

# Development of Metallic Substrate Supported SOFC at DLR Stuttgart

G. Schiller  
German Aerospace Center (DLR)  
Institute of Technical Thermodynamics  
Stuttgart, Germany

## 1. Introduction

Improvement of power density and lifetime and, above all, reduction of production costs which are still far too high are common objectives of all development work presently done on solid oxide fuel cells. Recent development concentrates therefore on possibilities allowing for reduction of operating temperature, on improved cell and stack designs and on more cost-effective processes for the production of relevant materials and also of cell components. The modular principle with a large number of single cells enables principally inexpensive series manufacturing. Additionally to stationary applications of SOFCs, such as combined heat and power for domestic use, larger buildings and industrial plants, recently also smaller SOFC stacks in the power range up to 5 kW gained special attraction for mobile applications, for instance for on-board electricity supply in vehicles. Such Auxiliary Power Units (APU) can be operated independently from the combustion engine to cover the increasing demand of electrical energy in passenger cars with high efficiency. This contributes to higher comfort, for example through auxiliary air conditioning, telecommunication etc., as well as to saving of fuel [1].

Plasma spray technologies as an alternative approach to conventionally applied sintering techniques have been applied for SOFC components such as interconnection strips of Siemens Westinghouse cathode tubes [2], functional layers in the planar Sulzer Hexis concept [3] and in the tubular concept of Mitsubishi Heavy Industries [4] as well as for protective coatings of interconnect plates [5]. Based on advanced plasma deposition processes with both DC and RF generated plasmas which have been further developed and adapted to the needs of electrochemical energy conversion processes DLR Stuttgart has developed a concept of a planar SOFC with consecutive deposition of all layers of a thin-film cell onto a metallic substrate support [6]. The current state of this DLR spray concept and its further potential is summarised in this paper.

## 2. Plasma deposition technologies for SOFC fabrication

Standard manufacturing techniques for SOFC are based on conventional ceramic wet powder processing and sintering methods such as tape casting, screen printing or wet powder spraying that are further developed in terms of improved product quality and process economy. In an alternative approach DLR concentrates in its SOFC development activities on specially adapted thermal plasma deposition processes with DC and RF plasmas. Fig. 1 shows the principles of DC and RF plasma torches. DC plasma generation is based on the interaction of a gas, mostly argon, with a high current arc discharge, ignited between a finger-shaped cathode and a surrounding hollow anode forming a fast and very hot plasma jet ( $T > 10.000\text{ K}$ ) which leaves the torch exit. Laval-type nozzle contours providing a controlled expansion of the plasma jet accelerate the jet to supersonic velocities of 2000 – 3000 m/s. The powders to be sprayed are injected radially to the plasma where they are accelerated, melted and finally projected onto a substrate. The coating is formed by solidification and flattening of the particles at impact on the substrate. By applying the high-velocity Laval nozzles enhanced spray particle velocities of up to 900 m/s are achieved which is about twice as high as that of standard torches [7].

The RF induction plasma is generated by coupling radio-frequency (RF) energy by means of a coil into the gas volume of a plasma torch [8]. Spray powder can be injected axially in the hot plasma core ( $T > 10.000\text{ K}$ ). Compared to a DC plasma the RF plasma jet has a larger volume but a lower velocity guaranteeing a long and intensive interaction of feedstock and plasma in a long jet. This offers additionally the possibility of plasma chemical reactions in order to synthesise and simultaneously deposit materials originating from simple liquid precursors. The liquid precursors are fed to the plasma torch by means of an antipulse peristaltic pump and atomised through an atomisation probe [9].

