FINAL PUBLISHABLE SUMMARY REPORT

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Contents

METSAPP project executive summary

Most SOFC demonstrations with ceramic cells in real system operation have revealed problems regarding reliability issues. Attention to reliability and robustness has especially been paid for mobile applications. Modelling studies as well as practical experience have shown how up-scaling of cells and stacks to more industrially relevant sizes generally leads to lower reliability in real system operation and intolerance towards system abuse and operation failures. Due to the ductility and mechanical strength of metals, metal supported cells have robustness advantages compared to anode supported cells. Also, the long term durability of anode supported cell and stack components requires a reduction in the operation temperature to ≈ 650 ºC, which is feasible with metal supported SOFCs. Therefore, METSAPP aims at developing novel cells and stacks based on a robust, reliable and up-scale-able metal supported technology for stationary as well as mobile applications.

Prior work demonstrated significant progress towards durability by using unconventional half-cell design, where the major material and durability problems associated by the use of Ni-YSZ anodes are circumvented by alternative anode structure, composed of a FeCr-ceramic porous conductive backbone, into which electro-catalysts are infiltrated. In previous project, oxidation issues of the FeCr metallic phase appeared to be the major durability issues. The METSAPP cell robustness was significantly improved with the LSFNT anode material development and its integration into the cell. The resulting cells with LSFNT based anode designs showed significant improvement in electrochemical stability. In addition, high performance cathodes were also developed and integrated into various sizes of cells successfully. Furthermore, the cell fabrication process was optimised to enhance the cost-efficiency and environmental friendliness by developing the co-casting process using non-toxic materials that enables mass manufacturing. More than 500 good quality cells in different sizes up to 300 cm^2 were fabricated during the course of the project.

Several new interconnect coatings were investigated for the anode and cathode sides. The developed coatings result in much lower oxidation rates, inhibition of Cr evaporation and oxide scale resistance reduction. Furthermore, it was demonstrated that the coatings possess a self-healing capability so that even severe deformation damages during shaping of the interconnects can be tolerated. Thus, it is possible to mass produce the interconnect coatings before deformation. The data obtained with respect to oxidation rates and Cr evaporation were used to develop a new lifetime model, expected to describe the situation in a stack more realistically.

Modelling and computer simulations represented some important activities in METSAPP and major progresses were achieved. In particular, in order to assess the degradation failure mode, an oxidation model has been developed and implemented. The model describes the growth of the oxide scale and the change of the pore volume, which in turn influences the gas diffusion in the microstructure. In addition, the extensive electrochemical characterization and stability of the FeCr-LSFNT based cells enabled extraction of the electrochemical parameters for the validation of the developed 2D Finite Element Method (FEM)FEM model for I-V curves. These extracted parameters are in excellent agreement with the simulated I-V curves using 2D FEM model at different temperatures.

ElringKlinger AG took over the stack assembly after TOFC closure at the project end. The welding process parameters were adapted to the METSAPP cell and the stack design was optimised regarding the cell integration into the cell frame, illustrating the flexibility of METSAPP cells for different stack designs (both TOFC and EK designs). The necessary future steps for stack demonstration were defined.

Summary description of METSAPP context and main objectives

State of the art SOFC technology for stationary as well as for transportation application is being demonstrated with either planar or tubular ceramic anode-supported or electrolyte-supported SOFC cells. However, the SOFC technology faces many challenges when it comes to commercialization, since cost reduction, reliability and extended lifetime is required. In order to improve durability and cost efficiency of the cells the stacks and the system much of the development has in the past been focused on lower operation temperature, increased power density and material savings based on reduced cell and stack component thickness. Nevertheless, most of the demonstrations with ceramic cells in real system operation have until now revealed problems regarding these issues in combination with low robustness. Attention to these issues has especially been paid in connection with SOFC technology for mobile application, such as in APUs. Modelling studies as well as recent practical experience has proved how up-scaling of cells and stacks to larger more industrially relevant sizes generally leads to lower reliability in real system operation and intolerance towards system abuse and operation failures. These observations conform to the statistical distribution of mechanical properties governing the probability of failure of cells based on ceramic materials, whether it is for mobile or for stationary applications.

The metal-supported technology has many potential advantages such as cost, good thermal conductivity and ductility of the metallic substrate, which will ensure safe operation including thermal shock resistance and tolerance towards internal temperature gradients and operation cycles. Finally, reduction in the operation temperature to ≈ 650 ºC is feasible with metal supported SOFCs. Therefore, METSAPP aims at developing novel cells and stacks based on a robust, reliable and up-scale-able metal supported technology for stationary as well as mobile applications.

The preceding EU FP7 METSOFC project has been aiming at improved reliability and robustness for mobile applications by the introduction of metal supported cells based on cost effective, industrially relevant manufacturing processes and has shown potential for the use in APU units. Degradation tests have revealed that the novel METSOFC metal supported stack technology has a potential for 5.000-10.000 operation hours at 650-750 ºC stack temperature fulfilling the well known requirements for APU applications. However, the knowledge gained from the project as well as from other parallel projects on metal supported cells highlighted the need for further improvements of the cell components in order to fulfil durability requirements in stationary applications (such as: Distributed generation, and CHP) where lifetime of 20.000 to 60.000 hours is mandatory. The objective of the METSAPP project is to improve the lifetime of SOFC stacks based on metal supported technology to beyond 10.000 hours aiming at 40.000 hours for stationary as well as mobile applications with increased power densities. The established experience indicates that long term durability requires a further reduction of the operation temperature to 600 – 700 ºC. METSAPP is targeting at a novel improved cell concept with a cell ASR of 0.5 Ωcm^2 at 650 ºC with a degradation rate of less than 0.25% / 1000 h.

For this, the oxidation effects on the metal support and the anode has to be further investigated by combining mathematical oxidation models with testing, characterisation and screening of new materials. This includes further understanding of how microstructural parameters such as porosity or tortuosity change over time with oxidation. It also includes fundamental modelling of physical material parameters such as creep and deformation as a function of mechanical and thermo-mechanical load during operation. Finally, feedback from modelling and testing of cells and stacks are used to improve the materials in the cell and stack development work. Due to the limited project timeframe, this approach has to rely upon development and implementation of accelerated test protocols and extended simulation methods. Key development issues include:

- Metal powder development
- Development of novel anode designs and nano-structured coatings
- Integration of high performance stable cathodes
- Integration of developed components to full cells
- Component and cell manufacturing for testing and stacking
- Development of novel stack concepts
- Development of coatings for ferritic stainless steel interconnects.
- Electrochemical characterization and extraction of parameters for modelling and simulation.
- Development of advanced modelling tools and improved models to investigate the loss and degradation mechanism in cells and stacks
- Models to understand oxidation behaviour

The METSAPP project has the principal objective to improve the robustness and life time of the metal supported SOFC technology to significantly increase its appropriateness for cost effective up-scaling. For commercial breakthrough of the SOFC technology it is vital that the materials cost in case of large scale cell and stack production is reduced. The need for Ni-YSZ materials for the support layer in the current anode-supported cells or YSZ for the electrolyte-supported cells confines the raw material cost to a level of € 50-80 per kg. A metal-based SOFC stack technology has the potential to improve functionality, reliability and reproducibility and reduce the manufacturing cost of SOFC stacks. The objective of METSAPP is to bring the material cost for the major part of the cell and stack down to about € 10-20 per kg in case of stationary as well as mobile systems.

To reach these targets, METSAPP is to focus on improved nano-structured electrodes adapted to the metal-supported cell concept in METSOFC, as well as novel optimized stack designs to be introduced. In one of the work packages (WP2) new sulphur and carbon tolerant anodes based on doped titanates are to be developed, based on collaboration with the SCOTAS-SOFC EU/JTI-FCH project. DTU, USTAN as well as TOFC participated in the SCOTAS-SOFC project. In other cases, the new materials with increased performance are developed and implemented based on close collaboration with parallel national SOFC R&D projects. Furthermore metal supported cells and stacks developed in this project will lead to reliable and cost effective solutions suitable for up-scaling based on optimization in material selection and design. On stack level METSAPP will develop and introduce a new cost effective concept for thin metal interconnects with high oxidation resistance, long lifetime, low Cr evaporation rate and low area specific electrical resistance. The concept relies upon the continuous PVD thin film pre-coating technology for ferritic stainless strip steel developed by Sandvik (SMT) in the METSOFC project. METSAPP takes this breakthrough SOFC interconnect technology a big step further introducing novel in-situ multiple thin film coatings for prolonged life time.

Focusing on the objectives for long-term performance and up-scaling the project includes work on identification of relevant and critical material and design parameters through modelling, characterization, testing and post mortem analysis. An electro-chemical model of the repeatable stack elements will be developed and used for optimizing the cell size and flow patterns of interconnects. CFD & FEM modelling will be used for minimizing pressure drop across the cells and contact resistance between cells and interconnects. The improved understanding and knowledge obtained through modelling and testing will be transferred to other work packages for practical implementation through a close and effective link between the individual work packages and through efficient fast track iterations.

The project consist of a vertically integrated group of partners all supplementing each other and bringing the required competence, and experience into a focused and effective development approach. The project is front end loaded meaning that it first of all has a starting basis in the preceding METSOFC project with the same experienced partners plus two new supplementing partners needed to reach the project objectives. Reference materials whether metal powders for cell support, coatings, interconnects, cell seals or stacks are available for the project already from the starting point. The partners possess the required cross-functional competencies ranging from materials and electrochemical science, physical modelling and testing to materials and component processing and manufacturing. The partners possess all the necessary equipment for all the sequential steps of the whole development course such as: Advanced material characterization, testing stations for cells and stacks laboratory as well as industrial scale manufacturing equipment for powders, strip steels, thin film coatings, powder metallurgical as well as ceramic tape casting, screen printing, spray coating, lamination, powder metallurgical vacuum and hydrogen sintering, brazing, etc. There is a strong focus on industrially relevance by participation of three SOFC experienced industries. Furthermore, these industrial partners have a strong experience in coordinating R&D in collaboration with scientific institutional partners. High probability for success is ensured due to the mutual interest and vertical integration of the project partners avoiding contradictory interest.

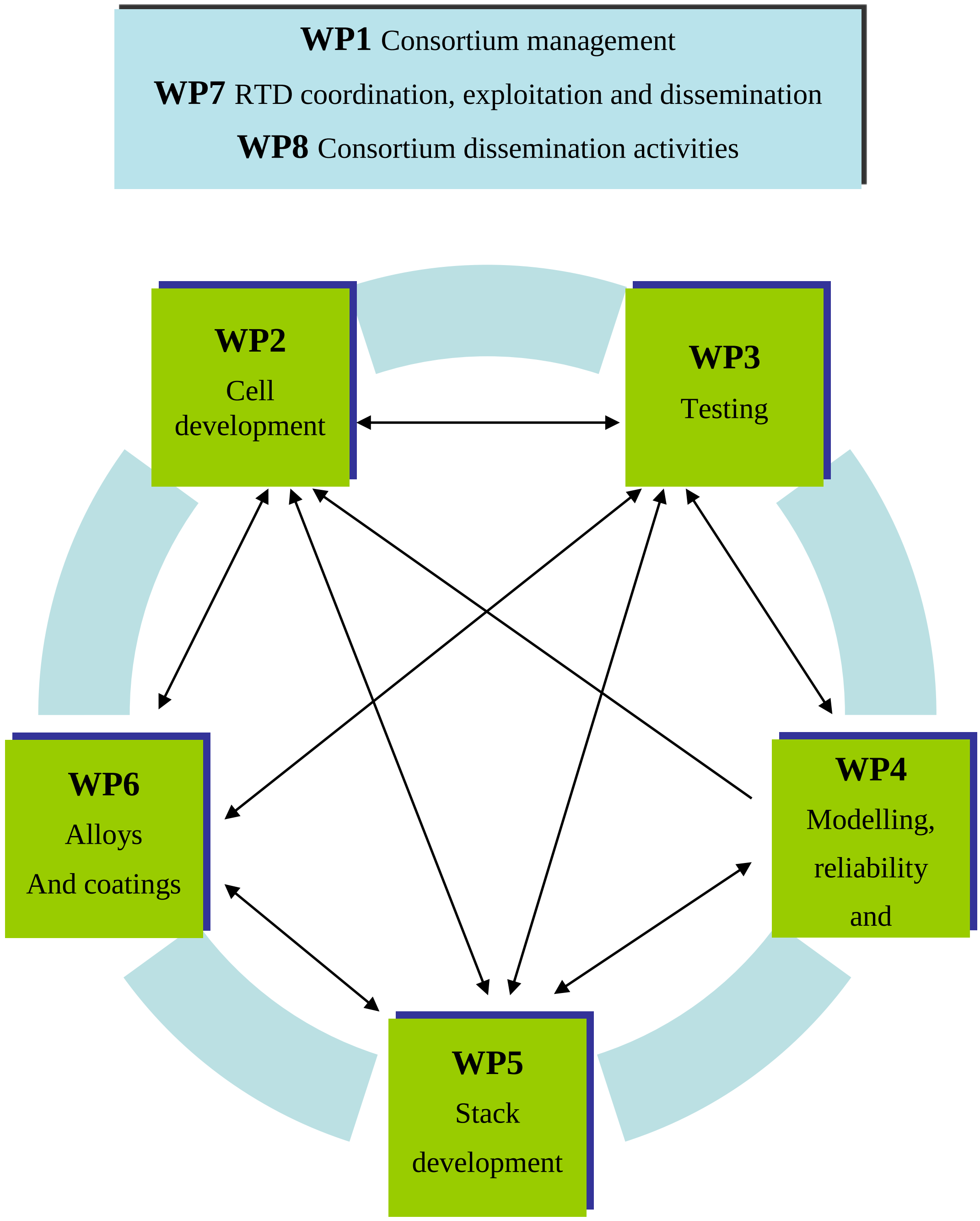
Primary objectives

- Robust metal-supported cell design, $ASR_{cell} < 0.5\ \Omega cm^2$, 650 °C
- Cell optimized and fabrication upscaled for various sizes
- Improved durability for stationary applications, degradation < 0.25% / 1000 h
- Modular, up-scaled stack design, stack $ASR_{stack} < 0.6\ \Omega cm^2$, 650 °C
- Robustness of 1-3 kW stack verified
- Cost effectiveness, industrially relevance, up-scale-ability illustrated

The work is organised in eight work packages. Three of which are related to overall management and dissemination across the whole project. The other five work packages deal with the five major technological areas to focus on.

WP Number	WP Title	Type of activity	Lead beneficiary
WP 1	Consortium management	MGT	DTU
WP 2	Cell development	RTD	DTU
WP 3	Testing	RTD	KIT
WP 4	Modelling, reliability and durability	RTD	AVL
WP 5	Stack development	RTD	AVL
WP 6	Alloys and coatings	RTD	Chalmers
WP 7	RTD Coordination, exploitation and other dissemination activities	RTD	DTU
WP 8	Consortium dissemination activities	OTHER	DTU

The work package interaction/interdependence is based on a LEAN spiral concept, with effective short cuts, avoiding sub-optimization and increasing speed of development.



METSAPP main S&T results/foregrounds

The METSAPP project scientific and technical main results for the development and integration of metal supported cells (MS-SOFCs) and stacks are covering mainly seven areas, presented below.

