DEVELOPMENT OF THIN-FILM SOFC FOR STATIONARY AND MOBILE APPLICATION BY USING PLASMA DEPOSITION TECHNOLOGY

Günter Schiller, Thomas Franco, Rudolf Henne, Michael Lang and Patric Szabo
German Aerospace Center (DLR)
Institute for Technical Thermodynamics
Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany

O. Finkenwirth, B. Kuhn, F.-J. Wetzel
BMW Group, Future Powertrain Technology Projects
D-80788 Munich, Germany

ABSTRACT

At the German Aerospace Center (DLR) in Stuttgart, a concept for planar SOFC using a metallic substrate support and thin-film layers, which are deposited by plasma spray processes (spray concept), has been developed. This concept enables the fabrication of the entire membrane-electrode assembly in a single consecutive spray process without any sintering steps or other thermal post-treatment after spraying, thus promising fast and cost-effective cell fabrication. Based on this concept adequate stack designs and stack technologies for the assembly of stacks have been developed for both stationary and mobile applications. The nature of the cell supporting substrate has a significant influence on the electrochemical performance of plasma sprayed cells; hence substrate development is a key issue. This paper describes the current status of development of the DLR spray concept including the stack designs, scale-up aspects of the fabrication technology, recent developments with substrates and the electrochemical characterization of single cells and short-stacks for both stationary and mobile applications.

INTRODUCTION

DLR Stuttgart has developed a planar thin-film concept of a metallic substrate supported SOFC - called “spray concept” - which is based on plasma spray technology for the manufacture of the entire cell. The characteristic properties of the plasma spray process such as short process time without any post-treatment after spraying, high material deposition rate and the ability to be transferred to an automated production line enable cost-effective and rapid cell fabrication with large active cell areas.

The principle of the substrate supported DLR spray concept is schematically shown in Figure 1 and has been described in detail previously (1). The mechanical strength of the thin-film cell as well as excellent electrical and thermal conductivity is provided by an
open porous metallic substrate, which also serves as a fuel gas distributor. All functional layers of the cell – anode, electrolyte and cathode – are consecutively deposited onto this substrate by a multi-step vacuum plasma spray (VPS) process in a single procedure.

The thickness of the electrolyte can be reduced to 20-30 μm resulting in a membrane-electrode assembly (MEA) with a total thickness of 100-120 μm due to the high strength of the substrate support. The contact from the cathode to the ferritic steel interconnect is provided by a flexible and ductile perovskite-type foil or coating and an additional protective coating is deposited onto the metallic interconnect by VPS to prevent the evaporation of chromium species from the metal alloy.

The plasma spray technology and the VPS installation used have been described previously (2). Special features of the facility that are essential for SOFC cell fabrication are high-velocity DC plasma torches with own-developed Laval-type nozzles to be operated at supersonic conditions, internal powder injection through different injection ports along the torch nozzle and robot-controlled torch manipulation.

The spray powders used for the deposition of the different layers of the MEA consist of conventional SOFC materials such as YSZ (7 mol %, 5-25 μm) for the electrolyte and in combination with NiO (10-25 μm) and LSM (20-40 μm) for the anode and the cathode, respectively.

**Figure 1.** Principle of planar SOFC design according to DLR spray concept.

**STACK DESIGNS OF DLR SPRAY CONCEPT**

A stack design based on plasma sprayed cells and machined ferritic steel interconnect plates and an adequate stack technology for the assembly of stacks in the power range of
1-5 kW has been developed (3). An exploded view of this design with interconnect plate, frame and cell assembly is shown in Figure 2. Internal manifold for fuel gas and air is used with gas distribution in counter flow mode. Sealing of the ferritic steel interconnects is done with punched green foils of glass seal consisting of alkaline earth borosilicate glass which are laminated with the metallic plates by using the foil binder or a screen printed glass paste.

The porous metallic substrate offers advantageous such as possible integration of the interconnect plate through welding and brazing techniques. The interconnect consisting of two parts, a plate and a frame, allows for adaptation of the frame height to the thickness of the different substrates used. The functional ceramic layers of the cell are then plasma sprayed onto the brazed substrate-interconnect unit. The brazing of the substrate provides an excellent electrical contact to the cell’s anode.