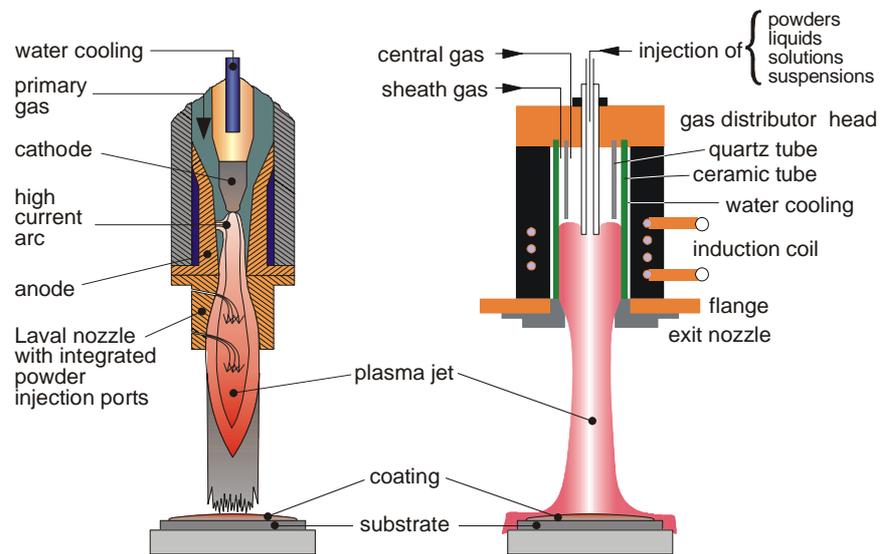


Fig. 1: Principles of DC (left) and RF plasma torches (right)

The development and fabrication of solid oxide fuel cells at DLR is primarily based on the DC plasma process but the RF plasma technology using liquid precursors – the so-called thermal plasma chemical vapour deposition (TPCVD) process – is increasingly applied particularly for the formation of highly porous cathode layers.

DLR is equipped with several plasma spray facilities as it is shown in Fig. 2 with a view to one of the plasma spray laboratories. The main facilities are:

- 3 DC plasma installations of different sizes. Recently, a new large facility with a diameter of the vacuum vessel of 2.4 m allowing for the deposition of high quantities of substrates was set into operation in addition to the installation shown in the background of the picture where the plasma torch is manipulated by a robot system.
- 2 RF plasma installations, where the torch is moved vertically and the substrates are moved in x-y directions.

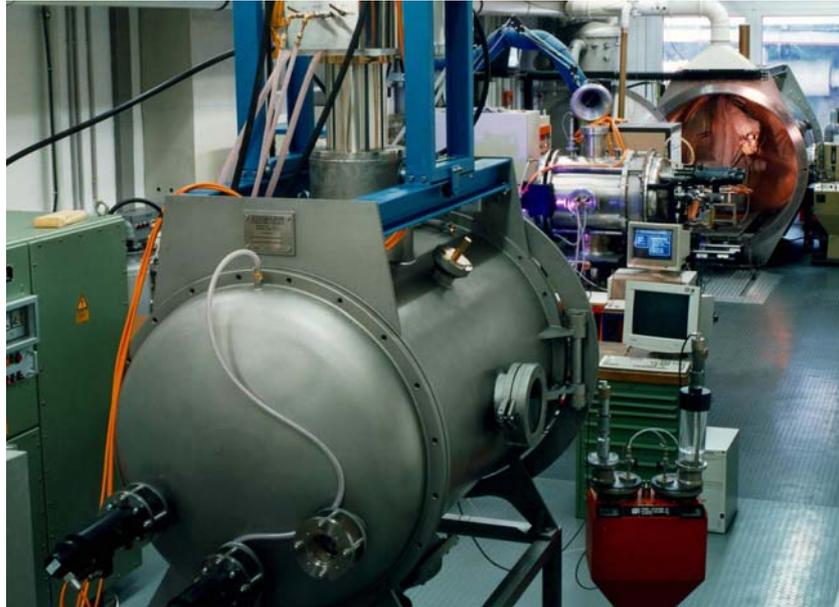
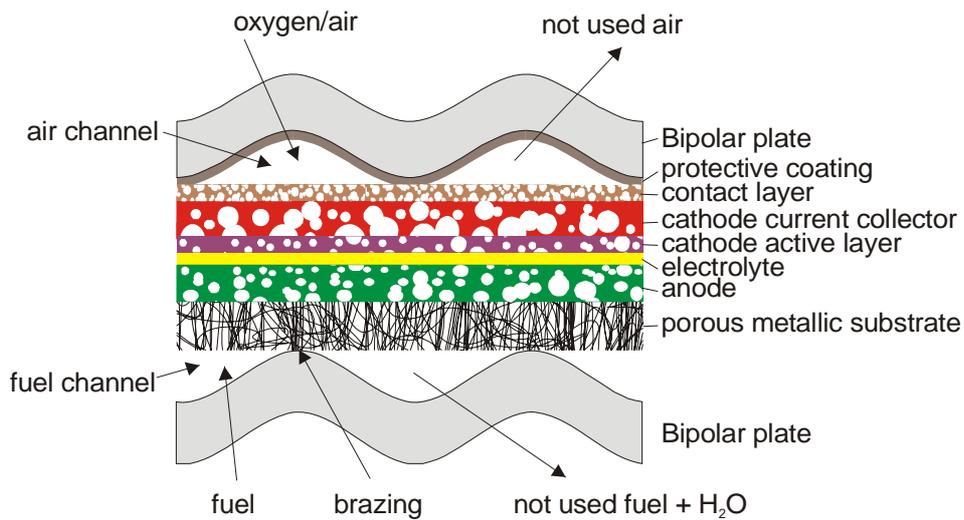