Development and characterisation of novel MS-SOFCs

Development and integration of robust anode

The use of conventional Ni and Y_2O_3 stabilized ZrO_2 (Ni-YSZ) cermet based anode functional layers (AFL) in the MS-SOFCs lead to problems such as Ni inter-diffusion with the metal support and as a result poor redox stability. One solution is the use of Ni-free AFL backbones, into which the electrocatalytically active materials are infiltrated to make the electrode fully functional. In the previous EU METSOFC project, anode designs based on FeCr-YSZ with infiltrated Ni:GDC (Gd doped CeO_2 (GDC) with small amount of Ni) were developed successfully (see Figure 1).

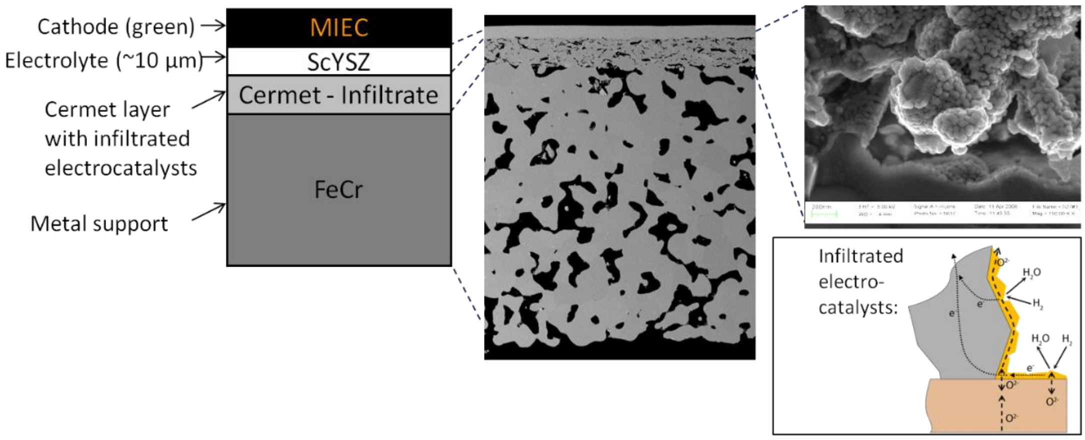


Figure 1: Schematic illustration together with SEM images showing the concept of the MS-SOFC cell design and electrocatalyst infiltration.

The cells developed in the EU-METSOFC project demonstrated highly promising electrochemical performance. However, going to more realistic operating conditions, i.e. reformates and high fuel utilization, high degradation was observed due to the severe oxidation of FeCr metal phase in the AFL. Thus, in the current EU METSAPP project, one of the focus is centered on the development of high performing oxidation resistant anodes, based on the infiltrated AFL design presented in Figure 1. Three major routes were considered in order to obtain robust anodes. While the development of oxidation resistant alloys and nanocoatings showed potential although insufficient improvements, the development of alternative anodes was successful and resulted in robust anodes, though further understanding and control of the infiltrated electrocatalyst is a remaining development task. In addition, the electrocatalyst influence was studied for its impact on the anode performance and reasonable stability was demonstrated.

Development of oxidation resistant alloys

The metallic phase used in the anode cermet backbone has to

- Have a relatively low particle size distribution due to the anode thickness. This is detrimental to the lifetime, as smaller particle size results in higher surface area for a given volume and thus breakaway oxidation occurs faster.
- Be highly oxidation resistant at SOFC operating conditions. Modelling showed that the parabolic rate constant (Kp) values, with the required low particle size distribution, has to be around 10^{-16} – 10^{-17} $g^2cm^{-4}s^{-1}$ (or even lower) are needed for lifetime above 10.000 hours.

- Be compatible with manufacturing process, in particular sintering at high temperature in low pO2

The investigation of different alloys showed that FeCr ferritic alloys are the best compromise, although the oxidation resistance is still not sufficient. Other alloys such as 316L, IN718 and F75 are more oxidation resistant, although still not sufficient. These alternative alloys as first produced are though incompatible with the sintering process. Modification of their physical characteristics and addition of other alloying elements to tune their sintering behaviour might render them suitable as alternative alloys. However, the improvement in oxidation resistance is expected minor in comparison to the needed effort to tempt matching the sintering behaviour and not focused on.

Development of protective nanostructured coatings:

Nanocoatings are intended to have two functions as represented in Figure 2. The primary function of the coating is to limit the formation of Cr_2O_3 on the FeCr particles. The coating is also expected to move the reaction zone away from the FeCr surface to lower the accelerated oxide formation upon drawing a current. These coatings have to possess high electronic and low oxygen ion conductivities, prevent Cr-diffusion, be compatible with electrocatalyst and demonstrate physical, chemical and microstructural stability. Potential nanocoatings of reactive elements, chromites, titanates, metal oxides and spinels were therefore investigated.

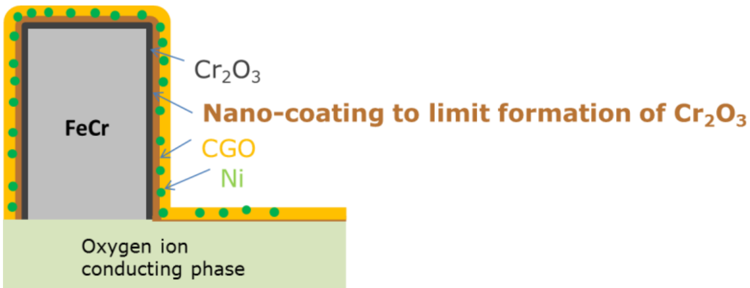


Figure 2: Hypothetical schematic illustration showing how the nano coatings are intended to inhibit the formation of Cr_2O_3 on the FeCr-based material in the METSAPP cell. The electrocatalytically active phase infiltrated on top of the protective coating is composed of CGO and minor amount of Ni (10 wt.% with respect to CGO), which is currently the state-of-the-art (SoA) infiltrate used.

The titanate based coatings such as doped $SrTiO_3$ and doped TiO_2 were either difficult to form at low temperature or unstable at operating conditions. Metal oxide coatings such as CuO were successfully formed at low temperatures (< 400 ^{o}C). However, during testing, CuO was reduced to Cu and the coating was disintegrated into discrete particles in the fuel electrode environment. This coating disintegration resulted in an inefficient protection of FeCr surfaces.

The chromites and spinels coatings were found to be the most promising, although insufficient. The major challenge with these materials was to obtain a continuous and uniform coating on the FeCr surfaces. It was demonstrated that the coating reaches into the anode layer, and thus provides a protection of the AFL backbone (see Figure 3 right). The obtained coating quality was strongly dependent on the FeCr surface quality (impurity content, see Figure 3 Left and Center), as well as the coating precursor solution wettability. The coatings adherence and uniformity requires further optimization to completely realize their potential in improving the oxidation resistance of metal surfaces.

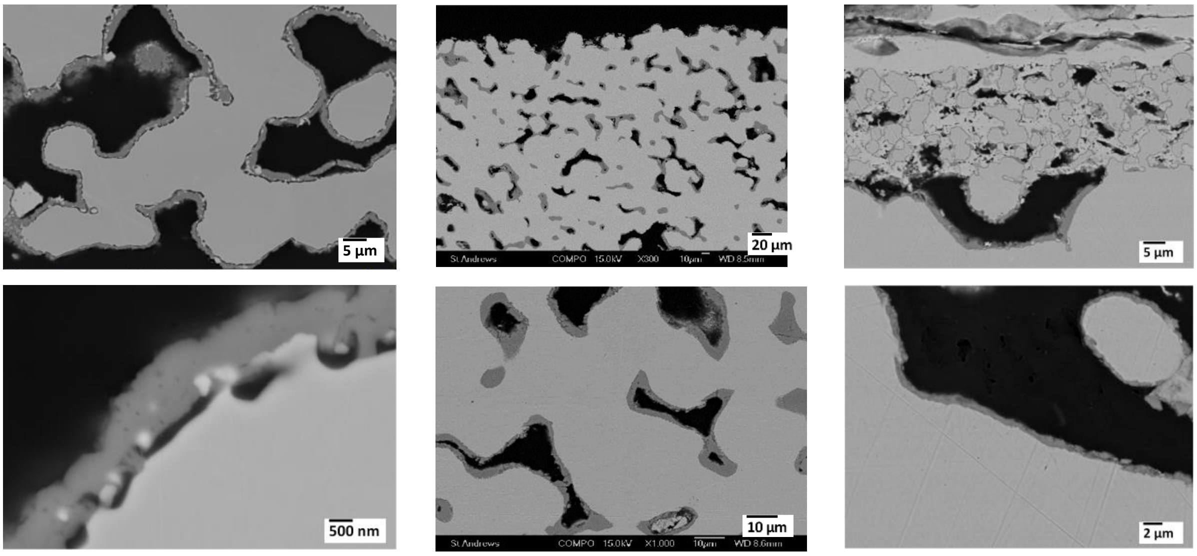


Figure 3: Impact of FeCr surface quality on the coating uniformity: Left) FeCr surface contaminated by silicon (dark region between the coating and metal); Center) clean metal support. Demonstration of material infiltration into the AFL Right) SEM of AFL backbone infiltrated.

Development of alternative anode designs

In this third approach, new materials were investigated. Doped $SrTiO_3$ is an electronically conducting ceramic material that should be stable under sintering at highly reducing conditions and high temperatures, possess good electronic conductivity and be compatible with other cell components. Among the doped $SrTiO_3$ materials, DTU focused on the Nb-doped $SrTiO_3$ (STN) materials and USTAN focused on the (La,Sr)(Ti,Fe,Ni)O_3 (LSFNT) materials. First, specific results on each type of material regarding material development and integration are presented, followed by the results obtained on oxidation resistance and electrochemical properties when using these materials in the AFL backbone.

Development of STN based anode backbone

By replacing the YSZ phase by STN, the oxidation resistance was significantly improved (Figure 5 b) and the electrochemical performance was encouraging (see “Electrochemical properties improvement using doped $SrTiO_3$ based anodes”, page 13), though not reproducible due to the cell quality inconsistency. Variations in cell quality were caused by the sintering mismatch of the different half cell components resulting in poor adhesion with electrolyte and leaky electrolyte layer. Also, loss of Cr was observed from FeCr particles and it appeared that the Cr was migrating towards electrolyte through STN, allowing for the formation of Cr-rich oxides in the anode and electrolyte pores.

Development of LSFNT based anode backbone

LSFNT based anode backbone showed the most promising characteristics. The special characteristic of these materials, exsolution of the nanoparticles ((Figure 4 A), compatibility between LSFNT and FeCr ((Figure 4 B), compatibility between LSFNT and YSZ ((Figure 4C) resulted in excellent adhesion with other cell components and probably also enhanced their electrochemical performance. In addition, these materials possess good electrical transport ((Figure 4 D) and redox stability ((Figure 4 E) and favourable sintering behaviour to be matched with other cell materials (Figure 4 F), making their integration into the MS-SOFCs successful.

Different anode backbone designs were formulated using this material and their integration behaviour was investigated to further develop the cells with novel anode backbones. These anode backbone designs consist of LSFNT, LSFNT-FeCr, LSFNT-ScYSZ and LSFNT-FeCr-ScYSZ. The latest showed the most promising microstructure with significantly improved adhesion with electrolyte and metal support. The addition of small amount of ScYSZ significantly improved the adhesion between the anode backbone and the electrolyte and the FeCr addition ensured adhesion with the metal support. As shown in “Oxidation resistance improvement using doped $SrTiO_3$ based anodes”, page 12, oxidation resistance was significantly improved, and the preliminary investigation did not show the issue of Cr diffusion from the FeCr particles to the electrolyte through LSFNT, as when using STN backbone. Electrochemical testing showed significant improvement in the stability with nice performance (see details in “Electrochemical properties improvement using doped $SrTiO_3$ based anodes”), advancing the cell development towards project objective, i.e., development of robust MS-SOFCs.

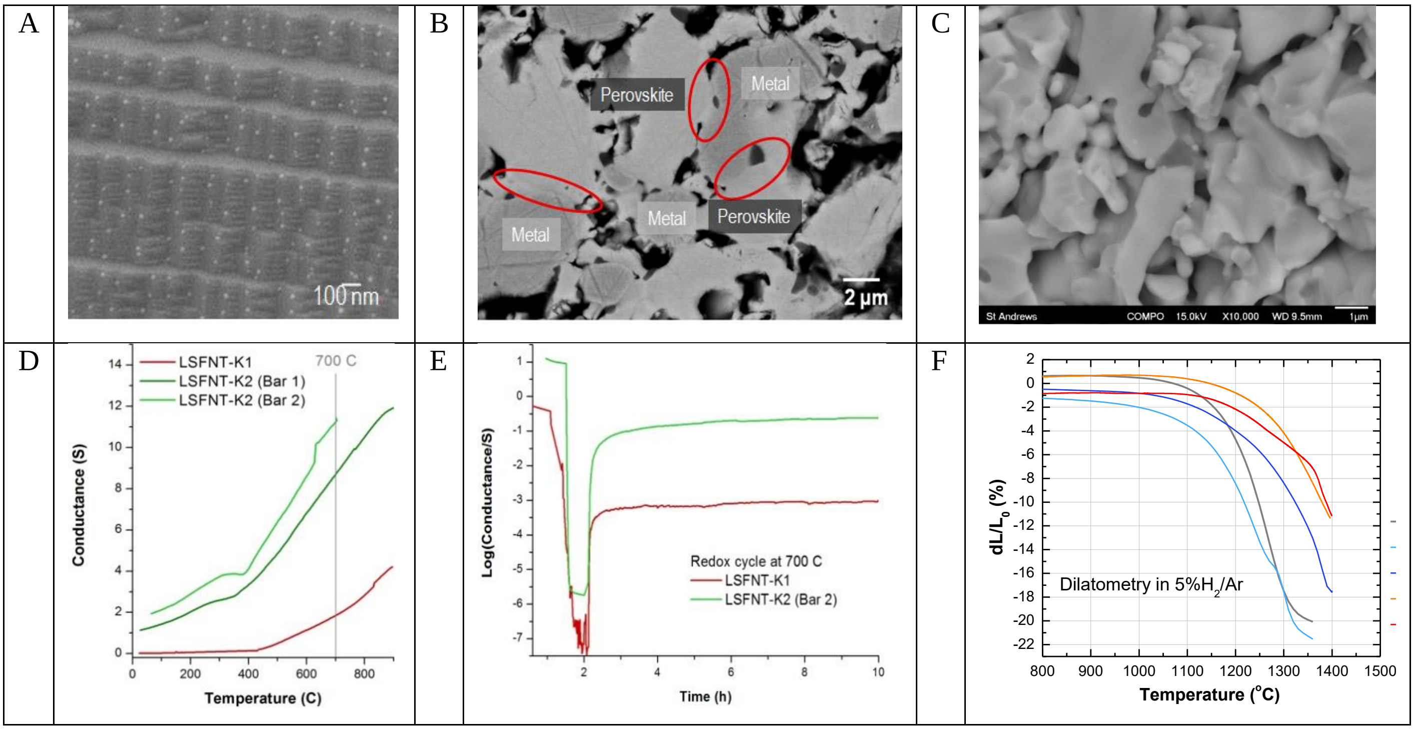


Figure 4: Properties and microstructure of selected LSFNT materials. (a) Metal particles exsolved on the perovskite surface. (b) Interface between perovskite and metal after sintering highlighted in red. (c) Typical electrode microstructure-fracture. (d) Conductivity vs temperature for different samples. (e) Conductivity on redox. (f) Dilatometry in reducing conditions showing the sintering profile of various samples: grey – YSZ, blue – LSFNT (with various particle size), orange/red – other LSFNT materials with lower A-site deficiency.

