STATUS AND RECENT PROGRESS IN SOFC DEVELOPMENT AT HALDOR TOPSØE A/S AND RISO

Niels Christiansen, Steen Kristensen and Helge Holm-Larsen
Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark
Peter Halvor Larsen, Mogens Mogensen, Peter Vang Hendriksen and Søren Linderoth
Riso National Laboratory, DK-4000 Roskilde, Denmark

ABSTRACT

The SOFC technology under development at Haldor Topsøe A/S and Risø National Laboratory is based on an integrated approach ranging from manufacturing of planar anode-supported cells and compact stacks to analysis of total systems. The standard cells are thin and robust with dimensions of 12 x 12 cm² and cell stacks are based on internal manifolding. Production of cells is being up-scaled continuously. The durability of the standard stack design with standard cells has been tested for more than 13000 hours including nine full thermal cycles with an overall voltage degradation rate of about 1% per 1000 hours. Recently, the degradation rate has been significantly reduced by introduction of improved stack component materials. 75-cell stacks in the 1 kW power range have been tested successfully, so far for several hundred hours. Stacks have been delivered in a pre-reduced state to partners and tested successfully in test systems with natural gas as fuel. The consortium of Haldor Topsøe A/S and Risø has an extended program to develop the SOFC technology all the way to a marketable product. Stack and system modelling including cost optimisation analysis is used to develop 5 kW stack modules for operation in the temperature range 700-850°C. To ensure the emergence of cost-competitive solutions, a special effort is focused on manufacturing and testing of larger anode-supported cells. The SOFC program comprises development of next generation cells and multi stack modules for operation at lower temperature with increased durability and mechanical robustness. Development of cells with porous metallic support and new electrode materials is in progress in order to ensure long-term competitiveness.

BACKGROUND

Haldor Topsoe A/S (HTAS) and Risø National Laboratory (Risø) are jointly carrying out a development programme focusing on low cost manufacturing of flat planar anode-supported cells and stacks employing metallic interconnects. In several studies, planar SOFC technology was identified as one of the most promising technologies for future power generation in commercial and industrial CHP applications. The challenge today is to integrate the fuel processing system (FPS) with the cell stacks in order to maximize the system efficiency for various applications. However, the road to success will first and foremost depend on the ability to produce high performance and cost-effective cells and stacks.
In 2002 HTAS and Wärtsilä Corporation entered into a co-operation agreement to start a joint development program within the planar SOFC technology. The development program aims to market highly efficient, clean and cost-competitive fuel cell systems with power outputs above 200 kW for distributed power generation, CHP and marine application.

Establishment of partnerships such as HTAS/Riso/Wärtsilä will serve to strengthen the technology platform and accelerate the development. The outcome of a conceptual study carried out by HTAS and Wärtsilä of a 250 kW planar SOFC system for CHP application and the results from the first 1+ kW HTAS stack tested at Wärtsilä are reported in [1, 2].

**Cell Production Pilot Plant**

The HTAS/Riso cell production pilot plant has now been in operation since early 2002. The production line comprises equipment for large-scale slurry preparation, a 20 meter long continuous tape casting machine, automated spray deposition facilities, automated cell punching equipment and several large batch sintering furnaces. The cell production capacity is approximately 500 cells per week and a rejection rate lower than 10% has been demonstrated. After commissioning of an automated continuous spraying process line in the spring of 2005 the production capacity will reach an amount of more than 1000 cells per week. In order to ensure a high quality and continuous cell improvement all the processing steps are computer-logged, and an extensive on-line database comprising all the relevant material, component and process details has been established in the pilot plant. The standard cells are 12 x 12 cm² with a thickness of 0.350 mm and with a thin 10 micron YSZ electrolyte as previously described [3]. Cells up to 18 x 40 cm² have been manufactured. Currently 18 x 18 cm² cells are tested in stacks.

The cells possess high mechanical strengths of 270 and 220 MPa measured at RT and 800°C respectively in addition to high flexibility. The flexibility of the cells is primarily due to the relatively thin anode support, but because of the inherent difference in thermal expansion coefficient between the NiO/YSZ anode support and the YSZ electrolyte, the cells have a small curvature from edge to edge. The curvature may be reduced to about 2 mm, if the anode support thickness is increased to about 0.500 mm (see Figure 1). However an increased cell thickness will decrease the cell flexibility. A continued cell development has diminished the curvature even for thinner cells as shown in Figure 1.