Fig. 2: DLR plasma spray laboratory with DC (background) and RF plasma installation (front)

### 3. DLR SOFC spray concept

First generation SOFCs consisted of electrolyte-supported cells with an electrolyte thickness of 150 – 200  $\mu\text{m}$ . As the ohmic losses are mainly caused by the thick electrolyte development work focused on the reduction of the electrolyte thickness in the next SOFC generation which means a move to an electrode- (mainly anode-) or a substrate-supported design. These new concepts such as the anode-supported cell concept of Research Center Jülich and others [10] as well as the DLR spray concept exhibit such a new design principle with an electrolyte thickness of 10 – 30  $\mu\text{m}$ .



(not in scale)

Fig. 3: Principle of planar SOFC design according to DLR spray concept

Fig. 3 shows the principle of the planar DLR thin-film concept of a metallic substrate-supported SOFC which is based on plasma deposition technology for the manufacture of the entire cell. The mechanical strength of the thin-film cell as well as excellent electrical and thermal conductivity are 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 move from a ceramic to a metallic substrate support reduces considerably the problem of crack formation resulting in large cell size and simplified stack design. A precondition for such a cell and stack design with porous metallic substrate support is of course the availability of a long-term stable and corrosion-resistant material with an adequate thermal expansion behaviour related to the ceramic cell components. The development of such an appropriate metallic substrate in co-operation with industrial partners is presently a main activity with the realisation of the spray concept.

Two stack designs for stationary and mobile application have been developed on the basis of plasma sprayed cells and ferritic steel interconnects. Fig. 4 a shows the stack design for stationary application with relatively thick machined interconnect plate, frame and cell assembly. Internal manifold for fuel gas and air is used with gas distribution through machined gas channels in counter-flow mode. Prior to deposition the metallic substrate is fixed onto the interconnect plate by brazing and laser welding with the rim of the surrounding frame. The functional ceramic layers of the cell are then plasma sprayed onto the substrate/interconnect unit. Additional sealing between the interconnect plates is done by punched green foils of glass seal. For application of an SOFC as an auxiliary power unit (APU) for on-board electricity generation in vehicles and airplanes the stack technology has been modified to meet the very strict requirement of low volume and weight. This technology is based on thin stamped metal sheets which are laser welded to form a metallic cassette arrangement with integrated brazed metallic substrate as it is shown in Fig. 4 b.

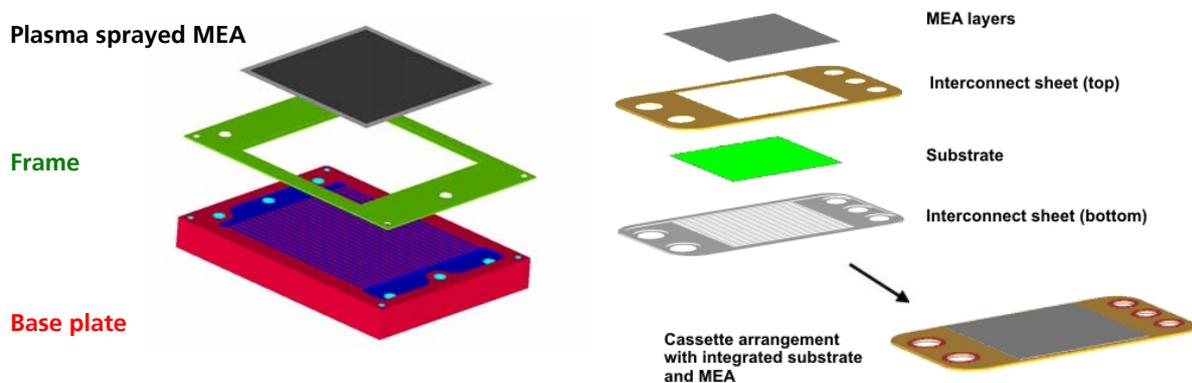


Fig. 4: 3-D view of DLR stack design for a) stationary (left) and b) APU application (right)