Oxidation resistance improvement using doped $SrTiO_3$ based anodes

The oxidation behaviour of the newly developed anode backbone made of FeCr-STN and FeCr-LSFNT was compared to the reference anode backbone based on FeCr-YSZ (Figure 5). The ceramic phase (STN/LSFNT) appears to cover almost all FeCr particles. Therefore, it seems to block the inward diffusion of oxygen ions (if it covers the FeCr surface) and prevent the formation of Cr_2O_3 and further oxidation. The oxidation resistance is significantly improved using doped $SrTiO_3$ based anodes instead of YSZ.

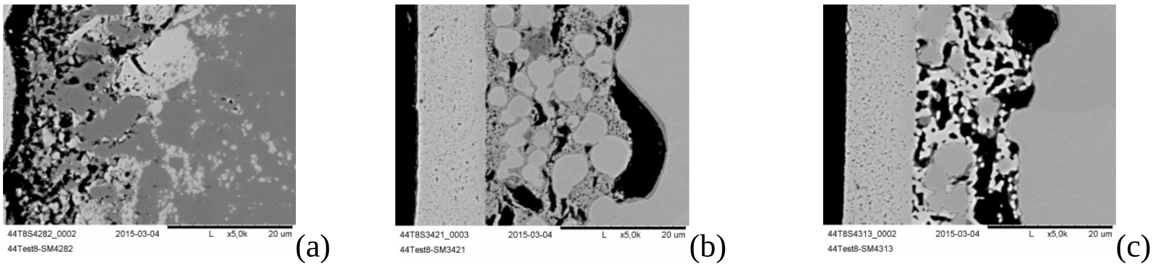


Figure 5: SEM micrographs of the different anode designs after oxidation testing at 650ºC for 250 h (a) FeCr-YSZ, (b) FeCr-STN and (c) FeCr-LSFNT.

Electrochemical properties improvement using doped $SrTiO_3$ based anodes

To supplement the development of robust anode designs, the newly developed anode designs FeCr-STN and FeCr-LSFNT were tested and compared to the initial anode design FeCr-YSZ for their short-term and long-term electrochemical performance. FeCr-STN based anodes showed promising performance and especially stability [1]. However, the reproducibility was challenging due to the variation in cell quality. In Figure 6, the impedance spectra of the best performing cells with the new anode backbones developed (FeCr-STN and FeCr-LSFNT) are compared to the initial best performing cell FeCr-YSZ, all infiltrated with Ni:GDC electrocatalyst.

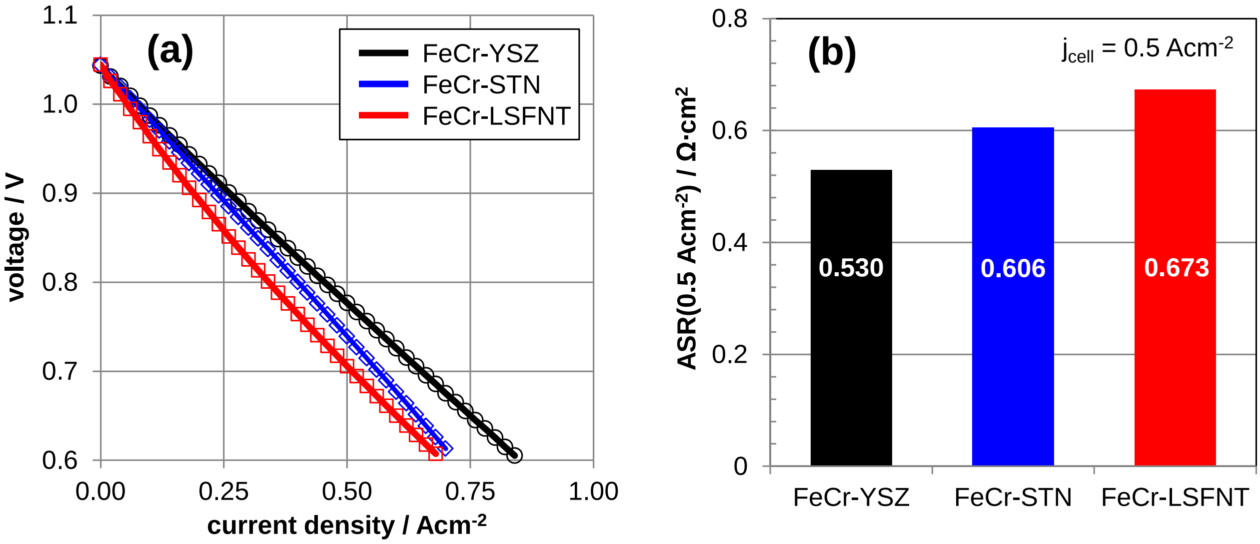


Figure 6: (a) Comparison of C/V-measurements recorded on METSAPP MS-SOFCs with different anode design and (b) $ASR_{total}(0.5\ Acm^{-2})$. Operating conditions: T = 650 °C, 20% humidified H_2 as fuel and air as oxidant. Gas flow rates for anode/cathode were set at 250 sccm.

In order to understand the individual loss mechanisms contributing to the internal resistance of the METSAPP cell generations, a detailed electrochemical analysis by means of electrochemical impedance spectroscopy (EIS) was carried out by recording series of impedance spectra at stepwise varied operating conditions (anode/cathode gas composition, operating temperature, current load). The recorded spectra were subsequently analyzed by the distribution of relaxation times (DRT), allowing a deconvolution of individual electrochemical processes in order to analyze their dependencies on operating conditions, if the change of polarization resistance is < 5% for the measurement period. This required cell stability was only observed for the last cell generation with

FeCr-LSFNT anode design. Cells with FeCr-YSZ anodes showed a strong degradation rate, even at low water vapor contents in the fuel gas, whereas cells with FeCr-STN anodes showed improved stability, but the measured results were not reproducible, probably due inhomogeneous distributed catalyst during fabrication.

Therefore, only a qualitative comparison between the different cell generations is presented in Figure 6a-b by using EIS/DRTs , as quantification via CLNS-fitting would not deliver meaningful results. However, the cell with FeCr-YSZ anode (Fig. 6b, black) shows the lowest serial resistance, while the cell with FeCr-STN anode (Fig. 6b, blue) exhibited the lowest polarization resistance. On the cell with FeCr-LSFNT anode (Fig. 6b, red) the highest serial and polarization resistance was measured, mostly owing to an increased contribution between 10-100 Hz, where the anode electrochemistry shows its highest sensitivity (cf. Figure 7b).

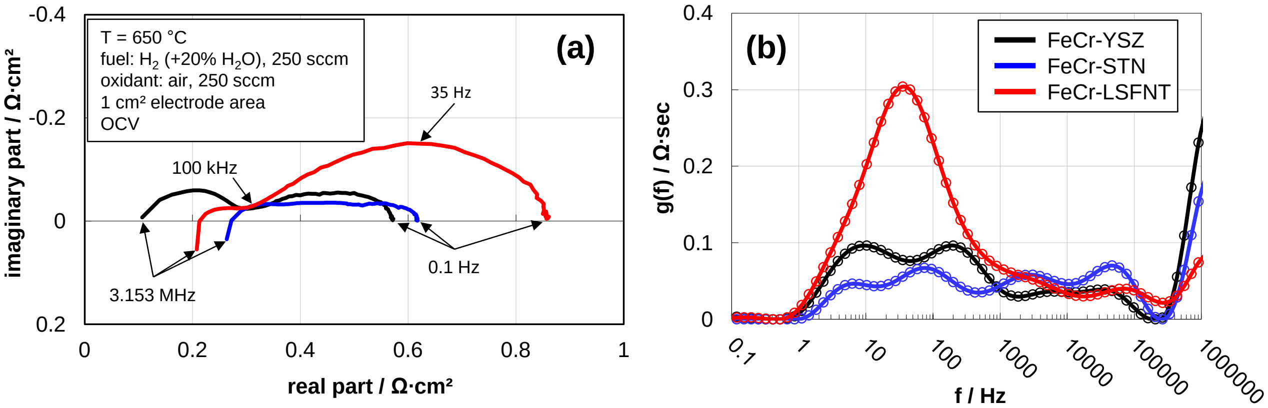


Figure 7: (a) Electrochemical impedance spectra (EIS) recorded on METSAPP MS-SOFCs with different anode design and (b) corresponding DRTs calculated from EIS. Operating conditions: T = 650 °C, 20% humidified H_2 as fuel and air as oxidant. Gas flow rates for anode/cathode were set at 250 sccm

Consequently, the measured current/voltage characteristics displayed in Figure 6a matched the EIS results, where the best performance with the lowest ASR was measured on the cell with FeCr-YSZ anode. In the sum, the difference in serial resistance was higher compared to the difference in polarization resistance between the cells with FeCr-YSZ and FeCr-STN anode, whereas the most stable cell with FeCr-LSFNT anode exibited the highest total resistance (0.67 Ω-cm^2) and consequently lowest performance among the three, which is still nice performance (see Figure 6).

Nevertheless, a great step towards a durable MS-SOFC has been made by developing the FeCr-LSFNT anode and integrating it into the METSAPP cell design. The long term measurements at constant current load of j = 0.25 A/cm² at T = 650 °C performed on corresponding cells under low fuel gas humidity (only leakage) and 20% H_2O in the fuel gas demonstrated great improvement in stability, expected to be due to the higher oxidation resistance demonstrated (see "Oxidation resistance improvement using doped $SrTiO_3$ based anodes", page 12). The results are displayed in Figure 8. Assuming a linear degradation rate, an average performance degradation rate of ~0.5 % / 100 h for the cell operated with H_2+leakage as fuel was calculated and ~1.2 % / 100 h for the cell with H_2+20% H_2O. The improved cell stability allowed the extraction of parameters for the electrochemical modelling, which was a challenge with the MS-SOFCs with FeCr-YSZ anode backbones. Although the FeCr-LSFNT anode designs showed relatively inferior performance, the greater stability paves the way for the development of robust MS-SOFCs. It is also strongly believed that the initial performance can be further improved by a microstructure optimization, an improved control of the infiltration process and understanding of the backbone/electrocatalyst interaction.

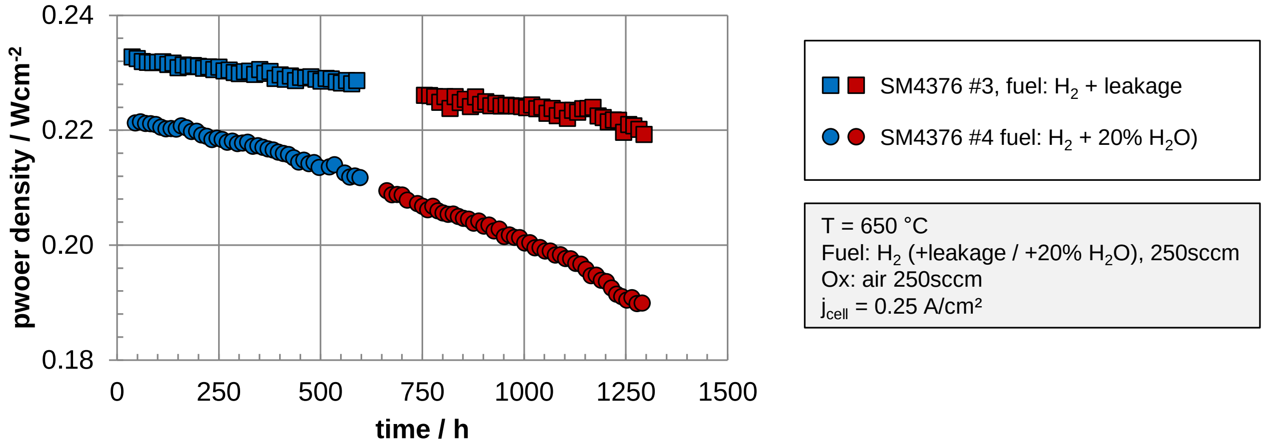


Figure 8: Performance of two FeCr-LSFNT type cells under load for ~1000 hours with different water vapor content in the fuel gas

Loss processes evaluation of FeCr-LSFNT based cells

With the help of an established, physical meaningful equivalent circuit model, the occurring loss processes were evaluated and quantified. Unfortunately, due to insufficient cell stability of FeCr-YSZ and cells, the method could only be applied to FeCr-LSFNT type cells, as the change in polarization resistance during the whole measurement should not exceed 5% in order to maintain meaningful results in the CLSN-fitting process. The determined losses for FeCr-LSFNT type cells are depicted in the Arrhenius-plot in Figure 9 with corresponding activation energies.

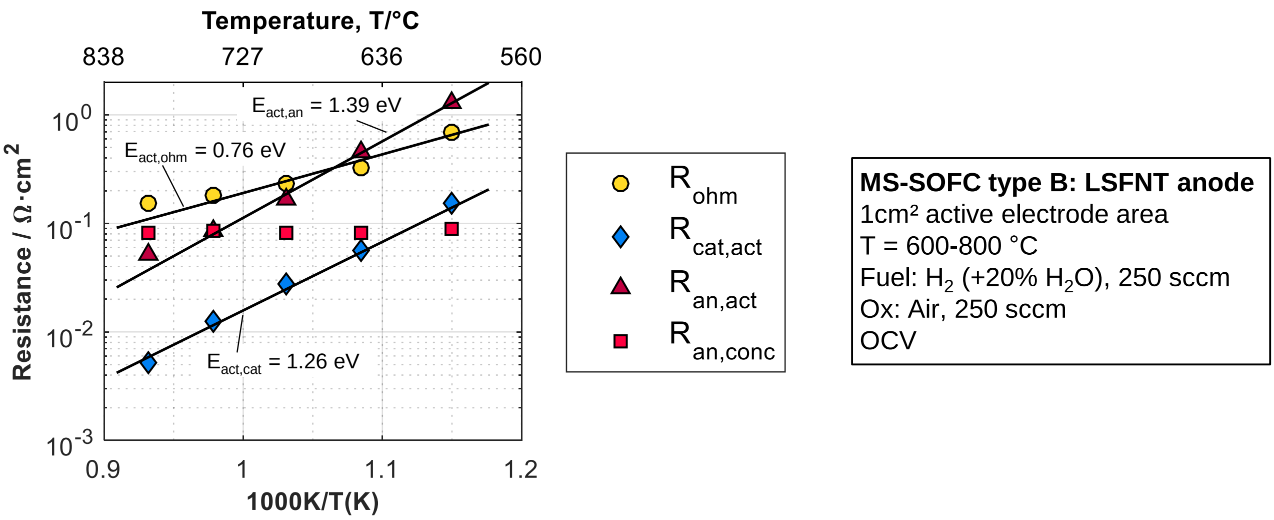
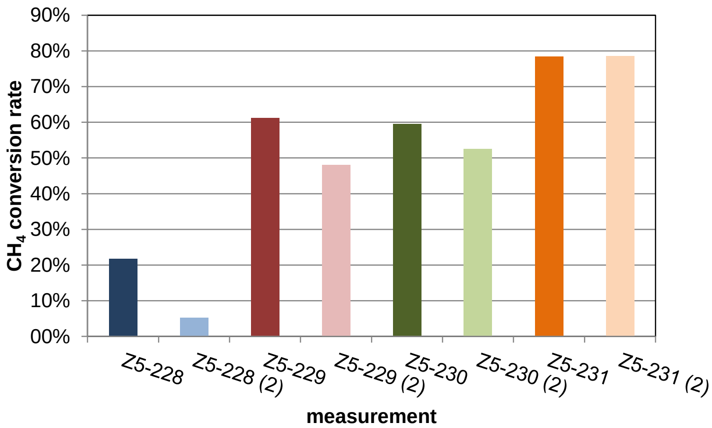


Figure 9: Arrhenius-plot with by CLNS-fitting determined losses of FeCr-LSFNT type cells.

