The application of solid oxide fuel cells as an auxiliary power unit (APU) for the supply of electrical energy on board of road vehicles and aircraft requires some additional and technically ambitious properties compared to those needed for stationary application. These are such as a compact design with light weight and small volume, fast start-up time and long-term stability under severe operating conditions including some thousands of thermal and redox cycles. DLR Stuttgart has developed a concept of a planar metallic substrate supported SOFC which is based on advanced plasma deposition processes as the manufacturing technique. A cell and stack design has been developed to meet the very strict requirements as mentioned with regard to the APU application. The present paper focuses on the electrochemical performance of plasma sprayed cells with special concern on constant operation, rapid start-up and thermal and redox cycling experiments.

## INTRODUCTION

In recent years, SOFC technology has attained high interest as an APU system for the electrical power supply in vehicles in a small power range of around 5 $kW_e$ and, in the longer term, for the replacement of the turbine-based auxiliary power unit on board of aircraft being in the range of 200-400 $kW_e$ for the supply of electrical consumers. Such a SOFC APU system can operate independently from the main engine that might be optimized only for propulsion whereas the SOFC APU can maintain the electrical supply of all other functions. Conventional fuels such as gasoline and kerosene, respectively, are used which are converted to hydrogen and carbon monoxide via a reforming system to feed the fuel cell. Such an arrangement with a gasoline powered APU represents a paradigm shift in the power supply of vehicles leading to a significantly enhanced system efficiency and favorable consequences concerning a reduction of fuel consumption and emissions. A successful development of an automotive APU system would be of high importance as base technology also for other applications such as for utility vehicles, ships and airplanes.

## DLR SPRAY CONCEPT AND CELL AND STACK DESIGN

DLR has developed a concept of a planar metallic substrate supported SOFC based on advanced plasma deposition processes. This concept with consecutive deposition of all functional cell layers – anode, electrolyte and cathode – in a single multi-step vacuum plasma spray (VPS) process onto a porous metallic substrate support has been described in detail previously [1]. To meet the very strict requirements of low volume and weight for APU application a cell and stack design has been developed in cooperation with industrial partners. The repeating unit of this design is based on two thin stamped ferritic steel sheets consisting of CroFer22APU which are laser welded to form a metallic cassette configuration. The porous substrate is integrated in this cassette by brazing and welding techniques. Subsequently, the functional cell layers are consecutively deposited on the metallic substrate incorporated in the cassette. The single cassettes are assembled to compact, lightweight stacks by means of contact layers and glass seal material. More details on the cassette design are given in [2].

## EXPERIMENTAL

In order to investigate the behavior of VPS cells under APU relevant conditions small plasma sprayed cells of circular shape with an active area of 12.5 $cm^2$ were electrochemically characterized during thermal and redox cycling conditions and at rapid start-up. Cells with an anode consisting of NiO (Becon, Switzerland) and YSZ (Medicoat, Switzerland), a YSZ electrolyte (Medicoat, Switzerland) and a LSM cathode (EMPA, Switzerland) were prepared by VPS. During activation of the cell the NiO of the anode was reduced during operation by hydrogen to Ni forming anodes with a porosity of 25-30 vol.%. As substrate both a porous knitted wire structure consisting of CroFer22APU (Rhodius, Germany) and a powder metallurgically manufactured porous plate (Plansee, Austria) consisting of IT14 alloy (Fe-26Cr-(Mo,Ti,Mn,$Y_2O_3$)) [3] was used. The porosity of the Rhodius substrate is in the range of 80 vol.%, that of Plansee has a porosity of approximately 50%.

The thermal cycling experiments were performed after activation of the cells at 800 °C at a constant load of 200 mA/cm$^2$ for approximately 150-200 hours. The thermal cycle included cooling down of the furnace in Ar/10% $H_2$ atmosphere and air from 800 °C to 180 °C and heating again to 800 °C. The temperature gradient during heating was 3 K/min whereas the cooling procedure was done with approximately 1-2 K/min. Before and after cycling the cells were characterized by I-V characteristics and impedance spectroscopy. Between the different cycles the cells were operated at a constant load of 200 mA/cm$^2$ with 0.5 slpm $H_2$ + 0.5 slpm $N_2$ and 2 slpm air. For the redox cycling experiments at 800 °C the gas flow to the cells was stopped in each cycle for 2-3 hours and subsequently standard operating conditions (200 mA/cm$^2$ , 0.5 slpm $H_2$ + 0.5 slpm $N_2$ / 2 slpm air ) were applied again. For the fast start-up experiments the furnace used was heated up as fast as possible to 600 °C within approximately 32 minutes in an atmosphere of 0.25 slpm air at the air side and 0.25 slpm Ar+5% $H_2$ at the fuel side. At 600 °C the gas supply was switched to 2 slpm air and 0.5 slpm $H_2$ and 0.5 slpm $N_2$ as the fuel, respectively. The time needed to reach 800 °C was approximately 45 minutes.

