NEW DEVELOPMENTS IN STACK TECHNOLOGY FOR ANODE SUBSTRATE BASED SOFC

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ABSTRACT

During the last two years the development program on anode supported SOFC in Jülich has focused on the improvement of three major aspects of the stack technology; low resistance contacts between cells and interconnects, gas tight glass-ceramic seals and assembly procedures. These activities are targeted at producing and testing a 20 kW SOFC system in 2003. One of the intermediate milestones in this program is the building and testing of stacks of 20 cells with an electrochemical footprint of 361 cm². At a power density of 0.3 W/cm² a stack of this size will generate over 2 kW of electrical power at 800 °C. The modified stack design used for these kW-class stacks is presented as well as the results of a number of short stacks of different sizes and numbers of cells, tested under various conditions leading up to this milestone.

INTRODUCTION

During the past few years R&D on the planar anode substrate based solid oxide fuel cell (SOFC) at the Forschungszentrum Jülich has progressed steadily. In the most recent years the emphasis in the program was directed towards the improvement of stack technology. The major aspects investigated have been the electrical contact between the successive layers in the stack and the sealing technology, next to the development of improved assembly procedures (1, 2). Until 1999 the basis of the Jülich stack design was a block comprising of substrate cells and interconnect plates that was placed inside a metallic housing constituting the external manifolds (2). This design allowed the stacks to be operated in a cross-flow configuration only. The design put severe demands on the sealing materials used. During the sealing procedure, perpendicular surfaces in three directions had to be sealed simultaneously causing large deformation and shearing in the glass-ceramics during curing. This frequently led to a loss of gas tightness in the stacks.
To counter these problems the design was modified. In the new design the sealing surfaces are all in planes perpendicular to the stacking direction, i.e. only in two directions, omitting the large deformations observed before in the stacking direction. This could only be realised by changing from an external to an internal manifold. A number of stacks tested in such a design with internal manifold and cross-flow configuration showed good electrochemical data. Especially the problems with gas tightness of the stacks were solved.

Adopting an internal manifold design opened the possibility to change the gas flow configuration. Modelling calculations showed that with the Jülich substrate based single cells, temperature distributions across the cells depended strongly on gas flow directions. Operating a stack in cross-flow generates an asymmetric temperature distribution with rather large temperature gradients (3). These effects are mitigated by operating the stack in either a counter-flow or a co-flow configuration. A final design modification was therefore made to facilitate this mode of operation.

STACK DESIGN

Stack configurations with an internal manifold and a counter-flow configuration have been designed and tested before for planar type self-supporting electrolyte SOFCs (4, 5).

Extensive modelling of the gas flow was performed to optimise the geometry and the dimensions of the feed tubes, the manifolds and the gas channels in the interconnect plate.

Fig. 1 shows a schematic view of a 2-cell stack in the so-called E-design with internal manifold and counter-flow configuration. Fuel and oxidant gases enter the stack both from the bottom through two tubes each on the corners of opposite sides. In each layer, containing only one cell, the gases are distributed over the entire width of the cell inside the manifold. Through the channels in the interconnect the gases are distributed over the entire surface of anode and cathode, respectively. In the exit manifold the gases are collected in the centre and leave the stack through one tube on each side. In Fig. 1 the manifolds and gas channels on the fuel side are visible, although not all gas channels are drawn. Those on the air side are an exact mirror image.

Fig. 1 Schematic view of a 2-cell stack in E-design with internal manifold and counter-flow configuration
STACK ASSEMBLY

Stacks with 2, 4 and 5 cells, 10 cm x 10 cm or 20 cm x 20 cm in size, were assembled. These cells have an effective electrode area of 81 cm² and 361 cm², respectively. Details on cell manufacturing have been reported previously (1).

Interconnect plates were made from the commercial available ferritic steel 1.4742 (X10CrAl18). Gas channels and manifolds were machined into the steel plates. On the fuel side a Ni-mesh was spot-welded to the ribs separating the gas channels in order to form an electrical contact between the interconnect and the anode substrate. On the air side a layer of lanthanum cobaltite (LC) was applied on to the ribs using the Wet Powder Spraying (WPS) technique for contacting the interconnect with the cathode (see Fig. 2).

For sealing and insulation a glass-ceramic with a defined composition from the BCAS-system (BaO-CaO-Al₂O₃-SiO₂) with minor additions of other oxides was used. The glass powder was suspended in an organic solvent using ultrasonic agitation. After placing the cell in the interconnect plate the suspension was applied to the circumference of the cell and the manifolds using an automated dispenser (see Fig. 2). Before piling the layers on top of each other the glass powder suspension was allowed to dry for 2 h at 60 °C.

