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The status of metal-supported SOFC development and industrialization at Plansee

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Benefiting from a strong cooperation with Forschungszentrum Jülich, Karlsruhe Institute of Technology (KIT), and AVL List GmbH respectively, Plansee has been focusing on the development and industrialization of metal-supported SOFC and components for mobile applications. In the scope of some challenging development projects a novel MSC configuration and a first pilot fabrication route could be demonstrated successfully. Currently, the work is ongoing towards a continuous and reliable manufacturing of standard cells as well as the demonstration of system-relevant stack tests. This paper gives an overview about the latest results in cell and stack development as well as about the manufacturing route for cost-effective metal-supported cells.

Introduction

The need of a low-emission and efficient energy supply for mobile applications has led to a world-wide political and social controversial discussion. In this context, for example, the German government intends to increase the amount of electrical vehicles to nearly one million cars until 2020 (1). Other governments in Europe and the U.S. have planned to do nearly the same. The ways to approach to this goal are different but with one thing the most experts agree: to bridge the gap between a conventional combustion engine and a pure electrical engine, a hybrid solution (a mixture between both engines) is needed. This common meaning can mainly be attributed by the fact that the range of pure battery vehicles is generally insufficient. In this spirit many car manufacturers, e.g. like Toyota, Ford, Volkswagen etc., have started the development and commercialization of hybrid cars already many years ago.

In recent years, this common trend has also led to an increasing interest on alternative devices to extend the limited range of pure battery vehicles without using a relatively inefficient and polluting combustion engine. For this purpose, highly efficient fuel cell systems have attained world-wide interest to be used as range extender or even as main propulsion system in hydrogen-driven cars (2-4). Furthermore, there are also some other interesting approaches for using fuel cell systems in mobile applications.

For example, by so-called fuel cell based auxiliary power units (FC-APUs) the electrical power, e.g. for air conditioning, can be provided highly efficient. World-wide development activities in terms of FC-APUs have triggered by the fact that in heavy duty vehicles, e.g. trucks and/or commercial vehicles like forklifts, wheel loaders, shovel dozers and others, the power demand has increased considerably and this demand is still rising (5). For this reason, the increasing interest in this technology has also triggered the development efforts of a special kind of APU, the SOFC-APU. Compared with other fuel cell technologies an SOFC-APU system provides specific advantages:

(i) possibility to operate with on-board fuels (e.g. Diesel)
(ii) higher electrical efficiency
(iii) higher volume specific power density
(iv) no need for expensive precious metal catalysts

In the past, the world-wide SOFC development activities of research institutions and companies have focused their work mainly on alternative cell materials and cell designs. Whereas the system requirements, e.g. frequent redox and thermo cycles as well as fast start-up times, were significantly increased it had to be commonly recognized that the ceramic SOFC cell types, the anode-supported (ASC) and the electrolyte-supported (ESC), get into severe difficulties to meet them. Therefore, specific development efforts have led to an outstanding novel cell generation, the metal-supported cell (MSC) technology (6, 7, 8). Due to its metallic cell support the MSC is promising to have a significant higher mechanical stability, and thus a much better thermal and redox behavior compared with ceramic cell systems, attributes that meet most of the important requirements for mobile APU applications.

Development Approach

Cell Development and Manufacturing

Plansee's generic cell development program is located mainly in the scope of the project "NextGen MSC" and in parts in the project "MetAPU". Both projects are financially supported by the German Ministry of Economics and Technology (BMWi). The following paper gives an overview about the project-related work that is coordinated by Plansee within a co-operation between Forschungszentrum Jülich, Karlsruhe Institute of Technology (KIT), and AVL List GmbH respectively. Whereas Jülich and KIT provide a high level of basic scientific support in terms of cell development and cell testing, Plansee and AVL are engaged in the industrial commercialization, e.g. the establishment of a pilot manufacturing line of MSC cells, repeat-units, and finally, system-relevant tests of MSC stacks for the AVL SOFC system.