#### 4. Current state of development of DLR SOFC spray concept

The core element of a cell, the membrane-electrode assembly (MEA), should exhibit high porosity (> 20 vol. %) of the electrode layers but, on the other hand, a very low closed porosity of the electrolyte of less than 2 vol. %. Furthermore, a graded structure of the interfaces of the different layers with extended three-phase boundaries is recommended. In order to achieve optimum qualities of the different MEA layers extended experimental work and adaptations referring to materials and process parameters have been necessary. Table 1 summarises the preferred powder feedstock at present for the fabrication of the MEA compound.

|                   |                   |  |   |   |
|-------------------|-------------------|--|---|---|
| Powder            | NiO               | ZrO <sub>2</sub> -7mol%Y <sub>2</sub> O <sub>3</sub> | ZrO <sub>2</sub> -10 mol%Sc <sub>2</sub> O <sub>3</sub> | (La <sub>0.8</sub> Sr <sub>0.2</sub> ) <sub>0.98</sub> MnO <sub>3</sub> |
| Short name        | NiO               | YSZ  | ScSZ  | LSM   |
| Morphology        | sintered, crushed | sintered, crushed                                    | sintered, crushed                                       | sintered, spherical   |
| Size distribution | 10 - 25 μm        | 5 - 25 μm  | 2 - 20 μm   | 20 - 40 μm  |
| Supplier          | Cerac, USA        | Medicoat, Switzerland                                | Kerafol, Germany  | EMPA, Switzerland   |

Table 1: Powders used for cell fabrication by DC plasma spraying

Metallic substrates to be used are either nickel felts or ferritic steel structures such as felts, foams or woven wire meshes with a porosity in the range of 50 – 80 vol. %. Nickel exhibits excellent oxidation-resistant properties but a too high mismatch in thermal expansion with the ceramic cell components which causes severe problems in the case of large substrate size. Ferritic steel shows a much better adapted thermal expansion coefficient but corrosion stability is less pronounced. Hence, novel and combined substrates with improved oxidation behaviour are presently under development. The application of special high-velocity DC torches for supersonic conditions is an essential requirement for the deposition of dense high-melting YSZ electrolyte coatings with a thickness of only 20 – 40 μm. Fig. 5 shows the metallographic cross section of an entirely DC plasma sprayed thin-film cell consisting of a 35 μm thick porous NiO/YSZ cermet anode, a 25 μm thick dense electrolyte and a 30 μm thick porous cathode deposited onto a porous metallic felt substrate. Measurements by means of quantitative image analysis reveal a residual porosity of the electrolyte layer in the range of 1 – 2 vol. % with few closed pores. After reduction of NiO to Ni in the anode during operation a further increase of the anode's porosity results in a sufficiently high porosity in the range of 20 – 25 vol. %. But at the cathode side the lack of such a "pore forming process" leads to a limited porosity of only 10 – 15 %. Impedance spectroscopy measurements reveal the by far highest contribution to the cell's polarisation resistance from the cathode due to its relatively low porosity. Therefore, strong efforts are needed to improve the cathode's pore structure.

