A0904

Stack Tests of Metal-Supported Plasma-Sprayed SOFC

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Abstract

The development of metal-supported plasma-sprayed SOFC has shown impressive progress in recent years. The main focus of this development was to create a functional stack. Integration of the cell into interconnects has been simplified leading to a lightweight cassette design with a fully integrated cells. Short stacks have been tested for proof of concept with good results at thermal and redox cycling. This shifted the main tasks of the development to scaling up the number of layers and increasing the lifetime of the stacks.
In the project MS-SOFC new cassettes using the Plansee ITM alloy have been developed and new plasma spray processes for the electrode layers were introduced. Changes in the manufacturing processes also allowed for the reduction of the number of manufacturing processes for the cassette.
Stacks were built up using the new developments. Two 10-layer stacks, one with a vacuum plasma sprayed electrolyte and one with a low pressure plasma sprayed electrolyte, were assembled to evaluate the power density and one 4-layer stack was used for long-term testing. Results of these experiments are presented in this paper.

Introduction

The development of metal-supported SOFCs (MSC) at DLR focuses on the development of stacks for mobile applications. For this a lightweight stack design was developed around the metal supported plasma-sprayed SOFC. This design has advantages concerning the integration of the cell in the bipolar plate and an improved heating-up time due to the reduced overall cell thickness.
The project MS-SOFC was started with the aim of applying industrial manufacturing technologies for all cell and stack components. This included the use of new plasma torch technologies for the manufacture of the ceramic layers as well as the stamped interconnects from sheet metal.
Another aim of the project was the improvement of the power density of plasma-sprayed cells and stacks. Up to now the best power density achieved with a cassette-type short stack was 170 mW/cm² for the LPPS-electrolyte and 205 mW/cm² for the VPS electrolyte with an operation temperature of 800°C and a fuel gas flow of 1 slpm H_2+1 slpm N_2 and 2 slpm air [2]. There was only one test with a two layer stack. It was therefore planned to set up two multi-layer stacks, one for each of the two different plasma-spray processes.
Another major challenge is the long-term stability of these metal supported cells. TEC mismatch between the ceramic layers and the metal support and the oxidation of the metal substrate lead to increased degradation of this cell type. For the measurement of the long-term stability a 4-layer stack was tested for 5000 h.

Experimental

In the project MS-SOFC an updated cassette design, the MSC1 design was introduced. It consists of two stamped metal plates and the porous metal substrate. The new design uses the Plansee ITM alloy because it has a higher mechanical strength compared to Crofer 22 [1]. This allowed the reduction of the material thickness of the stamped plates from 0.5 mm to 0.3 mm. The active cell area was reduced from 100 cm² to 81.4 cm² to improve the gas distribution, see figure 1.

Figure 1: CP- (left) and MSC1-cassette (right)

In the older CP design the substrate was integrated by welding along the perimeter and brazing in the area to ensure good contact on the anode side. The brazing process was delicate since the liquid braze tended to infiltrate the porous metal substrate and thereby reduced the porosity. Moreover, the brazing material was also expensive. In order to improve this assembly it was decided to replace

brazing by laser-welding. This exchanged a protracted batch vacuum process for a quick, continuous process at ambient conditions.
The welding process as well as the use of ITM for all the metal cassette parts had an additional advantage since the porous metal substrate which is integrated into the cassette is also made of the ITM alloy, the whole assembly now was a combination of the same alloy and there is no built up of mixed alloys neither in the welding zone where the CP cassette has an interface between Crofer 22 and ITM nor in the brazing zone where the parts of the CP cassette are made of Crofer 22, Ni-based braze and ITM. Such mixing of alloys can have unfavorable properties with regards to oxidation behaviour and mechanical strength. Without the solder infiltrating the substrate it was also no longer necessary to measure the permeability of the integrated substrate which further reduced the number of manufacturing steps.
The cassettes were then coated with the functional layers of the fuel cell by plasma-spraying. The active area of the cell is 81.4 cm². In the project MS-SOFC two different plasma spray processes were used to manufacture the electrolyte, the vacuum-plasma-spraying (VPS) as the state-of-the-art process at DLR and the low-pressure-plasma-spraying (LPPS) at Sulzer-Metco. The cathodes were applied with atmospheric-plasma-spraying (APS) using a Sulzer Triplex torch. The cassettes designated for the long-term test received a slightly thicker electrolyte of 60 µm compared to 40 µm of the standard stacks in order to improve gas tightness. On all of these cassettes no diffusion barrier layer [3] between the anode and metal substrate and no oxidation protection layer on the cathode side were applied. Figure 2 shows the configuration of the stack repeating unit and Figure 3 shows a coated cassette.