## RESULTS AND DISCUSSION

### THERMAL CYCLING EXPERIMENTS AND RAPID START-UP

During operation of a SOFC under APU conditions interruptions may occur for different intervals when the APU is switched off. Although a very efficient thermal insulation will be realized with integration in the vehicle it can not be avoided that the operating temperature decreases, even to ambient temperature in some cases after long interruptions. When starting the SOFC system again, the operating temperature of 800 °C must be reached within a few minutes. These thermal cycling conditions represent very severe requirements in terms of long-term stability needed for SOFC application in a vehicle. In order to test plasma sprayed cells under these conditions thermal cycling experiments were carried out as described in the previous section.

The monitored behavior of a VPS cell using a knitted wire CroFer22APU substrate from Rhodius is shown in Fig. 1.

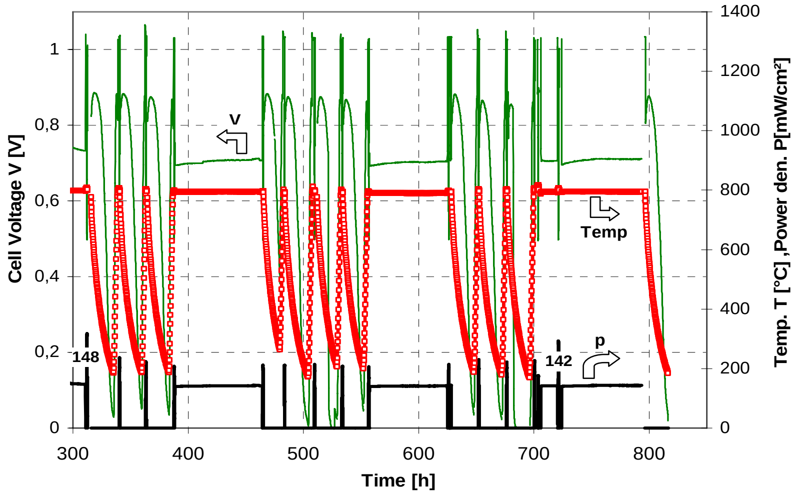


Fig. 1 Electrochemical behavior of a VPS cell with CroFer22APU substrate during 10 thermal cycles between 800 °C and 180 °C at a load of 200 mA/cm$^2$

During 10 thermal cycles at a load of 200 mA/cm$^2$ within a period of approximately 400 hours a decrease of the power density from 148 mW/cm$^2$ to 142 mW/cm$^2$ was observed which is a change of approximately 4%. The open circuit voltage decreased in the same period from 1037 mV to 1028 mV indicating only a slight degradation which may be attributed to thermo mechanical stresses introduced in the substrate/cell unit. After each thermal cycle I-V curves were recorded showing a more severe degradation of approximately 16% when comparing the power density at 0.7 V at the beginning (190 mW/cm$^2$) and at the end (160 mW/cm$^2$) of the experiments. Impedance spectroscopy measurements performed at a load of 200 mA/cm$^2$ revealed a slight increase of the total cell resistance of approximately 8% from 1.14 Ωcm$^2$ to 1.23 Ωcm$^2$ which is mainly attributed to the polarization resistance of the electrodes since the ohmic resistance was found to be practically unchanged. Analogues thermal cycling experiments performed with IT14 substrate from Plansee revealed similar results as shown for the cells containing Rhodius substrates. When evaluating these results it must also be taken into account that at constant operation without any cycling a degradation of the cells of approximately 2%/1000 h has been detected.