![Figure 1. Cell curvature as a function of anode support thickness.](image-url)
To assess the degree of reproducibility, ten batches of nominally identical cells were produced and the electrical characteristics of cells from different batches measured. This study led to an increased understanding of the critical processing steps in the cell manufacturing. Variations in the cathode performance seem to be the dominant source of difference in cell performance [4]. Over the period from 2003 to 2004 the spread in cell performance was reduced from 20 to 10% and the average ASR from 0.24 to 0.19 using the same general material composition (see Figure 2).

![Figure 2. ASR measured at 850°C for nominally similar cells (ASR is corrected for the effect of fuel utilisation).](image)

**Cell Test with Different Fuels**

Cells are routinely characterised with hydrogen or syngas as fuel. The performance in synthesis gas and methane/water-vapour (S/C = 2) is generally close to the performance in moist hydrogen. After correcting for fuel utilisation, the ASR was 10-15% higher when running on syngas or methane compared with hydrogen. Recently, ammonia was tested as a fuel with good result. A higher open circuit voltage and increased diffusion losses led to a slightly higher ASR in the case of dry N2/H2 or NH3 as fuels. The results are summarised in Table 1.

**Table 1. Measured area specific resistances at 850°C in various gas mixtures.**

| Fuel          | H2/5%H2O | H2/20%H2O | Syngas | CH4/H2O | N2/H2  | NH3 |
|---------------|----------|-----------|--------|---------|--------|-----|
| ASR [Ωcm²]    | 0.291    | 0.260     | 0.282  | 0.283   | 0.354  | 0.350 |

**Durability Test of Cells**

The durability of the standard anode-supported cells with LSM cathodes was tested at different temperatures, electrical loads as well as different fuels [5]. The cells were in this study operated at a high fuel utilisation of 80% for 1500 hours. The cell polarisation was
found to be the most dominating operation parameter decisive for degradation rate. Under a polarisation corresponding to a current density of 0.25 A/cm² (at a cell voltage of 850 mV) the cell degradation over 1500 hours is very small (about 2 mV/1000 h) regardless of temperature and fuel. Under stronger polarisation (bringing the cell voltage below 750 mV) a larger degradation is observed in the range of 5-20 mV/1000 h at 850°C. At a lower cell operation temperature of 750°C the degradation increases even further to 20-100 mV/1000 h depending on the polarisation in question. These results are further discussed in [5]. Examples of electrical performances under three different constant current densities are given in Figure 3.

![Figure 3. Voltage degradation over time for cells tested at different current densities at 850°C with synthetic pre-reformed methane (S/C 2) at 80% fuel utilisation.](image)

In the cell degradation studies a considerable effort is made to study the presence and effect of foreign phases, which are due to the segregation of impurities and dopants at the interfaces between the electrolyte and electrodes of the current cells [6].

**Distribution of Losses**

To be able to focus the further development it is necessary to be able to split up the resistance in terms emanating from individual components or processes. Such a splitting was achieved based on a careful analysis of impedance spectra obtained on full 4 x 4 cm² cells [7]. The analysis shows that the cathode is the component with the highest resistance, and consequently significant effort is directed to further developing the cathode part of the cell.

**Stack Development**

The HTAS/Risø SOFC stack development is focusing on a low cost reliable design based on thin multi-layers with metallic bi-polar plates (interconnects) with a high volume power density. The stack development is subdivided in a number of important tasks such as: Component machining and shaping, contacting, stack component interfaces, seals, metallic interconnects, coatings and modelling.
The properties of the metallic alloy have proven to be crucial for the stack performance and long-term durability. Oxidative behaviour and contact resistance of a significant number of potential iron-chromium based alloy candidates were investigated [8]. Furthermore, intermediate contact layer candidates were studied in European collaboration projects [9, 10]. The initial contact resistance between a selected steel (Crofer 22APU) and a perovskite ceramic contacting plate was found to be about 7 mOhmcm² for the coated steel increasing with time at a rate of 0.5 mOhmcm² per 1000 h (see Figure 4). Since the life time target for an SOFC stack for residential applications is about 40,000 hours it will be important to establish knowledge concerning the development of the total contact resistance between the interconnect and the cell. The primary contribution to the contact resistance is attributed to the oxide scale. Studies on oxide scale growth as a function of time and temperature have revealed that operation of the actual materials at 950°C for 1000 hours results in similar oxide scale thicknesses as seen during operation at 750°C for 40,000 hours. Recently, accelerated contact resistance measurements based on Crofer 22APU steel coated with a patent pending LSMC perovskite resulted in an initial contact ASR of 3 mOhmcm² increasing by a rate of 1 mOhmcm² per 1000 hours at 950°C in air [11].