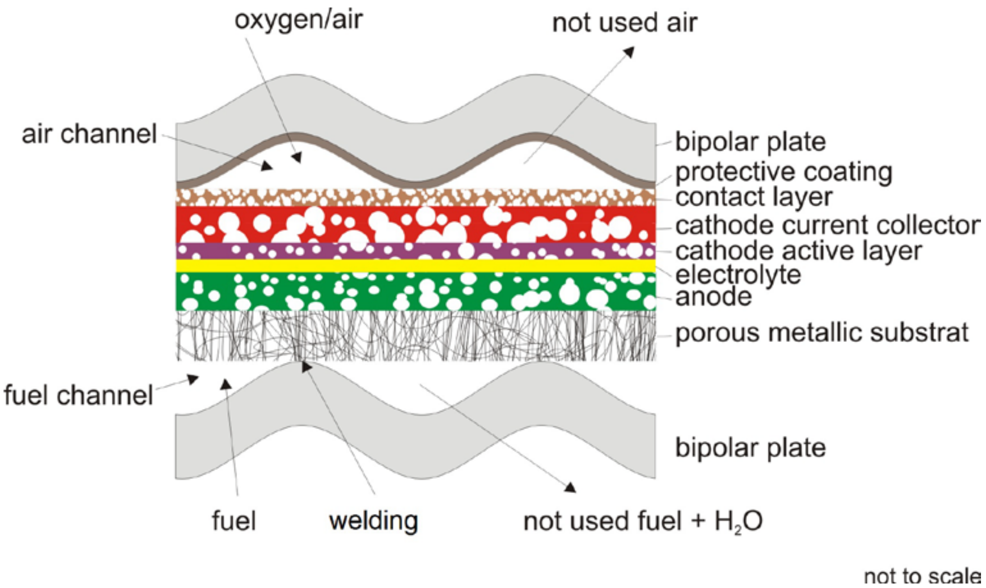

Figure 2: Configuration of a repeating unit in a stack

Leak tests on the electrolyte layer and permeability tests on the porous anode were performed with self-designed equipment. It is capable of performing permeability tests according to ISO 4022. Gas leakage of the electrolyte layer was measured by differential pressure.

Figure 3: Cassette with integrated SOFC

First tests with short stacks indicated that the cassettes were not flat enough to ensure good contacting. Therefore 3D-laser topography was introduced for assuring quality. It showed that the cassettes needed to be flattened in order to improve contacting. This was done in a vacuum furnace at 800°C. After the heat treatment the leak rate and the flatness of the cassettes was measured again. The cassettes with low leak rates were selected for stack test and coated with glass seal and the cathode contact layer.
In order to qualify the cassette production lot a single layer stack was measured before the bigger stacks were built. The multi-layer stacks were built in the DLR test benches #3 for long-term testing and #10 for stack tests. In total two 10-layer stacks were built, one each with VPS-electrolyte and one with LPPS-electrolyte and one 4-layer stack with VPS-electrolyte for the long-term test. Figure 4 shows a 10-layer stack.

Figure 4: 10 layer stack

Results and discussion

The test of the first single layer stack with a flattened cassette proved the success of this additional process. The 3D topography of the same cassette as-sprayed and after the flattening shows a notable difference, see figure 2.