For automotive application to be used as an APU (auxiliary power unit) for on-board electricity generation in vehicles (4) the DLR stack technology has been modified to meet the very strict requirements for reduced volume and weight. This stack design has been developed within a consortium of companies led by BMW AG which bring in their specific know-how as proven automotive suppliers such as ElringKlinger AG, RHODIUS GmbH and ThyssenKrupp Stainless (Nirosta and VDM).

This technology is based on thin stamped metal sheets which can be laser welded to form a metallic bipolar cassette arrangement with integrated brazed metallic substrate. A 3-D view of the cell design for APU application is shown in Figure 3. For the sealing of the gas ducts between the different cassette units rings of ceramic material are used.
A key issue for the cell fabrication with the spray concept is the substrate material which should combine different properties such as high electrical conductivity, an adapted thermal expansion coefficient related to the ceramic layers, a suitable porous structure with high mechanical strength and excellent corrosion stability during operation. Conventional SOFC substrate materials such as a nickel felt, a porous sintered Cr-ODS alloy and a porous stainless steel plate fulfill only partially the required properties which necessitates a separate substrate development in co-operation with partners from industry and research establishments.

A variety of commercially available materials mainly with ferritic structure was intensively investigated under SOFC relevant conditions (5). The best material studied with regard to oxidation stability turned out to be a nickel felt, but a problem arises with this material with large cell areas of 10 x 10 cm² and above because of the quite high mismatch of the thermal expansion coefficients of Ni and YSZ. A material with much better adapted thermal expansion behavior and high oxidation resistance at high temperatures are FeCrAlloy materials, such as for example Fe-22Cr-5Al-0.1Y which can be processed to foams or woven wire structures. The reason for the excellent oxidation stability can be attributed to the formation of a thin alumina scale, which protects the basic material through a dense coating, and the oxidation process is practically stopped. On the other hand, the electrical conductivity of the substrate is decreased due to alumina formation. This implies that for an ideal substrate a secondary conducting material which is not oxi-
dized, such as for instance Ni, has to be integrated into the substrate structure which might be a porous foam, a felt, a fiber texture or a knitted or woven wire structure. A very promising material is a ferritic steel with low Al content (CroFer22APU), which was developed at Research Center Jülich (6) and is produced by ThyssenKrupp. Knitted wire structures of this material prepared by RHODIUS are currently under investigation. More details on the investigation and test of metallic substrates are given in this proceedings volume (7).

**ELECTROCHEMICAL PERFORMANCE**

In the course of the scale-up process from laboratory scale cells with an area of some cm\(^2\) to the targeted final size of 20 x 20 cm\(^2\), presently plasma sprayed cells with an area of 5 x 5 cm\(^2\) and 10 x 10 cm\(^2\) were fabricated and electrochemically investigated in metallic housings and short-stack arrangements. Figure 4 shows the set-up of a cell of 10 x 10 cm\(^2\) for stationary application in a metallic housing as well as a metallographic cross section of a plasma sprayed cell on a porous substrate.

![Figure 4. Plasma sprayed cell of 10 x 10 cm\(^2\) in metallic housing and metallographic cross section of the cell on a porous metallic substrate.](image)

The nature of the cell supporting substrate has a significant influence on the electrochemical performance of plasma sprayed cells. Figure 5 shows the current density/voltage characteristics of two cells of 10 x 10 cm\(^2\) (85 cm\(^2\) active area) in a metallic housing, which contain different substrates, as are a porous FeCrAlY foam and a Ni felt, respectively. The cells were operated at 900°C with 2 SLPM H\(_2\) and 2 SLPM air. The open circuit voltage (OCV) of the Ni felt containing cell is much lower compared to the cell with the FeCrAlY substrate. The reason for this might be the higher thermal expansion of Ni, which promotes microcracks in the thin plasma sprayed YSZ electrolyte. However, the cell with the Ni felt support achieves a higher power density compared to the cell with the
FeCrAlY substrate. More detailed information particularly on investigations with impedance spectroscopy are given in this proceedings volume (8).

