Final technical report

Fuel Cells Put to Work

Market-driven solutions for high performance power

EUDP Project J. No 64010-0052

Period 01.07.2010-30.06.2012
Project responsible:
Topsoe Fuel Cell A/S
Nymøllevej 66
2800 Lyngby
CVR No. 28308523

Project partners:
Department of Energy Conversion and Storage, DTU
Frederiksborgvej 339
4000 Roskilde
Supported by

Report prepared by Christoffer Graae Greisen, July 2012

Contents

Summary

In this project, Solid Oxide Fuel Cell (SOFC) system prototypes for three market segments have been developed, namely a mCHP PowerCore, an APU stack module, and a DG stack module. These have allowed us to establish strong collaborative projects with system integrators, such as Dantherm Power, SK, AVL and Eberspächer. Through this development work, the test capability and capacity has been radically improved, especially for the 5-10 kW stack modules. Stack manufacturing capability and capacity has also been improved. A number of production methods have been upgraded in order to allow establishment of industrial scale production facilities and to obtain more environmentally friendly processes.

Introduction

Project structure

The present project, EUDP Project J. No 64010-0052, is a 24 month project organised in 3 work packages, addressing the system level, the stack level and the cell level, respectively. The project included a review in August 2011. This report covers the entire span of the project. The overall objectives of the project are listed below, followed by a brief record of the final status on the project milestones. Subsequently a detailed report on each work package is provided.

Overall fulfilment of project objectives

“Solid oxide fuel cells offer clean and efficient production of power and heat from a wide selection of readily available fuels. This project will mature solid oxide fuel cell systems to a level where they are meeting critical user requirements for efficiency, lifetime and costs. Three different systems will be developed, each targeting a key market segment: micro combined heat and power (mCHP), auxiliary power units (APU) and distributed generation (DG). For mCHP and APU, product prototypes will be developed. For DG, fuel cell stacks in 50 kW systems as well as a new design of stack modules for 250 kW systems will be demonstrated. To meet system requirements, high performance cells and stacks are needed. As part of the project, improved manufacturing methods which are suitable for industrial scale manufacturing of cells and stacks will be developed and validated. The focus will be on cost reductions, improved cells and stacks with higher power density.”

For the mCHP and APU segments, the overall project objectives have been met, in that product prototypes are now available, and being implemented by integrator partners into their demonstrator systems. In the DG segment the path to 250 kW systems has not been demonstrated but stack modules for smaller demonstration units (10-50 kW) have been developed. Manufacturing methods for industrial scale are now available at the cell level, while on the stack level this is the case for only some manufacturing processes.

Overall completion of milestones

				jul-10	aug-10	sep-10	okt-10	nov-10	dec-10	jan-11	feb-11	mar-11	apr-11	maj-11	jun-11	jul-11	aug-11	sep-11	okt-11	nov-11	dec-11	jan-12	feb-12	mar-12	apr-12	maj-12	jun-12
Milepæls ID	Milepæl (Dansk Titel)		Status	Måned																							
				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
A	mCHP produktdesign defineret	🟩	15.02.2011									🟩															
B	mCHP produktdesign verificeret	🟩	31.03.2012																		🟩						
C	Levetidsmodel for PowerCore samt demonstration af over 20.000 timers staklevetid (i henhold til SOFC-roadmap)	🟥	Not met																								🟥
D	APU Produktdesign verificeret	🟩	31.12.2011																		🟩						
E	Evaluering af eksisterende 50 kW Wärtsila system	🟩	31.12.2010						🟩																		
F	Validering af 250 kW DG stakmoduldesign i forhold til brugerbehov	🟥	Not met																		🟥						
G	Evaluering af muligheder for automatisering	🟩	31.12.2010				🟩																				
H	I alt 4 stakdesign overført til produktion	🟥	Not met																								🟥
I	Vandbaseret anode udviklet	🟩	30.11.2011																	🟩							
J	Karakterisering af svovltolerante celler med scandium	🟩	31.10.2011												🟩												
K	Multilags-tapecasting testet	🟩	01.04.2011										🟩														

Milestones A,B,D,E,G,I,J,K have all been met, and as milestones B, D, I and K the expectations are even somewhat exceeded. See the individual work packages for an elaboration.

During the project 3 milestones have not been met. These are

- Milestone C: “Lifetime model for PowerCore and demonstration of 20000 hours of stack lifetime.” Lifetime assessment for PowerCore components are available as well as long term test setup, but since no PowerCore has run more than 750 hours, extrapolation to 20000 hours is too speculative to claim such a lifetime.
- Milestone F: “Validation of a stack module for 250 kW systems against user needs”. The currently developed DG stack module is too small for usage in 250 kW systems, but it is suitable for systems in the 10-50 kW range. The DG stack modules have been tested in conditions which resembles such systems.
- Milestone H: “A total of 4 stack designs transferred to production” was not met. Work on transferring stack designs to production revealed a number of failure modes, especially related to quality control of stack components and conditions outside nominal operation. This has lead to a delay and a change of focus towards an extensive effort on solving QA problems in the stack production.

WP 1 Fuel cell systems

In the 3 different segments pursued by Topsoe Fuel Cell, there are different requirements. For DG, lifetime and efficiency is most important. For mCHP, tight integration and lifetime is important. For APU, pressure drop is the key, the fuel is very different from the stationary applications and mechanical robustness is more important than lifetime under stable conditions.

WP 1.1 Development of Topsoe PowerCore for the mCHP market

A new Topsoe PowerCore called the Stage 3 PowerCore has been developed within this project. The PowerCore development is based on all the know-how gained from developing, manufacturing and testing of the Stage 2 PowerCore. There are two fundamental design principles behind the Stage 3 PowerCore. The first one is minimizing the heat losses by having a very tight thermal integration of the stack and the hot balance of plant components within the PowerCore. This allows operation with a high electrical efficiency as well as operation with load variations within a broad range while still maintaining a high electrical efficiency. The second design principle is to use the natural gas reforming concept developed from the Stage 2 PowerCore testing which is based on cold desulphurisation, adiabatic steam reforming together with anode recycle operation. This combination gives the simplest balance of plant configuration together with the highest electrical efficiency for a mCHP system.

There are a number of major technological advancements within this work package including the development of a completely new open air manifold stack design, a new stack module with high temperature stack compression, and an integrated heat exchanger/burner module developed together with an industrial partner/sub-supplier. These improvements led to the meeting of milestone A “mCHP product design defined”. This very successful development work continued with some highlights listed below:

- 10 PowerCores have built and tested with very uniform and high performance up until now.
- The PowerCore is undergoing an extensive testing program where we have so far achieved an accumulated testing time of more than 1200 hours where the longest test is more than 700 hours, 22 load cycles between full power and 50% power, and 18 complete thermal cycles.
- PowerCores have been shipped to two different external partners that are currently in the process of developing a system around the PowerCore.
- Through 2 major design revisions of the stack module, leaks have been minimized, compliance with regulatory requirements has been obtained, steel material intercompatibility has been achieved, and the architecture of the system has been simplified.

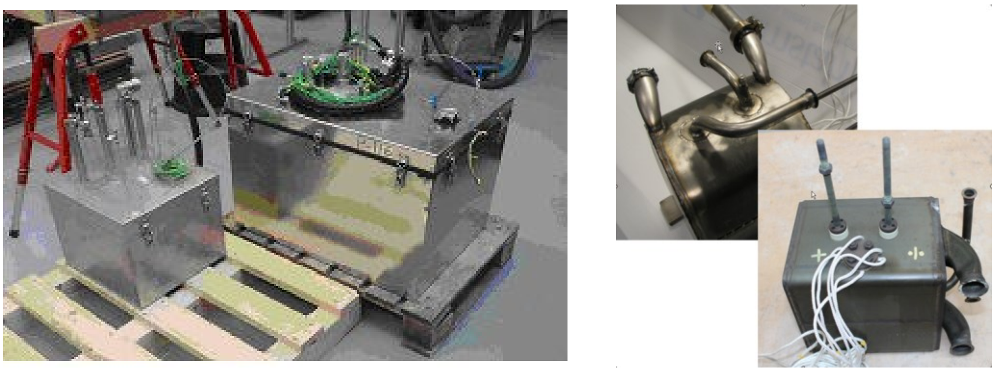

Figure 1: Left: The stage 3 Topsoe PowerCore next to the much larger stage 2 PowerCore. Right: The mCHP stack module in two design iterations for (a) robustness and (b) manufacturability.

While the power output has been kept constant, the Stage 3 PowerCore is designed with a number of improvements regarding the performance in comparison with the Stage 2 PowerCore. All of these specifications are proven in PowerCore testing apart from the lifetime assessment. Some of the major improvements are:

- Increased electrical net efficiency from 52% to 62%
- Volume reduction from 148 L to 35 L
- Weight reduction from 90 kg to 30 kg
- Heat loss reduced below 300 W
- Start-up time reduced from 15 hours to below 3 hours
- Start-up and shut-down performed without protection gas

A major impact of these very promising results is that commercialization activities have now been agreed with Korean partner SK. This is further elaborated in the section on market and network activities.

These results lead to claiming milestone B: “mCHP product design verified”.

The lifetime assessment of the PowerCore is coming from numerous sources where one of the most important parts is long-term PowerCore testing internally and in partner laboratories, as well as demonstrations. The capabilities for PowerCore testing have been increased by a custom built functionality tester. The functionality tester gives us the possibility to test PowerCores on long-term tests in a close to real-life environment. This in combination with internal long-term stack testing and both internal and external component testing gives us confidence in the total lifetime assessment.