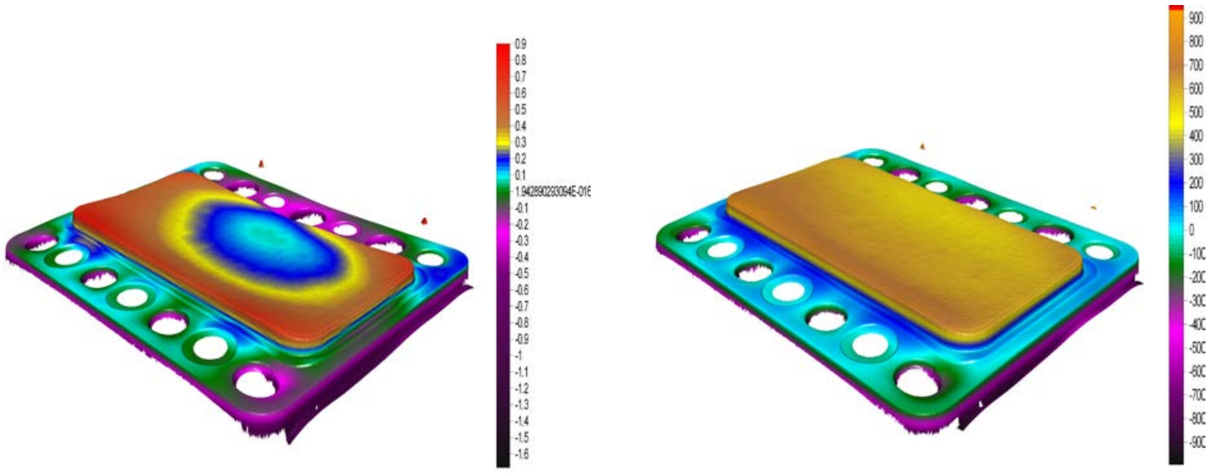

Figure 5: 3D topography of cassette as-sprayed (left) and flattened (right)

The dent in the cell area was successfully removed and also the seal area was leveled out. This should lead to improved contacting and easier sealing of the stack. The heat treatment of the cassettes only slightly affected the leak rate of the electrolyte. The cassette leak rates that were measured were around 330 mbar in the as-sprayed state. After flattening the leak rates were reduced by about 10% to 300 mbar. Cassettes below 280 mbar were not considered for stacks.

The cell also received a new contact paste from Ceramtec. The stack was tested and achieved a power density of 260 mW/cm² at 800°C with a fuel gas flow of 1 slpm H2 + 1 slpm N2 and 2 slpm of air on the cathode side, see figure 3.

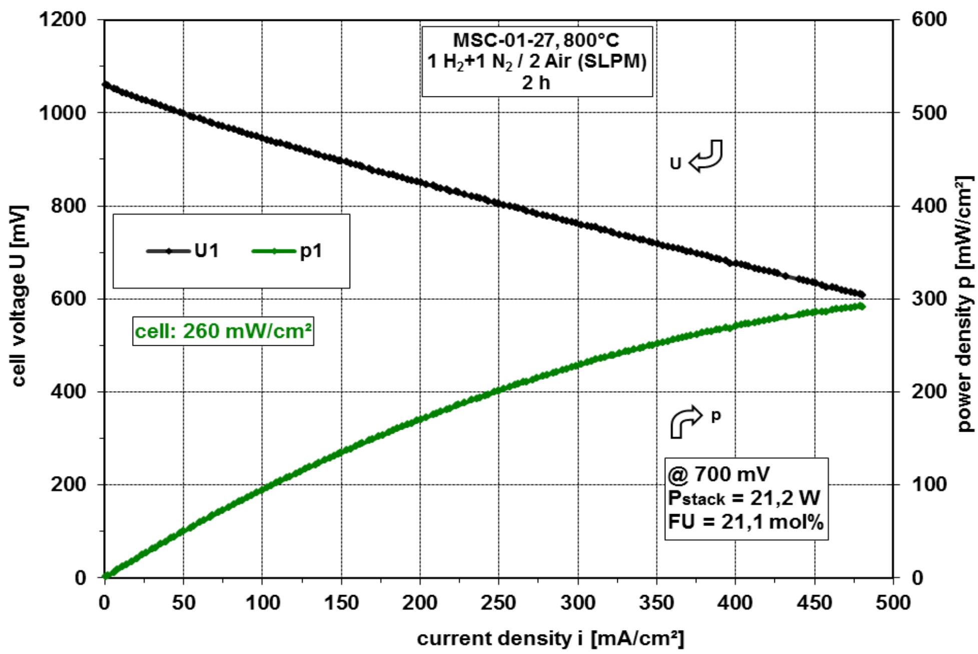

Figure 6: i-V curve of short stack MSC-01-27

Two 10-layer stacks were set up, one with VPS electrolyte and one with LPPS-electrolyte. Both stacks were operated at 800 °C with a fuel gas flow of 10 slpm H_2 and 10 slpm N_2 and 20 slpm of air as oxidant. After heat up, the anode was reduced by gradually increasing the amount of H_2 in the fuel gas to the desired target value.