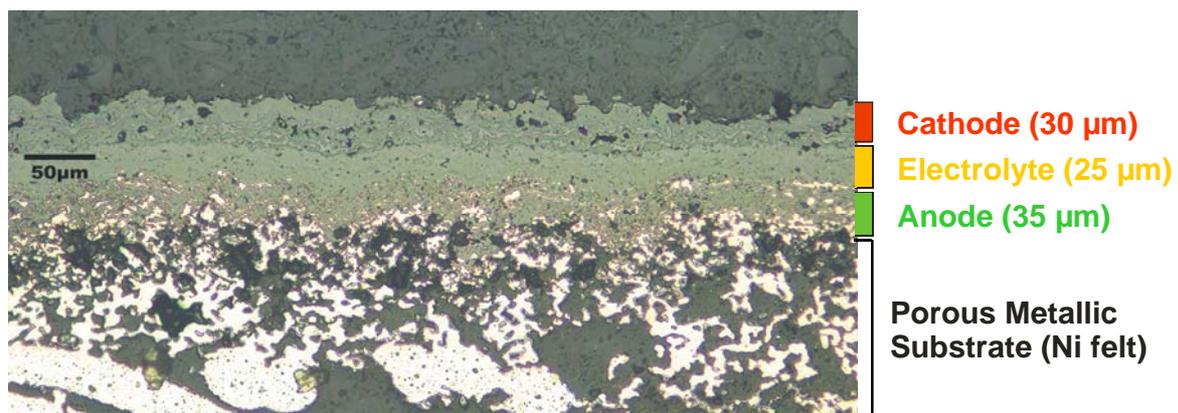


Fig. 5: Metallographic cross section of an entirely plasma sprayed cell on a Ni felt substrate

The electrochemical characterisation of plasma sprayed cells is performed with small circular cells with an area of 12.5 cm<sup>2</sup> which are operated with simulated gasoline reformat consisting of H<sub>2</sub> and N<sub>2</sub> (40 smlpm/cm<sup>2</sup> each) and air (160 smlpm/cm<sup>2</sup>). The performance of cells consisting of a NiO/YSZ anode, YSZ electrolyte and LSM cathode is shown in Fig. 6 as a function of the operating temperature in the range of 700 – 850 °C. At the operating conditions which will be

applied for APU application of 800 °C a power density has been achieved of about 300 mW/cm<sup>2</sup> at a voltage of 0.7 V and at 850 °C a power density of about 400 mW/cm<sup>2</sup> was obtained. When applying an improved cathode of LSCF material a further significant improvement of cell performance is expected.