The assembly of this unit is progressing with the facilities, auxiliaries and hardware in place (see Figure 2). Custom programming of the control system is ongoing. The final assembly and commissioning of the test system pending, but it will support the testing needs for validating the PowerCore development.

Concurrently the individual components of the PowerCore are being tested and mapped individually in the component testing facilities of Topsoe Fuel Cell. These validation tests include main heat exchanger module, pre-reformer activity, electrical heater, stack module and anode recycle system. This adds to the overall confidence and validation of the PowerCore. But the delays in these activities also means that milestone C: “Lifetime model for PowerCore and demonstration of 20000 hours of stack lifetime” is not met.

The progress on the PowerCore development has been presented at Fuel Cell Seminar 2011 in Florida [17], at HFC 2011 in Malmö [18] and at FC EXPO 2012 in Japan [3].

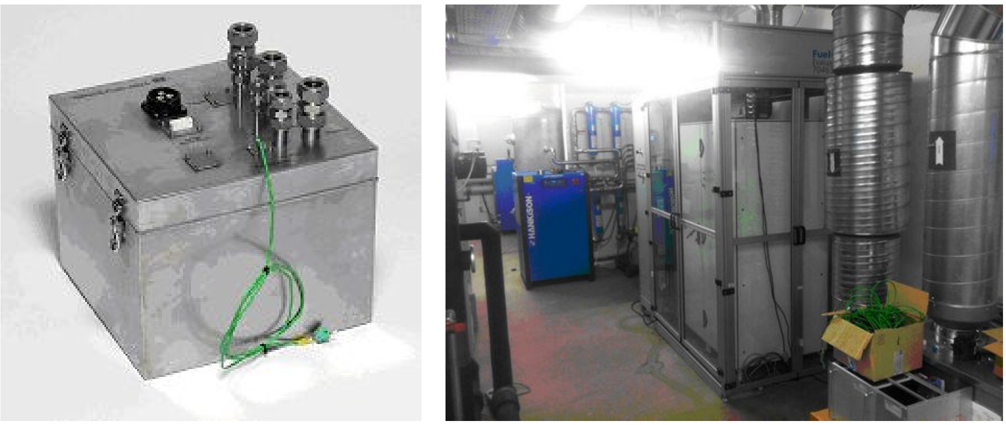

Figure 2: The Stage 3 PowerCore and the functionality tester.

WP 1.2 Development of APU stack and APU stack module

In the APU market segment, scope was in December 2010 changed from the initial plan that included development of a PowerCore. Thereafter the work has focused on the development of stacks and stack modules dedicated for use in auxiliary power units in heavy duty vehicles such as trucks. In this field the technical challenges are mechanical ruggedness, easy installation, high volumetric power density and robustness to relevant thermal and load cycling. A patent application is filed for the design of the cast casing and the flat interface.

The scope change has proven to be highly successful as it has lead to a much faster APU system development. The new stack module is now in use at three different system integrators, one company in the USA, the company Eberspächer in Germany and the company AVL in Austria. Another US integrator is expected to join after the summer 2012.

AVL presented their “APU Gen1 system” at the Hannover Fair 2012 and made a presentation at the CMCEE conference in May 2012 [5]. In their presentation, AVL quoted: ”The new Topsoe stack is a straight forward design. You just bolt it onto your system.”

Figure 3. The new APU stack. Weight 10 kg. Dimensions are 184 x 159 x 166 mm. Two threaded power outlets are seen. Voltage probes leave from the side. Depending on the fuel, the duration of operation and efficiency trade-offs, each stack can deliver an electrical power in the range 2-3 kW.

A total of 29 of these stacks have been built and tested. The most unknown and crucial performance characteristic was durability during load cycling and thermal cycling. We have therefore given the traditional stationary operation test a low priority in the favour of a testing procedure in which multiple load changes take place. The graph below shows a sequence of nine thermal cycles.

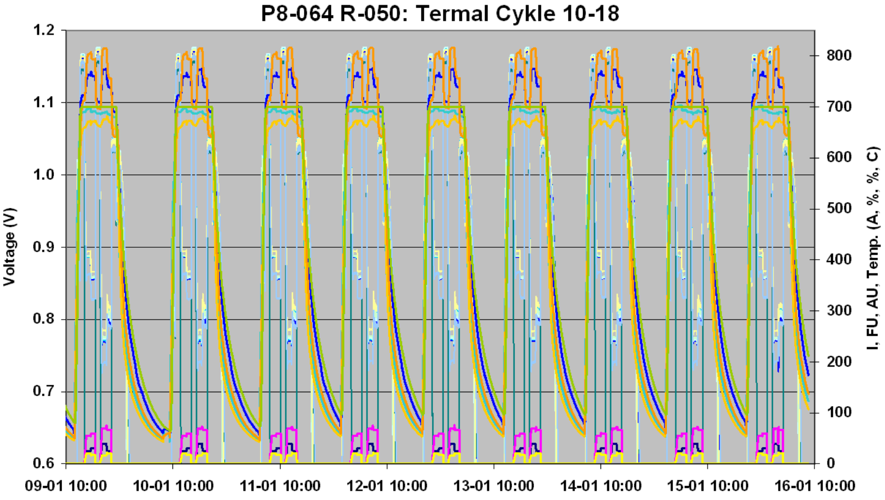

Figure 4. Nine fast, full thermal cycles, repeated one after another. No performance loss is seen.

The graph in Figure 5 compiles 60 full thermal cycles. Each dot represents a full thermal cycle. A slight degradation is seen over time. This degradation is however in the range expected for stable operation over the same time span, here 750 hours, i.e. there is no sign that the stack is affected by the thermal cycling as such. We believe that we have by now demonstrated our designs ability to withstand several dozens of full thermal cycling @ ~1h start up time.

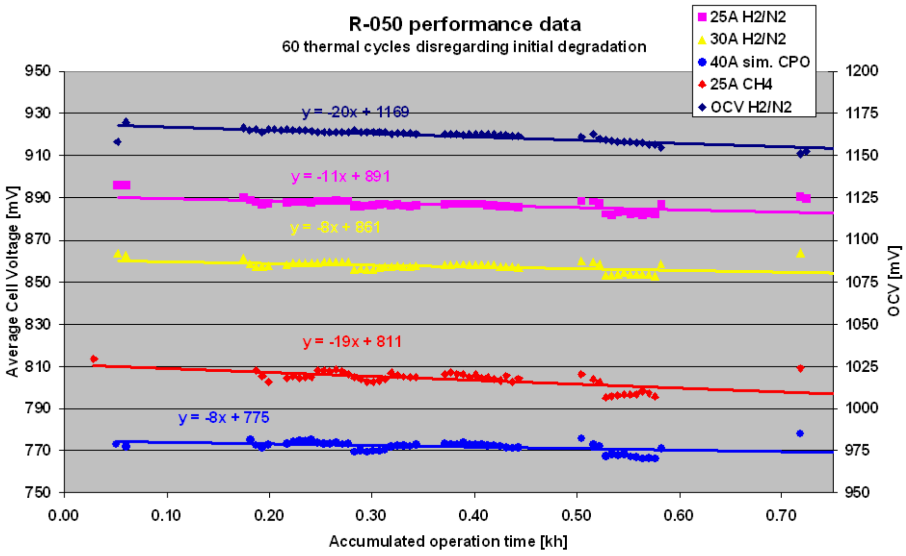

Figure 5: Each dot represents a full, fast thermal cycle followed by operation on various fuels.

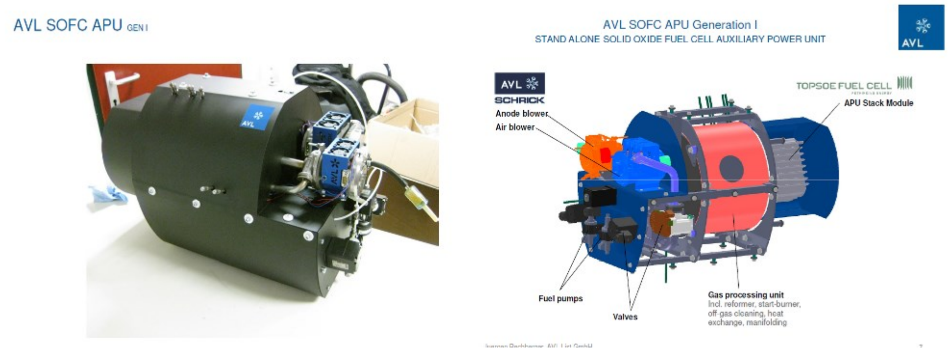

Figure 6: The stack mounted in an AVL system. From [4]

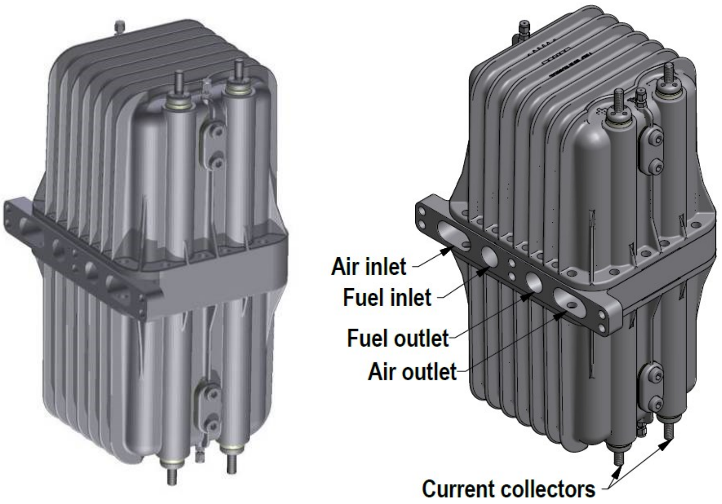

Figure 7: APU Stack module. Twin configuration. Approx. 24 kg, H350 mm x W232 mm x D168 mm

The APU stack modules and test results have also been presented at a number of technical conferences i.e. [41] and [3]. They also lead to meeting milestone D: “APU product design verified”.

