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Christiansen, N.; Hansen, J.B.; Kristensen, S.; Holm-Larsen, H.; Linderoth, Søren; Hendriksen, Peter Vang; Larsen, Peter Halvor; Mogensen, Mogens Bjerg

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SOFC Development Program at Haldor Topsøe/Risø National Laboratory - Progress Presentation

N. Christiansen[1], J. B. Hansen[1], S. Kristensen[1], H. Holm-Larsen[1], S. Linderoth[2], P. V. Hendriksen[2], P. H. Larsen[2], M. Mogensen[2]

[1]Haldor Topsøe A/S, Lyngby, Denmark

[2]Risø National Laboratory, 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. Today, 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. The standard cells are thin and robust with dimensions of 12 x 12 cm^2 and the cell stacks are based on internal manifolding. Production of cells in a pilot production plant is being up-scaled continuously. Stack and system modelling including cost optimisation analysis is used to develop 5 kW stack modules for operation in the temperature range 700-850^{o}C. High volume power density stacks based on thin plate metallic interconnects have been tested for more than 10000 hours including thermal cycling with encouragingly small degradation. Stacks in the 1+ kW size classes have been tested in methane as well as CO rich gas. 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 cathode materials is in progress in order to ensure long-term competitiveness.

Background

Haldor Topsøe 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. The challenge today is to integrate the cell stacks with the fuel processing system (FPS) in order to maximize the system efficiency for various fuels and applications. However, the road to success will first and foremost depend on the ability to produce high performance, cost-effective, robust cells and stacks.

HTAS has in 2002 entered into collaboration with the Finnish company Wärtsilä for large-scale SOFC systems (200kW+). Wärtsilä's responsibility in this regard includes system level integration and marketing. Establishment of partnerships such as HTAS/Risø/ 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 is reported in [1].

Cell production and development

The cell production capacity of the HTAS/Risø pilot production line is approximately 500 cells per week and a rejection rate lower than 15% has been demonstrated. A further upscale to 1000 cells per week is underway in 2004 - 2005. 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 cm^2 with a thickness of 0.350 mm as described previously [2]. However, the cell size has also been successfully scaled up and 18 x 40 cm^2 cells are currently being included in the stack development for testing.

A study of the reproducibility of the cell production campaigns in 2003-4 has been carried out. This study clearly pointed out the cathode as the least reproducible component of the cell [3]. To be able to focus the further development it is necessary to be able to split up the overall cell resistance in terms emanating from individual components or processes. The analysis based on impedance spectroscopy of full cells [4] shows that the cathode is the component with the highest resistance at temperatures below 850^{o}C, and consequently significant effort is directed to further developing the cathode part of the cell, (see the following).

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 have been investigated [5, 6]. Furthermore, intermediate contact layer candidates have been studied in a European collaboration project [7, 8]. The initial contact resistance between a selected steel (Crofer 22APU) and a perovskite ceramic contacting plate was found to be about 7 $mOhmcm^2$ for the coated steel increasing with time at a rate of 0.5 $mOhmcm^2$/1000h. This is acceptable for a durable stack. Thermal cycling experiments have revealed that the contact couple alloy/LSM may be thermally cycled more than five times from room temperature to 750^oC with no detrimental effects.

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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 cm^2 and shaped metallic interconnects have been tested in the temperature range 650-850^oC with hydrogen, methane or syngas as fuels. Metallic interconnects without coatings or with ceramic and/or metallic coatings have been tested giving rise to different stack ASR and different durability properties.

Long-term stack test

A 5-cell (12 x 12 cm^2) stack based on thin plate metallic interconnects with a proprietary ceramic coating has now been tested for more than 9000 hours including seven full thermal cycles between room temperature and 800^oC. The gas composition is 160 Nliter H_2 + 90 Nliter N_2 and 400 Nliter air per hour.

