RECENT RESULTS OF THE SOFC APU DEVELOPMENT AT DLR

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ABSTRACT

In recent years, SOFC technology has attained high interest for electrical power supply in vehicles as an Auxiliary Power Unit (APU) that operates independently from the main engine. In this paper, recent results are reported that have been achieved at DLR in adapting the DLR spray concept to the needs of an APU design based on plasma sprayed cells. Some major issues such as the porous metallic substrate, the characterization of the plasma sprayed cathode, the behavior of plasma sprayed cells during cycling experiments, and the development and application of an analytical tool for spatially-resolved electrochemical characterization are addressed.

INTRODUCTION

Solid oxide fuel cells have been developed in the last two to three decades mainly for stationary applications as highly efficient and environmentally friendly energy converters for power stations in the high power range and for decentralized energy supply in the medium to low power range. In recent years, a more short-term realizable application field for SOFC has attained high interest – SOFC systems in a small power range of around 5 kW for the engine-independent electrical supply in vehicles, and, in the longer term, for the replacement of the turbine-based auxiliary power unit (APU) for the supply of electrical energy on board an aircraft.

The demand on electrical energy on board of vehicles has increased dramatically in the past years to fulfill the clients’ desire of comfort and safety by applying additional electric consumers. As this development will continue it is desirable, for economic and ecological reasons, to develop an aggregate independent from the main engine – an auxiliary power unit (APU) - for which SOFC technology is an interesting option. The car manufacturer BMW favors such a hybrid solution where the conventional internal combustion engine (ICE) takes over only the propulsion of the vehicle with optimum rate of revolution and the SOFC APU system can maintain the electrical supply of all other functions in the automobile. 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. The application of SOFC APUs with some kW electrical power having significantly higher cost targets than that for fuels cells for traction seems...
to be realizable much earlier than the market entry of fuel cell powered vehicle drivetrains which has been prolonged for some more years because of the presently too high production costs. On the other hand, the operation of SOFC in vehicles means additional requirements, besides of high volume- and weight-related power density and 5,000 hours lifetime, such as fast start-up time of some minutes and stability during some thousand thermal and redox cycles.

A successful development of an automotive APU system would be of high importance as a base technology also for other applications, such as for utility vehicles, ships and airplanes. In order to solve the problems associated with SOFC application as an APU on board of a vehicle an industrial consortium has formed in Germany consisting of 8 companies mainly from the automotive industry headed by BMW Group. For the SOFC stack development also two research centers are involved in the consortium, the German Aerospace Center (DLR) in Stuttgart and the Research Center Jülich (FZJ). FZJ concentrates on their production process based on wet powder and sintering techniques whereas DLR uses plasma deposition technologies for the fabrication of the entire cell. This paper reports some results of recent developments being performed at DLR to adapt the DLR spray concept to the needs of an APU design based on plasma sprayed cells in a cassette configuration. Some major issues such as the porous metallic substrate essential for the DLR concept, the characterization of the plasma sprayed cathode, the behavior of plasma sprayed cells during cycling experiments and the development and application of an analytical tool for spatially-resolved electrochemical measurements are addressed.

CELL AND STACK DESIGN

As an alternative approach to standard SOFC manufacturing techniques which are based on wet powder processing and sintering methods, DLR has developed a concept of a planar SOFC based on advanced plasma deposition processes. This concept with consecutive deposition of all layers of a thin-film cell onto a porous metallic substrate support has been described in detail previously [1].

The porous metallic substrate offers advantageous possibilities for integration in the interconnect plate incorporating welding and brazing techniques. The cell and stack design which has been developed within the German industrial consortium to meet the very strict requirements of low volume and weight for APU application is shown in Fig. 1. The repeating unit of this design is based on two thin stamped ferritic steel sheets (CroFer22APU) which can be laser welded to form a metallic cassette configuration consisting of a bottom and a top interconnect sheet. The porous substrate is integrated in this cassette by a brazing technique. Subsequently, all functional layers of the cell – anode, electrolyte and cathode – are consecutively deposited on the substrate/interconnect unit by a multi-step plasma spray process. The single cassettes (Fig. 2) are then assembled to compact, light-weight stacks by means of contact layers and glass seal material.