WP 1.3 Development of stack modules for the DG market

The aim for WP1.3 has been to develop building blocks for large systems (up to 250 kW). Extensive work has been carried out in order to achieve this. Highlights of this work are described in the following as well as in the chapter covering WP2.

Systems with large foot print stacks

During 2010 two 50 kW units, LARGE SOFC and DEMO SOFC, constructed by Wärtsilä Fuel Cell were started up. 24 Topsoe Fuel Cell Gen-II stacks (large footprint stacks)[i] were installed in each of these systems. The start-ups were successful; however, no significant operating time was obtained due to lack of stack robustness towards the operation conditions. But the experience gained with these systems was sufficient to meet milestone E: "Evaluation of existing 50 kW systems". Extensive work was carried out with the aim of producing sufficiently robust Gen-II stacks. This work is covered in WP2.

Stack modules with Open Air Manifold stacks

In order to mitigate the risk caused by the large cell footprint of the Gen-II stack it was during 2011 decided to change focus into developing stack blocks including stacks of smaller foot print. The smaller power output of each stack is compensated for by coupling stacks together into compact units of four stacks each sharing both anode and cathode flow connections; those units are called OAM (Open Air Manifold) stack modules. The close collaboration between Wärtsilä Fuel Cell and Topsoe Fuel Cell have ensured that the IPM module (constructed by Wärtsilä Fuel Cell), which were originally intended for Gen-II stacks, is suitable for OAM stack modules. The change of focus has caused a delay but has also created a possible road to development of larger systems.

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[i] Topsoe Fuel Cell has operated with a number of stack types. These can be divided in to two major groups; one with cells size 18 cm x 18 cm (large footprint stacks) and one with cell size 12 cm x 12 cm (small footprint stacks). For the DG program both of these have been used.

The OAM stack module consists of three sub-modules; a core module including four stacks, a feed through module, and an end module. Such sub-modules combined in one module are shown in Figure 8. The core modules consist of four stacks placed symmetrically such that the thermal conditions for all stacks are similar; ensuring close to equal performance of the four stacks, each delivering 1,5 kW. The major advantages of this are that it prevents a shortened lifetime and limitations of the operation window caused by different conditions for the stacks while at the same time ensuring compactness of units. The core module also includes a compression system, bypass gaskets around the stacks, and a fuel manifold. The feed-through module functions as the air inlet manifold and includes feed troughs and connections to the core module. The end module functions as the air outlet manifold. Figure 9 shows a feed through module mounted to a core module.

Production of all components of the modules, except the stacks, has been successfully outsourced, while assembly and tests are done at Topsoe Fuel Cells A/S. The stack module materials are chosen for long-term operation. If the parts should be damaged despite of this, the modules are built such that all parts of the modules can be exchanged without damaging other parts.

Tests have been carried out to verify the performance of the module components and the complete module. The accuracy and sustainability has been verified for the compression system and a number of other parameters have also been verified. In Table 1 key target parameters reported in January 2012 are given. Most of these targets have been reached except those for which validation require long operating time or test of a large number of module tests.

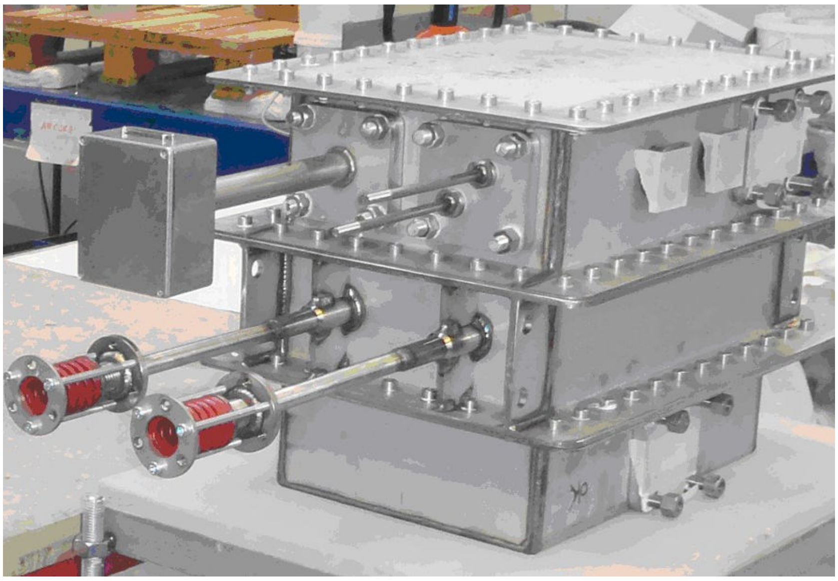

Figure 8: Stack module consisting of three sub-modules.

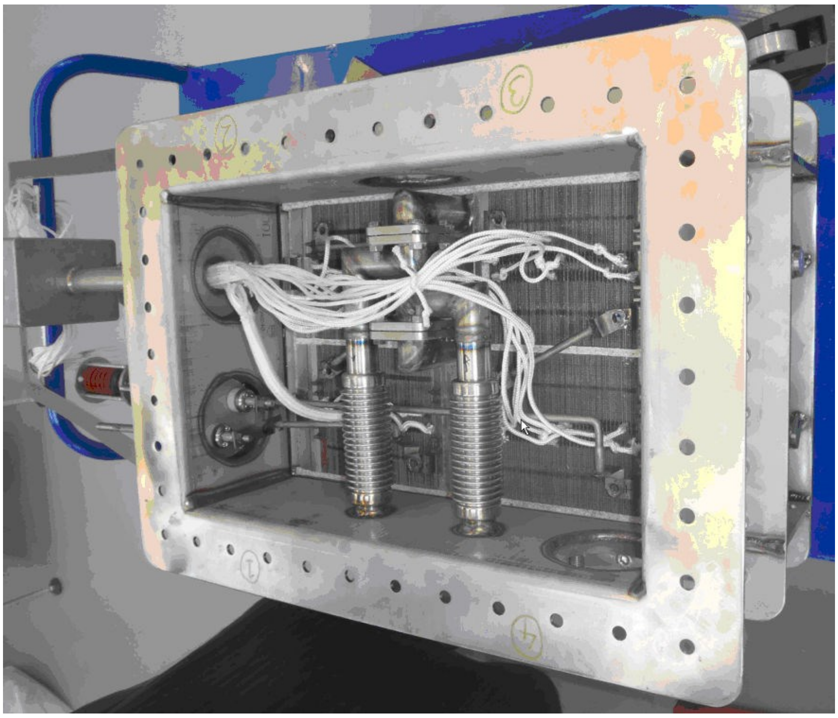

Figure 9: Feed-through module mounted to core module.

Table 1: Target key parameters for OAM stack modules.

Parameter	Value	Verified
Design lifetime module (Not stack) before hard-failure	≥40,000 h	
Number of modules allowed to hard-fail before lifetime	10%	
Module Begin of Life (BOL) power @ Verification operating point (VOP)*	6,000W @ 240V	√
Cathode pressure drop @ VOP	<20 mbar	√
Cathode pressure drop variation between modules @ VOP	<20%	
Anode pressure drop @ VOP	<25 mbar	√
Anode pressure drop variation between Modules @ VOP	< 7%	
Endured start-up time	< 5 h	√
Orientation of module	Free	√
IMR interval (Inspection, Maintenance, Repair)	>5,000 h	
Endured air flow	>120 Nm^3/h	√
Endured fuel flow	>15 Nm^3/h	√
External leakage air @ VOP	<0.1% @ 0.2 barg	√
External leakage fuel @ VOP	<0.01% @ 0.2 barg	√
Bypass air leakage @ VOP	<1% @ 50 mbar difference	√
Endured inside pressure	>250 mbarg	√
Weight	~70 kg	√

In addition to the key parameters listed above, it was clear by the end of 2011 that a better solution for the electrical insulation between the stacks and the fuel manifold was needed. The previously used gasket was only resistive enough for having two stacks electrically in series. A sub-project has identified several possible options and tested their electrical resistance both instantaneously and over time. The result is that a suitable material has been identified such that the four stacks in one module can be operated in a serial configuration. This is of significant importance for the system cost, as it decreases the required number of load supplies and increases the maximum obtainable output voltage.

With funding through the CATION project AVL LIST GmbH have in collaboration with Wärtsilä Fuel Cell and Topsoe Fuel Cell completed risk analysis, DFMEA, on OAM stack modules, for which they have also made a damage model. Data from tests of the OAM stack modules are at the time of writing being implemented in this model. Additionally, AVL have prepared their 10 kW test station for a degradation test of one module. At Topsoe Fuel Cell FEM analysis has been applied to the stack module design and materials to ensure that no unwanted deformations occur and CFD analysis has been applied to both the cathode and anode flow to ensure proper flow distributions.

Two prototypes of OAM stack modules have been testes with a so called D1 (decision point 1) test, which is a robustness test used to validate if the present module design can be used for further progress in the CATION project (EU funded project). The D1 test of OAM stack modules shall make sure that the modules are robust towards conditions they may be subject to in larger systems where several OAM stack modules will be coupled together. The conditions of an upcoming test by Wärtsilä Fuel Cell, where two to four modules will be tested together, has been used as an indication of which conditions that are relevant to test in order to ensure robustness towards realistic condition when up scaling SOFC systems. The OAM stack module tests also provide a means of testing four OAM stacks at a time.