Catalytic properties of MS-SOFCs

The advantage to use not only pure H_2 but also hydrocarbons as fuel via internal steam reforming (SR) and the water-gas shift reaction (WGS) extends the applicability of solid oxide fuel cells towards a market, where fuel flexibility is required. Consequently, the reforming abilities of the METSAPP cell were tested as well by probing and analyzing the local gas composition along the fuel gas channel. A special test rig designed for this purpose was employed, where the cell was operated at various elevated operating temperatures and fed with specified hydrocarbon gas compositions. The raw anode metal backbone showed only very low SR and WGS reforming abilities with a decreased performance few hours of operation. However, by adding an additional catalyst layer of Ni-GDC paste on top of the metal backbone, SR kinetics can be increased by a factor 3, depending on the layer thickness, thus increasing the fuel efficiency equally. However, as the WGS reforming performance is not affected, more research is required to unravel the underlying mechanism in detail. The results for SR conversion rate of 20% pre-reformed CH_4 are shown in Figure 10.



T = 650 °C
S/C = 3
CH_4: 18.18 %
H_2O: 63.64 %
CO: 4.55 %
H_2: 13.64 %
20% pre-reformed

	description
Z5-228	METSAPP
Z5-229	METSAPP + Ni/CGO 125 mg
Z5-230	8YSZ + Ni/CGO 119 mg
Z5-231	METSAPP + Ni/CGO 291 mg

Figure 10 Summary of internal steam reforming (SR) gas conversion experiments.

Impact of electrocatlyst material

Excellent initial performance was obtained with FeCr-YSZ anode backbone, best among the reported performance for MS-SOFCs worldwide, when infiltrated with Ru:GDC electrocatalyst instead of Ni:GDC (Figure 11). The stability of cells infiltrated with Ru:GDC was also found relatively superior. However, this seems to be strongly dependent on the anode backbone microstructure and uniformity of the electrocatalyst coating. Thus, further understanding and especially control of the infiltrate structure in the porous anode backbones is a remaining development task to improve stability of cells infiltrated with Ni:GDC, material industrially more relevant.

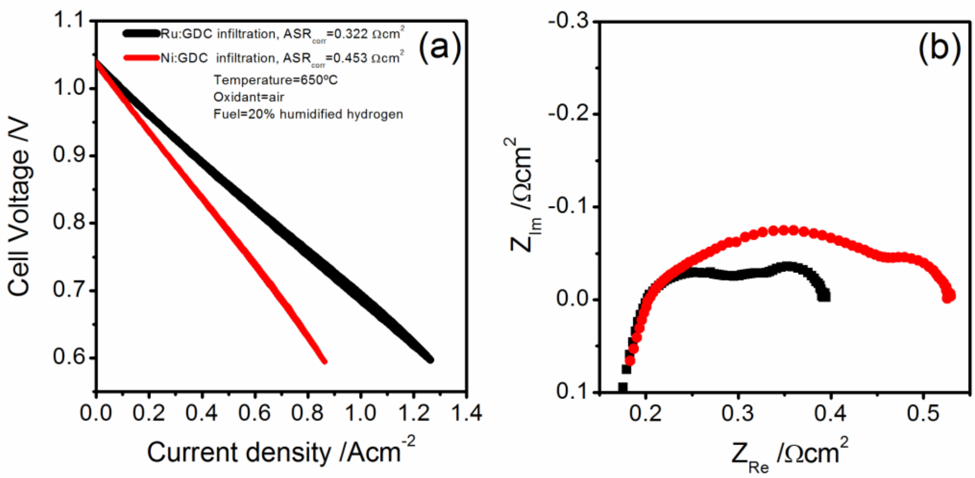


Figure 11: (a) Polarization curves and (b) Electrochemical impedance spectra of the Ru:GDC and the Ni:GDC infiltrated cells.

Selection and integration of high performance cathode

The current cell design requires that the cathode is sintered in-situ during the initial start-up used for electrochemical testing. The in-situ "sintering" temperature is significantly lower than the temperature usually used for purely ceramic based intermediate and high temperature SOFCs. Therefore, the effect of in-situ sintering temperature and time on the electronic conductivity, impedance and performance of two different cathodes ($(La_{0.6}Sr_{0.4})_{0.99}CoO_3$ (LSC) and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)) were investigated and compared in the temperature range of 650 – 950 ºC. In contrast to LSCF, the LSC-based cathodes showed excellent sintering capabilities, electronic conductivity and performance. Their polarization resistance (R_p) was 0.05 Ωcm^2, which to our knowledge is the best performance reported in the literature for a low temperature 800ºC in-situ sintered cathodes. The drawback of LSC based cathodes is a relatively high thermal expansion coefficient compared to other cell components. Consequently, the challenge was to make them mechanically robust towards thermal cycling. Efforts were made to address this issue by decreasing the cathode and current collecting layer (CCL) thicknesses down to a thin ~15 µm LSC layer, acting both as a cathode and CCL. Testing of such thin LSC cathodes on single cells (16 cm^2 active area) showed promising and reproducible results with no observable delamination. The same cathode layer was integrated on to the larger cells (12 cm x 12 cm cells for TOFC stacks and 15.3 cm x 8.3 cm cells for EK stacks). The conditioning and initial performance testing of such stacks did not show any damage of cathode. Thus, high performing LSC cathodes were successfully integrated in the METSAPP cell.

Mechanical properties characterisation

In order to understand the mechanical behaviour of the cells, cell components and stacks, particularly at elevated temperatures, the elastic and creep properties needs to be measured. Thus, mechanical testing payed particular attention to elastic response of the metal support and electrolyte as a function of temperature, creep behaviour of metal supports and interaction with oxidation and 3D simulation of the creep in metal supports. The elastic modulus at room temperature before the thermal treatment was measured to be 60.0±0.3 GPa. The Young's modulus "E" decreased more or less linearly with an increase in the temperature down to 32.5±0.6 GPa at 700 °C. Thermal treatments slightly increased the E due to the oxide scale formation. The ScYSZ electrolyte elastic moduli was found to have a significant peak around 450 °C, where the stiffness is believed to be lowered due to atomistic reorganizations. This will influence the stress distribution amongst the layers over a temperature cycle, but as it occurs mostly within the purely elastic temperature range, little impact is expected on stress distribution among cell components. A stack model is however needed to fully evaluate the impact.

For the stack metallic components, i.e. the interconnect (IC) steel and the metallic support (MS), the creep properties were measured and parameters for the constitutive creep laws for both primary and secondary creep were extracted from the measurements. The secondary creep is important for long-term steady operation, where as the primary is highly important for load cycling. In the non-oxidized state, both IC and MS samples showed same dependency with stress. In the oxidized state the material behaviour became complex. The oxide scale formed is a less creeping ceramic coating and thus minimizes the creep rate. However, if higher stresses are applied, the oxide scale peels off, and the creep rate increases compared to the non-oxidized material. This mechanism also increases the oxidation rate, as the protection from the oxide scale is lost and thus results in further oxidation. Infiltration minimizes the oxidation and thus also the amount of corrosive scale. Therefore, the infiltrated metal support creeps faster. Aging treatment of the infiltrated samples, found to be decreasing the creep rate.

The measured mechanical properties provide the insight into the mechanical behaviour of the individual cell components, however, the combined effect can only be evaluated in the stacks and thus forms the future scope of the work

The development of industrially relevant manufacturing processes and cell manufacturing

Making the multilayered structures using tape casting process can be more cost-efficient if the layers can be cast simultaneously, particularly for mass production. During the course of the project, a co-casting process, where all the layers were casted simultaneously, except cathode and barrier layer, was developed with different variations (wet-on-dry, semi wet-on-wet and wet-on wet with wet-on-dry and semi wet-on-wet being most successful). This co-casting and co-sintering of different layers in the cells makes the cell fabrication process significantly cost-efficient and economic. In addition, the process was made environmentally friendly thorough the replacement of toxic organic additives, such as MEKET, Phthalates with less toxic alternatives. During the course of the project, quality requirement of the raw materials was investigated systematically and the specifications for different raw materials were determined to enhance the tolerance and robustness of the cell fabrication process.

More than 500 cells and components of different sizes ranging from 25 cm^2 to more than 300 cm^2 were produced for various activities. This production demonstration with reasonably high cell production yield as well as the flexibility with cell geometry indicate that the METSAPP cell fabrication technology is up-scalable and industrially relevant. Although significantly improved, the infiltration process remains to be further developed and optimised for improving the reproducibility.

Development of robust stack components

One cell in a SOFC provides less than 1V. Thus many cells are connected to a fuel cell stack. Between the single cells, the interconnects are placed. Besides connecting the single cells into a stack, the interconnect separates the fuel compartment from one cell from the air compartment of the neighbouring cell. Thus it has to withstand both atmospheres and be electrically conductive. The material of choice are ferritic stainless steels that provide a good compromise between cost and durability.

The main technological challenge for steel interconnects are high temperature oxidation phenomena. In particular a) oxidation on the air side b) evaporation of Cr(VI) species on the air side, which deteriorates cell performance and depletes the steel in Cr c) oxidation on the fuel side d) increased electrical resistance due to the formation of poorly conducting oxide scales. All these issues have been addressed in METSAPP in particular by the use of conductive coatings. With the selection of the right coating, the surface properties of the material can be altered in a favourable manner. However, the use of a coating adds an additional manufacturing step and as a consequence extra cost. In order to minimize coating cost, Sandvik Materials Technology has developed a high volume coating process that allows to continuously coat entire steel coils. However, this high volume production process route relies on the coatings capability to sustain severe deformation during stamping into the final shape without losing its protective properties such as good adhesion, oxidation resistance, conductive oxide scale and low chromium volatility. This has been systematically studied within METSAPP on a fundamental level.

The main challenge on the air side is to inhibit the volatile Cr species formation. One of the proposed coatings is Co, which results in the formation of a Co-Mn oxide cap layer on the steel surface that reduces Cr evaporation effectively. Additionally, the oxide scale growth due to the high exposure temperature is a problem. In order to minimize this, the use of a Ce and Co coating has been investigated, where the Ce coating layer is closest to the steel surface. Figure 12 depicts two TEM micrographs of the oxide scales formed after 3,000 h exposure at 850 °C. Even though the Ce layer is only 10 nm thick, it significantly reduces the oxide scale thickness, while Cr evaporation characteristics are the same as for Co coated steel. Furthermore, it could be observed that the area specific resistance of the oxide scale is significantly lower for Ce+Co coated samples compared to Co coated samples.

In a further development step, a new generation of coatings has been developed with even improved high temperature oxidation performance. This laboratory coating consists of four layers of including Ce and Co, but also additional Cr, that is Ce+Cr+Ce+Co. This coating has not been studied in as much detail as the Ce+Co coating, however, all tests carried out show a similar performance with a superior oxidation resistance. Figure 13 shows the oxide scale after 20,000 h of oxidation at 800 °C. It is apparent that the oxide scale of the Ce+Cr+Ce+Co coated material is much thinner than the Ce+Co coated samples. This is expected to result in increased interconnect lifetime and reduced oxide scale, resulting in enhanced electric efficiency.

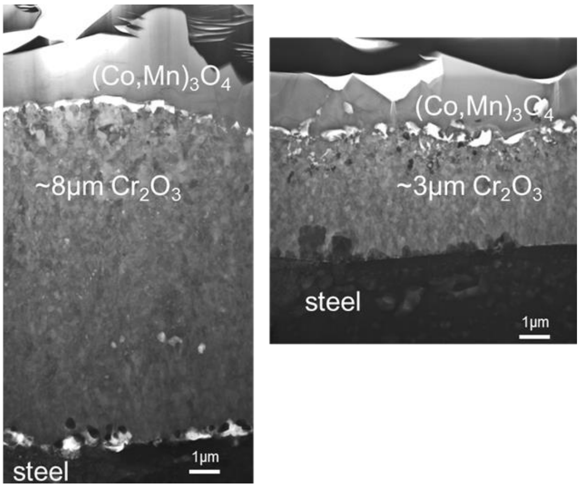


Figure 12: *TEM micrographs of the oxide scales formed after 3,000h exposure at 850°C. 800 nm Co coating (left) 10 nm Ce coating + 800 nm Co (right). Even though the Ce layer is only 10 nm thick it reduces the Cr_2O_3 oxide scale by almost two thirds.*

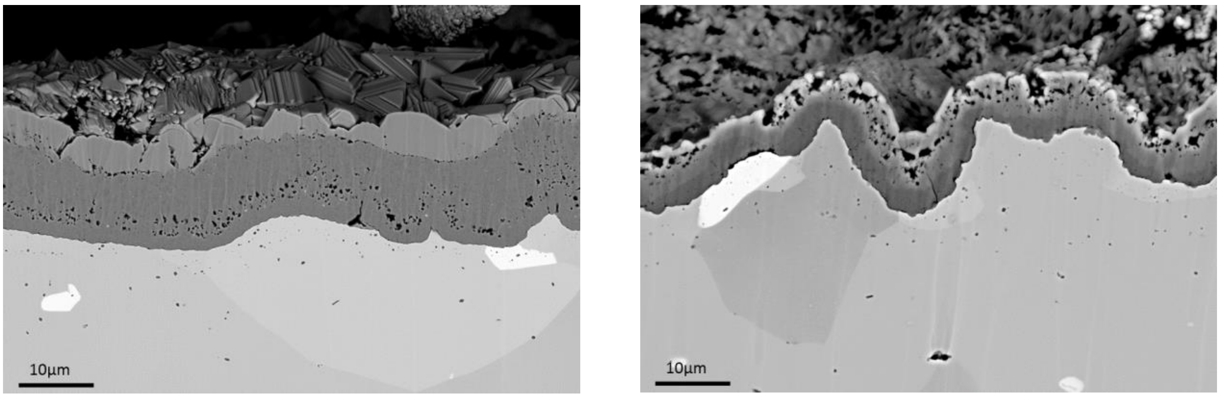


Figure 13: SEM micrograph of the Ce+Co-coated sample (left) and the Ce+Cr+Ce+Co-coated after 20,160 hours of cyclic oxidation at 800°C in ambient air.