The stack with the LPPS electrolyte achieved a power density of 222 mW/cm² at a stack voltage of 7.39 V. The total stack power was 180 W. It was not possible to get to 7.0 V due to a problem with the top cell. At a stack voltage of 7.39 V the voltage of the top cell was already down at 0.38 V, therefore the measurement was stopped at this point in order to avoid damage to this cell. Up to now the best power density of single layer short stacks with LPPS electrolyte was 170 mW/cm² [2].

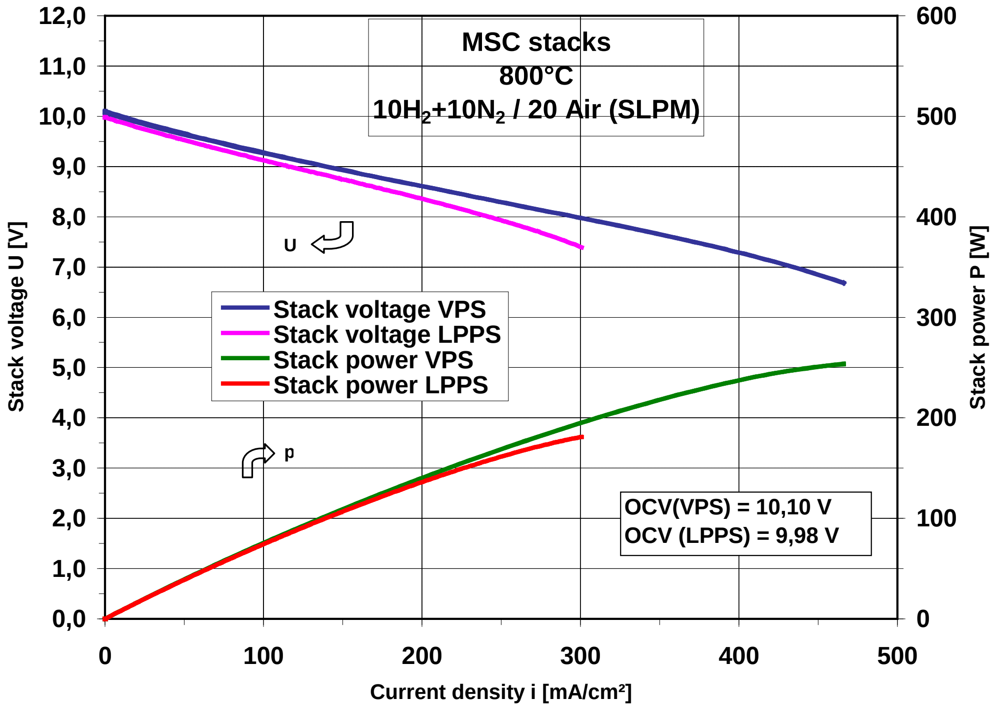

Figure 7: i-V-P curves of the two 10-layer stacks

The second stack with the VPS electrolyte reached a power density of 307 mW/cm² at a stack voltage of 7.0 V. The total power output of this stack was 248 W, see figure 4. The better performance was due to the better leak tightness of the VPS electrolyte. This also represented the best power density in a cassette with VPS electrolyte, where the maximum has been 260 mW/cm². Similar to the LPPS stack the top end cell showed the lowest performance. Due to time constraints each 10-layer stack was operated for 200 h.

The polarization curves of the single layers of LPPS stack showed except for the top cell a uniform behavior. At a stack voltage of 7.39 V individual cells had a power density up to 238 mW/cm². A similar behavior was found for the VPS stack. Again the top cell showed the lowest performance and the other 9 cells had a uniform curve, see figure 6. In order to avoid damage to the top cell both measurements were stopped before all cells could reach 0.7 V. The best cell in this stack had a power density of 329 mW/cm².