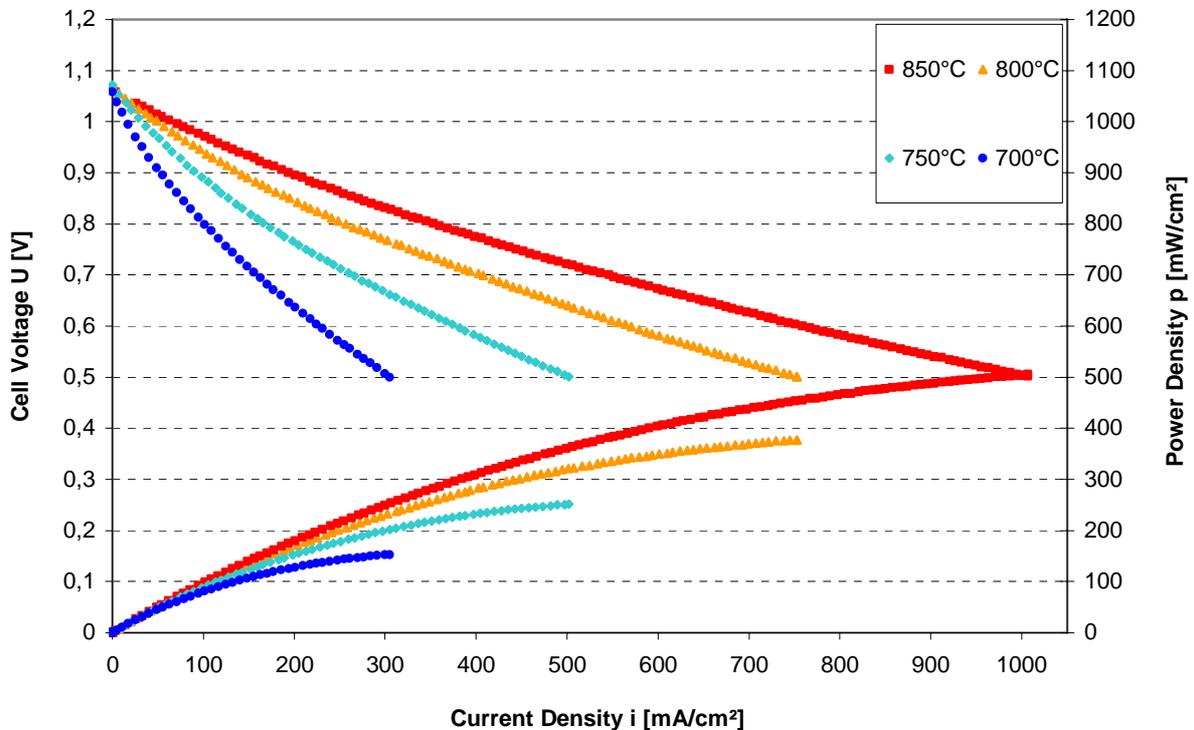


Fig. 6: I-V characteristics and power density curves of a plasma sprayed cell with 12.5 cm<sup>2</sup> area (anode: NiO/YSZ, electrolyte: YSZ, cathode: LSM) on ferritic steel substrate as a function of temperature

The results of a stack with 4 larger cells in cassette configuration with a size of 10 x 10 cm<sup>2</sup> are depicted in Fig. 7 showing a power of 78 W in operation with H<sub>2</sub>/N<sub>2</sub> (12.5 smlpm/cm<sup>2</sup> each) and air (80 smlpm/cm<sup>2</sup>) at a stack voltage of 2.8 V and an operating temperature of 800 °C. This corresponds to an average power density per cell of 175 mW/cm<sup>2</sup>. The maximum power density was 110 W corresponding to an average power density of 250 mW/cm<sup>2</sup>. At operation with hydrogen and air a higher power of 92 W (207 mW/cm<sup>2</sup>) at a stack voltage of 2.8 V and a maximum power of 121 W (272 mW/cm<sup>2</sup>) was obtained with the same stack.

Plasma sprayed SOFC cells fabricated according to the DLR spray concept prove a high potential for stable operation during cycling conditions. Both at redox cycling and thermal cycling conditions only small degradation was observed as is shown in the figures 8 and 9. Fig. 8 shows the electrochemical behaviour of a circular cell with 12.5 cm<sup>2</sup> area during 10 redox cycles. The power density at a load of 200 mA/cm<sup>2</sup> kept constant during cycling and the open circuit voltage (OCV) decreased slightly by 1 %.

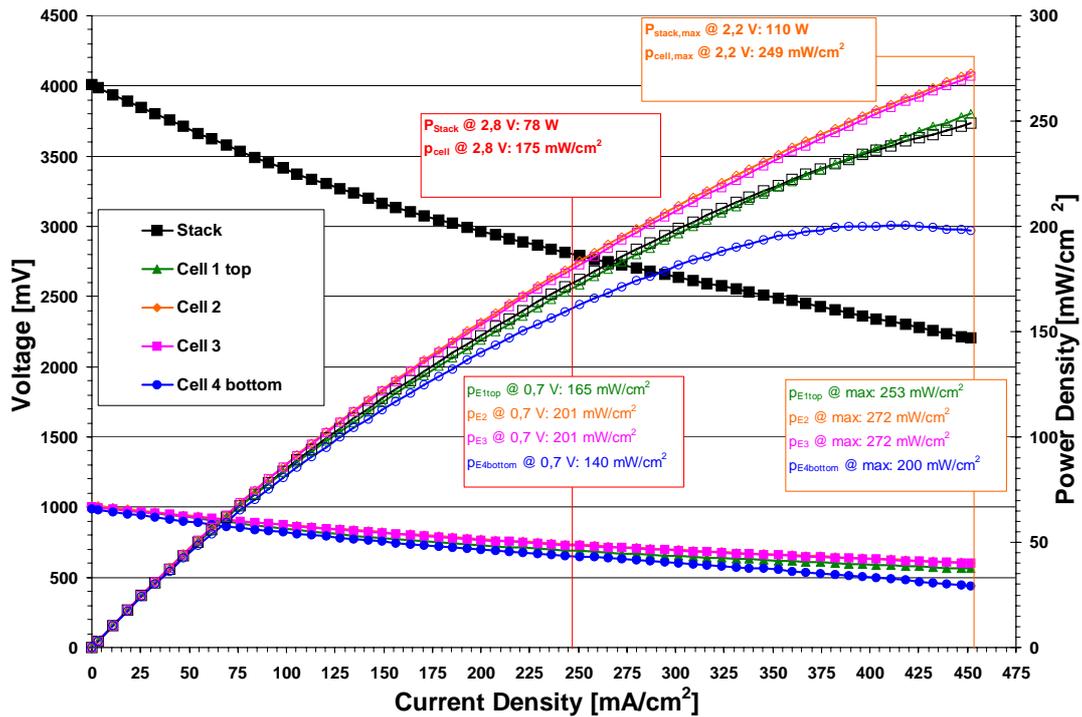


Fig. 7: I-V characteristics and power density curves of a 4-cell stack in cassette configuration (10 x 10 cm<sup>2</sup>) operated with H<sub>2</sub>/N<sub>2</sub> (1:1) and air at 800 °C