In order to predict the material lifetime for durations >40,000 h, a lifetime model has been developed. This model includes the Cr evaporation effect and with the data obtained in the project, calculations can be performed for different temperatures, times, material thicknesses and other critical parameters. Figure 14 shows the calculated Cr depletion profiles as a function of time for different coatings. It can be seen that with the application of a Ce+Co coating, a remarkable increase in calculated lifetime can be achieved. However, one has to be aware that the model is based on a number of simplifications and assumptions.

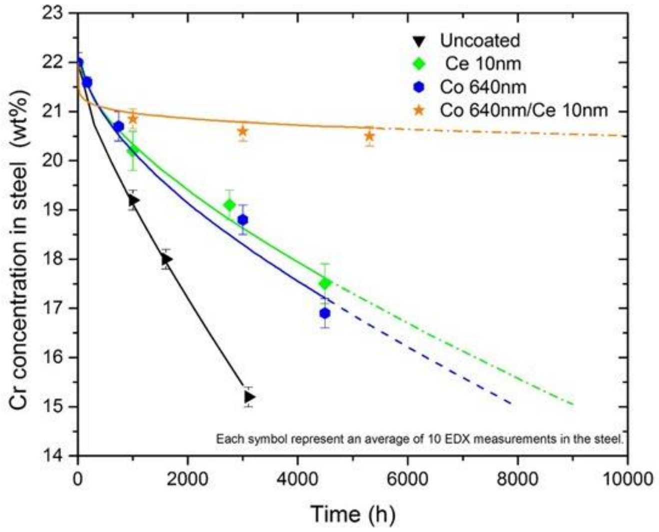


Figure 14: *Cr depletion chart for 0.2 mm thick samples exposed to air on both sides. This lifetime model takes both oxidation and Cr evaporation into account.*

As mentioned above the use of pre-coated material allows for a high volume manufacturing route. However, in the pre-coated steel concept, the steel is coated before stamping into a corrugated shape. The stamping causes significant deformation of the substrate and coating. In the course of the project, this was investigated in detail, both on simplified geometric forms and on real interconnect shapes defined by different stack manufacturers and produced by stamping. Furthermore, different steel substrate combinations have been investigated. Figure 15 is a schematic drawing of which kind of samples have been studied.

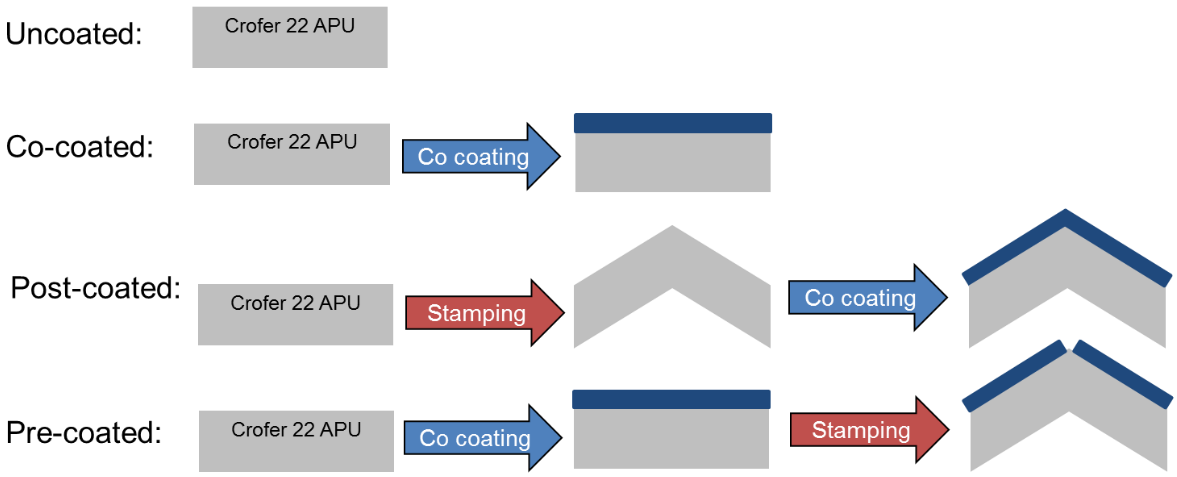


Figure 15: Schematic drawing of the four different types of materials investigated.

Figure 16 shows SEM images of the most severely damaged parts of a real interconnect shape. The Co map shows large areas lacking the protective Co coating after stamping of the pre-coated material. Nevertheless, it was found that the coated and undeformed, post coated and pre-coated material exhibit very similar Cr evaporation characteristics, although the coating has been subject to severe damage.

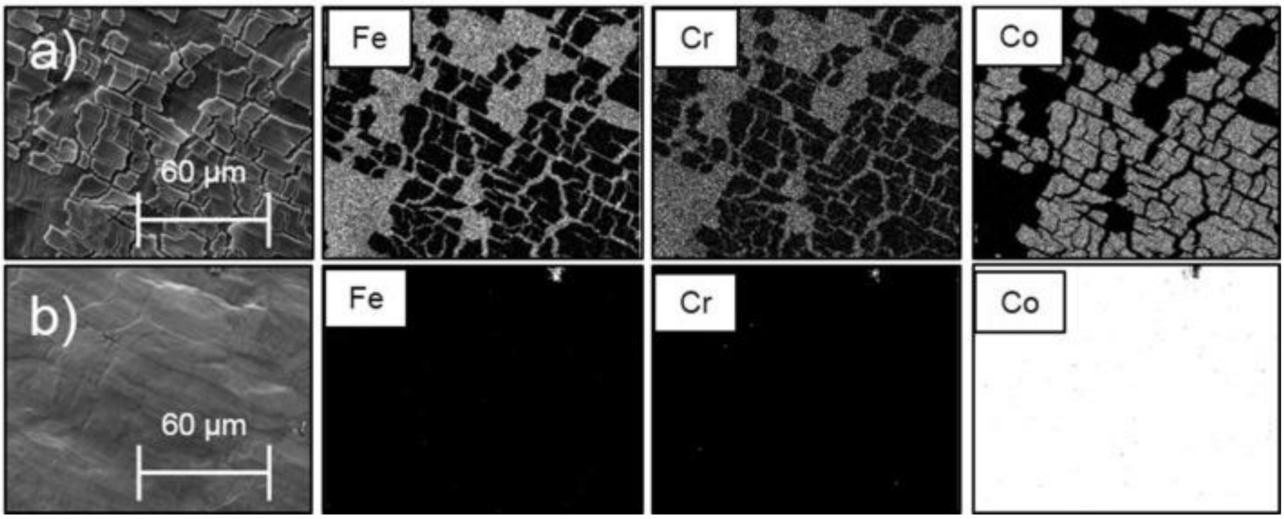


Figure 16: *Top view SEM image and EDX elemental maps before exposure for a) the pre-coated and b) the post-coated material.*

The reason for that is that the Co coating exhibits a self-healing capability. Due to fast surface diffusion at high temperature, a thin surface layer is formed that effectively blocks Cr evaporation. In order to illustrate this effect, another experiment was carried out. A partly Ce+Co coated sample was produced. In the uncoated region, a trench was milled using a focused ion beam (FIB). The trench was at a set distance (13 µm) away from the coated/non-coated border. This trench was then used as a reference point during oxidation trials. The sample was subsequently exposed for 504 hours (three weeks) at 800 °C. Then a second FIB trench was milled at a right angle towards the first trench. This second trench, which was about 26 µm wide, stretched from one of the short ends of the first trench and roughly 13 µm into the coated part of the steel, shown in Figure 17. The second trench therefore showed both the previously uncoated area and the coated part of the sample. Interestingly the oxide formation of the two had much resemblance. In fact, a Co rich oxide cap layer is formed over the entire cross section showing that even larger cracks can be filled by diffusion.

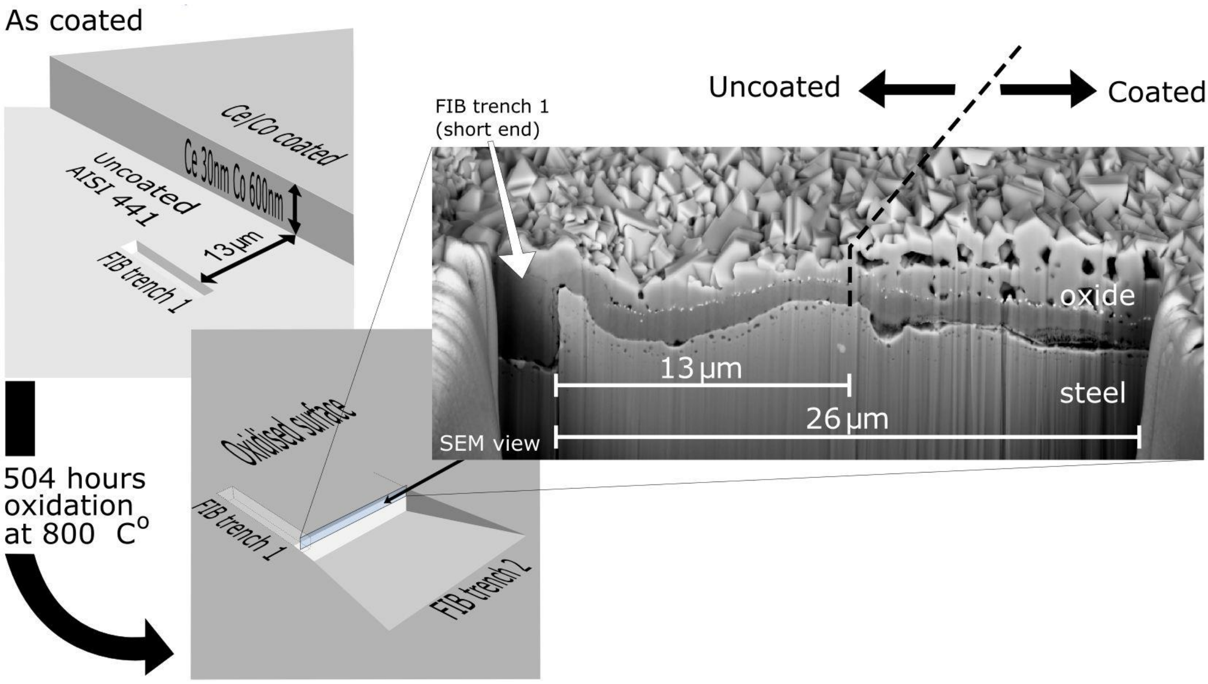


Figure 17: The AISI 441 sample was masked before being coated with 30 nm cerium and 600 nm cobalt, respectively. With the mask removed a sharp border between coated and uncoated surface was created. After oxidation at 800 °C the formed oxide of the uncoated part was examined. Cerium rich particles originating from the coated part were detected in the scale as far as 10 µm away from the coated area.

Development of characterization tools and numerical models

Relevant viable models are highly needed to understand failure mechanisms and to optimize material properties and cell and stack design. This understanding is crucial for the development of the stack in order to prevent them, or in the case of inherent mechanisms be able to set operation limits for the application of the stacks. The effect of various material parameter modifications is relatively more complex for metal supported cell technology compared to the anode-supported technology. The aim was that the models should be able to capture the governing mechanisms. By means of combination of physical models for the different governing failure modes and mathematical models for related random processes, accelerated test procedures (also already partly elaborated in METSOFC) were planned to be validated and updated if necessary.

The results of the modelling work were on the one hand validated models and test procedures for accelerated testing, which are mandatory for serial development due to the required long product life time and high reliability. These procedures will be applied for the investigation and validation of the actual metal-support-cell technology enhancing the chances for commercialization.

Identification on material parameters

The identification on material parameters and failure mode modeling has achieved fundamental results. Various material parameters needed for modeling of these MS-SOFCs. These material parameters have partly been found in the literature and partly measured through the METSOFC and METSAPP projects. It has also been chosen to state the conservation equations for physical phenomena for completeness. The innovative cell design is described in Figure 1.

Cell modelling

The cell modelling in METSAPP was performed to acquire quantitative information about the different loss mechanisms in different generation of the METSAPP cell. Based on this information a meaningful feedback to the cell developer was possible, enabling a targeted development of the individual cell components. Furthermore, a detailed cell model is required for repeat unit and stack modeling.

In order to classify the different MS-SOFC generations developed within the METSAPP project, an existing electrochemical model for MS-SOFCs was adopted, by which a separation and consequently a quantification of occurring loss processes can be realized. Furthermore, a determination of cell inherent material parameters for FEM models can be achieved with this modeling approach.

The physical origin of individual processes contributing to the overall loss in a MS-SOFC has been determined by varying purposefully specified operating parameters (temperature, anode/cathode gas composition), recording EIS each time and by analyzing the peak evolvement in the corresponding DRT series. Based on this procedure, the physical processes listed in Table 1 were found to occur in the METSAPP FeCr-LSFNT based MS-SOFCs and a physically meaningful electrochemical model was designed accordingly. Based upon this, an equivalent circuit is fitted via the complex nonlinear least-squares (CNLS) method. Exemplary, an EIS recorded on a METSAPP FeCr-LSFNT based MS-SOFC with the corresponding CLNS-fit result is shown in Figure 18 on the left and calculated DRTs on the right.

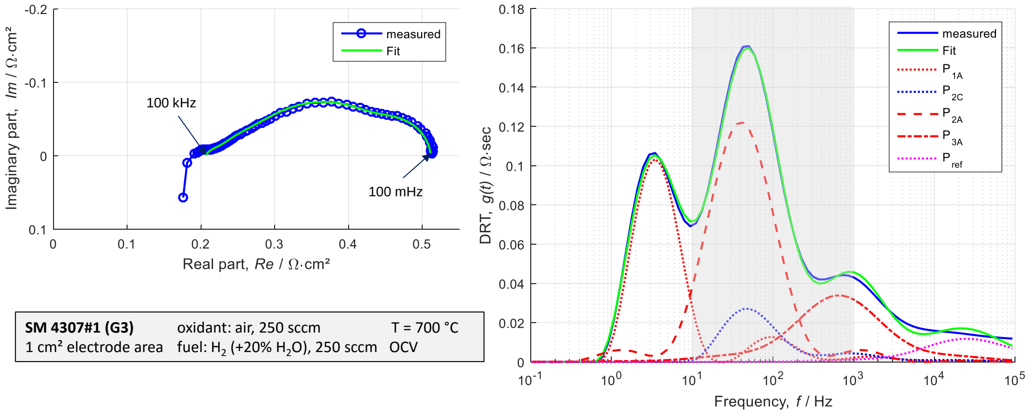


Figure 18: Measured and corresponding CLNS-fit of EIS (left). From measurement and fit results calculated DRTs and single process DRTs (right).

Fit residuals of all evaluated spectra were below 2% deviation, giving the generated results credibility, but the single process DRTs in Figure 18 on the right also reveals a non-negligible drawback. In the mid-frequency range between 10-1000 Hz, a great overlap of both anode and cathode related activation polarization losses ($P_{2/3A}$ and P_{2C}) show the highest sensitivity, thus preventing an unambiguous separation. Hence, an erroneously loss attribution is plausible and the achieved results should be regarded with certain care.