![Fig. 2 Assembly of a 5-cell E-design stack; air side of interconnect with LC-coated ribs and manifolds (top left), fuel side of interconnect showing the Ni-mesh and a 20 cm x 20 cm cell (bottom left), all five layers with cells and glass suspension coating and top plate (right).](image)

After assembling the stacks were transferred to a furnace for electrochemical testing. The stacks were heated with 1 K/min to a temperature between 700 and 850 °C depending on the softening temperature of the glass used. At this temperature a mechanical load was applied to the stacks. During heating and curing of the glass-ceramic the stacks were purged with air on the cathode side and argon on the anode side.
RESULTS

E-Design stack tests

The first stacks assembled in E-design were 2-cell stacks with cells of 10 cm x 10 cm with an electrochemically active area of 81 cm². After curing of the glass-ceramic seal the anodes were reduced at 900 °C by step-wise increasing the amount of hydrogen added to the purge gas on the anode side until pure humidified hydrogen flowed. The stacks were operated in a counter-flow configuration with 3% humidified hydrogen and air. Current-voltage characteristics were measured at various temperatures between 900 and 700 °C. Fig. 3 shows the current-voltage characteristics of three 2-cell stacks recorded at 800 °C with 3% humidified hydrogen as fuel gas. The three stacks showed good reproducible performance with the third stack in the series yielding slightly better results. At a working voltage of 1.4 V for the stack (0.7 V/cell on average) a current density of over 0.6 A/cm² was obtained, i.e. a power density of 0.42 W/cm². Fuel utilisation amounts to around 17% at this current density.

In order to simulate more realistic stack operation conditions current-voltage characteristics were recorded for one of these 2-cell stacks at 800 °C with lower hydrogen flows and higher steam contents. These current-voltage characteristics are shown in Fig. 4. A doubling of the fuel utilisation had only a minor effect on the performance. Increasing the steam content of the fuel gas to 50% lowered the stack voltage only with around 100 mV at current densities of 0.5 A/cm² and higher, whereas the open circuit voltage (OCV) dropped around 250 mV. With the lowest fuel flow rate used, but still with the 50% steam content, the performance of the stack tends to bend away at current densities above 0.3 A/cm² due to depletion of the fuel. Still, at a fuel utilisation of 60% (i.e. with a steam content of 50% in the inlet this simulates 80% fuel utilisation at stack outlet) reasonable power densities of 0.3 W/cm² could be obtained.

The modified stack design was further tested by assembling stacks with an increased number of cells (4-cells 10 cm x 10 cm) and with an increased active area (2- and 5-cells 20 cm x 20 cm). Fig. 5 shows both the current-voltage as well as the current-power characteristics of these stacks. The power output could thus be successively increased up to 800 W, which was reached for the 5-cell (361 cm²) stack at 800 °C. Noteworthy is the excellent performance of the 2-cell (361 cm²) stack, which showed a current-voltage characteristic that was even better than the stacks with the smaller (81 cm²) cells. At 1.4 V for the stack (0.7 V/cell on average) a current-density of 0.8 A/cm² was reached with a fuel utilisation (\( u_f \)) of 25%. This was very close to the best values obtained for single cells (16 cm²): 0.9 A/cm² at 0.7 V (\( u_f = 10\% \)). This demonstrates the potential of the anode substrate cells in the modified E-design, where power densities above 0.5 W/cm² at 800 °C can be obtained.

The 2-cell (361 cm²) stack produced a power of 400 W at a current density of 0.8 A/cm² (289 A @ 1.4 V). In comparison the 5-cell (361 cm²) stack produced less power as expected. This could be attributed to one of the cells, which showed a considerably lower performance than the other four cells in the stack, most likely due to a higher contact resistance at one of the interfaces.
Fig. 3 Current-voltage characteristics of three 2-cell E-design stacks.

Fig. 4 Current-voltage characteristics of a 2-cell E-design stack in dependence on fuel gas flow rate and fuel gas steam content.
Fig. 5 Stack voltage (open symbols) and stack power (closed symbols) vs. current density for selected 2-, 4- and 5-cell E-design stacks.

In Fig. 6 the power produced by the 5-cell (361 cm²) stack is shown at several operating temperatures. At 900 °C the maximum power obtained was 1084 W. This could have been considerably higher if not the stack had suffered from both air and fuel depletion. Fig. 7 shows the corresponding current-voltage characteristics of the stack together with the fuel and air utilisation during operation. At current densities above 0.8 A/cm² both are in the range from 60 to 80%. The low gas flow rates used were restricted by the test equipment. At these high current densities the voltage broke away due to insufficient air and/or fuel supply. Nevertheless, the results demonstrate the potential of stacking the anode substrate cells in the modified E-design in the kW range. Shortly tests of 10- and 20-cells (361 cm²) stacks will be conducted.