With FeCrAlY substrate supported cells (85 cm² active area) a first 2-cell stack test was performed at 900°C with H₂ and O₂ (2 SLPM). The high OCV of nearly 2200 mV indicates the proper sealing of the cells in the stack. The overall electric output at a cell voltage of 700 mV was 24 W, which means an average power density of approximately 140 mW/cm². The maximum power achieved was 31 W or 182 mW/cm², respectively.

Recent results of the electrochemical characterization of plasma sprayed cells of 10 x 10 cm² size with the cassette arrangement with thin metal sheet interconnect for automotive application are shown in Figures 6 and 7. A single cell revealed a power density of 180 mW/cm² with H₂/air and 150 mW/cm² with H₂/N₂ (1:1) as a simulated gasoline reformate (without CO) and air at a voltage of 700 mV and an operating temperature of 800°C (Figure 6).

A first 3-cell stack with this arrangement showed a power density of 115 mW/cm² per cell at 800°C when operated with H₂/N₂ (1:1) and air (Figure 7). The OCV of the 3-cell stack was 2750 mV. Further development work concentrates on the improvement of stack performance, reduced start-up time of approximately 10 minutes and stable behavior at multiple thermal cycles.

Figure 5. Current density/voltage characteristics of plasma sprayed cells (85 cm² active area) containing different substrates (Ni felt, FeCrAlY foam) at 900°C with H₂ and air (2 SLPM).
Figure 6. Current density/voltage characteristics of a single cell (81 cm² active area) in cassette arrangement at 800°C operated with H₂/air and H₂/N₂ (1:1) and air.

Figure 7. Current density/voltage characteristics of a 3-cell stack in cassette arrangement at 800°C operated with H₂/air and H₂/N₂ (1:1) and air.
CONCLUSIONS

Metallic substrate supported thin-film solid oxide fuel cells, which are completely fabricated by applying advanced plasma spray technology show promising properties for stationary as well as mobile application. The electrochemical performance of cells and short-stacks with a size of 10 x 10 cm² depends strongly on the material and structure of the cell supporting substrates. Further progress in cell performance is expected from the development and optimization of novel substrates, which combine the favorable properties of Ni and FeCrAlloy materials in terms of electrochemical activity and thermal expansion. Short-term and long-term electrochemical investigations and tests including thermal cycling experiments of stacks will prove the potential of plasma sprayed cells particularly for mobile application in the near future.

ACKNOWLEDGMENTS

Financial support through the German Federal Ministry of Economics and Technology (BMWi) and BMW Group for the development of the spray concept is gratefully acknowledged.

REFERENCES

1. G. Schiller, R. Henne M. Lang, R. Ruckdäschel and S. Schaper, Fuel Cells Bulletin – An International Newsletter, 21, 7, (2000).
2. G. Schiller, R. Henne and V. Borck, J. Thermal Spray Techn. 4 (2), 185, (1995).
3. P. Szabo, T. Franco, R. Henne, M. Lang, R. Ruckdäschel and G. Schiller, in Fifth European SOFC Forum, J. Huijsmans, Editor, PV 2, p. 806, (2002).
4. J. Zizelman, C. DeMinco, S. Mukerjee, J. Tachtler, J. Kammerer and P. Lamp, in Fifth European SOFC Forum, J. Huijsmans, Editor, PV 2, p. 1153, (2002).
5. T. Franco, R. Henne, M. Lang, G. Schiller and P. Szabo, in Fifth European SOFC Forum, J. Huijsmans, Editor, PV 2, p. 647, (2002).
6. W. J. Quadakkers, T. Malkow, J. Piron-Abellan, U. Flesch, V. Shemet and L. Singheiser, in Fourth European SOFC Forum, A. J. McEvoy, Editor, PV 2, p. 827, (2000).
7. T. Franco, R. Henne, M. Lang, P. Metzger, G. Schiller and P. Szabo, in SOFC-VIII, S. C. Singhal and M. Dokiya, Editors, this proceedings volume, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).
8. M. Lang, T. Franco, P. Metzger, G. Schiller, M. v. Bradke and S. Ziehm, in SOFC-VIII, S. C. Singhal and M. Dokiya, Editors, this proceedings volume, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).