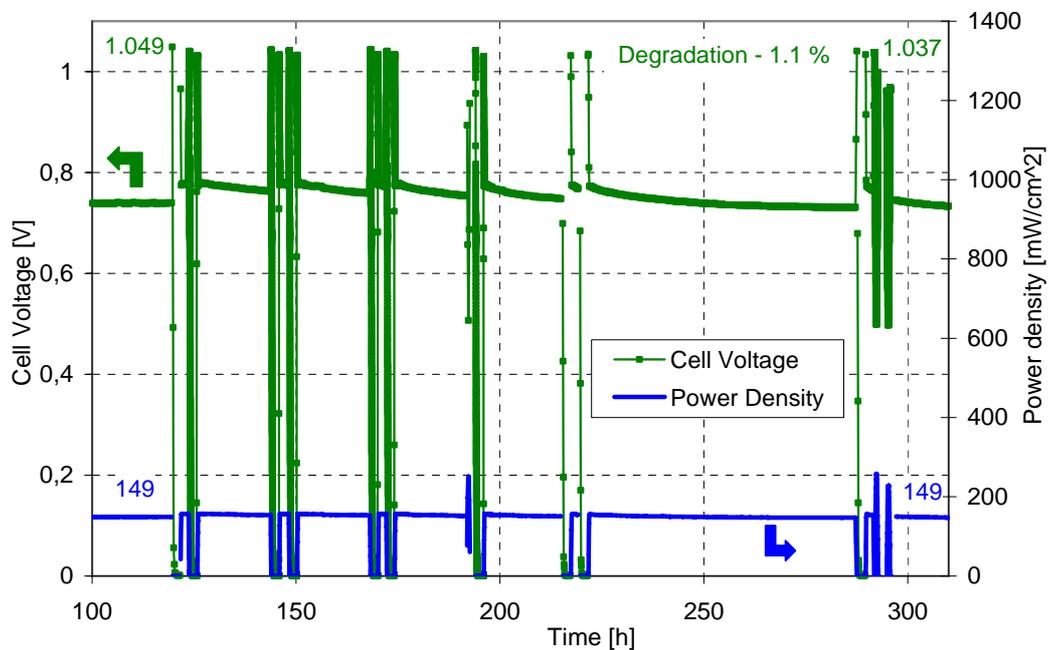


Fig. 8. Electrochemical behaviour of a plasma sprayed cell on a ferritic steel substrate during 10 redox cycles (200 mA/cm<sup>2</sup>, 800 °C, 0.5 slpm H<sub>2</sub> + 0.5 slpm N<sub>2</sub>/2.0 slpm air)

During thermal cycling a slightly higher degradation was observed compared to the redox cycling as can be seen in Fig. 9. After 10 thermal cycles at a load of 200 mA/cm<sup>2</sup> a decrease of the power density of about 4 % and of about 1.2 % of the OCV was found which might be

caused by thermomechanical stresses. During stationary operating of cells without cycling an average degradation rate of 2 % /1000 hours was detected.