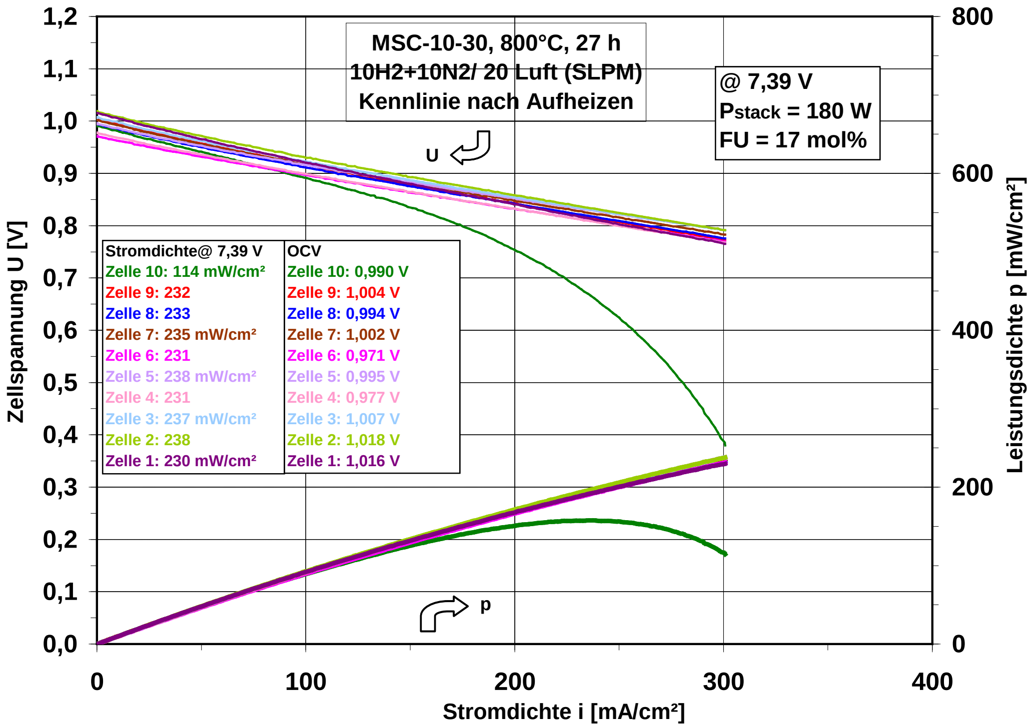

Figure 8: i-V-p curve of the LPPS 10-layer stack

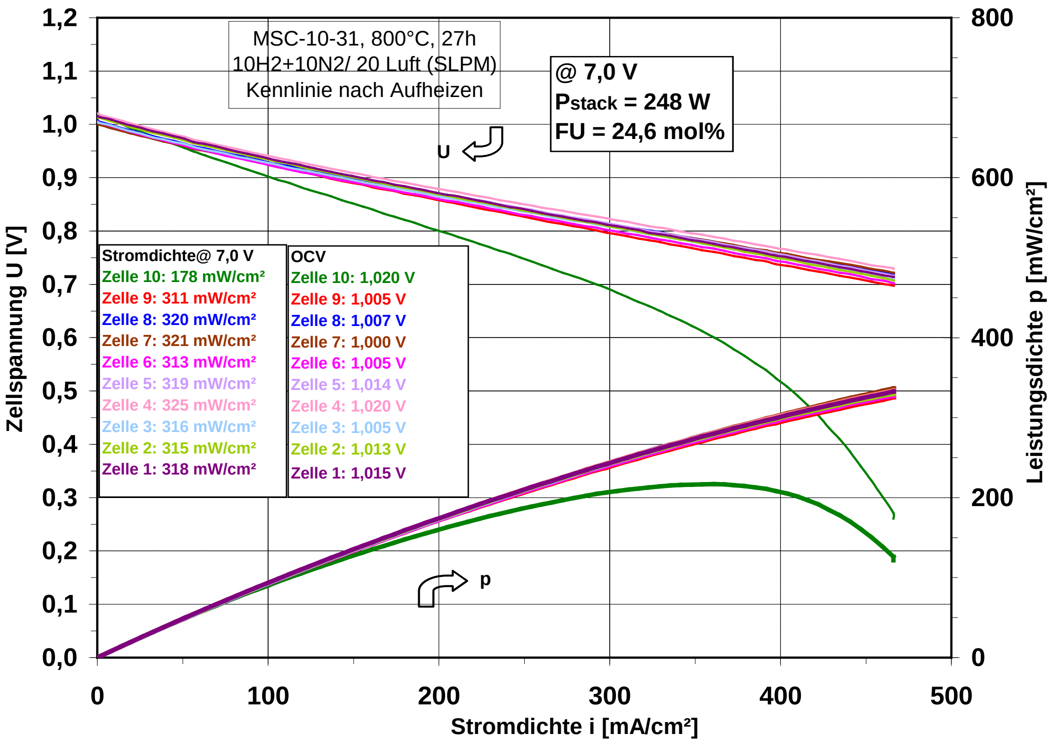

Figure 9: i-V-p curve of the VPS 10-layer stack

A long term test was performed with a 4-layer stack. The cassettes neither had an anode barrier layer nor an oxidation protection layer. The total operation time of this stack was in excess of 5000 h. Initial power density of the stack was 190 mW/cm², see figure 7. After 5000 h of operation the stack achieved 88 mW/cm², which results in a degradation rate of the stack of 10.7 %/1000 h. Again the top cell yielded the lowest power density but also showed a lower degradation compared to the other cells. The top of the stack is cooler than the rest because the heat generated by the stack can easily be transported away by the contact/seal weight of 60 kg which is stacked on top of the SOFC stack.