MS-SOFCs from the first project period (FeCr-YSZ based anode) exhibited an insufficient stability as the change of polarization resistance was > 5% after passing the whole measurement protocol, thus preventing a meaningful evaluation of parameter dependencies. In the second project period, MS-SOFCs with a new anode design (FeCr-LSFNT) were available, which demonstrated much improved cell stability, allowing (for FeCr-LSFNT based cells) a complete FEM modeling parameter determination.

Table 1: List of processes known to take place in METSAPP FeCr-LSFNT based cells, together with their characteristic frequencies, the corresponding operating parameter dependencies as well as the equivalent circuit element applied in the CNLS-fitting.

process	f_r, ASR	dependencies	physical origin	Element
P_{1A}	0.5..10 Hz	pH_2O_{an} , T (low)	gas diffusion in the anode support	G-FLWS
P_{2C}	30-60 Hz	$pO_{2,cat}$, T	oxygen surface exchange kinetics and O^{2-}-diffusivity in the bulk of the cathode	Gerischer
P_{2A}	10..80 kHz	pH_2O_{an}, T	(P_{2A}+P_{3A}) gas diffusion coupled with charge transfer reaction and ionic transport within anode	RQ
P_{3A}	0.8..10 kHz	pH_2O_{an}, T		RQ
$P_{hf,1}$	40..100 kHz	T	insulating interlayer at LSCF/zirconia interface	RQ
$P_{hf,2}$	> 100 kHz	T	yet unidentified	not included in model

Repeat unit modeling

In order to pre-evaluate different stack designs, a model framework has been developed based on the FEM. Due to the unavailability of reliable measurement data in the first years of the project, the model development and validation was carried out based on a state-of-the-art anode supported cells. The following physical processes are regarded in the model: (i) electronic/ionic conduction in the porous electrodes, (ii) metallic interconnectors (MIC) and electrolyte (iii) electrochemical charge transfer at the electrode/electrolyte interfaces and (iv) gaseous species transport within the porous electrode microstructures. The model geometry of consideration describes a so-called 2D repeat unit (RPU), covering a two-dimensional cross-section of a single stack level reduced to half of the flowfield contact rip and gas channel. Due to symmetry features, a whole stack level is accounted for and thus computational effort reduced massively.

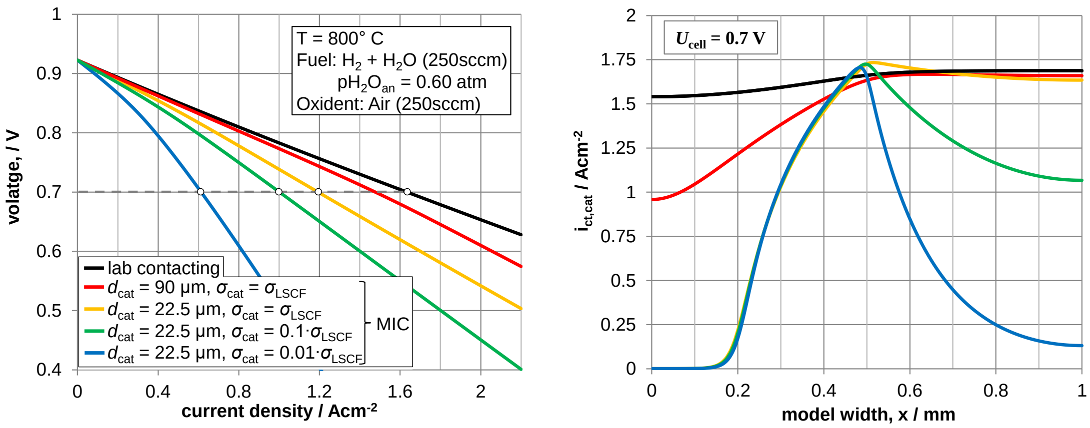


Figure 19: Simulated CV-curves for varied cathode layer thickness d_{cat} and electronic conductivity σ_{cat} (left). Current density distribution at cathode/electrolyte interface, U_{cell} = 0.7 V at T = 800 °C (right).

Based on anode supported cells parameters and a planar co-flow stack design, the performance for varied cathode layer thicknesses and electronic conductivity was simulated. Figure 19 displays predicted current/voltage (C/V) curves (left) and local current density distributions at the cathode/electrolyte interface (right) for an operating voltage of U = 0.7 V. An increasing loss in performance for thin cathode layers and less well electronic in-plane conducting cathode materials is predicted due to limited gas and electron transport properties. Depending on the cathode layer thickness, stack design and operating conditions, the additional losses can grow up to the dominating loss mechanism and deteriorate stack performance tremendously.

In the final stage of the project, required modelling parameters were available for the METSAPP MS-SOFC based on a FeCr-LSFNT anode. The results displayed in Figure 20 demonstrate excellent reproducibility of measured data in the regarded operating range.

The model enables a design matching of cell and stack. Depending on flowfield geometry and desired operating conditions suitable cell parameters as cathode thickness, porosity and electronic conductivity can be calculated. Therefore, such model will be helpful for the cell and stack development in the future.

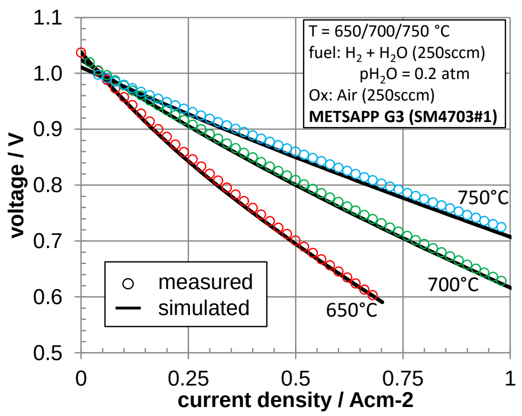


Figure 20: Comparison of on METSAPP FeCr-LSFNT cells measured and by the 2D FEM model predicted C/V curves for three operating temperatures.

Failure mode identification and assessment

One of the objectives of the METSAPP project is the development of stacks suitable for mobile application including mechanical robustness, i.e. suitable reliability. Hence, although durability and reliability failure modes of SOFC components and stacks are - at least - partly well known already, the effect of the superimposition of numerous failure mechanisms on the overall stack reliability is not fully understood today. Meeting reliability targets particularly under consideration of high expectations of end users put a lot of pressure on manufacturers to limit the risk of failure associated to particularly new components. Therefore, in the METSAPP project the AVL Load Matrix was applied, which is a method for defining validation programs in a very systematic fashion. Instead of using „global“ test acceleration factors, acceleration is considered separately for critical components (interconnector plate, sealing etc.) and failure modes, thus giving clue on the impact of certain tests on the component level. A complete process has been set up to identify critical components and failure modes. In this process, Failure mode and effects analysis (FMEA) results are linked with damaging driving conditions and allow the identification of damaging parameters. On this basis, damage models are set up to calculate the damage during certain tests compared to damage in the real duty cycle(s), thus leading to the acceleration factors. Research will be done to develop particular damage models on physical basis for the new materials and components investigated in order to achieve a higher level of accuracy of acceleration factors. The Load Matrix is used to eliminate weak points in the validation program while avoiding unnecessary over-testing.

The analysed stack and cell design correspond to the base case design, as defined by DTU and TOFC. The design has been analysed with regard to a stationary CHP application, with reformed natural gas as primary fuel. However, during the analysis, also problems in mobile applications have been kept in mind and added to the failure mode list, when not too remote from the base application.

In total, 88 possible failure modes for the whole stack have been identified. The result shows, that the majority of the possible failure modes is not relevant for the base case design. 34 failure modes need to be regarded in more detail and of those 17 are relevant for the validation.

For these failure modes, 10 main failure mechanisms have been identified, which need to be covered by the failure modelling.

Development of accelerated test procedures

The aim was to transfer the 10 identified failure mechanisms into an effective long term test program. Within the METSAPP project the total testing time for this purpose is limited to 18 000 hours in total. The overall goal was to generate a test program, which makes the best possible use of this time-frame and to enable a quantitative interpretation of the results. As reference application for the METSAPP stack, a stationary CHP-unit with pre-reformed natural gas fuel has been determined. A corresponding demonstration-system is available at AVL. To generate a representative duty cycle, data from this system has been combined with the long-term operating strategy by AVL and TOFC. In order to analyze the effectiveness of a long-term test program, first it has to be clarified for how long the stacks have to endure operation in the reference duty cycle. Thereby, different values for different requirements have been defined.

- 10 000 hours with 99.7% demonstrable reliability
- 20 000 hours with 98.7% demonstrable reliability
- 30 000 hours with 97.1% demonstrable reliability.

Test definition

In order to accelerate the 10 selected failure modes, two stack tests have been defined:

STK_SST_1 is an alternate load test, designed for the acceleration of most of the failure modes and STK_SST_2 is a constant load test designed for the acceleration of two failure modes.

For both tests the acceleration factors have been calculated with respect to the reference duty cycle.

In the final step, the test program was balanced. The aim of this process was to get an even coverage of failure modes and to maximise the demonstrable reliability for each failure mode. It has also been analysed how the test program would need to be balanced in order to reach all demonstrable reliability targets. It showed that one run of STK_SST_1 for 15 000 hours and one run of STK_SST_2 for 19 500 hours would be necessary.

Failure mode model development

The modelling work carried out aims at gaining a more detailed understanding of the processes taking place in MS-SOFCs and stacks. The developed models are validated as far as possible with data available and serve as a source of suggestions for improvement in cell- and stack-development.

The main focus was shifted from the development of a micro-scale SOFC model of the anode, to a oxidation model for the metal-support and AFL and its effects on the diffusion processes. oxidation was identified as one major failure mode. At the operation temperatures (650°C-750°C) and the presence of water vapour the metallic support, which consists of a sintered Fe/Cr powder, will corrode. The oxide growth will decrease the pore volume and the mass transport from the gas-channel to the AFL, where the electro-chemical reactions take place, will be impeded. In order to assess this degradation, an oxidation model is developed and implemented, which describes the growth of the oxide and the change of the pore volume, which in turn influences the diffusion in the microstructure. The species concentration is computed and homogenised material transport parameters are evaluated.

The effects of oxidation on the metal-support were analysed by implementing a mathematical model, which describes the growth of the oxide scale as a function of time (Figure 21).

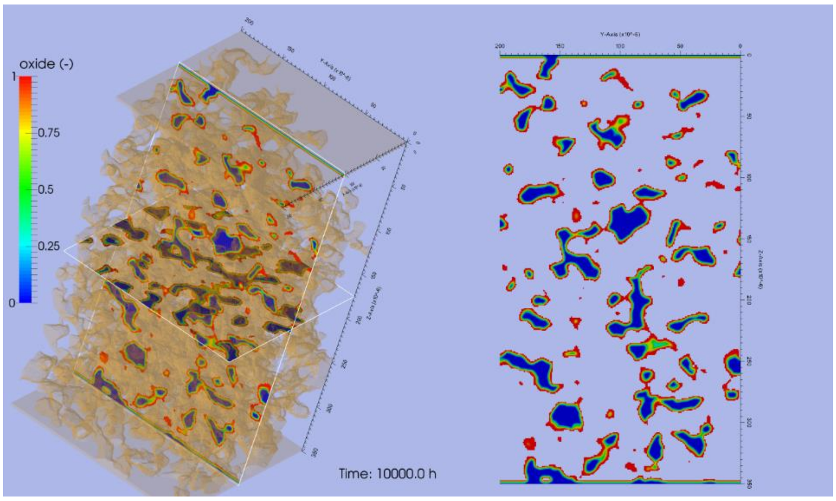


Figure 21: 3D regenerated metallic support microstructure with oxidation layer. The right-hand picture shows one slice through the geometry with corroded pores (red indicating fully corroded areas, while blue regions correspond to open pore space).

The parabolic rate law is widely used, to describe scale growth and is applied in this case because the underlying oxidation mechanisms are not as interesting as their effects on the microstructure. In a second step the oxidation of the metal particles in the anode functional layer were analysed. The program development is finished and gives an understanding of how microstructural parameters such as porosity or tortuosity change over time due to oxidation. The novel oxidation model is also capable of determining the evolution of the metallic support microstructure, and its influence on the mass-transport and the equivalent ASR caused by diffusion.

The oxidation and mass-transport models are not limited to the metallic support, but can also be applied to the AFL, where only the metal-particles are corroding. The only requirement is that the measurement quality is good enough and a difference between metal- and ceramic particles can be discerned. Furthermore, an analytical approach was elaborated, which allows estimating the impact of oxidation without the extensive simulation work, as a quick test to assess the applicability of the microstructure. The validated model was used in the METSAPP project to define accelerated test procedures for each particular failure mode.

Performance monitoring via THDA device

The goal of this task is to assist the development process of MS-SOFC stacks, as the use of THDA device was successfully demonstrated in the field of PEM fuel cells. This was accomplished for the first time on SOFCs in this project, using anode supported SOFC stacks with great success (Figure 22). Two tests were performed to successfully validate the method.

Unfortunately, this could not be tested on MS-SOFC stacks due to the lack of available stacks.

With those promising results on anode supported SOFC stacks, it was attempted to perform measurements with the THDA device at the cell level. However, this was not possible due to thermal stresses and leakages in the cell housing single cell tests. This could be the base of further development, with a new cell housing designed, or purchased.

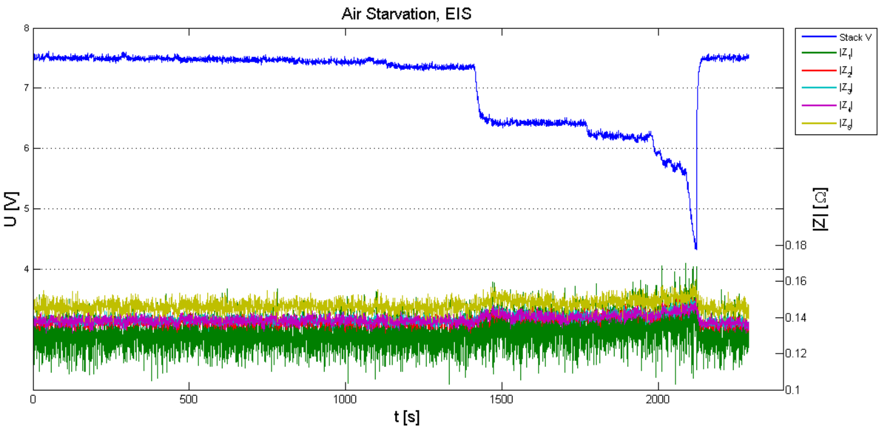


Figure 22   Air starvation, results of THDA diagnostics in EIS mode

Development of robust stack designs and building of stacks

The stack development started at the TOFC design and was taken over by EK, after TOFC closure.

Stack development on TOFC design

The focus of the stack-related work at TOFC was on the development of improved sealing technology and the implementation of a new stack design for MS-SOFCs. Laser welding was verified on multiple stacks, and other new design changes were tested on a component level.

TOFC showed successful integration of metal-supported cells having high power density at lower temperatures and operating for a few hundred hours. However, successful stack operation could not be guaranteed for every stack, because of failure modes that are initiated during the very first stack treatment at elevated temperature. Therefore, in addition to project goals of high performance and larger stack sizes, the principle objective of improving stack treatment without damage was brought into focus. During the project, TOFC made changes in stack sealing strategy, geometrical and material designs, as well as procedures for high temperature treatment.