Figure 1 shows an overview of Plansee's manufacturing line of MSC single cells and repeat units (here schematically demonstrated as a production line with single cells and light-weight repeat units for APU stacks). After a substrate and/or a repeat unit manufacturing, a 1-2 µm tick diffusion barrier layer (DBL) consisting of CGO is directly deposited on top of the substrate by a magnetron sputter process. Subsequently, the porous 40 µm graded Ni/8YSZ anode is screen printed in a dust-free clean room environment, in a multi-pass printing/drying procedure to generate a microstructure with a gradually decreasing pore size, which is finally sintered. Afterwards, the thin-film 8YSZ electrolyte with a thickness of 3-5 µm is applied by a gas flow sputter process (9) followed by a 1-2 µm thick CGO diffusion barrier layer which is integrated by magnetron sputtering as well. Finally, a 40-50 µm thick LSCF cathode is added which is applied by screen printing, likewise the graded anode structure, and finally activated in-situ during initial cell operation. The detailed cell set-up as well as the development of the cell components, e.g. the novel gas flow sputtered thin-film electrolyte, is already described in detail elsewhere (6-10).

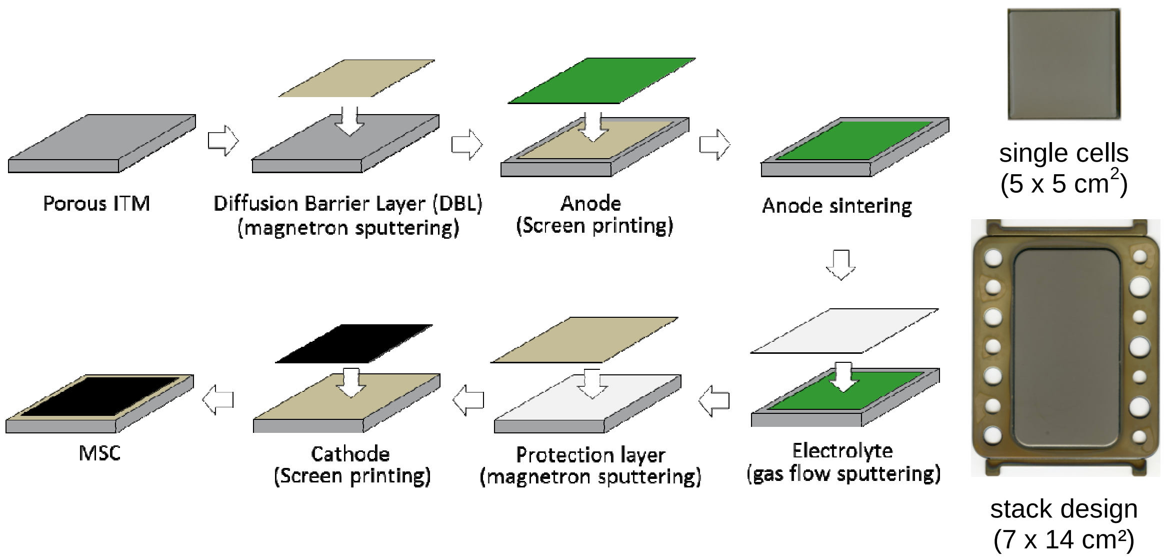

Figure 1. Pilot manufacturing process of single cells and cells for stack-relevant light-weight cassette technology (“repeat units”)

As a result of consequent cell and manufacturing process development, a novel MSC configuration and a first fabrication line, for the production of up to 25.000 cells per year, could be demonstrated successfully. Currently, the work is ongoing towards a continuous and reliable manufacturing of standard cells as well as the demonstration of first system-relevant stack tests.

Applications and System Requirements

In the scope of numerous projects (11, 12), a consequent development work has performed by AVL List GmbH to establish a reliable and affordable 3 kW SOFC APU system (Figure 2). Within the project “NextGen MSC” AVL has focused to develop and increase the stack and system reliability as well as the test of a novel and unique system feature, the recirculation of anode exhaust gas (13), under real operation conditions.

Such an APU system is probably one of the most challenging applications for an SOFC. The system requirements which are directly given from the application itself, e.g. from the truck industry, dictates the requirements to an adequate SOFC, respectively MSC stack. The most challenging requirements to the stack are such as: (i) the European road diesel as fuel, with high carbon and sulfur contents, (ii) a small system, and hence stack weight of < 100 kg, (iii) a fast system start-up time < 30 min, and (iv) the ability for thermo (300/3000, cold/warm) and redox (30/5, operation/ambient) cycles respectively.

Figure 2. Prototype of a 3 kW AVL SOFC APU for heavy duty trucks (12)

Beside this high challenging application AVL and its industrialization partner, “HighRef Power”, have been focusing to enter also into some other relevant markets, e.g. for military, camping, and marine applications (13).