In short, the D1 test includes the following:

- Standard operation. Pre-reformed Natural gas, 25 A, 60% Fuel Utilization, 21% Air Utilization.
- Load variations: +/-30% (17.5 A, 25 A, 32.5 A).
- FU variation: 65%, 60%. Variation parameter: fuel flow.
- AU variation: 24%, 21%, 18%. Variation parameter: air flow.
- Load cycles: Abrupt 25A (standard operation) → 0 A. Step at 10 A on the way to 25 A. All other conditions are kept the same.
- SU/SD cycles.

Both prototype modules passed the test and it was decided to continue with the present OAM stack module design. Additionally one of the modules has been tested for a total of more than 1100 h, including more than 400 h at nominal operation, six thermal cycles, five load cycles, three rounds of fuel and air utilization variations, and operation at 32.5 A. At nominal operation the BOL (Beginning Of Life) power is 6 kW for one OAM stack module. Overall, eight OAM stack modules have been tested under varied conditions, the first six setting the basis for the two prototypes.

Due to the change of focus and the resulting delay, long-term tests have not yet been carried out for OAM stack modules, and therefore milestone F: Validation of 250 kW stack module against user needs", is not met. The tests are, however, upcoming. In addition, long-term testing on a 20 kW system is presently running in the New Energy unit constructed by Wärtsilä Fuel Cell, which includes 24 Topsoe Fuel Cell Alpha stacks. The last stack delivery for this unit has at the time of writing been running for 3048 h. The average degradation, which is linear over time, is ~37 $m\Omega*cm^2*kh^{-1}$ and the estimated lifetime is 15400 h.

Two OAM stack modules have been shipped to Wärtsilä Fuel Cell where they will be tested in the IPM module.

The work on the DG module has been presented at a number of conferences, e.g. [3] and [41].

WP 2 Stack manufacturing

WP 2.1 Conditioning[ii] and test of stacks

In the stack conditioning process the components of the stack including cells, interconnects, spacers, materials for sealing etc. are heated and compressed before reduction.

During the first half of 2011, a number of stacks were built with a process in which conditioning, reduction and test was performed in one thermal cycle and this process was validated on two different stack designs. A total cycle time of less than 36 hours was achieved. However, due to the significant height reduction in the conditioning process, it has not been straightforward to implement this combination on open air manifold stacks (see WP 2.4).

[ii] Earlier and in internal Topsoe Fuel Cell jargon, the term ”birth” has been widely used.

Accelerated reduction with higher hydrogen content and half of the reduction time was also tested in a short-term test. However, the feasibility of this approach has shown to be rather dependent on the particular stack design.

Decrease of the reduction time by aid of electrical potential showed very promising results and it has been found that stack reduction will require very little hydrogen supply. A number of stacks have been built and tested in order to determine the process parameters and impact on performance. Furthermore the process has been used in the APU stacks discussed in WP 2.2 and some of the new stack designs discussed in WP 2.4. A patent application has been filed for this process [8], and hence no further details will be given in this report.

Through the use of less organic contents, it was proven possible to decrease the cycle time of conditioning from about 40 hours to less than 19 hours, thereby a goal of 20 hours conditioning time is reached. This accelerated cycle time is also implemented in two of the new stack designs.

WP 2.2 Stack cost reduction

Milestone G: “Evaluation of possibilities for automation” was completed on time. This and other studies induced a number of activities in order to decrease the stack cost. The following graph shows the impact of these activities on the cell and IC package cost as well as on the cost of a stack for a 1 kW NG mCHP system.

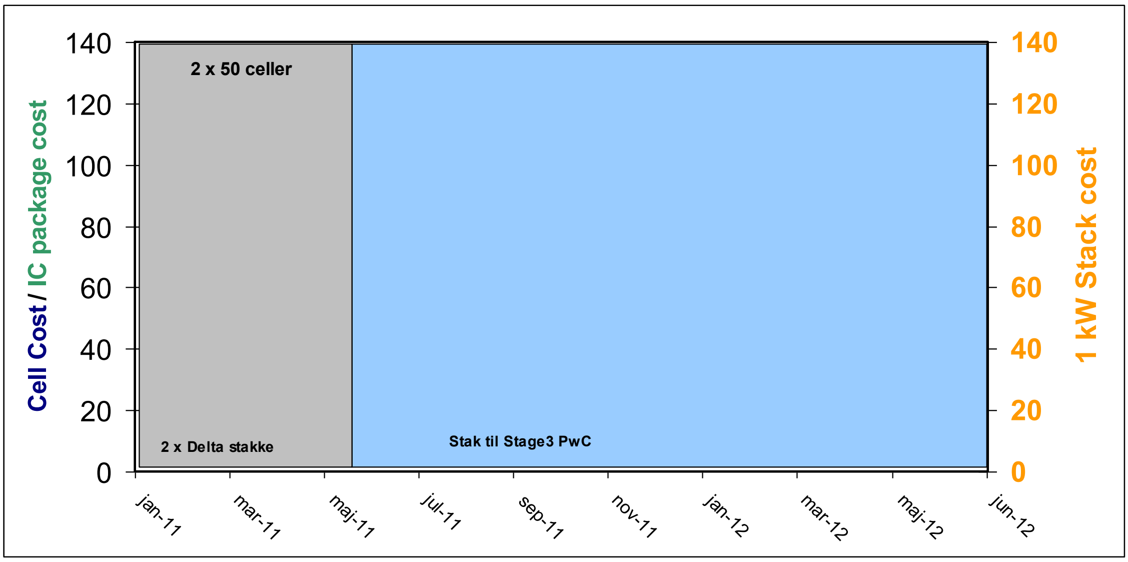

Figure 10: Result of cost reduction efforts, excluding depreciation on the stack conditioning equipment. The large step in cell cost is due to the change to 2,5 G cells (see WP 3)

Screen printing was chosen for improving the sealing materials and processes. The screen printing ink was developed in collaboration between Topsoe Fuel Cell and RISØ DTU. Process feasibility of the print as well as the final sealing properties has been investigated. It did not quite meet the tightness requirements, but it is expected that better control of the print homogeneity can solve this issue as soon as the actual production volume increases.

Equipment for automated measurement of interconnects has been implemented.

The latest work on cost modelling has emphasized that depreciation of the conditioning, reduction and test equipment is one of the main cost contributors.

WP 2.3 Stability of stacks

As mentioned under WP 1.3, an unforeseen issue with the stack robustness towards some thermomechanical conditions under operation was identified on the large footprint stacks. This spurred a number of activities to improve the mechanical strength of the anode support and to better understand it's correlation with process parameters.

To this end, test equipment was developed in order to test cells at high temperature and controlled atmosphere (see Figure 11).

Thermomechanical modelling of the stress field in the stack as a function of the operating conditions (see Figure 12) has improved capabilities in defining the allowable window of operation for the current cell design. The results of this work is further elaborated in [52].

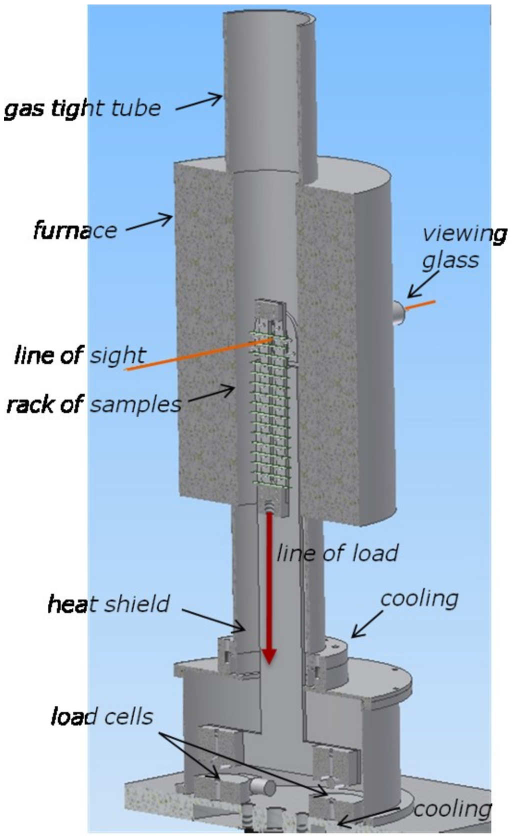

Figure 11: 3D sketch of the assembly of the experimental setup. It can measure up to 30 samples at a time and operate at about 800°C.

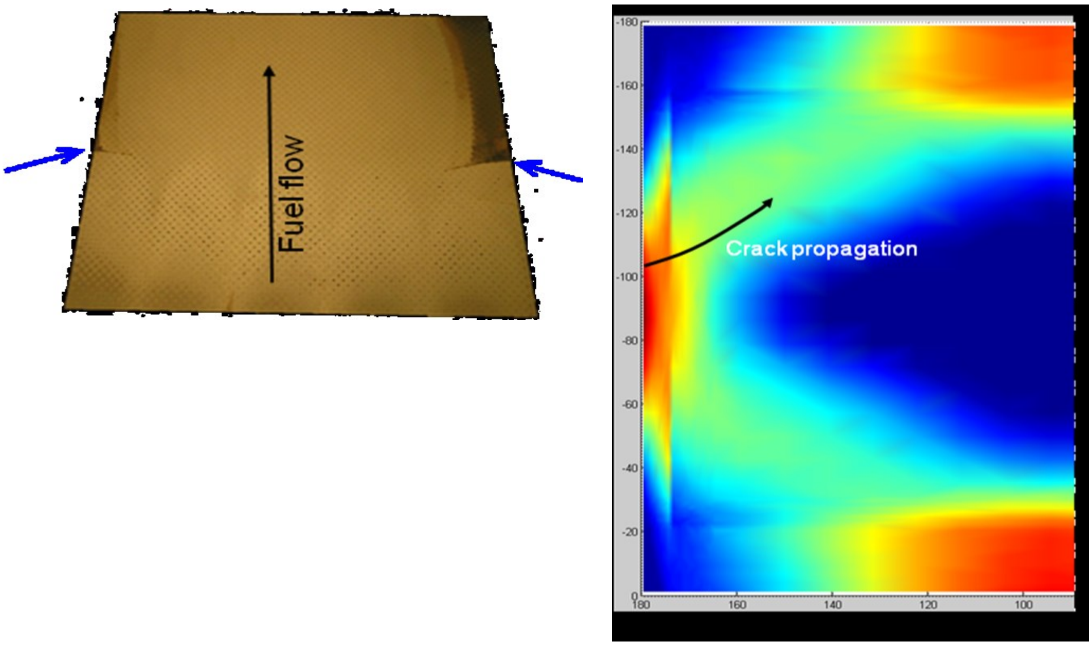

Figure 12: Cracks in a cell exposed to harsh operation and stress distribution from the thermo-mechanical model.