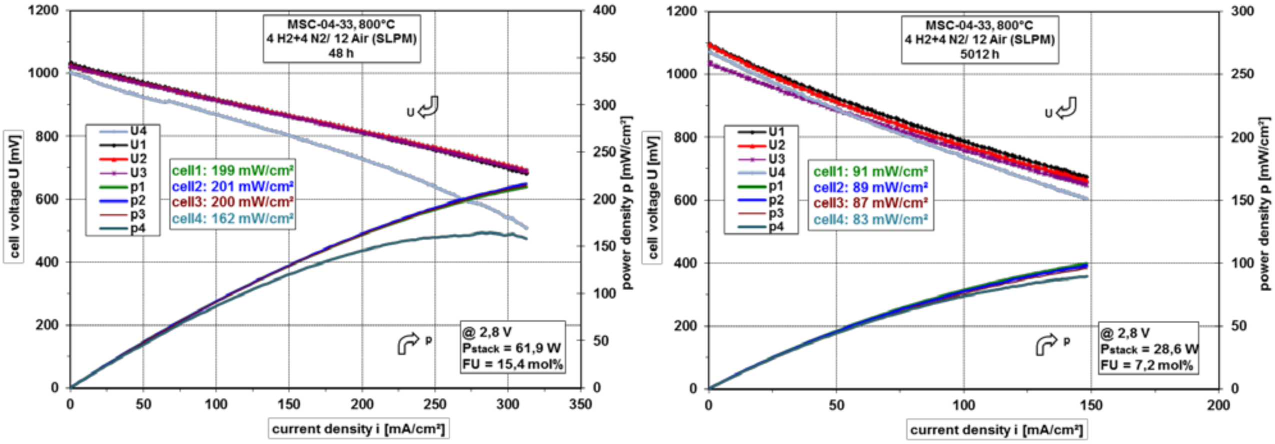

Figure 10: i-V-p curves of the long term test

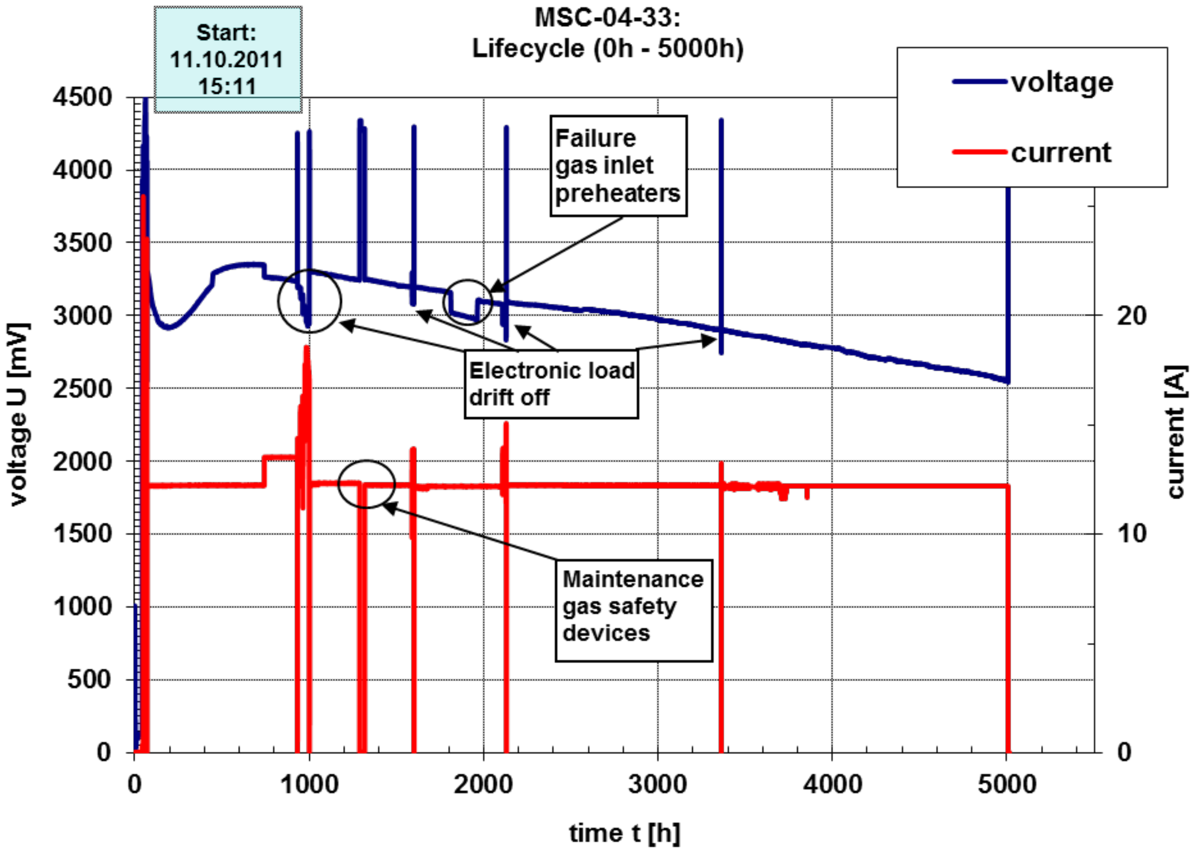

Figure 11: Life cycle of stack MSC-04-33

Up to 2500 h the degradation rate was lower at only 4 %/1000 h. This was attributed to the long burn-in time of the contact layer which led to ~1000 h of operation with virtually no degradation. This effect of the contact layer in the first 1000 h is visible in the life cycle of the stack, see figure 8. Under the static load of 150 mA/cm² there was an initial sharp decrease in stack voltage and after 150 h the voltage started to rebound to the original level with a large increase up to 600 h. From that

point the increase slowed down until it finally reached the starting level after 800 h. When no further change was observed, the load was increased to 200 mA/cm² but after 150 h the electronic load started to drift to even higher loads and it was shut off. For restart it was set to a load of 150 mA/cm² on which the stack then ran for the remaining 4000 h.
Since the stacks that were measured before never were operated for such extended periods new degradation mechanisms are likely to be found but the stack is still in operation. Apart from the standard degradation effects like Cr_2O_3-poisoning, oxidation of metal components, nickel agglomeration and cracks in the electrolyte, the LSCF as cathode material seems to have a higher degradation than the standard LSM [4]. The overall degradation rate of the stack is still high at 10.7 %/1000 h but much lower than previous tests where rates of 13-15 %/1000 h were found.

Conclusion

The new heat treatment process to increase the flatness of the cassettes lead to a large improvement of contacting and this resulted in an improved power density of the stacks. The 10-layer stacks were tested successfully and yielded the highest power densities for both electrolyte concepts. A maximum of 307 mW/cm² was achieved for a stack with VPS electrolyte and 222 mW/cm² for the stack with LPPS electrolyte.
All stacks showed a problem with the top end cell which is due to contacting and gas distribution problems. Additionally this part of the stack is cooler than the rest of layers. Therefore this layer shows a lower performance. A new top end plate and a new way of applying the load on the stack need to be developed.
Taking into account that the SOFC short stack was not specifically prepared for durability, e.g. without protection layers the obtained performance loss and 5000 h of operation is considered a promising result. It represents the longest stack test with plasma-sprayed SOFCs at DLR. The long burn-in time for the contact layer needs to be addressed. A new stack incorporating the protection layers is in production and an external mechanism with a push rod to apply the contact/seal load is under development to eliminate the high thermal mass of this weight in the furnace.

Acknowledgements

The results in this paper were obtained in the project MS-SOFC supported by the German Federal Ministry of Economics and Technology (BMWI) under the contract number 0327779A.

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