![Figure 4. Contact resistance between Crofer 22APU steel (coated and uncoated) and an LSM contacting plate at 750°C in air.](image)

The current HTAS stack design consists of thin-layer repeatable stack components with internal gas manifolds. Several stacks containing 5, 10, 25, 50 or 75 cells with the dimensions 12 x 12 cm² and shaped metallic interconnects were tested in the temperature range 650-850°C with hydrogen, methane or syngas as fuels. Metallic interconnects without coatings or with ceramic and/or metallic coatings were tested giving rise to different stack ASR and different durability properties.

**Long-term Stack Test**

A 5-cell (12 x 12 cm²) stack based on thin plate metallic interconnects with a proprietary ceramic coating was tested for more than 13000 hours including nine full thermal cycles between room temperature and 800°C. The gas composition was 160 Nliter H₂ + 90 Nliter N₂ and 400 Nliter air per hour. The stack current at 800°C was 20 A corresponding...
to a stack ASR of about 1 Ohmcm$^2$ and a stack volume power density of about 2 kW/liter. The thermal cycles have not affected the voltage degradation which stayed at a constant low level slightly below 1%/1000 hours. This reduction of total stack power over time is predominantly due to the voltage loss of two cells in the stack. Figure 5 shows the encouragingly modest degradation of this long-term stack durability test where three out of the five cells (including interconnects) exhibited a very low measurable degradation.

During the long-term durability test of the five-cell stack the electrical losses in the stack was investigated by in situ impedance analysis. The analysis of the stack revealed that the series resistance $R_s$ is dominating from about 3500 hours of operation, whereas the polarisation resistance $R_p$ increases after 9000 hours and reaches an overall level similar to $R_s$. The impedance spectra measured on different repeatable cell/interconnect units at different time intervals since the start was used to break down the losses. Figure 6 shows that one part of the stack has a very constant $R_p$ as well as $R_s$, whereas another part has a constant $R_p$ and an increasing $R_s$. A third part of the stack has constant $R_s$ but an increasing $R_p$. Such measurements on individual segments of the stack are very valuable in connection with post mortem analysis of the stack components. In general, the results revealed that a significant spread in stack component performance was apparent in the early period of stack manufacturing. However, the very low degradation of one part of the stack proves that long-term durability based on controlled stack manufacturing is within reach.

The latest stacks use a new metallic alloy for the interconnect (Crofer 22APU) and a new perovskite coating. This improvement reduced the overall ASR of the stack to about 0.5 Ohmcm$^2$ and further improved the durability. A 5-cell stack had no measurable voltage degradation over 1000 hours and the typical initial decrease in stack voltage was also eliminated. The new coating has eliminated the detrimental deposition of chromium in the LSM cathode, that has typically been observed until now during the first 1000 hours.

**Figure 5.** Durability test (13000 hours +) of 5-cell (12 x 12 cm$^2$) stack at 800°C, 20 A. Ordinate is in mV per cell. (★ all cells, ■ cell 1, ▲ cell 2, x cell 4, x cell 5).

Electrochemical Society Proceedings Volume 2005-07 173
of stack operation in the case of uncoated or insufficiently coated metallic interconnects. The chromium deposition and cathode degradation were studied by TEM-EDAX mapping of the electrolyte-cathode interface (to be published).

Figure 6. Series resistance $R_s$ (solid lines) and polarisation resistance $R_p$ (dot lines) as a function of operation time up to 13000 hours, (800°C, 20 A), determined by in situ impedance analysis on different stack segments (cell Nos. 1, 2 and 4).

A 10-cell stack has been operated with a fuel utilisation of 93% on hydrogen and 55% on methane/water. Due to the very compact stack design the stack volume power density is 2.4 kW per litre stack volume under a conservative safe operation condition of 0.38 W/cm².

Figure 7. Test of a 75-cell (12 x 12 cm²) in the 1 kW+ power range at 800°C, operated with 2000 Nliter H₂ + 1200 Nliter N₂ and 5075 Nliter air per hour, 28% fuel utilisation at a current of 18 A.
A 75-cell stack was delivered to Wärtsilä’s test system and successfully started on September 16, 2004 with natural gas as system fuel. One stack provides about 1.2 kW power to the Finnish national grid. In 2005 a total of four stacks will be used in the system to achieve up to 5 kW electrical power.