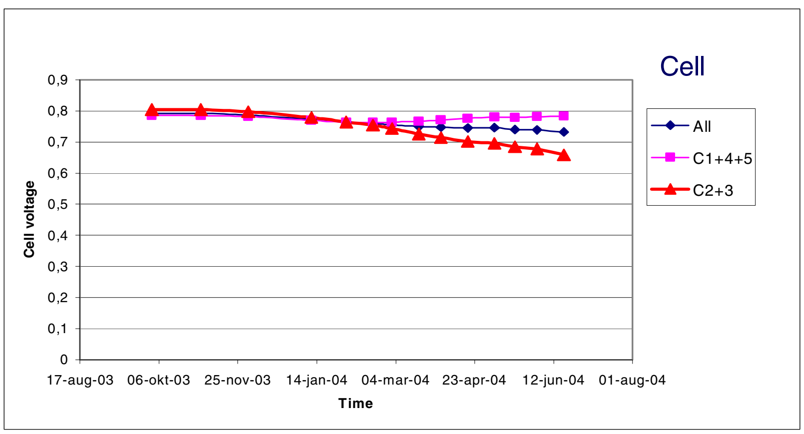

Figure 1. Durability test (9000 hours +) of 5-cell (12 x 12 cm^2) stack at 800^oC, 20 A.

The stack current at 800^oC is 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 stays 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. Impedance spectroscopy analysis on the stack has revealed that the series resistance is dominating until about 3500 hours of operation time, whereas the polarisation resistance dominates after 9000 hours. Figure 1 shows the encouragingly modest degradation of this long term stack durability test where three out of the five cells (including interconnects) have no measurable degradation.

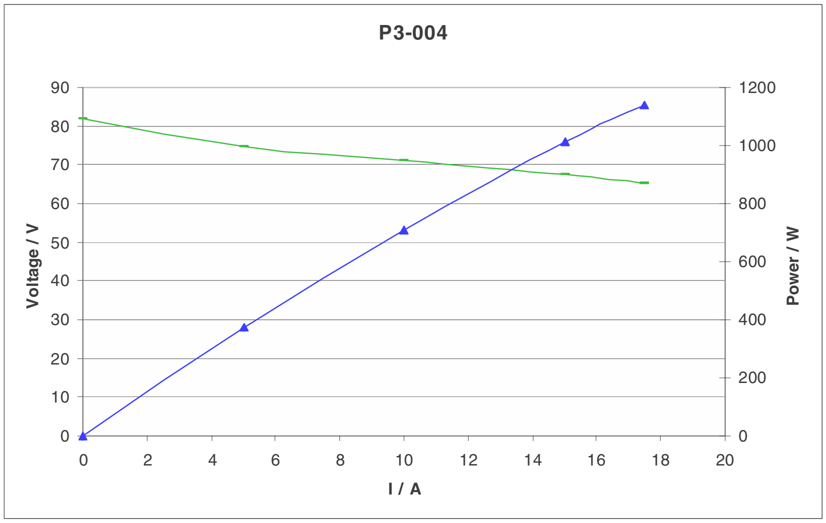

Figure 2. Test of a 75-cell (12 x 12 cm^2) in the 1 kW+ power range at 800°C, operated with 2000 Nliter H_2 + 1200 Nliter N_2 and 5075 Nliter air per hour, 28% fuel utilisation at a current of 18 A.

The latest stacks use a new metallic alloy for the interconnect (Crofer 22APU) and a new perovskite coating. This improvement has reduced the overall ASR of the stack to about 0.5 $ohmcm^2$ and further improved the durability. A 5 cell stack has no measurable voltage degradation over 1000 hours and the typical initial decrease in stack voltage has also been eliminated. Due to the very compact stack design the stack volume power density is 2.4 kW per liter stack volume under a conservative safe operation condition of 0.38 W/cm^2.

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 2 x 2 cm^2 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. 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.

Modelling and system analysis

The basis case is using natural gas as fuel. The system which has been further described in [1] features an adiabatic pre-reformer for conversion of higher hydrocarbons and an anode recycle to provide steam and heat for the reforming reactions. The unspent fuel which is not recycled is burned in a catalytic combustor. For process simulation a 3-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 has been further described in [9] where it has been 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.

The system analysis has now been extended to include diesel, methanol and DME as fuels. Two different routes for diesel processing have been studied. One is based on Catalytic Partial Oxidation, the other on HydroDesulphurisation. The Methanol/DME systems are based on a new proprietary lay-out where the fuel is methanated before the stack. These studies are further described in [10]. In Table 1 is shown a comparison of the efficiencies calculated for the different 250 kW_e SOFC CHP systems. The relative stack sizes are also included.

Table 1

Fuel	El eff. %	Total eff. %	Stack size %
Natural gas	55.5	83.6	100
Methanol	51.5	84.6	93
DME	49.2	83.5	93
Diesel CPO - O_2/C= 0.30	42.9	85.4	114
Diesel HDS	51.5	79.7	81

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