Results

Cell Development

As we have already described in detail our cell development activities with focus on our standard MSC cell, MSC06B, Type C (6-10), we want to give at this point a short overview about further development work which has related to cathode and anode optimization. At first, in this work we have focused in particular on improved and alternative cathode materials like $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC), $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ (LSCF), and a mixture of LSC, LSCF and graphite (GF). The graphite content in the LSCF-paste material was targeting in improvement of the cathode adhesion to the electrolyte layer as well as of the electrochemical activity by a specific exothermal reaction of the graphite with oxygen, during the in-situ cathode activation. At second, we carried out some specific structure improvements to our screen printed anode layers by using new powder compositions. Figure 3 shows the results of these measures.

It is clear to recognize that the highest cell performance could be reached by cells with standard LSCF cathodes and improved anode structures (type D) as well as by a cell with LSC cathode and a standard anode (type C). In all cases the operation point of 0.7 V couldn’t be reached by our measurement technique. But with an extrapolation of the curves it was possible to estimate the cell performances at this operation point of significantly more than 2 A/cm^2 at 850°C. In contrast, the current density of our standard cell, MSC06B, at 0.7 V is approx. 1.6 A/cm^2 at the same temperature.

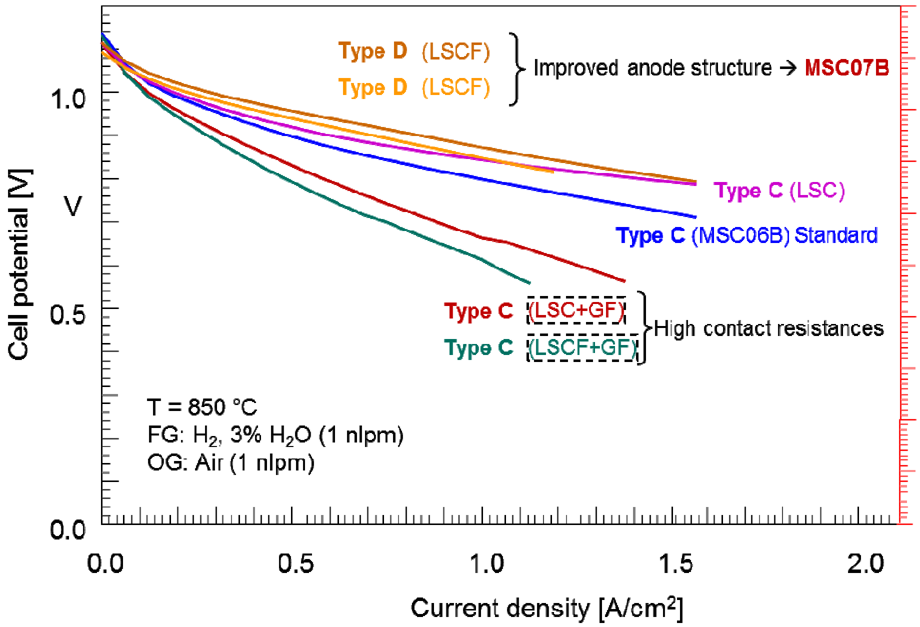

Figure 3. Single cell tests (5 x 5 cm^2, active cell area: 16 cm^2) of cells (based on the standard cell, MSC06B, type C) with special optimizations to cathode and anode structure

The fact that the thermal expansion (CTE) as well as the sintering temperature of the LSC material is in general significantly higher than those of LSCF (14) makes the decision easy to neglect a LSC in-situ cathode for enlarged cell areas. In contrast, the good results of the cells with improved anode structures, but with standard LSCF cathodes, indicate a next generation of an MSC cell type, the MSC07B.

In the case of the cells with optimized graphite cathodes (LSC+GF and LSCF+GF) only current densities of 0.65 A/cm^2 (LSCF+GF) respectively 0.8 A/cm^2 (LSC+GF) at 0.7 V could be achieved. Impedance measurements at KIT have indicated significant higher contact resistances which could be attributed to a relatively strong warping of the cells, and hence of a diminished cathode contact area.