After recording a first set of current-voltage characteristics all stacks were subsequently operated at 800 °C under a constant load of 0.3 A/cm² up to a few hundred hours to study the initial degradation behaviour. All stacks suffered from a relatively high degradation rate. Most likely reasons are the corrosion of and Cr-evaporation from the unprotected steel used as interconnect. Also the deterioration of the contact layers between cells and interconnect may account for the rapid performance loss of the stacks. These reasons are under investigation (6) and improvements will be transferred to a next series of stack tests. One possible cause for the observed degradation of the stacks, i.e. the deterioration of the cells, can be excluded as is shown in the next section.
Fig. 6  Power vs. current density characteristics of the 5 cell (361 cm²) E-design stack in dependence on the temperature.

Fig. 7  Voltage vs. current density characteristics of the 5-cell (361 cm²) E-design stack in dependence on the temperature; fuel and air utilisation are also shown.
Single cell tests

Long term operation tests were conducted in order to study the performance stability of single cells in an inert environment. The cells (5 cm x 5 cm; effective electrode area 16 cm²) were tested in an all ceramic (alumina) housing using a gold seal and Ni- and Pt-meshes for current collecting at anode and cathode side, respectively (7). Fig. 8 shows the time dependence of the voltage recorded for the longest running single cell operating at a current density of 0.3 A/cm² at 750 °C. In the first 300 h of continuous galvanostatic operation the cell voltage dropped 25 mV to a value of around 800 mV. This behaviour is, however, particular for this single cell. Other single cells, mainly in short term experiments, showed the opposite behaviour, i.e. in the first 200 h of galvanostatic operation the voltages increased, usually 10 to 20 mV, before reaching a constant level. The degradation observed in this particular case is also distinctly different from the behaviour observed for the stacks.

![Fig. 8 Time dependence of the voltage of a single cell during operation at 0.3 A/cm² at 750 °C.](image)

In the period between the 4200th and the 5700th hour of operation an off-set in the galvanostatic control caused the decrease and increase of the cell voltage. In this period also, the cell had to be shut off completely (cooled down to room temperature) for a period of 200 h. Nevertheless, after more than 6500 h of almost continuous galvanostatic operation the cell voltage is still around 800 mV, i.e. for the single cell the degradation rate is below 0.1 %/1000 h. A similar degradation result was obtained in the long term operation test over 5000 h of another cell, which showed the more common behaviour in the first 200 to 300 h of operation.
CONCLUSIONS

A modified stack design with internal manifold and counter-flow configuration has been constructed and tested with anode substrate SOFCs. Stacks with up to 5 cells, 20 cm x 20 cm in size, have been assembled and produced more than 1 kW power at 900 °C and 0.8 kW power at 800 °C with 3% humidified hydrogen as fuel gas. For the large cells (361 cm² effective electrode area) assembled in the modified stack design power densities over 0.5 W/cm² have been reached at 800 °C.

Single cells operation under a constant load of 0.3 A/cm² at 750 °C with hydrogen/air showed stable operation over a period of over 6500 h.

ACKNOWLEDGEMENTS

The authors wish to thank all members of the Jülich SOFC substrate concept team, especially Mr. G. Blaß and his group for cell manufacturing and Mr. R. Erben and Mr. H. Wesemeyer for conducting the cell and stack electrochemical tests.

REFERENCES

(1) P. Batfalsky, H-P. Buchkremer, D. Froning, F. Meschke, H. Nabielek, R.W. Steinbrech and F. Tietz, in Proceedings of the 3rd International Fuel Cell Conference, p. 349, Nagoya (1999)
(2) D. Stöver, U. Diekmann, U. Flesch, H. Kabs, W.J. Quadakkers, F. Tietz, I.C. Vinke, in Solid Oxide Fuel Cells VI, S.C. Singhal and M. Dokiya, Editors, PV 9919, p. 812, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).
(3) D. Stolten, D. Froning and L.G.J. de Haart, in 4th European Solid Oxide Fuel Cell Forum, A.J. McEvoy, Editor, p. 347, European Fuel Cell Forum, Oberrohrdorf (2000).
(4) T. Hikita, M. Hishinuma, T. Kawashima, I. Yasuda, T. Koyama and Y. Matsuzaki, in Solid Oxide Fuel Cells III, S.C. Singhal and H. Iwahara, Editors, PV 93-4, p. 714, The Electrochemical Society Proceeding Series, Pennington, NJ (1993).
(5) Y. Akiyama, T. Yasuo, N. Ishida, S. Taniguchi and T. Saito, in Solid Oxide Fuel Cells III, S.C. Singhal and H. Iwahara, Editors, PV 93-4, p. 724, The Electrochemical Society Proceeding Series, Pennington, NJ (1993).
(6) C. Gindorf, L. Singheiser and K. Hilpert, in This issue; V. Shemet, J. Piron-Abellan, L. Singheiser and W.J. Quadakkers, in This issue; O. Teller, W.A. Meulenberg, F. Tietz and W.J. Quadakkers, in This issue.
(7) L.G.J. de Haart, K. Mayer, U. Stimming and I.C. Vinke, J. Power Sources 71, 302 (1998).