**Development of Future Generation Cells**

The next generation of cells (3G) being developed in the HTAS/Risø consortium is thin film electrolyte cells with a ferritic stainless steel support on the anode side. The status is that 4 x 4 cm² half cells have been fabricated with dense electrolytes. Currently the effort is on up-scaling this to larger cell sizes. Work on utilizing ceria as an anode component is continued in order to enhance the robustness towards red-ox cycles and carbon precipitation. $R_p$ values around 0.1 Ohmcm$^2$ were obtained in CH$_4$ fuel with 3% H$_2$O at 650°C using cone electrodes of gadolinia doped ceria. A promising new LSCF cathode material, which has an area specific resistance of 0.11 ohmcm$^2$ at 600°C on ceria electrolyte, has been identified. These cathodes are also being applied on the existing anode supported cells for operation temperatures in the intermediate range of 700°C.

**Modelling and System Analysis**

The basis case for fuel processing when the feedstock is natural gas is shown in Figure 8. The system which has been further described in [1] features an adiabatic pre-reformer for conversion of higher hydrocarbons and an anode recycle blower to provide steam and heat for the reforming reactions. The unspent fuel which is not recycled is burned in a catalytic combustor. In the system analysis the electrical efficiency at the design point is predicted to be 55%, whereas the total system efficiency is around 84%. For process simulation a three-dimensional mathematical stack model has been established and integrated into the HTAS proprietary heat and mass balance program called GHEMB. This forms a very suitable basis for flexible and accurate system analysis. The system analysis is further described in [12] where it is demonstrated that a low to moderate stack degradation of about 1%, as verified experimentally above, can be counteracted by allowing a combination of reduced fuel utilisation and (from 85 to 75%), and an increased stack temperature (by 40°C) maintaining the rated output over 40,000 hours of operation and an efficiency penalty of only 3 percentage points.

![Figure 8. Process flow diagram for an SOFC system.](image-url)
REFERENCES

1. E. Fontell, T. Kivisaari, N. Christiansen, J. B. Hansen and J. Pålsson, *Journal of Power Sources*, **131**, Issues 1-2, (2004).

2. E. Fontell, J. B. Hansen, T. Kivisaari, J. Pålsson, M. Jussila, J. U. Nielsen, *Design and Construction of 5 kW planar SOFC System for System Development*, poster presented at Fuel Cell Seminar, San Antonio, (2004).

3. N. Christiansen, S. Kristensen, H. H. Larsen, P. H. Larsen, M. Mogensen, P. V. Hendriksen, S. Linderoth, in *SOFC-VIII*, S. C. Singhal and M. Dokiya, Editors, *PV2003-07*, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).

4. A. Hagen, M. Menon, S. Ramousse, P. H. Larsen, R. Barfod, P. V. Hendriksen, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

5. A. Hagen, R. Barfod, P. V. Hendriksen, Effect of Operational Parameters on Long-Term Stability of SOFCs, *in these proceedings*.

6. K. V. Hansen, M. Mogensen, in *SOFC-VIII*, S. C. Singhal and M. Dokiya, Editors, *PV2003-07*, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).

7. R. Barfod, A. Hagen, S. Ramousse, P. V. Hendriksen and M. Mogensen, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

8. T. F. Petersen, S. Linderoth, J. Laatsch, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

9. P. Huckowski, N. Christiansen, V. Shemet, J. Piron-Abellan, L. Singheiser, W. J. Quadakkers, Oxidation Induced Lifetime Limits of Chromia Forming Ferritic Interconnector Steels, *First International Conference on Fuel Cell Development and Deployment*, Storrs, (2004).

10. E. Konycheva, J. Laatsch, E. Wessel, F. Tietz, N. Christiansen, L. Singheiser and K. Hilpert, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

11. L. Mikkelsen, A. R. Dinesen, P. V. Hendriksen, Interface Resistance between FeCr Alloys and La$_{0.85}$Sr$_{0.15}$MnO$_3$, *in these proceedings*.

12. J. B. Hansen, J. Pålsson, J. U. Nielsen, E. Fontell, T. Kivisaari, P. Jumppanen and P. V. Hendriksen, *Design Aspects of a 250 kW NG fuelled SOFC System – Strategies to counteract Stack Performance Degradation*, 2003 Fuel Cell Seminar, Florida, (2003).