System Relevant Single Cell Tests

Further development activities have targeted in single cell tests in laboratory scale (5 x 5 cm^2, active cell area: 1cm^2) under real SOFC APU operation conditions to determine a characteristic performance map. For this purpose, the real diesel reformate gas composition (50% N_2, 15% H_2, 14% CO, 11% H_2O, 10% CO_2) from AVL was used. Due to a selective variation of the operation temperature and simulation of the fuel utilization (by a stepwise replacement of the oxidizable gas components like CO and H_2 with CO_2 and H_2O) it is possible to determine the cell performance of all possible stack conditions. Figure 4 shows exemplarily such a characteristic performance map of a standard MSC cell at 750°C. The diagram shows I-V curves at different simulated fuel utilizations (0-80%).

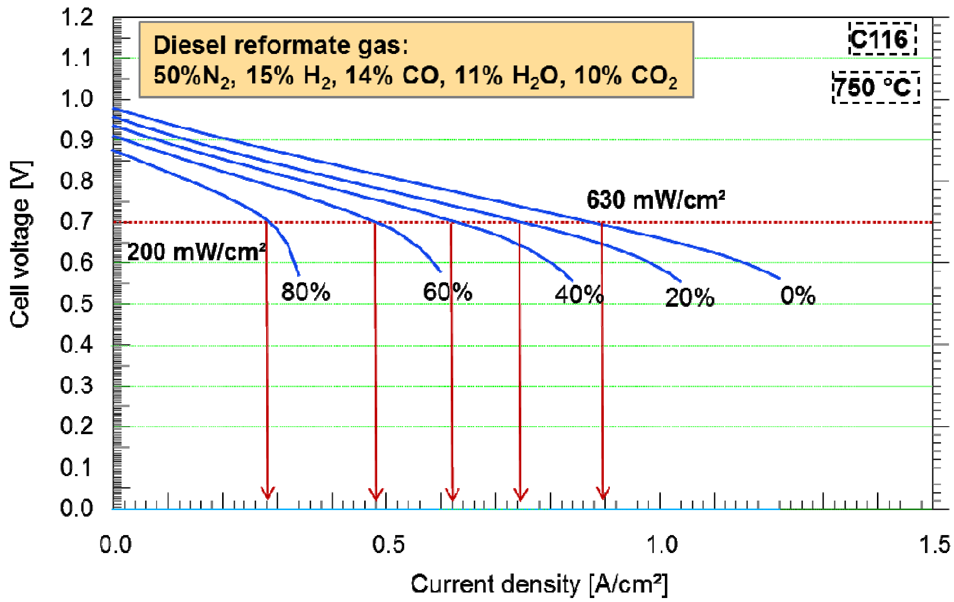

Figure 4. Characteristic performance map with simulated fuel utilizations of a standard cell (MSC06B) at 750°C operated with system-relevant diesel reformate gas (50% N_2, 15% H_2, 14% CO, 11% H_2O, 10% CO_2) (cell size: 5 x 5 cm^2, active cell area: 1 cm^2)

In spite of this hard stack operation conditions, at a fuel utilization of 80% a standard MSC can still achieve a cell performance of 200 mW/cm^2 at 0.7 V. In contrast, within 1 cm behind the gas inlet (simulated fuel utilization of 0%) the cell reaches a performance of approx. 630 mW/cm^2 at 0.7 V.