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The porous metallic substrate is a key component in the DLR spray concept which must meet many requirements such as high electrical conductivity, adapted thermal expansion to the ceramic layers, high gas permeability and sufficient mechanical strength and corrosion stability. Due to the high porosity of > 40 vol% and the resulting high surface/volume ratio a very severe and important task is to improve significantly the long-term corrosion stability in SOFC anode gas atmospheres. Various ferritic steel materials from different suppliers based on a melt metallurgical production line have been investigated and tested under SOFC relevant conditions [2]. A predominant reason of the relatively low corrosion stability of porous ferritic steel substrates with high Cr (> 20 wt%) and low Mn content (0.02 - 0.05 wt%) which show adequate corrosion stability as dense material is seen in the melt metallurgical manufacturing process. During that process a segregation of elements in the melt and evaporation of components of the alloy can occur leading to an inhomogeneous element distribution and an insufficient formation of protective oxide scales on the particle surface during cell operation. A promising material in this respect is a powder metallurgically (PM) manufactured porous substrate from Plansee AG, Austria, consisting of Fe-26Cr-(Mo,Ti,Mn,Y2O3) alloy [3]. Substrate samples of this alloy with a porosity of approx. 50% which have been fabricated by tape casting and subsequent sintering were studied under SOFC relevant conditions. Fig. 3 shows SEM pictures of the substrate's morphology with two magnifications (100 x and 300 x) proving the well pronounced sinter contacts between the particles and the fine porous structure. In annealing tests, the PM substrates showed excellent corrosion stability both after 200 h and 1,000 h at 800°C in the simulated anode gas atmosphere H2-50% H2O (Fig. 4). The oxide phases formed after 1,000 h consist of non-stoichiometric Mn-Cr spinel, Cr2O3 and an intermetallic Fe-Cr phase. The sinter contacts between the particles are not affected by oxide phases. Thus, a significant increase of ohmic cell losses is not expected during electrochemical cell operation for the first 1,000 h.
First electrochemical tests of plasma sprayed cells on PM substrates revealed a power density of about 210 mW/cm$^2$ at 0.7 V and 900°C when using a simulated reformat gas (H$_2$/N$_2$) and air. This is in the same power density range than that of cells on other ferritic steel substrates. In future investigations, the corrosion behavior during cell operation for more than 1,000 h has to be studied. Particular concern has to be paid on interdiffusion processes of iron and chromium from the substrate into the anode and of nickel from the anode into the substrate which usually occurs during long-term operation of ferritic steel substrates. In this case, a diffusion barrier coating between substrate and anode is needed to prevent the interdiffusion processes.

**CATHODE DEVELOPMENT**

Plasma sprayed LSM cathodes revealed relatively high electric losses due to their limited porosity as reported in previous publications [4]. For this reason, much effort has been paid on the improvement of the vacuum plasma spray (VPS) fabrication process and improved cathode spray powders. When using La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) powder...
from H.C. Starck, Germany, and optimized spray parameters, significantly higher power densities could be achieved than reported before with LSM and LSF cathodes [5]. Table 1 shows a comparison of the power density of VPS cells with this new LSCF cathode with the former state-of-the-art VPS cathodes exhibiting a significant increase of power density at 0.7 V of up to approximately 300 mW/cm$^2$ at 800°C. The gas flows used for these measurements were 40 sccm/cm$^2$ hydrogen and 40 sccm/cm$^2$ nitrogen as fuel, and 160 sccm/cm$^2$ air as oxidant.