Computer simulations

Computer simulations advanced in several regards during the project. The knowledge was used e.g., to build a multiscale model of MS-SOFC stacks at TOFC. Specialized FEM and other mechanical simulations have been investigated in order to understand the creep behavior of the stack interconnects. The results yielded important information about the sensitivity of cell mechanics to creep phenomena at different loads and temperatures. Preliminary conclusions / findings from this work:

- Modelling of metal support creep based on Norton Power law constitutive formulation seem untrustworthy – improved equations are needed.
- More complex flow rule formulations should be evaluated, which take into account different dislocation and diffusion mechanisms in different temperature regimes.
- Effect of coatings and impregnations are not sufficiently understood in relation to composite creep behaviour description

In addition to these mechanical studies, tools have been developed for design optimization. Most notable is a flow-homogenization tool (see Figure 23), which is a universally applicable tool with the intention to be used to optimize flow patterns. This was especially important as new interconnect geometries were to be considered, since new geometries can contain complex patterns—and yet require fast feedback concerning stack operation in order to apply appropriate design tweaks.

AVL continued the development of AVL FIRE ® v2014, which contains a comprehensive 3D electrochemical model for the simulation of solid oxide fuel cells. The model is applicable to single cells, stacks, steady and transient analyses with pure hydrogen or hydrocarbon as fuel. In future, the model shall be extended in order to account for degradation mechanisms (e.g. carbon formation) and in order to enable stress and deformation analysis.

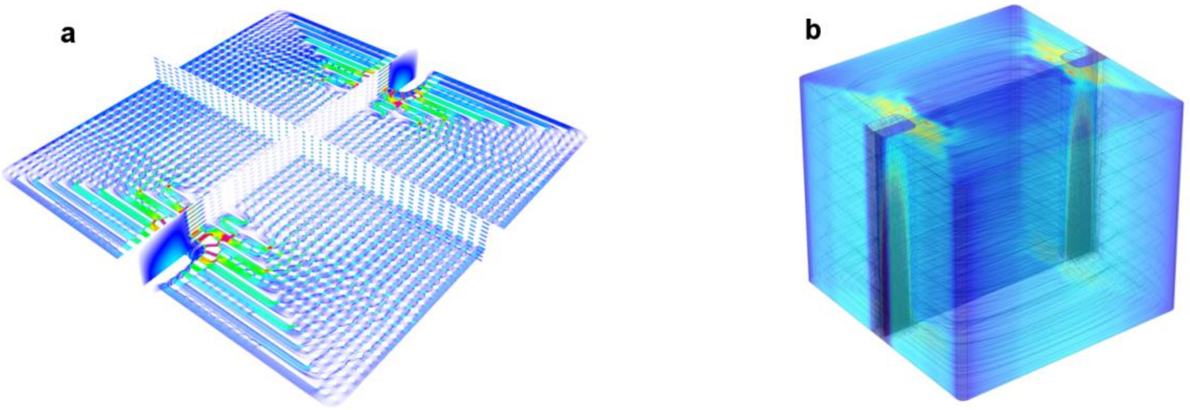


Figure 23. Homogenization process of fluid flow in a stack. A) Detailed Navier-Stokes model of a 10-unit-cell stack. B) Homogenized model of a 75-unit-cell stack based on simplified Darcy flow in porous media. B) was obtained from the full Navier-Stokes solution using topology optimization procedure

Stack design optimisation

Several stack trials were conducted during the project, with variations in stack composition and treatments. The stack treatments included variations in the application and duration of compression forces, in order to determine the importance of mechanical force and metal creep. The conclusion from those tests and others was that too little load adversely affected stack start-up, whereas higher loads could be tolerated in some cases without catastrophic failure. Therefore, the was to find an optimal compression, at which there was no cross-over leakage and also no severe creep. This meant to develop and implement a new stack design with the purpose to have minimal impact of creep, so that safer (higher) compression forces will induce only a low amount of creep.

The focus of the work was to develop 10-25 cell stacks with optimal compression forces, improved laser welds (of cells to interconnects), improved stack conditioning and glass sealing procedures, capability of internal reforming in the stack, and to eventually test them for at least 1000 hours. The work resulted in improvements on all aspects of the stack fabrication steps and conditioning, which lead the development of promising stacks that were intended for stack testing towards the end of 2014. However, due to the closing of TOFC in August 2014 the stacks were unfortunately never tested. Some of the development highlights are given below:

*Laser welding of cells to interconnects (IC):*The laser welding parameters for welding the MS-SOFCs to ICs were significantly improved. With the introduction of a “double-weld” together with improved laser weld parameters the leak rates from the cell-IC component became sufficiently low for proper implementation into stacks.

Stack birth and conditioning: This step involved assembly of the cell-IC single-repeat units into stacks and forming a good seal between the cell of one cell-IC component and the IC of another cell-IC component (see Figure 24). Here, progress was made in finding a proper procedure including choosing an appropriate glass material, finding a suitable temperature profile during the sealing process, as well as optimal compression during the sealing step to form a leak tight stack without damaging the electrolyte.

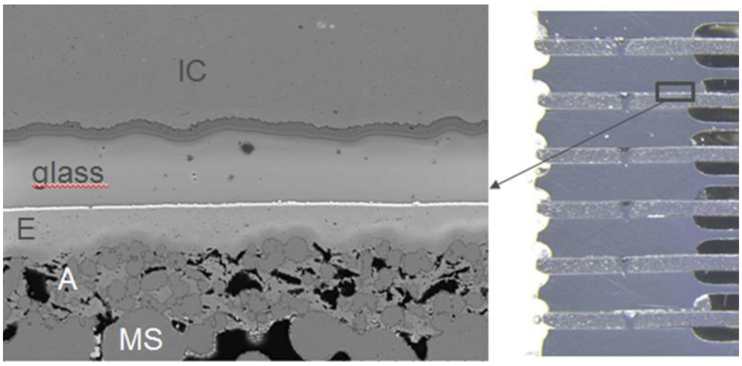


Figure 24. Cross-section of a trial 6-cell stack at the edge (right image) with the corresponding good glass seal (left image). Note the good adhesion of the glass to both the IC and the electrolyte (E) (no cathode on the edge of the cell).

Cathode sintering; ex-situ vs. in-situ: One of the challenges with the MS-SOFC technology developed in the project was how to solve the issue with sintering of the cathode. One of the suggested changes included a new strategy of *ex-situ* cathode sintering, which required several modifications in the stack fabrication procedure. A patent application was completed and submitted during the second project period. TOFC was eventually able to prove that an *ex-situ* process indeed is possible, however, the process was unfortunately deemed too difficult to use with respect to ensuring sufficient reproducible quality of the cathode after stack assembly, as well as from a cost perspective when the process was going to be upscaled.

An alternative route with *in-situ* cathode sintering, where the cathode is sintered when the stack has been assembled and is sealed with glass at elevated temperatures, was therefore developed in the second project period. The *in-situ* sintering route required testing and implementation of new glass materials for sealing and new methods for their application and processing (heat treatment and compression). New insights into the different fabrication steps of the stacks made it eventually possible to fabricate a very promising stack (see Figure 25), which after assembly showed promising low leak rates The developed stack fabrication route resulted in a stack that could be handled without compression and was approved with regards to the leak rates. The stack was unfortunately never characterized in a stack test due to the closing of TOFC at the same time as this stack had been produced.

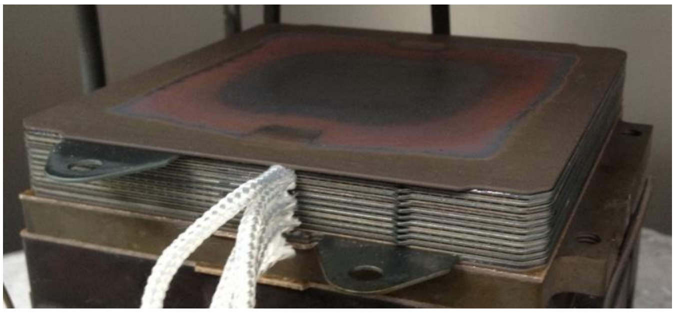


Figure 25: A 10-cell stack with MS-SOFC after assembly and conditioning with in-situ sintering of the cathode. The stack was approved with regards to the leak rates and was intended for stack characterization as the next step.

Stack development on EK design

The main objectives for the project were as follows:

- Development of welding processes for the general applicability of METSAPP cells into EK stacks.
- Development of a small EK-Design stack with MS-SOFCs
- Post mortem analysis of a tested stack in respect to creep resistance and mechanical compression of the cell (depending on successful stack building)
- Feasibility study for the integration of coated steel stack components in standard EK-stacks (anode supported cells)

The main challenge for EK was to develop a design and a process to implement the METSAPP cells into a standard EK stack within a short time frame.

Welding trials: First welding trials were performed to find the right orientation of the cell to the cell frame and to obtain the right welding parameters. An evaluation of different welding options, as shown in Figure 26, was performed. The best results were obtained applying orientation (a). Other orientations yielded to welding defects, like inclusion of ceramics into the welding seam.

Due to the fact that the cell orientation relative to the cell frame in option (a) is opposite to the ceramic cell orientation in the EK stack (the electrolyte is oriented towards the cell frame), a new cell frame design had to be developed.

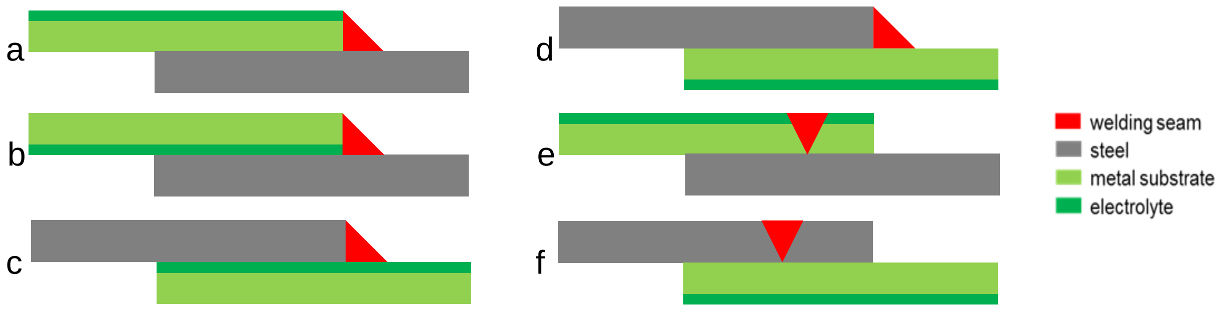


Figure 26: Illustrations of the various welding variants in order to weld the cell (composed of the metal substrate and electrolyte) onto the cell frame (steel).

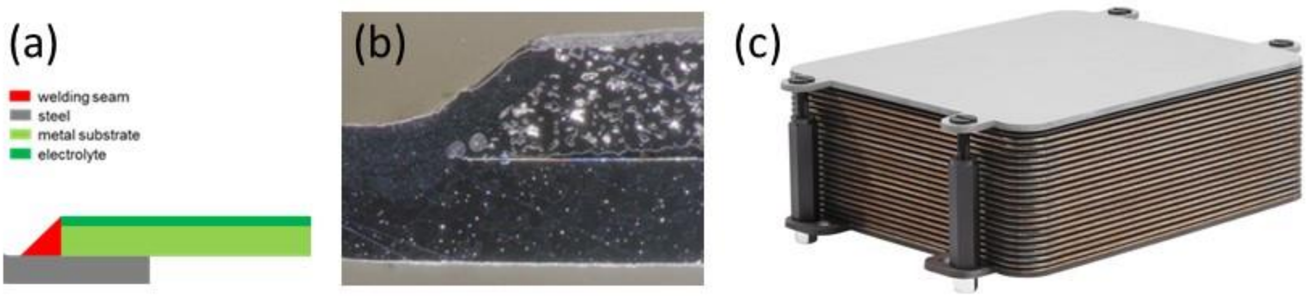


Figure 27: Drawing (a) and micrograph (b) of a cross section of a frame part to host the cell, and (c) picture of a stack.

Design optimization: Figure 27 shows a cross section of the cell frame, which allows to integrate the metal supported cell into the stack. The micrograph in Figure 27 also shows that a dense metal layer has been obtained, covering the cell from the electrolyte down to the anode into the cell frame. Due to the new design, standard quality procedures did not apply. Hence, the general leak tightness of the welding seam could not be tested initially. For the second stack, the cell containing parts were tested. A sufficient leak tightness could not be obtained due to the limited time frame.

Stacking and conditioning: Two five cell stacks were built during the participation of EK in METSAPP.

First each of the cells was welded into a cell frame part. This item could not be tested for leak tightness, as there was no testing device suitable for this design available yet. As a consequence, the first stack was built containing cells, which were only optically checked for potential leaks. The results obtained from the welding trials, in particular a certain bending of the welded part, made the stacking advisable. This stack proved to potentially contain several leakages. Nevertheless, this stack was set up in a test rig and conditioned for further testing. The conditioning of the stack had to be adjusted to suit cells, which did not need to be reduced before operation. During the conditioning process the stack degraded rapidly, further testing was not possible. The post mortem analysis of the stack showed that the electrolyte detached itself from the metallic substrate in the vicinity of the welding seam.

To improve the leak tightness of the welding seam, a second set of welded cells was prepared, adding a “green” glass sealing on top of the welding seam. This glass sealing melted during stack conditioning, sealing the welding seam successfully. Nevertheless, during stack conditioning, the stack also degraded rapidly and the same type of failure was detected in the post mortem analysis. A more detailed analysis of the welded cells shows micro fissures in the electrolyte starting at the welding seam and reaching several millimeters into the cell. These micro fissures explain the observed damages only to a limited degree. The fact, that the electrolyte is damaged only where the cell frame covers the anode, cannot be explained by damages caused by laser welding. Nevertheless, the experiments show that the stack can physically host the METSAPP cell. Now further development is necessary to improve the integration of the METSAPP cell into the stack, e.g. the welding seam should be moved away from the electrolyte. This would require changes in the cell production. Another possible way forward is to change the laser source from a standard pulsed laser to a continuous disk laser. This way the energy necessary for welding can be reduced and the thermal input into the cell can be minimized.

Effect of stack design on mechanical compression: Previous evaluations of stacks within METSAPP and METSOFC indicated that the mechanical compression applied to the stack at operating temperature leads to creep of the MS-SOFC and can cause leakages in the cell and ultimately total failure of the stack. Hence the aim of this task was to evaluate these findings within EK stacks and compare the applied mechanical pressure previously suggested (appr. 25 – 100 kPa) with the pressure applied to EK anode supported cell based stacks. Due to the fact that none of the stacks built went into operation, the effect of the stack design on the mechanical compression and potential creep in the cell could not be analysed.

METSAPP potential impact, dissemination and exploitation of results

Potential impact

Metal supported cells as a key technology, especially for mobile applications

So far, SOFC is mainly used for stationary power generation, as the technology allows very efficient conversion of hydrocarbon based fuels into electricity. In this market segment, there are already various products on the market like from Bloom Energy (US) and Aisin Seiki (JP). Due to the high operating temperature, SOFCs can directly convert hydrocarbon feedstocks into electricity via direct electrochemical oxidation of carbon monoxide and internal reforming of hydrocarbons. This capability represents the main advantage compared to state-of-the-art PEM fuel cells, which can only convert pure hydrogen.