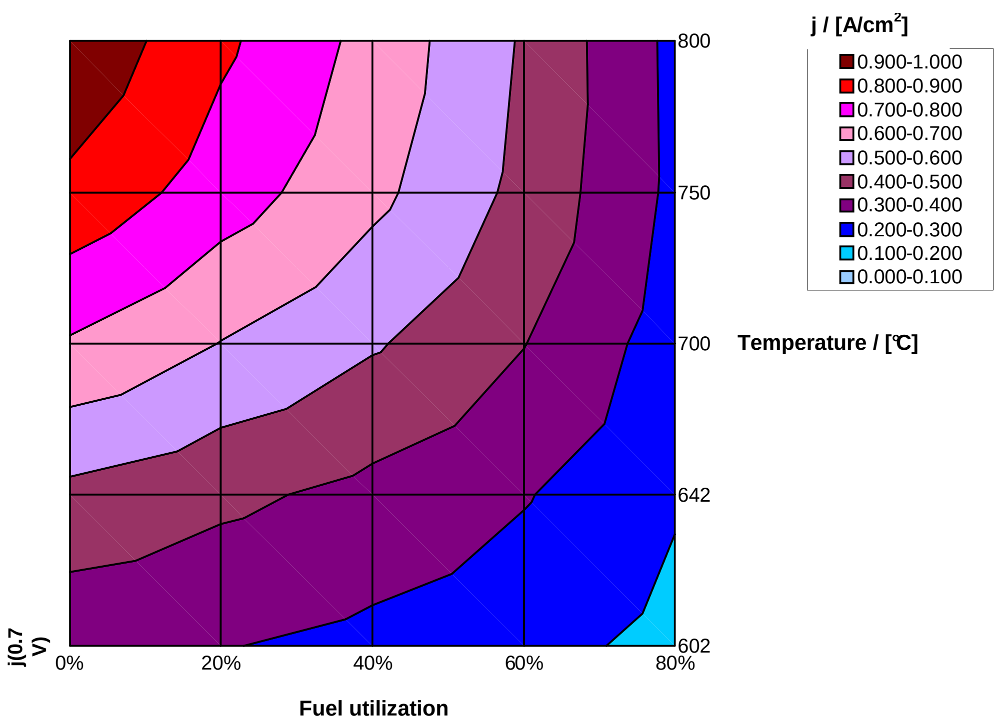

Figure 5. Characteristic performance map of a standard MSC for the operation with diesel reformate (50% N_2, 15% H_2, 14% CO, 11% H_2O, 10% CO_2) in dependency of simulated fuel utilization and operation temperature; measured at 0.7 V

This is a remarkable result that gives the possibility to estimate the cell performance of a potential stack under real system operation conditions. For example, in the case of the AVL SOFC APU system (Figure 2) a fuel utilization of only 60-70% in the SOFC stack is targeted (the fact that the system runs with a recirculation of anode exhaust gas (14) allows to aim at lower fuel utilizations in the stack). Therefore, a cell performance of 280-340 mW/cm^2 can be estimated under system-relevant conditions.

In Figure 5 a characteristic performance map is given, showing the distribution of current densities j at a cell voltage of 0.7 V in dependency of possible operation temperatures as well as simulated fuel utilizations. This map allows determining different possible system-relevant operation points. For example, it can be recognized that between a fuel utilization of 60-70%, at a temperature of 600°C, current densities of 0.2-0.3 A/cm^2, and thus cell performances of 140-210 mW/cm^2 can be achieved. In contrast, at an operation temperature of 800°C, at a simulated fuel utilization of only 0-10%, it is possible to achieve 0.9-1.0 A/cm^2, and hence power densities of 630-700 mW/cm^2. This demonstrates the broad operation field of the performance (140-700 mW/cm^2), and thus the high potential of this cell technology under stack-relevant conditions. Of course, with a system-relevant point of view only the operation points at high fuel utilizations are really interesting.

Further system relevant single cell tests, in general in terms of the very interesting redox behaviour under APU conditions, are presented in detail by D. Roehrens et al. (15).

Stack Development and Stack Tests

In the scope of the “NextGen MSC” project a first scale-up of standard single cells (MSC06B), with a size of 5 x 5 cm^2, to a stack-relevant cassette design (“CM1”), with a cell size of 7 x 14 cm^2, could be carried out successfully. The measured leakage rates of the “repeat units” have corresponded relatively well with those of small single cells. During the stack development and testing work, which has performed by Jülich, first two-level stacks could be assembled (Figure 6) and tested successfully. In Figure 7 some results of a first successfully measured two-level stack are shown.