Table 1. Comparison of power densities of VPS cells with different cathodes at 800°C with 40 sccm/cm$^2$ H$_2$ and 40 sccm/cm$^2$ N$_2$ as fuel, and 160 sccm/cm$^2$ air as oxidant.

| Cathode Material | Powder Supplier | Power density (@700mV) |
|------------------|-----------------|------------------------|
| VPS LSM          | EMPA            | 167 mW/cm$^2$          |
| VPS LSF          | EMPA            | 219 mW/cm$^2$          |
| VPS LSCF         | H.C. Starck     | 293 mW/cm$^2$          |

Table 2. Area specific resistance $R_Q/R_P$ and power densities obtained from measurements at 800°C: variation of oxygen partial pressure (160 sccm/cm$^2$ O$_2$/N$_2$).

| Condition (% vol O$_2$ in N$_2$) | 100% | 60% | 21% | 10% | 5% |
|----------------------------------|------|-----|-----|-----|----|
| OCV                             | $R_Q$ [Ω cm$^2$] | 0.32 | 0.32 | 0.34 | 0.33 | 0.34 |
|                                 | $R_P$ [Ω cm$^2$] | 0.42 | 0.51 | 0.83 | 1.15 | 2.41 |
| 200 mA/cm$^2$                   | $R_Q$ [Ω cm$^2$] | 0.32 | 0.33 | 0.34 | 0.33 |
|                                 | $R_P$ [Ω cm$^2$] | 0.32 | 0.38 | 0.55 | 0.54 | –   |
|                                 | $p$ [mW/cm$^2$]  | 173 | 173 | 167 | 167 | –   |

In Fig. 5, the impedance spectra (Nyquist plot) obtained at load condition of 200 mA/cm$^2$ at the same fuel and oxidant flows. The area specific resistance $R_P$ increases by about 70% with decreasing fraction of O$_2$ in nitrogen from 100% to 10%. Two overlapping arcs (depressed semicircles) can be related to two apparent processes: a process at about 8 Hz which increases with decreasing pO$_2$ (more dominantly at fractions of less than 21%), and a process at about 2 kHz which also increases with decreasing pO$_2$. Table 2 summarizes the corresponding values of the area specific resistance $R_Q/R_P$ and the power densities at OCV and at a load of 200 mA/cm$^2$.

In Fig. 6, a SEM picture of an unpolished cross-section of the cathode of the cell with the VPS LSCF cathode is shown. The VPS cathode layer is finely structured and porous. Measurements for the determination of the permeation and diffusion coefficients of the different cathode functional layers are in progress.

**CELL BEHAVIOR DURING CYCLING EXPERIMENTS**

In order to investigate the behavior of VPS cells under cycling conditions plasma sprayed cells on knitted wire CroFer22APU substrates (Rhodius, Germany) and Ni felt substrates (Bekaert, Belgium) were electrochemically characterized during thermal and redox cycling. The circular cells with Ni/YSZ anode, YSZ electrolyte and LSM cathode layers
had an active area of 12 cm². The thermal cycling experiments started after operation of 150 hours under constant galvanostatic load of 200 mA/cm² at 800°C by cooling down the furnace in Ar/10% H₂ atmosphere and air 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 constant load of 200 mA/cm² at 800°C with 0.5 slpm N₂ + 0.5 slpm H₂ and 2 slpm air.

The monitored cell's behavior during thermal cycling is shown in Fig. 7. During 10 cycles at a load of 200 mA/cm² within approximately 300 hours a decrease of the power density of the cell with the CroFer22APU substrate from 150 mW/cm² to 143 mW/cm²
was observed which means a change of 5%.
The open circuit voltage decreased during this period from 1048 mV to 1013 mV indicating an increased leakage probably due to induced thermomechanical stress in the substrate/cell unit.

Figure 7. 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/cm².

Impedance spectroscopy measurements revealed a slight increase of the total cell resistance of approximately 2% which is attributed to the polarization resistance of the electrodes since the ohmic resistance was found to be constant during the thermal cycling experiment. Analogous thermal cycling experiments as described before with cells on Ni felt substrates showed a degradation of 2% in power density during 10 thermal cycles. The OCV proved constant behavior during the cycling period indicating a satisfactory gas tightness of the cell. Impedance spectra revealed a slight increase of the total impedance of about 15% and a constant ohmic resistance.