Detailed investigations on the correlation between cell strength and cell microstructure are reported under WP 3.3.

During the second half of 2011, a thorough test programme was put together in order to evaluate two stack designs against a combined set of requirements and find limits of the window of operation of these stack designs. Furthermore, in this work package a significant effort was put into post mortem analyses (PMA, taking the stack apart, either after conditioning or after test) in order to identify and quantify the probability and severity of phenomena that do not show in stack testing. Also the production stack (Delta) has been run through a number of tests, and an extensive sequence of PMA's were performed, indcluding a large number of stacks that had never been in stack test due to various other rejection criteria in production. The work on accelerated testing continued throughout Q1-2012, especially on the APU stack and the mCHP/DG stack. The total number of stacks investigated is given below.

Design	Number of stack tests	Number of PMAs
Delta	34	45
APU stack	22	7
mCHP/DG stack	44	22

The results gained from these experiments have been used to iteratively adapt the conditioning and reduction processes developed in WP 2.1 for the specific stack designs.

WP 2.4 New stack designs

During the first year of the project two stack design entered the process of being transferred to production. These were both of the large footprint type with internal manifold. In the first pilot series, an unforeseen sensitivity of stack performance on interconnect steel composition was identified. Since narrowing of the steel composition was no option from a cost perspective, the production process was adjusted. The result is shown in Figure 13.

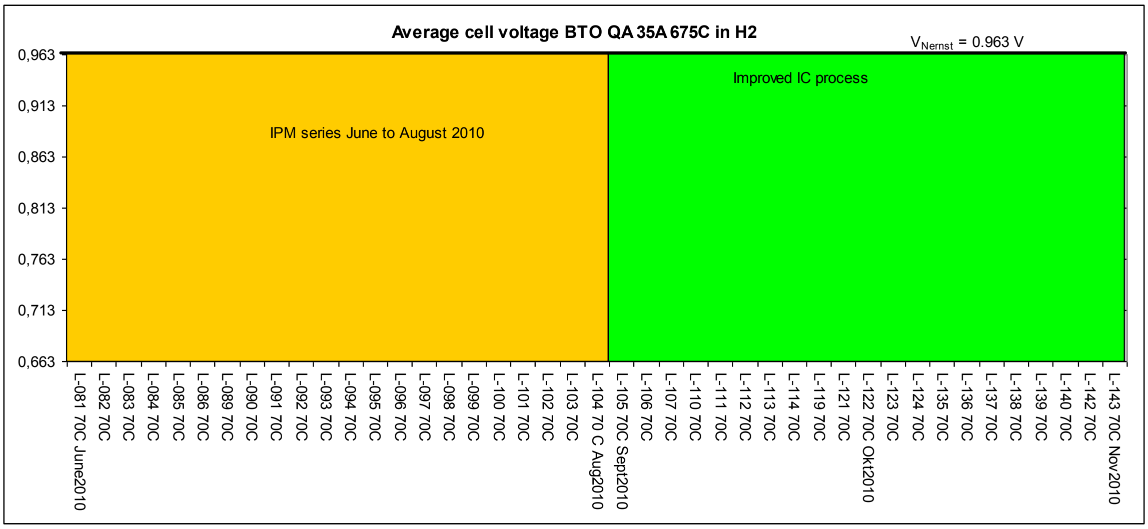

Figure 13 shows the performance of the pilot series, and the verification series after the process adjustment. It shows clearly the rather large number of stacks used for adjustment of processes at such a late point.

The second stack followed the new transfer procedure after the robustness issue mentioned in WP 1.3 was solved. However, transfer of this stack was stopped at design verification level, since it failed to fulfil a requirement to robustness, due to another failure mechanism, elaborated e.g. in [3].

A number of lessons have been learnt in these transfer activities:

- Design verification at prototype level did not capture the sensitivity to IC steel composition. For the next designs, a larger number of prototype stacks were included to assure proper design verification. This in turn will reduce the total number of stacks used in the transfer process.

- Test capability of the combined conditioning, reduction and test systems was insufficient to serve as Outgoing quality control (OQC).
- The production database (CAOS) could be improved for smoother feedback of production data to development.
- Manufacturing process instructions were too detailed, inflating workload and risk of errors when introducing new stack designs. Therefore instructions were limited to stack specific parameters and details and split from generic machine instructions.
- Product documentation level during the development phase was clearly insufficient.

In the second half of the project a number of these improvements were implemented, To this end, the cell QC was further developed through the project to include:

- A sample cell from each batch is committed to measurement of area specific resistance under hydrogen on a single cell tester.
- A number of mechanical and electrical measurements on the different layers of the cell.

Interconnect QC consists of

- Coat integrity and homogeneity.
- Electrical resistance of interconnect with coat.
- Control of geometrical specifications.

The production basis is the documentation required to make the production flow work without continuous attention from R&D. In this regard, a number of control procedures, especially on subcomponents going through multiple external services, were developed and implemented, in order to move towards manufacturing on demand.

As the project has progressed, the methodologies, reviews and other transfer procedures were integrated into the Topsoe Fuel Cell QA system. Production process analysis, Design for Manufacture and Design Failure Mode and Effects Analysis (DFMEA) have become part of the development phase. The transfer in its more narrow definition is part of the implementation phase, including i.e. Process Failure Mode and Effects Analysis.

The next stack on the transfer plan is the 12x12 cm open air manifold type used in the mCHP and DG stack modules. This stack is far in the development phase, but learning from WP 2.3 and 1.3, it has been acknowledged that significantly more test data must be available before a stack design is mature enough to transfer to production. Hence no stacks have been fully transferred, but the mCHP stack module and the aforementioned OAM stack are built in small series as prototypes and must still be kept under control by R&D in order to capture and address relevant failure modes.

STACK DESCRIPTION	STATUS
mCHP stack module for stage 3 PowerCore	Module encapsulation fully outsourced to a Danish supplier.
APU stack module	Is being built in small volumes and delivered as prototypes. Outgoing quality control still followed closely by development.
mCHP/DG stack for stack modules	Basis of production partly completed. Fully manufacturable by supply chain. Outgoing quality control still followed closely by development.

The overall milestone H: "Totally four stack designs transferred to production" has therefore not been met, but the activities and improvements originally foreseen to be sufficient have all been implemented.

WP 3 Cell manufacturing

WP 3.1 Water-based cell manufacturing

In this work package, the possibility of substituting the organic solvent in the cell production with water has been evaluated with special emphasis on slurry stability, compatibility of materials and process window for tape casting with water-based slurries. Finally a number of half cells have been manufactured using water-based tape casting having a performance comparable to that of half cells made using the standard ethanol based tape casting technique.
Milestone I in this work package "Water-based anode developed" has been fulfilled and further more a number of water-based half cells have been manufactured and tested. The tested cells have performances as good as ethanol based cells.

Manufacturing

The main challenge with regard to water-based tape casting has been the formulation of the slurries. Several possible formulations have been evaluated as described in the technical reports BC-1254, BC-1287 and BC-1370 [21],[23],[29]. A commercially available product family was chosen for the continued experiments as described in BC-1344 [24].

The stability of the ceramic particles in water has been evaluated and it was found that the particles are stable at pH values relevant for processing with the chosen formulation [22],[28]. As leaching of yttrium increases with decreasing pH, changing the formulation in a way that leads to lower pH might increase the risk of compositional changes of the YSZ particles.

The processing steps have been optimized in order to minimize the formation of foam and obtain the desired viscosity of the slurries resulting in the formulation of standard recipes for water based electrolyte, anode and anode support slurries for water based tape casting. The slurries have been tapecast both as individual layers which were subsequently laminated to form the half cell as well as multilayer tapecast. Both manufacturing routes have shown good, reproducible results. It has furthermore been shown that the half cells can be sintered under the same conditions as standard ethanol based half cells.