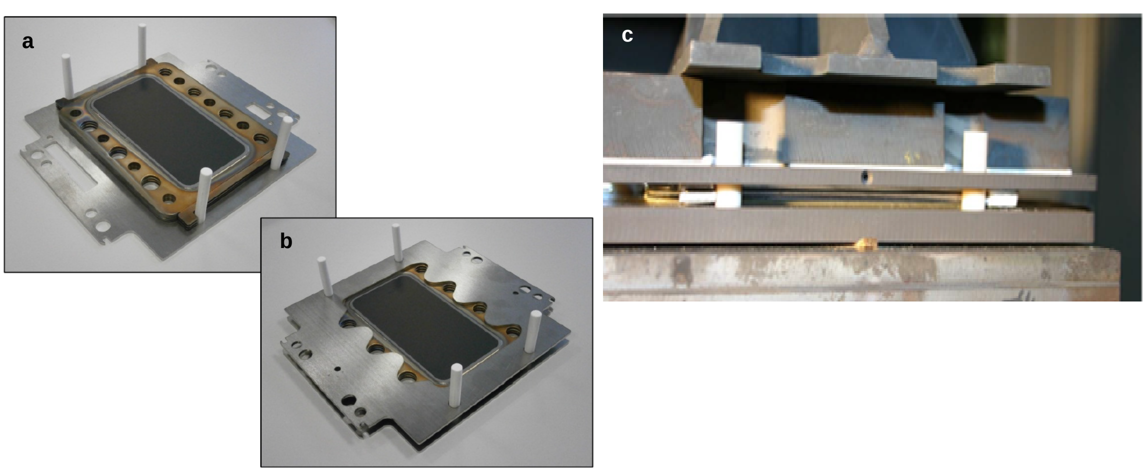

Figure 6. Stacking of a two-level stack (a, b) and integration and set-up of a contacted stack in a furnace chamber of the test bench at Jülich (c)

Because of some minor problems with voltage contacts (loosened wire contacts) at the test bench, the potential of cell level 2 has decreased significantly in the first 50 h of operation time during the sealing procedure of the stack (Figure 7, above). After a fixing of that problem the stack levels have reached OCV of approx. 1 V; stack level 2 has reached even significantly more than 1 V. In general, the relatively high cell potentials indicate low leakage rates of the electrolytes and the glass solder outside the cassette levels. After the sealing and start-up phase (until 140 hrs.) both cell levels were characterized carefully at different operation temperatures (700 °C, 750 °C and 800 °C). Some of these measurements are exemplarily shown in diagram 7 (below).