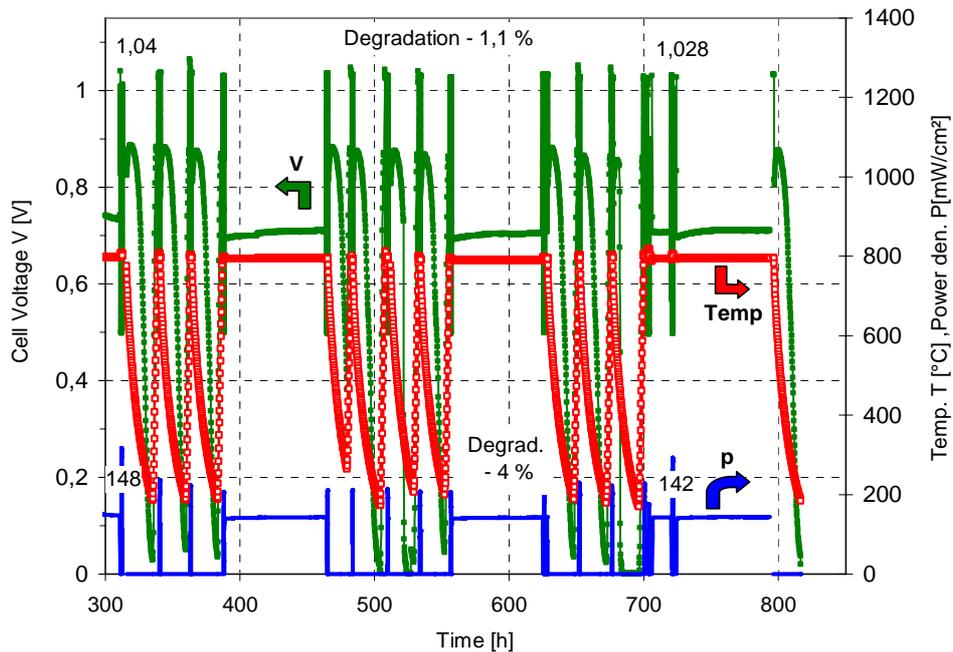


Fig. 9: Electrochemical behaviour of a plasma sprayed cell on a ferritic steel substrate during 10 thermal cycles (200 mA/cm<sup>2</sup>, 800 °C, 0.5 slmp H<sub>2</sub> + 0.5 slpm N<sub>2</sub>/2.0 slpm air)

## Conclusion

Vacuum plasma sprayed cells prove a promising behaviour during fast start-up and thermal as well as redox cycling which is an important requirement for application in an automotive APU system. This behaviour is supported by the cell design with a metallic substrate and only thin functional ceramic layers of 100–120 µm for the entire membrane-electrode assembly. But further improvement of the cells' cycling capability is needed to meet the requirements for APU operation with some thousands of thermal and redox cycles. Hence, future development work will concentrate on the optimisation of the metallic substrate and the microstructure of the cells.

## References

- [1] J. Zizelmann, C. de Minco, S. Mukerjee, J. Tachtler, J. Kammerer, P. Lamp, Proc. 5<sup>th</sup> European SOFC Forum, Vol. 1, 1153-1164 (2002)
- [2] S. C. Singhal, Proc. 5<sup>th</sup> International Symposium on SOFC (SOFC-V), The Electrochemical Society, Pennington, NJ, Proc. Vol. 97-40, 37-50 (1997)
- [3] R. Diethelm, M. Schmidt, K. Honegger, E. Batawi, Proc. 6<sup>th</sup> International Symposium on SOFC (SOFC-VI), The Electrochemical Society, Pennington, NJ, Proc. Vol. 99-19, 60-67 (1999)
- [4] N. Hisatome, K. Ikeda, K. Tomida, T. Kurihara, H. Omura, 1998 Fuel Cell Seminar, November 16-19, 1998, Palm Springs, CA, USA, 28-31 (1998)
- [5] G. Schiller, R. Henne, R. Ruckdäschel, Journal of Advanced Materials, Vol. 32(1), 3-8 (2000)

- [6] G. Schiller, R. Henne, M. Lang, R. Ruckdäschel, S. Schaper, Fuel Cells Bulletin – An International Newsletter, No. 21, 7-12 (2000)
- [7] W. Mayr, R. Henne, Proc. 1<sup>st</sup> Plasmatechnik Symposium, Vol. 1, Luzern, Switzerland, 87-97, (1988)
- [8] M. I. Boulos, J. Therm. Spray Techn., 1(1), 33-40 (1992)
- [9] M. Müller, E. Bouyer, M. v. Bradke, D. W. Branston, R. B. Heimann, R. Henne, G. Lins, G. Schiller, Mat. Sc. Eng. Techn., Vol. 33(6), 322-330 (2002)
- [10] L. G. J. de Haart, I. C. Vinke, A. Janke, H. Ringel, F. Tietz, Proc. 7<sup>th</sup> International Symposium on SOFC (SOFC-VII), The Electrochemical Society, Pennington, NJ, USA, Proc. Vol. 2001-16, 111-119 (2001)