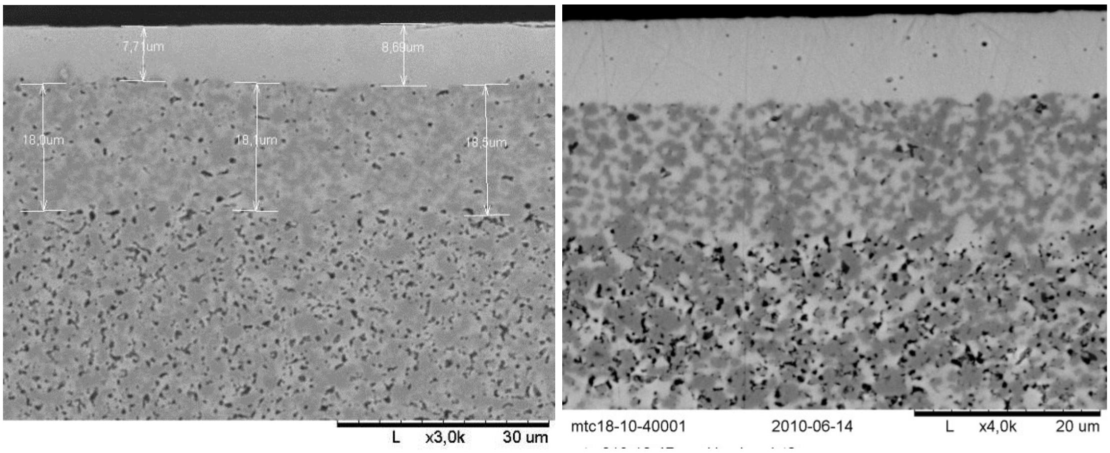

Figure 14: Microstructure of water based (left picture) and ethanol based (right) half cell

Testing

The details of electrochemical and micro-structural analysis are given in the internal technical note BC-1347 [26]. Two water-based half cells have been tested electrochemically. The performances of the two cells are similar and comparable to that of multilayer tapecast ethanol based half cells as shown in Figure 15 where the performance is compared to that of a standard 2G half cell (sprayed electrolyte and anode). The water-based cell shows a very good performance comparable to that of the best ethanol based cells.

The microstructure of the water-based cells has been compared to that of ethanol based cells as well showing a good percolation of the Ni particles and a sufficient porosity to allow proper distribution of the gases during operation.

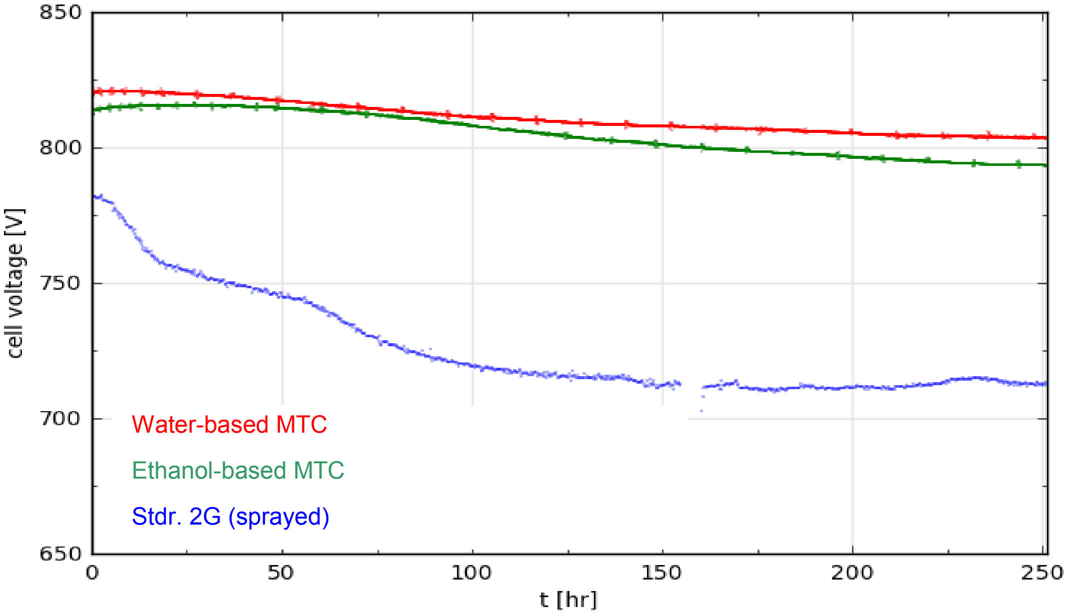

Figure 15: Cell voltage curves for the water-based tape cast laminated cell (red line), for a non-water-based tape cast laminated cell (green curve) and for a stdr. sprayed 2G cell (blue curve). The cells were operated at 750°C, 12 A (0.75 A/cm^2), air to the cathode, 40% H_2O in H_2 to the anode with a flow resulting in a fuel utilization of 26% during durability testing.

WP 3.2 Cells with higher efficiency

Stack cost can be reduced either by reducing the operating temperature to gain a cost reduction in other components of the stack, or by increasing the cell efficiency to reduce the number of cells needed for a given electrical effect of a stack.
Three different paths to higher efficiency were followed in this task:

- Implementation of 2.5 generation cells,
- Scandia-doped zirconia based cells,
- Improved impregnation of cells.

Cells with 2.5G technology in production at Topsoe Fuel Cell

2.5G cells consist of 2G half cells with a screen-printed CGO barrier layer and LSCF/CGO cathode. With these cells, the operating temperature of the fuel cell can be reduced significantly which in turn allows longer interconnect lifetimes. The barrier layer has to be dense in order to prevent reaction between cathode and electrolyte material and it also has to be very thin to limit increases of the specific resistance of the cell.

2.5G has been implemented as a standard product at Topsoe Fuel Cell. Both cell and stack tests show that efficiency of production cells is as good as for the development cells. Equipment for Quick Cell Testing (QCT) has been established and QCT-measurements are implemented in the production QC program. Results shows 25% lower resistance of 2.5G cells compared to 2.1G. (0.36 Ω*cm^2 for 2.5G compared to 0.48 Ω*cm^2 for 2.1G cells). Using the developed cost model we find that higher cost efficiency is obtained with 2.5G cells.

Printability of the CGO barrier layer has shown to be very dependent on the quality of the half cell, since screen printing processes are inherently sensitive to edge curl and unevenness of the substrate. But optimization of the organics in the barrier ink has resulted in significant improvements in printability. The yield of the screen-printing process for 12 cm x 12 cm cells has been increased from 40% to more than 95%.

The 2.5G cathode ink is currently produced in a planetary ball mill. Using this equipment, pre-milling of both LSCF and CGO is necessary in order to avoid agglomerates. As a result, the process is very time-consuming. Pearl milling gives a much more uniform microstructure and eliminates the need for pre-milling. Furthermore, ink leveling of the original cathode formulation is not sufficient as seen from Figure 16. An optimized binder system ensuring good flow properties of the ink has been identified and pearl milling is scheduled to be implemented in production late summer 2012. This will improve quality and dramatically reduce production time. A method to characterize the rheology of screen printing inks has been developed and will be implemented and used as a QC parameter in ink production.

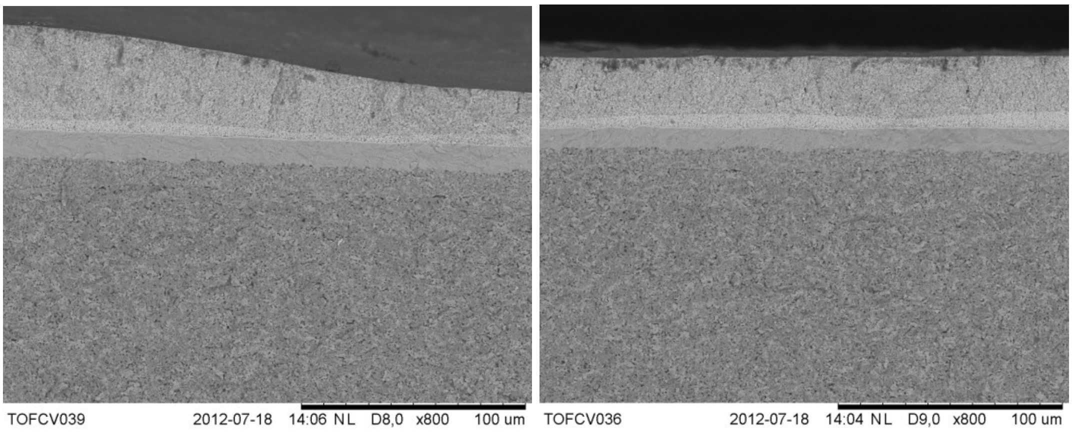

Figure 16: Levelling of Original cathode formulation (left picture) and cathode with improved binder system (right).

Scandia–doped zirconia based cells

Cells with scandia-doped zirconia in electrolyte and anode (‘Scandium cells’) have in earlier projects been shown to have not only lower specific resistance than cells without scandium but also lower degradation in performance. Within the current project flat cells with no edge defects have been manufactured for cell and stack testing. These cells have been manufactured using the lamination technique where the layers of the half cells are tape cast individually and laminated together before co-sintering.
Durability tests of these cells have shown a very low anode degradation that indicates a lifetime of 53.000 hours at 700°C before reaching the critical value of 1 Ω $*cm^2$. This is a dramatic improvement compared to standard 2G cells, and comparable to the predicted requirement for commercialization.

The promising results from cell tests have not been reproduced on stack level. The Sc-doped cells showed an increased leak current and specific resistance was not decreased as expected, even though the cells were applied an optimised LSC:CGO cathode. Increased anode support porosity and short circuits created by the cathode most likely caused this. Adherence of the cathodes was found to be too weak, as delamination was observed after testing. Process and cathode related circumstances disturbed the results, and made it impossible to evaluate the effect of Sc-doping and process changes with respect to specific resistance, sulphur tolerance and degradation behaviour on stack level.

An ongoing task within the project has been to transfer the manufacturing of Scandium cells to a pilot production scale. The preferred technique for the upscaled production is multilayer tape casting and good microstructural results have been obtained by multilayer tapecasting the three thin layers (barrier layer, electrolyte and anode) in the Scandium cell. Due to uncertainties in the supply possibilities and tremendous cost increase of Scandium three layer multilayer tapecast processing was done on the non-Scandium system as well.