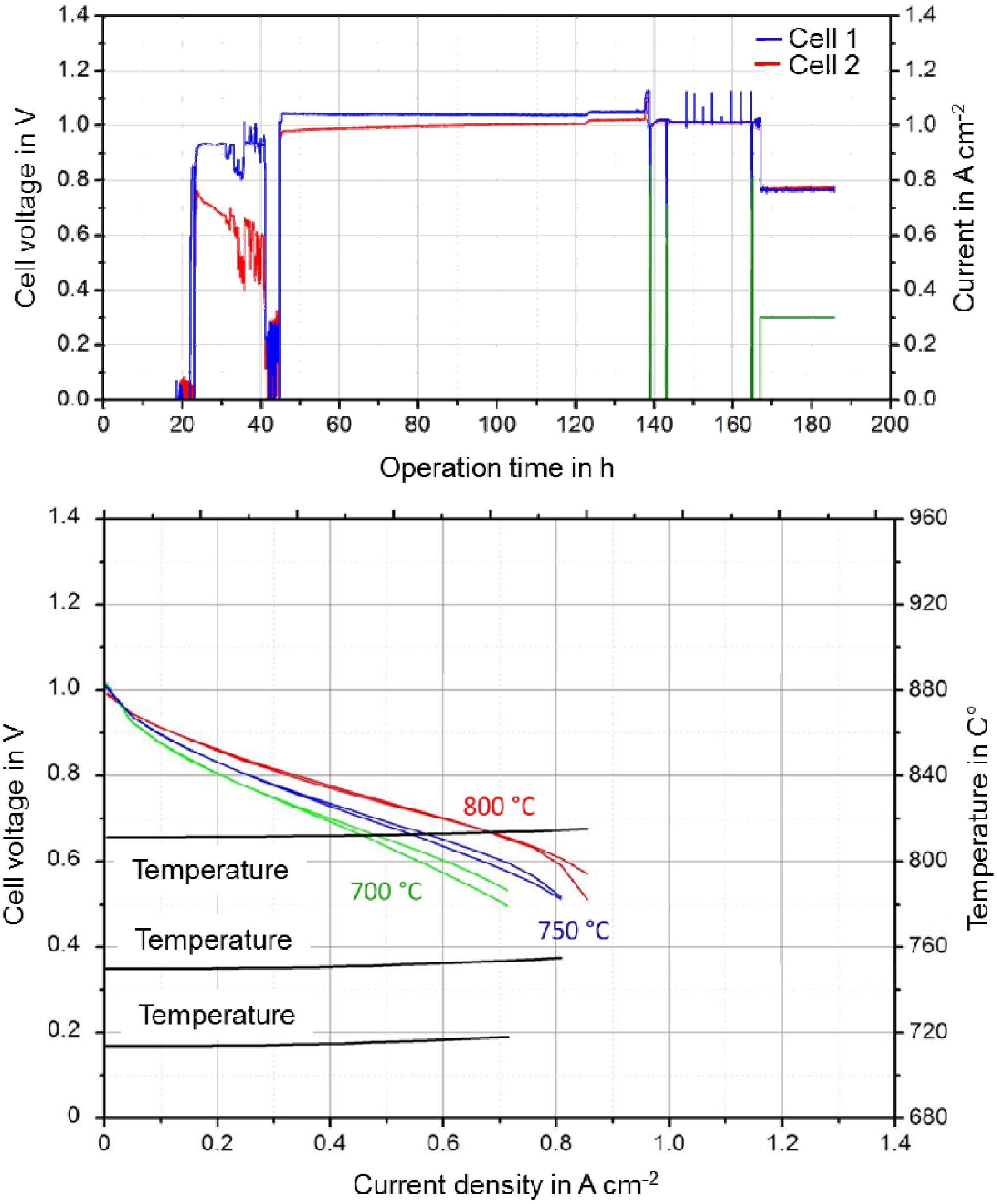

Figure 7. Electrochemical characterization of a first two-level MSC stack (fuel gas: 2 slm H_2, 2 slm Ar, 10% H_2O; oxide gas: 10 slm Air). The diagram above shows the cell voltages of both levels over the stack operation time. The diagram below shows typical I-V-characteristics in dependency of the operation temperature.

It is obvious, that at higher operation temperatures both stack levels have also reached higher current densities. Furthermore, both levels show only small differences in its I-V characteristic. The highest power density of the stack could be reached at 800 °C. At an operation point of 0.7 V the stack provides a power density of 430 mW/cm^2 of each cell. Related to the active cell area (88 cm^2) each level shows approx. 38 W. In contrast, at 700°C each stack level has achieved 280 mW/cm^2 or 25 W. In the focused standard operation temperature of the AVL system, at 750°C (Figure 2), the stack has reached approx. 350 mW/cm^2 or 31 W per level.

Due to a progressive aging of stack level 2 the whole stack unfortunately had to be switched off already after 381 h operation time. A post mortem analysis in Jülich has indicated that the aging effect can be attributed mainly to problems with the glass sealing. However, this first stack characterization has demonstrated impressively the feasibility and the high potential of the MSC technology for a light weight stack design.

One of the biggest challenges by stacking of these light-weight cassettes is the fact that the design was originally established for the well-known plasma sprayed cell concept of the German Aerospace Center (DLR), Stuttgart (16). The design is adapted to an overall cell thickness of 120-140 µm. In the case of the thin-film MSC of Plansee the overall cell thickness is in the range of only 80-90 µm which resulted in constructive problems during the glass sealing procedure (short circuits in the sealing area by the significant thinner sealing gap in case of using the thin-film MSC). For this reason, Plansee and its Partners are developing in the scope of the MetAPU project a specific light weight design for sintered thin-film cells.

Conclusion

In the present paper an overview over the development and industrialization work in the scope of the "NextGen" MSC project has presented. Benefiting from a strong cooperation with Forschungszentrum Jülich, Karlsruhe Institute of Technology (KIT), and AVL List GmbH respectively, a first pilot fabrication for metal-supported single cells as well as for a stack-relevant light weight design for mobile applications, e.g. the AVL SOFC APU, could be established successfully. Furthermore, the highlights of cell and stack development could be pointed out. So, the development of single cells with special optimizations of cathode and anode structures could be demonstrated, whereas novel single cells were presented which achieve more than 1.5 W/cm^2 at 850°C and 0.7 V under humid H_2 and air operation conditions. Moreover, single cell tests under real system-relevant conditions (in AVL diesel reformate) have demonstrated the high potential of the standard cell technology. Finally, a first two-level stack test, with MCS standard cells on top of a light-weight cassette design, could be operated successfully demonstrating its high potential for mobile stack applications. Currently, the work is ongoing towards a continuous and reliable manufacturing of standard cells as well as the demonstration of system-relevant stack tests with 5 and 10-level stacks. Furthermore, a novel stack design is currently in progress which provides a significantly higher reliability during stacking.

Acknowledgments

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