % of the contact area on the cathode is in contact with the contact layer. This leads to an increase of the contact resistance and to a reduction of the stack power while operating the SOFC at high temperatures. With the addition of pore forming materials the porosity of the contact layer is increased, hence providing higher deformation. This pore forming material, either in the liquid or in the solid state, burns out without residue and leads to an increased porosity. The volume fraction of the pore formers in the dried contact layer can reach 50 vol.%. This reduces the green density to 1.7 g/cm³ and provides a higher ductility of the contact layer. In spite of the increased porosity the contact layer has still a sufficiently high electrical conductivity and the contribution to the total ohmic resistance is negligible.

**Sealing technology**

For the sealing of the stack components a typical alkaline earth borosilicate glass is used (12). The base composition of this glass ceramic is 51 wt.% SiO₂, 24 wt.% BaO, 14 wt.% B₂O₃, 11 wt.% Al₂O₃ with an addition of 0 - 10 wt.% MgO. This is a slowly crystallizing glass with hexacelsian and cristobalite as crystalline phases. The sealing temperature can vary between 900 °C and 1000 °C. Crystallization kinetics are to a large extent adjustable through the MgO concentration and through the sealing temperature. Whereas the thermal expansion coefficient of the glass is only 4.5 · 10⁻⁶ K⁻¹, it is in the crystallized state nearly 10 · 10⁻⁶ K⁻¹. The viscosity increases with the crystallisation by a factor of 10⁶.

For sealing the stack components a green foil is made from glass powder by tape casting. The sealing parts are punched and ground to a definite thickness. These parts are laminated with the metallic plates by use of the foil binder or a screen printed glass paste. This is a simple and cost-effective technique. An important problem in the case of a green foil as sealing material is the suppression of the lateral shrinkage. Therefore, the green foil has to be held under compressive stress during the shrinkage period between 700 °C and 820 °C. Under pressure the shrinkage takes place only in the foil thickness.
and the lateral design is not changed. With this material gastight sealings with long-term stability at the working temperature of the SOFC are possible.

**SCALE UP OF CELL AREA**

Based on the spray conditions for the single layers entirely plasma sprayed cells have been fabricated in a consecutive spray process using both porous metallic plates and metal felts as substrates. Details on the fabrication of circular cells with active areas between 5 and 54 cm² are reported in (8). For the stack design as described above the scale up of square-shaped cells up to a final size of 20 x 20 cm² is required which is currently under development. When using porous plates whose thermal expansion coefficient is well adapted to the MEA layers large area cells up to 350 cm² active area can easily be fabricated. For the application of thin Ni felts as substrate for large area SOFC cells, however, these substrates have to be fixed on the metallic bipolar plate with a metallic solder prior to spraying. The thermal expansion behavior of large felt substrates during the coating process depends strongly on process parameters and the characteristics of substrate fixation. Square-shaped cells with dimensions between 5 x 5 cm² and 20 x 20 cm² by using both porous plates and brazed interconnect/Ni felt compound units are exemplarily shown in Fig. 6.

![Fig 6: Vacuum plasma sprayed square-shaped cells with the dimensions 5 x 5 cm², 10 x 10 cm² and 20 x 20 cm²](image-url)
ELECTROCHEMICAL PERFORMANCE

The electrochemical characterization of plasma sprayed cells up to a size of approximately 50 cm² active area by means of I-V characteristics and impedance spectroscopy measurements prove high power densities and allow for the reduction of the operating temperature to below 800 °C with still reasonably high electrochemical performance. At 900 °C power densities in the range of 800 mW/cm² with ScSZ containing cells and of 600 mW/cm² with YSZ containing cells are achieved at 0.7 V when operated with hydrogen and air as operating gases. At reduced operating temperatures down to 750 °C the power densities decrease to approximately 300 mW/cm² with ScSZ containing cells and 200 mW/cm² with YSZ containing cells, respectively. Fig. 7 shows the electrochemical performance of a plasma sprayed thin-film cell using ScSZ as electrolyte material as a function of temperature.

The evaluation of impedance spectroscopy measurements reveals low ohmic and total resistances. The ohmic resistance of the thin electrolyte contributes with around 10 % only little to the overall cell resistance whereas the highest contribution by far is caused by the cathode. Recently performed investigations indicate that highly porous LSM/carbon cathodes, as described before, reveal a significantly reduced polarization resistance.

Fig. 7: Electrochemical performance of a VPS thin-film cell (ScSZ/Ni anode, ScSZ electrolyte, ScSZ/LSM cathode) as a function of temperature (operating gases: 0.9 SLPM H₂, 1.5 SLPM air)
CONCLUSIONS

Metallic substrate supported thin-film solid oxide fuel cells are fabricated by using advanced plasma spray technique according to a novel “spray concept”. Entirely plasma sprayed cells of laboratory scale show promising high electrochemical performance also allowing for operation at reduced operating temperature below 800 °C. The present development work is essentially dedicated to the further improvement of materials and components such as the metallic substrate, the cathode and the sealing technology as well as the simultaneous scale up of cell fabrication to a final cell size of 20 x 20 cm². The stack technology is currently being developed in order to build up short stacks and stacks to shortly perform short-term and long-term operational tests.

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