Impregnation of cells
Impregnation of the cells by active materials is another way to improve efficiency.
Efficient use of fuels such as i.e,. diesel reformate or JP-8 (jet fuel) calls for a water gas shift reaction (converting CO and H_2O to CO_2 and H_2), which is catalysed by Ni in the anode. These fuels also contain S, a known poison to the Ni catalyst. Impregnation of the anode with nano-particles has been shown to improve sulphur tolerance, both by limiting the S-based increase in area specific resistance of the anode (poisoning of active sites) and by limiting the S-based inhibition of the shift reaction.

A method to infiltrate stacks after reduction with desired active materials has been developed and tested successfully. By applying an underpressure in the stack, it is possible to flush the stack with an infiltration solution. This water based solution contains the precursor of the active materials. Mild heating after the infiltration process assures the formation of nano-particles in the primary electrode structure.

The performance of stacks with and without impregnation was evaluated in diesel reformate at 2 and 25 ppm sulfur levels. The performance of impregnated stacks was superior to the non-impregnated stack and long term tests were used to further characterize the stacks. The main conclusion from the tests was that impregnation increased the shift activity but further work is needed to evaluate if the impregnation process should be implemented.

Test with Scandium-based cells were also accomplished in this part of the project to check the electrochemical activity of Scandium cells with sulfur present. The stacks available for testing have only been mapped for low-sulphur performance. The effect of sulfur up to 10 ppm has been studied and performance of Scandia cells were found to be 12 % better than unimpregnated 2 G cells.

All in all, these results meet the milestone J, “Characterization of sulphur tolerant cells with scandium”.

WP 3.3 Cell cost reduction

Improved production methods are one way to reduce cell cost. In this project we have looked in to Multilayer Tape Casting (MTC), flexo/gravure printing and ultrasonic spraying. All of these processes generate less waste than the current spraying process. Initial results with ultra sonic spraying and flexo/gravure did not show improved anode-electrolyte interface (see below) as obtained from multilayer tape casting. Due to this ultrasonic spraying and flexo/gravure were not considered further. Slot die is another process which on a longer term will be further investigated and evaluated.
By the multilayer tape casting technique the half cell is made in a continuous process in which the layers of the half cell are cast consecutively.

The microstructure of a MTC 2G half cell is comparable to that of a standard 2G half cell with respect to porosities etc. Improved interfaces between layers can be observed and the Ni-percolation seems to be improved as well.

Single cell test was performed on an MTC half cell with a screen printed 2.1G cathode, showing much lower ASR than cells based on tapecasted anode support and sprayed anode and electrolyte (0.25 Ω*cm^2 compared to 0.33 Ω*cm^2 at 750°C).
Detailed impedance analysis shows that the improved performance of the MTC cell is mainly due to a significant decrease of the Ni-YSZ anode charge transfer resistance at the triple phase boundary, suggesting that the improved initial performance of the MTC cell is due to the structural changes observed in the anode either by the slurry processing or by the multilayer tapecast process. The MTC cells are in general higher electrochemically performing when compared to cells having a half cell produced via tape casting of the support and spraying of the active anode and electrolyte.

Not only is the initial performance of the MTC cell better than that of the standard 2G cell, but the initial degradation (first few 100 hours) of the MTC cells is lower as well as illustrated in Figure 17, where the red curve is a std. 2G cell and the blue a MTC cell [29].

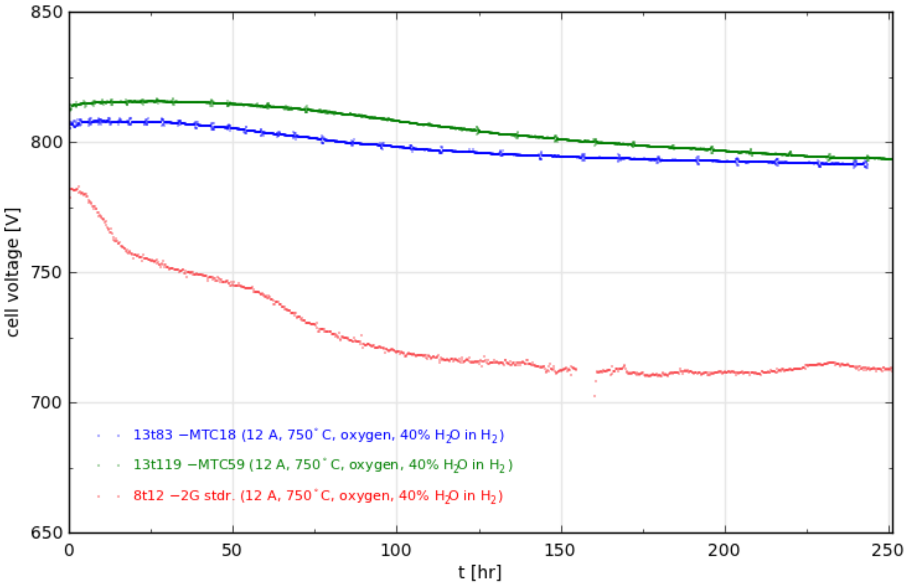

Figure 17: Comparison of short-term durability of MTC cells and the standard 2G production cell. All cells are tested under the same conditions. (750°C, 0,75 A/cm2, 40% H_2O in H_2, =2 to cathode)

A very important prerequisite for the MTC process is the ability to control thickness of thin layers, by placing several doctor blades over a very stable and flat substrate. To obtain the necessary stability at Topsoe Fuel Cell, an extension to the existing tapecasting equipment has been constructed. The above results obtained at Risø DTU have been transferred to Topsoe Fuel Cell where flat, dense half cells with a microstructure comparable to that seen for MTC cells made at Risø DTU have been produced.

When reproducing the original MTC formulation some defects were occasionally observed and the slurry formulations were further developed to avoid these defects.

Standard sintering temperature for half cells is 1315°C. Sensitivity towards sintering temperature has been tested by sintering MTC half cells at varied temperatures 1255°C, 1275°C, 1295°C, 1315°C and 1335°C. Half cells with dense electrolytes have been produced in the full temperature range and the electrochemical performance of the MTC cells is similar even though the sintering temperature was changed 80 °C. Sintering temperature affects the porosity but mechanical strength of these samples is not yet known [30].

The used tape casting slurries contain undesired additives with impact on environment and work has been carried out in order to substitute these with more environmental friendly raw materials.

Three-layer MTC with environmentally friendly slurries (one of two substances substituted) has been tested and showed good results with respect to microstructure and cell performance, referring to the green curve in Figure 17. A high reproducibility in sintering shrinkage, leak tightness, porosity and microstructure is obtained for half cells from the reproduced MTC batches. Reproduction of continuously multilayer tape-casting is thus demonstrated with success and milestone K “Multilayer tape casting tested” is fulfilled. Anode support with both substances substituted has been produced with promising results but is yet to be reproduced.

Mechanical strength is affects cell yield and thereby over all cell cost. Mechanical strength of cells is very dependent on half cell microstructure and work was carried out to further understand the correlation between milling conditions, particle size distribution, sintering shrinkage, porosity and strength. Results show a clear correlation between milling energy and porosity. The mechanical strength of the sintered cells from both standard and environmental friendly MTC-slurries is higher than the standard produced 2G half cells.

Cathode thickness affects efficiency of the cell as well as cell raw material cost and is thereby another important parameter in cost optimization. In order to identify the optimal thickness of the screen printed cathode, a series of different cells were made and tested in the same stack, freezing the cathode thickness to be used in production.

Market and network activities

The national SOFC strategy finalized in autumn 2010 and the strategy for stationary fuel cell application (due in February 2011) has been made with the group of companies, technical institutes and research institutes. This has contributed significantly to the frequent interaction between Topsoe Fuel Cell and the relevant companies in for a, where the technology progress and customers need is discussed. Within the Danish micro combined heat and power project the discussions have continued at workshops every half year. These activities also meant that a project specific forum like the planned sounding board was not necessary, and hence was not established.

As a result of the dedicated development efforts and a range of network activities, in May 2011 a memorandum of understanding was made between the mother company, Haldor Topsoe and Korean SK Holding. This was followed up with the signing of two collaboration agreements in Seoul on May 15, 2012.

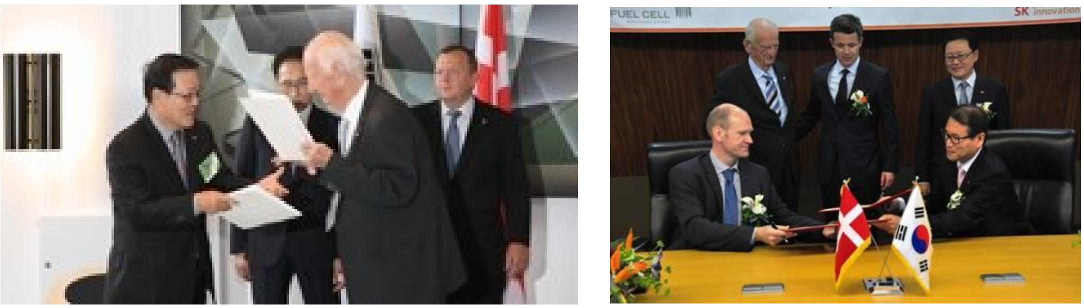

Figure 18: Left: Man Won Jung, Executive Vice Chairman of SK Holding and Dr. Haldor Topsøe, Chairman of Haldor Topsoe at the MoU signing ceremony in Eigtveds Pakhus, Copenhagen on 12 May 2011. Right: Man Won Jung and Lars Martiny, CEO of Topsoe Fuel Cell, at the signing of the cooperation agreements on May 15 in Seoul, Korea.