After completion of the thermal cycling, redox cycling experiments were performed at 800°C. In each cycle the gas flow to the cells was stopped for 2-3 hours and subsequently standard operating conditions (200 mA/cm², 0.5 slpm H₂+0.5 slpm N₂ / 2 slpm air) were applied again. During 10 redox cycles a decrease of the power density at a load of 200 mA/cm² of 13% was observed for the CroFer22APU substrate supported cell and a decrease of 3.4% for the Ni substrate supported cell.

The results of the cycling experiments prove that the thermal expansion mismatch between the ferritic steel substrate and the ceramic cell layers can cause thermomechanical stresses resulting in a decrease of the gas tightness of the electrolyte. Thus, further development work is needed to improve the cycling capability of plasma sprayed cells to achieve the objectives required for APU operation.
SPATIALLY-RESOLVED ELECTROCHEMICAL CELL CHARACTERIZATION

For a more detailed local electrochemical characterization of cells, a new measuring system has been developed and built up at DLR [6]. This system allows the characterization of SOFCs at 16 distinct measuring points along the flow path of the gases in the cell allowing to determine concentration gradients of the reactants and the products. These concentration gradients cause different electrochemical potentials at the SOFC electrodes and varying corrosion conditions of the metallic substrate. With the measuring system that has been built up, current, voltage, temperature and impedance data as well as their distribution can be measured. Additionally 16 capillaries are integrated to take gas samples of the anode gas atmosphere to be analyzed. As a result of the installation of the system the limiting components and/or processes in the system could be identified more easily.

Fig. 8 shows the schematic of the cathode interconnect and the segmented cathode. Insulation material at the outer edges of the segments prevents the contact to the common metallic housing, and also the wires for current flux and voltage measurement are isolated from the common plate. In addition, thermocouples are placed in the metallic segments to maintain the temperature distribution at different gas flow rates and also to correlate experimental data of the impedance measurement with the local temperatures. The common plate ensures a uniform contact pressure over all segments. The capillaries that are used to take gas samples from the anode gas atmosphere are not illustrated in the scheme.

As an example for the capability of this new analytical tool the power density distribution of the 16 segments, each 4.6 cm² wide, of a plasma sprayed metallic substrate supported cell (100x100 mm²) is shown in Fig. 9 for 800°C. The gas flow rates are 12.5 sccm/cm² H₂, 12.5 sccm/cm² N₂ as fuel and 80 sccm/cm² air as oxidant.
The current density distribution varies tremendously over the cell. Maximum differences of 116.6 mW/cm² could be identified in Fig. 9. The worst segment reaches only 23.6% of the power density of the best segment. The average power density of the cell was 125.6 mW/cm² at 0.7 V. It can be seen that there is a power density gradient from the air inlet to the air outlet on the outer edges of the system adjacent to the glass sealing. In the lines of the segments 5 and 9 the opposite behavior is observed.

There is a slight increase of the power density of about 15.1% in average from air inlet to air outlet. The main effect could be attributed to the inhomogeneous gas distribution at the inlet and to the sealing. The differences in the electrochemical behavior are also caused by local water production as a result of the not absolutely gas tight electrolyte. It could be seen by local impedance spectroscopy that the current distribution is in good accordance with the local resistances. The local temperatures (Fig. 10) directly affect the ohmic resistances and should therefore be taken into account.
The measurement routine revealed that the anode overpotential at an overall cell voltage of 0.7 V with the selected gas supply is nearly not existent and can therefore be neglected. As a consequence, the overpotential is mainly related to the cathode and further cell improvement should concentrate on this issue. The results obtained by these measurements show a variation of the behavior of the cell along the flow path. Current density, impedance and temperature can be associated with the observed effects. The obtained data can be used to avoid critical temperature gradients during operation and also to optimize functional layers to homogenize current density and heat production especially in a fuel cell stack.

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