After cooling down due to interruptions of SOFC operation the SOFC system should have the capability to start up again very rapidly. The objective here is to achieve 30% of the nominal power within 5 minutes and to attain full performance within approximately 10 minutes. Fast start-up experiments were carried out under conditions that have been described before. Since the speed of heating up the furnace used for these experiments was limited only a first approach in this concern was able to be conducted. Heating up the furnace from ambient temperature to 600 °C took approximately 32 minutes. Because of safety reasons the fuel gas composition of 0.5 slpm $H_2$ and 0.5 slpm $N_2$ simulating the composition of reformated gasoline was only applied at the elevated temperature of 600 °C. After switching on the fuel gas supply a nominal power density of 30% related to the power density measured at a voltage of 0.7 V was achieved within 6 minutes.

The results of the thermal cycling and rapid start-up experiments performed prove that VPS cells prepared according to the DLR spray concept show a promising potential for application in a SOFC APU system. The cell design using a metallic substrate with very high thermal and electrical conductivity and only thin functional ceramic layers exhibits advantageous properties to withstand fast heat-up and multiple thermal cycles. The existing thermal mismatch between the ferritic steel substrate and the ceramic cell layers can cause thermo mechanical stresses possibly resulting in a decrease of the cell's gas tightness and in enhanced cell resistances. By optimizing the structure of the substrate and the layers' microstructure particularly on the anode side further improvement in the cycling capability of plasma sprayed cells must be achieved in future work to meet the requirements needed for a successful operation of a SOFC system for APU application.

**REDOX CYCLING EXPERIMENTS**

At APU operating conditions it can not be totally excluded that the cell's anode is exposed to air for a certain period of time due to system failures that might occur. For this reason, the SOFC cells should be able to withstand reduction-oxidation cycles without exhibiting severe degradation behavior. In the experimental section redox cycling experiments were described to test plasma sprayed cells in this respect. During the stop of the gas flow air could penetrate into the tubes for fuel gas supply and get in contact with the anode. The behavior of a plasma sprayed cell on a Crofer22APU substrate with a knitted wire structure during 10 redox cycles is shown in Fig. 2. The cell had been operated for about 120 hours to ensure a stable electrochemical behavior before starting the redox cycles at a load of 200 mA/cm$^2$ and 800 °C operating temperature. In the oxidation state when the gases are switched off the cell voltage drops to zero. During the 10 redox cycles the power density decreased only slightly from 149 mW/cm$^2$ to 148 mW/cm$^2$ which is less than 1%. The open circuit voltage changed from 1049 mV to 1037 mV in the same period. The impedance spectra which were monitored during the 10 redox cycles reveal that the ohmic resistance remains constant at 0.44 Ωcm$^2$ and is not affected by the redox cycles indicating that no severe irreversible oxidation processes occur in the VPS cell. This behavior was also confirmed by I-V curves which were recorded before starting redox cycling and after the 5th and 10th cycle.

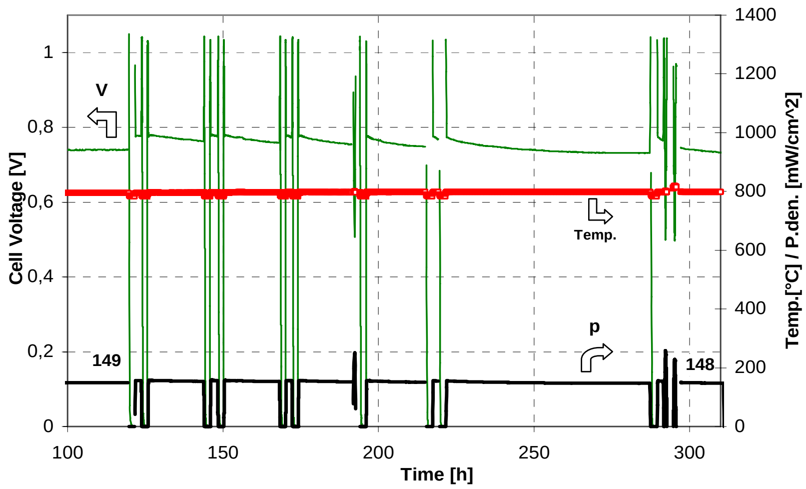


Fig. 2 Electrochemical behavior of a VPS cell with CroFer22APU substrate during 10 redox cycles at a load of 200 mA/cm$^2$ and 800 °C

## CONCLUSION

Vacuum plasma sprayed cells prove a promising behavior during fast start-up and thermal as well as redox cycling which is an important requirement for application in an automotive APU system. This behavior is supported by the cell design with a metallic substrate and only thin functional ceramic layers of approximately 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 optimization of the metallic substrate and the microstructure of the cells.

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