Publications and other references

1. Jens Ole Gulløv, Fuel Cells Put to Work, Project results with focus on markets and applications, Presentation given DKmCHP workshop in Sandbjerg, June 17, 2011.
2. H. Holm-Larsen, M. J. Jørgensen, N. Christiansen, J. H. Jacobsen: Recent progress in development and manufacture of SOFC at Topsoe Fuel Cell, presented at 2010 Fuel Cell Seminar and Exposition, www.fuelcellseminar.com
3. Sune Danø, Henrik B. Elmose, Niels Erikstrup, Joachim H. Jacobsen, Magnus W. Larsson, Søren Primdahl, Henrik F. Weineisen, Andreas B. Richter, Review of Progress in Development and Manufacture of SOFC at Topsoe Fuel Cell, presented at the Fuel Cell Expo 2012, Tokyo Big Sight
4. Jürgen Rechberger, “First operating experience with AVL SOFC APU Systems”, presented at Fuel Cell Seminar, Orlando, FL, Oct 31-Nov 3, 2011
5. J. Rechberger CMCEE Dresden, “Test experience with the AVL SOFC APU system”
6. J. Rechberger, M. Reissig, M. Hauth, P. Prenninger, AVL List GmbH; Graz/ Austria ”SOFC System Development at AVL”. 10th EUROPEAN SOFC FORUM 2012.
7. Patent application on Electrical Anode Protection, filed May 5, 2010, TOFC-NPS-022 / PCT/EP2010002765: Process for operating a high temperature fuel cell stack
8. Patent application filed May 26, 2011, PCT/EP20112603: Electrical anode reduction of Solid Oxide Fuel Cell
9. N. Christiansen, H. Holm-Larsen, S. Primdahl, M. Wandel, S. Ramousse & A. Hagen: Recent Progress in Development and Manufacturing of SOFC at Topsoe Fuel Cell A/S and Risø DTU, ECS Transactions, 35 (1) 71-80 (2011)
10. C.Gadea et.al: Development of Solid Oxide Fuel Cell components by tape casting of water-based systems, accepted for the 12th Conference of the European Ceramic Society in Stockholm
11. BC-1286: Michela Della Negra, Christina Knöfel: Study of the behaviour of YSZ (TZ8Y) dispersions in water, internal Risø technical report
12. BC-1287: M.Della Negra et.al: Studies of different water-based binder systems and formulations for YSZ electrolyte tape casting, internal Risø technical report
13. BC-1305: C. Gadea: Comparison of assembling methods of water-based half-cell components, internal Risø technical report
14. Anne Hauch, Karen Brodersen and Marie Wandel, Risø: High performing Ni/YSZ anode produced by cost-effective multilayer tape casting, Electrochem and Solids-State Letters, submitted 2011

15. M. Della Negra, C. Knöfel, M. Wandel: Study of the behaviour of YSZ dispersions in water, presented at the 12th Conference of the European Ceramic Society in Stockholm, 2011

16. C.Gadea et.al: Development of Solid Oxide Fuel Cell components by tape casting of water-based systems, presented at the 12th Conference of the European Ceramic Society in Stockholm, 2011

17. Helge Holm-Larsen et al, “Recent progress in Development and manufacture of SOFC at Topsoe Fuel Cell”, presented at Fuel Cell Seminar, Orlando, FL, Oct 31-Nov 3, 2011

18. Magnus Larsson, “SOFC development towards a mCHP market" presented at HFC 2011 - Hydrogen and Fuel Cells in the Nordic Countries", Malmø 26/10-2011.

19. BC 1338: Karen Brodersen (DTU), Jens Vang og Sif Kjølby Topsoe Fuel Cell; Substitution of MEKEt in tape cast anodesupport, Internal Risø DTU report

20. BC -1341: Mads Gudik-Sørensen and Søren Foghmoes; Dispersion of NiO particles in ethanol, a quick test approach, Internal Risø DTU report

21. BC-1254: Water-based slurries for tape casting: stability of suspensions and study of binders

22. BC-1286: Study of the behaviour of YSZ (TZ8Y) dispersions in water

23. BC-1287: Studies of water-based binder systems and formulations for electrolyte tape casting

24. BC-1344: Water based tape casting 2G anode: Optimization with Polymer Innovation system

25. BC-1345: Water based tape casting 2G electrolyte: Influence of casting parameters on final thickness

26. BC-1347: Water based tape casting: production of tape casted laminated and multilayer tapecasted

27. BC-1305: Comparison of assembling methods of water-based half-cell components

28. BC-1353: Study of the behaviour of YSZ dispersions in water solutions having different pH

29. BC-1370:Water based tape casting of YSZ electrolyte with Duramax B1000 binder

30. Hauch, C.Birkl, K.Brodersen, P.Jørgensen; Multilayer tape cast SOFC – Effect of anode sintering temperature; A1007, 10th European SOFC Forum 2012

31. Karen Brodersen, Anne Hauch, Per Hjalmarsson, Peter Stanley Jørgensen and Johan Hjelm, Risø: High performance anode supported SOFC produced by multilayer tape casting, presented at ECerS XII, 2011

32. Helge Holm-Larsen, Mette Juhl Jørgensen, Niels Christiansen, J. H. Jacobsen, Recent Progress in Development and Manufacture of Solid Oxide Fuel Cell at Topsoe Fuel Cell , Fuel Cell Seminar, San Antonio (2010).

33. John Bøgild Hansen, Jørgen Madsen, Jens U Nielsen, Niels Christiansen, Ammonia as SOFC fuel - Assessment from natural gas, coal or biomass to power and heat, Journal of Power Sources, (2010).

34. N. Christiansen, H. Holm-Larsen, S. Primdahl, M. Wandel, S. Ramousse, A. Hagen, Recent Progress in Development and Manufacturing of SOFC at Topsoe Fuel Cell A/S and Risø DTU, ECS transactions vol. 35 no.1, SOFC XII, Montreal (2011)

35. J.B. Hansen, N. Christiansen, J.U. Nielsen, Production of Sustainable Fuels by Means of Solid Oxide Electrolysis, ECS Transactions, vol. 35. no.1. SOFC XII, Montreal (2011).

36. Helge Holm-Larsen, Mette Juhl Jørgensen, Niels Christiansen, J. H. Jacobsen, Recent Progress in Development and Manufacture of Solid Oxide Fuel Cell at Topsoe Fuel Cell, Fuel Cell Seminar, Orlando (2011).

37. Niels Christiansen, Future Fuel Cells, Springer Verlag (in press 2012)

38. Mogens Mogensen, Søren H. Jensen, Sune D. Ebbesen, Anne Hauch, Christopher Graves, Jens V. T. Høgh, Xiufu Sun, Shital Das, Peter V. Hendriksen, Jens U. Nielsen, Aksel H. Pedersen, Niels Christiansen, John B. Hansen, Production of "Green Natural Gas" Using Solid Oxide Electrolysis Cells (SOEC): Status of Technology and Costs, World Gas Conference, Kuala Lumpur, (2012).

39. John B. Hansen, Niels Christiansen, Is SOFC technology ready for the market or is the market ready for SOFC technology, Spriger Verlag, (in press 2012).

40. Anke Hagen, Niels Christiansen, Risø/Topsoe SOFC Activities, Werkstofffragen der Hochtemperatur Brennstoffzelle (SOFC), Juelich (2012).

41. Niels Christiansen, Søren Primdahl, Marie Wandel, Severine Ramousse and Anke Hagen, Status of the Solid Oxide Fuel Cell Development at Topsoe Fuel cell A/S and Risø DTU, 10th European SOFC Forum, Lucerne (2012).

42. Brandon J. McKenna, Niels Christiansen, Richard Schauperl, Peter Prenninger, Peter Blennow, Trine Klemensø, Severine Ramousse, Alexander Kromp, André Weber, Advances in Metal Supported Cells in the METSOFC EU Consortium, 10th European SOFC Forum, Lucerne (2012).

43. BC-1279 Optimization of anode thickness for multilayer “wet on wet” tape-casting of 2G half cells

44. BC-1374 Sintered multilayer tape-cast half cells

45. BC-1278 Laminated 2G half cells based on slurries with DBP and MEKEt free binder and solvent

46. BC-1307 Processing of binder solutions for tape-casting
47. BC-1373 Multilags tape-casting af 2G halvceller med ECO bindersystem
48. BC-1329 Overvejelser om minimering af tapesplid ved multilags tape-casting.
49. BC-1371 Tape-castings erfaringer med henblik på at forstå ”Orme-defekter”
50. BC-1372 Adjustments of binder viscosity in PVB binder solutions
51. BC-1364 Ethanol based Anode Support for SOFC
52. H.L. Frandsen,T. Ramos, A. Faes, M. Pihlatie, K. Brodersen; Optimization of the strength of SOFC anode supports; Journal of the European Ceramic Society 32 (2012) 1041–1052

List of abbreviations

APU:	Auxiliary Power Unit
ASR	Area Specific Resistance
AU	Air Utilization
BOL	Beginning Of Life
CGO:	Cerium gadolinium oxide
CHP:	Combined Heat and Power
D1	Decision point 1
DBP:	dibutylphtalate
DFMEA	Design Failure Mode and Effects Analysis
DG:	Distributed power generation
FU	Fuel Utilization
LSC	Lanthanum Strontium Cobaltite
LSCF:	Lanthanum strontium cobalt ferrite
mCHP:	Micro Combined Heating and Power, other common abbreviations are m-CHP and µ-CHP.
MTC	Multi Layer Tapecasting
NG	Natural Gas
OAM	Open Air Manifold
QCT	Quick Cell test
ScYSZ:	Scandia-doped zirconia
SOFC	Solid Oxide Fuel Cell
SU/SD	Start-Up/Shut Down
TOFC:	Topsoe Fuel Cell
YSZ:	Yttria-stabilized zirconia