SOFC technology still needs significant improvements to reach the requirements for automotive applications. Typical SOFC cell architectures today are based on a ceramic-metallic sandwich design with two major parts: 1) a ceramic supported cell consisting of ceramic functional layers and a ceramic support layer and 2) a metallic interconnectors to stack various individual cells electrically in series. Up-to-date cell designs use a ceramic support layer (anode or electrolyte). Ceramic layers are in general very vulnerable to mechanical and thermal stress. Hence, heat-up time and mechanical strength of these cells are limited and prohibit an application in passenger cars.

Therefore, the ceramic support layer is replaced by a metallic layer in METSAPP. This dramatically enhances the cell characteristics towards thermal gradients, rapid start-up and mechanical robustness. On the system development side, a major advantage is that the stack protection system during heat up and cool down is not required any more. In addition, another advantage of the MS-SOFC is the complete process change in how the cell is implemented into the SOFC stack, compared to ceramic supported cells. This allows pursuing a manufacturing strategy, which should reduce manufacturing cost substantially. Finally MS-SOFCs are manufactured in an already reduced state. The stack is almost fully operational after assembly.

Thus, the MS-SOFC technology is expected to have an impact in the following markets.

APU for trucks

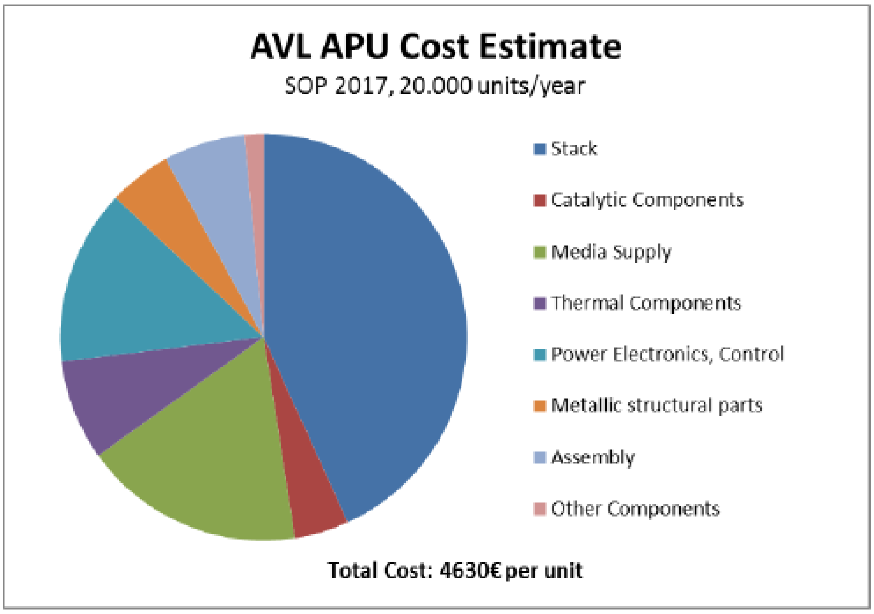
The dissemination work for MS-SOFC APU systems in heavy duty truck applications as compiled in METSAPP can be applied generally and are in continuous use at AVL during discussions with partners and end customers (e.g. Eberspächer, Peterbuit, Kenworth).

The primary end user segment dealt within this project were APU for mobile applications. APUs based on fuel cell technology allows producing electricity for instance on board of a truck without idling of the main diesel engine. Similarly, such units can be used on board of recreation special purpose vehicles like military, construction (Off-Road) emergency and boats to provide electricity required.

Cost analysis for MS-SOFC in APU for trucks

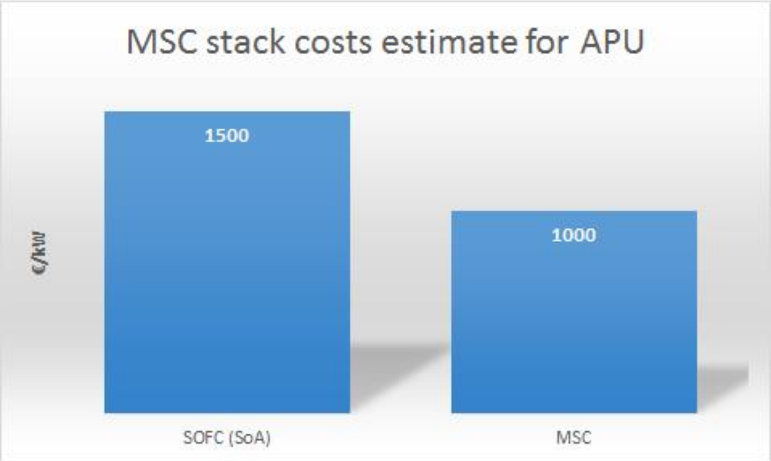
Within the DESTA project, AVL performed a business case and industrialization study for the AVL SOFC APU product towards an Anti-Idling product on the North American Heavy Duty Truck market. The study can be transferred directly to the MS-SOFC technology.

As shown in the figure below, slightly above 40 % of the system cost account for the stack. The other major cost contributors are media supply (blowers) and power electronics/control. For a successful truck, APU products stack costs of below 800 €/kW have to be reached on a mid to long term basis. This represents costs of a single cell + interconnector of around 20 €. A first commercial market introduction might be realistic with costs of 1500 €/kW or 40 € per repeating unit.



AVL SOFC APU cost estimate (SoA)

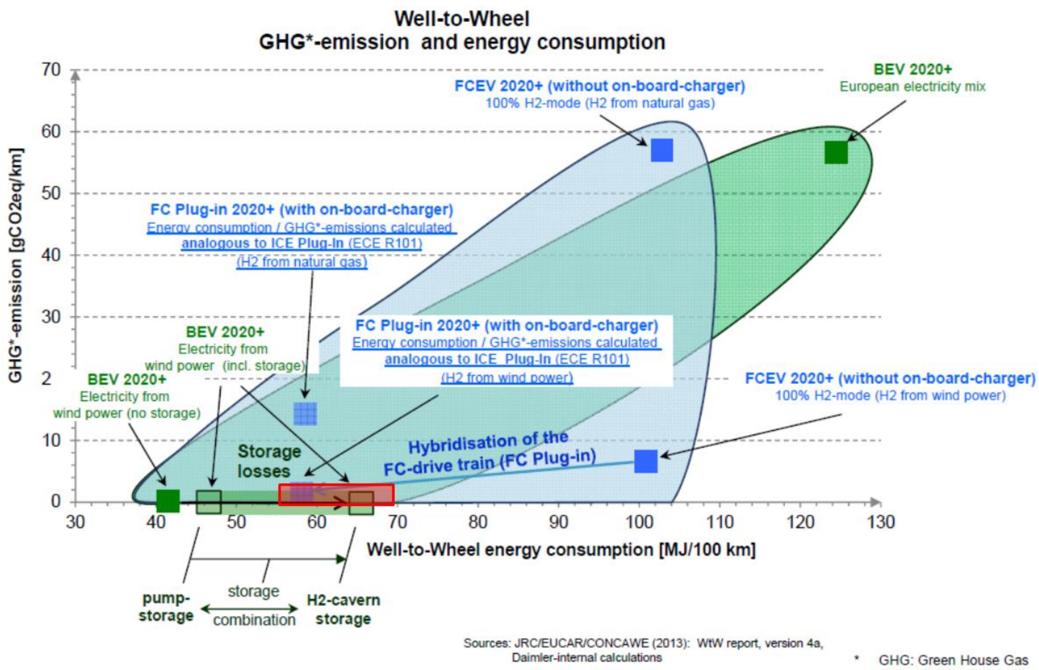
Therefore, the METSAPP concept is based on a metallic supporting layer, replacing the conventional ceramic supporting layer. This dramatically enhances the characteristics and reduces costs of the cell. As shown in the picture below, the goal for MS-SOFC might be realistic with 1000€ / kW.



SOFC for electric vehicle (SOFC EV)

As widely recognized battery electric vehicles (BEVs) have major challengers regarding recharging times and vehicle range. To overcome these challenges various BEVs are already today offered with an optional range extender system based on a combustion engine (e.g. BMW i3). However, combustion engine based range extenders are not either an optimal solution due to the rather low efficiency, noise and pollutants. Lots of original equipment manufacturer (OEM) want to evaluate SOFC based range extenders, which offer significant advantages especially towards high efficiency. An addition, biofuel can also be used, which enables a zero-CO_2 and a zero-emission propulsion concept.

The following picture shows different EV technology like battery and fuel cell in comparison with the total energy consumption (well-to-wheel) and green house gas emissions. It can be seen that the SOFC range extender approach can reach similar energy and emission levels like pure BEVs and H_2 PEM fuel cell vehicles (both with electrical energy from wind). Regarding the BEV, an interesting effect can also be seen if energy storage losses are taken into consideration. For a large scale roll-out of zero-emission BEVs, the electrical energy needs to come from renewable sources. Due to the stochastic appearance of this energy form, storage need to be applied. This increases significantly the overall energy consumption of pure BEVs. If this energy loss is considered, all three powertrain concepts (pure BEV, H_2 PEM Fuel Cell and SOFC range extender) reach a similar total energy consumption in the range of 45-70 MJ/100km.



MS-SOFC stack with all the advantages compared to CSC is definitely a key technology for SOFC EV'S. MS-SOFC is much better suited because of the following requirements:

- High power to volume and weight ratios
- Mechanical robustness and durability
- Improved thermal conductivity
- Fast start up (<10min)
- Thermal cycle ability
- Low investment costs (simple system architecture)
- Compatibility with existing fuel infrastructure (preferably liquid fuels).

MS-SOFC for μ-CHP

Metal-supported SOFC is clearly better suited for the use in mobile applications, for instance for APU and EVs, than state-of-the-art ceramic based anode-supported or electrolyte-supported SOFC. The use of MS-SOFCs for μ-CHP has also clear potentials. However, MS-SOFCs should be first demonstrated for mobile applications, as the potentials are greater. Further investigations for μ-CHP will be more beneficial at a later stage.

Exploitation of results

The METSAPP project demonstrated the feasibility of a stable metal supported cell, based on a FeCr-LSFNT anode backbone infiltrated with Ni-GDC electrocatalyst. This cell design showed significantly improved oxidation resistance and electrocatalytic stability, with potential for further improvement of the stability and initial performance. The current stability level reached makes the cell usable for mobile applications. Further development would be needed for stationary applications.

Hundreds of cells were produced using relevant industrial techniques. However, the cell manufacturability has to be further improved with focus on the electrocatalyst integration process. This, in addition with further understanding of the backbone/electrocatalyst interaction is expected to result in superior stability as well as improved initial performance.

New highly performant coatings that can be mass produced on thin interconnects can be exploited for the METSAPP based stack concept, as well as for any SOFC stack concept using thin metallic interconnects.

The extensive electrochemical characterization and stability of the FeCr-LSFNT based cells enabled extraction of the electrochemical parameters for the validation of the developed 2D FEM model for I-V curves. These extracted parameters are in excellent agreement with the simulated I-V curves using 2D FEM model at different temperatures.

The advanced models for flow-homogenization optimization, developed at TOFC, partly under METSAPP, are in used for SOEC (HTAS) and SOFC (Resolvent I/S) applications.

The project also demonstrated the use of THDA device to assist the development process of SOFC stacks for the first time, using anode supported SOFC stacks with great success. This method can be exploited further for all types of SOFC stacks and is expected useful also on the cell level.

The project demonstrated that the METSAPP cells can be used for different stack designs, though demonstration potential for stacking with ElringKlinger's design was shown and the necessary knowledge was obtained to promote MS-SOFC development even further.

The main industrialisation is foreseen on special markets, , which are mobile home, a houseboat, a yacht, etc.. The advantages of a SOFC APU, like silent and efficient power generation, and potentially of a combined production of heat and power are highly desirable and valuable. Furthermore, these markets are open to new technologies and customers are willing to spend more on technologically advanced products. For the special markets, ElringKlinger assumes a volume of 5000 units for the year 2030.

Following these special markets, the larger markets for APUs in the transport sector and micro-CHPs become accessible and the upscaling into the new markets will help to reduce cost even further. Even an assumed small percentage of 1% of the total amount of boilers sold in Europe each year (approximatively 5 million) will increase stack sales up to 50.000 units per year. This is equivalent to over 1.5 million cells.

This method should help to establish the SOFC technology in the European market and will help to achieve the goals for 2020 (20% cut in greenhouse gases, 20% increase in energy efficiency and 20% energy from renewable sources).

Dissemination of results

The project results have been extensively communicated at several conferences (48 presentations), published in respective proceedings and 25 peer reviewed scientific journals within all technical areas represented by the different work packages (WP), see table below. In addition, not reported in the table below, a joint oral presentation within the METSAPP consortium that will take place at EFCF 2016, Lucerne. Therefore, the main dissemination addressed the respective scientific community. Open access journal was used whenever possible. Other dissemination included the presentation of the project at FCH JU and other EU project organised workshops and Review Days.

Type of dissemination	WP2	WP3	WP4	WP5	WP6	WP8	**Total**
Peer reviewed journal articles	7	2	4	0	11	1	**25**
Patents	0	0	0	2	0	0	**2**
Conference presentation oral / poster	5/3	2/0	6/7	1/0	9/6	8/0	**31/16**
Proceedings peer reviewed / not peer reviewed	3/0	2/0	5/1	1/0	12/1	2/0	**25/2**

For more details on the publications from this project, see the publication list as part of the Final Report.

Address of public website and relevant contact details

Project website:

A brief description of the project, the role of the different partners, and selected publications can be found on the project website:

www.metsapp.eu

Relevant contact details

Coordinator (from 1st of Oct 2014): Severine Ramousse

Address: Technical University of Denmark
Department of Energy Conversion and Storage
Frederiksborgvej 399
DK- 4000 Roskilde, Denmark

Email: rase@dtu.dk

Direct phone: +45 46775799

Mobile phone: +45 40201975

Partners

Beneficiary name	Short name	Country	Contact person
Technical University of Denmark	DTU	DK	Bhaskar Reddy Sudireddy bhsu@dtu.dk
Sandvik Materials Technology AB	SMT	SE	Mats Lundberg mats.w.lundberg@sandvik.com
Topsoe Fuel Cell A/S	TOFC	DK	Peter Blennow pebl@topsoe.dk
AVL List GmbH	AVL	AT	Richard Schauperl richard.schauperl@avl.com

Chalmers University of Technology	Chalmers	SE	Jan Froitzheim jan.froitzheim@chalmers.se
Karlsruhe Institute of Technology	KIT	DE	André Weber andre.weber@kit.edu
University of St Andrews	USTAN	UK	John Irvine jtsi@st-andrews.ac.uk
ICE Stroemungsforschung GmbH	ICE	AT	Andrea Thalhamer office@ice-sf.at
European Commission, Directorate - General Joint Research Centre, Institute for Energy	JRC	NL	Thomas Malkow thomas.malkow@jrc.nl
ElringKlinger AG	EK	DE	Stefan Hornauer stefan.hornauer@elringklinger.com