Improving Durability of SOFC Stacks
("IDUSOFC")

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Abstract

In the project the degradation rate as a function of time and thermal cycling of solid oxide fuel cell (SOFC) stack components was studied. The investigation included several types of electrolytes, anodes, cathodes and both ceramic and metallic interconnects. Also the time development of the contact resistances between cells and interconnects were investigated. Furthermore, both materials and fabrication procedures were developed in order to simultaneously decrease the cost and increase the electrochemical performance of the cells.

1. Introduction

It is known that SOFC lifetime may be very long, more than 50000h, if the tests are carried out with a low power density and not too high fuel utilisation. However, both high power densities, high fuel utilisation and long life times are necessary in order to make SOFC technology competitive with traditional power generation technology. A high power density means a high cell voltage and current density, which in turn means a low area specific resistance (ASR). Thus, there is an urgent need for a better understanding of the relationships between the parameters: ASR, operation conditions, manufacture procedures, materials composition and degradation rate. This need was the main background for launching this project.

Due to the confidential nature of some of the results, and in order to keep this open report reasonably short, only examples of results and the qualitative overall results are given. A list of publications derived from the project is given at the end of this report.

2. Partnership

The project was a co-operation between the five main European SOFC industrial developers (in the year 1995), all three European research centres involved in SOFC R&D and two of the leading universities in the field. The participants are listed below:

Risø National Laboratory (Co-ordinator)	DK
FZ-Jülich	DE
ECN, Petten	NL
Imperial College	GB
Oslo University	NO
Siemens	DE
Haldor Topsøe A/S	DK
Daimler-Benz/Dornier (until 30th Nov.1997)	DE
Rolls-Royce	GB
Statoil A/S	NO

3. Objectives

The objective of the project was the reduction of the cost of SOFC by improving the durability without increasing the production cost or decreasing the stack performance; preferably the production costs should be decreased and the cell performance increased. This was to be achieved through a better understanding of the fundamentals of the degradation processes of SOFC components, and through improved fabrication techniques of starting powders and ceramic cells, aiming at appropriate (rather than maximum) purity and quality levels of active components. The measurable objectives were:

1) A voltage degradation lower than 1% per 1000 h at steady state operation with 300 mA/cm^2, and at a reasonable temperature in the range between 800 and 1000°C. The internal area specific resistance should not be above 1 Ωcm^2 in a single stack element (i.e. a cell with interconnects on both sides). Fuel utilisation should be at least 80%.
2) A thermal cycling resistance resulting in less than 0.5% degradation per thermal cycle from operating to room temperature and back to operating conditions.

Regarding 1) it was mentioned that there was a considerable risk that it might not be possible in this project to fulfil all of the requirements for one given set of operating conditions.

4. Technical description

The most important project tasks are listed below:
- Fabrication of improved powders and samples
- Investigation of the effect of common YSZ-contaminants on stability and conductivity
- Interdiffusion at the cathode/electrolyte interface
- Mechanical testing of the electrolyte and influence of electrodes on strength
- Correlations between electrode structures and performance including durability testing
- Effect of internal reforming of natural gas on the durability of Ni-YSZ anodes
- Fabrication and testing of cells: Base cells, improved low cost cells, supported cells etc.
- Improvement of mechanical strength of cells
- Advanced non-destructive testing (NDT) of cells
- Endurance testing of single cells
- Oxidation, nitridation and carburization of metallic interconnect materials
- Reactions between metallic interconnect, cathode and anode
- Effects of water vapour on the properties of SOFC materials
- Chemical stability and compatibility of the stack materials
- Endurance testing of single cells (2 x 3 cm^2) with realistic current collectors
- Endurance testing of cells in stacks under realistic conditions
- Cost/benefit calculations

5. Results

Work has been performed on all these tasks and a wealth of results generated. The main results are briefly summarised in the list below:

- Low cost powders based on mixed lanthanide oxide instead of pure expensive lanthanum oxide were produced (patent obtained)
- The effects of small concentrations of Si, Mn, Ni, Fe and Cr on conductivity and stability of YSZ have been studied over prolonged periods
- The diffusion rate of MnO_X into YSZ has been determined as a function of temperature
- The area specific resistance (ASR) of cells with thick (ca. 180μm) 8YSZ electrolyte was improved from almost 1Ωcm^2 for base cells at 950°C to below 0.4Ωcm^2 at 950°C and 0.7Ωcm^2 at 850°C by improving the cathode
- Durability of electrodes and cells is sufficient at low current densities, but above 300mA/cm^2 degradation becomes more severe
- It was assumed at the beginning of the project that the degradation of cells and stacks was mainly due to thermally activated processes such as diffusion of materials into each other. This has proven not to be the case for the cells, which may be made rather stable even at high temperature as long as the current density is low. At high current density the situation is more complicated, and the degradation mechanisms are not yet fully understood
- Very long test periods of many thousands hours are needed in order to determine accurate degradation rates in the order of 1% per 1000h or lower
- When no current is drawn the electrodes are not seen to degrade within experimental uncertainties, even at 1000°C
- Degradation by thermal cycling of improved cells was about 0.01% per cycle, well below the target of 0.5% per cycle
- Methods of improving the mechanical strength of the cells have been demonstrated
- The main degradation problems are associated with the contact between cell and metallic interconnects. Establishment of stable contacts between cells and a metallic chromia forming interconnect has proven to be difficult even at temperatures of 850°C. Coating of the metal may be necessary at both the anode and the cathode side
- Two different coating systems for the cathode side, one based on different perovskite layers, and one based on spinel and perovskite layers, were shown to hold a low resistance over extended time. Similarly, coating technology was developed which counteracts corrosion problems at the anode contact
- Extensive studies of compatibility of cell and stack components have been carried out including the study of 14 compositions of sealing glasses
- Ten different non-destructive evaluation (NDE) techniques have been studied, and two of them, i.e. "through transmission ultrasonic" and "thermography", were shown to be good candidates for evaluation of cells in a mass production line
- Even though the objectives of the project were realistic for the three year project, cost calculations revealed (as expected) that these targets are not sufficient for commercialisation of SOFC technology. A further decrease of the degradation rate with time and a lowering of ASR, i.e. an increase of the power density, W/cm^2, is necessary

A few selected detailed results are presented below.

In case of the low cost powders based on mixed lanthanide oxide conductivity measurements were performed in order to see if any significant change compared to the pure lanthanum compounds. Fig. 1 show conductivity results for both $Ln(Sr)MnO_3$ (LnSM) and $Ln(Sr)CrO_3$ (LnSC) compounds. The results are very similar to data reported for the pure lanthanum compounds.

In the investigation of the effect of transition metals on the YSZ properties also the solubilities of these metal oxides in YSZ were determined through determination of the YSZ lattice parameter as a function of nominal concentration. Fig. 2 gives results. The solubility limit of FeO_x and MnO_x was found to be about 5 and 10 mol%, respectively (T_{sinter} = 1350°C) and for NiO a solubility limit of about 1 mol% (T_{sinter} = 1500°C) was found.

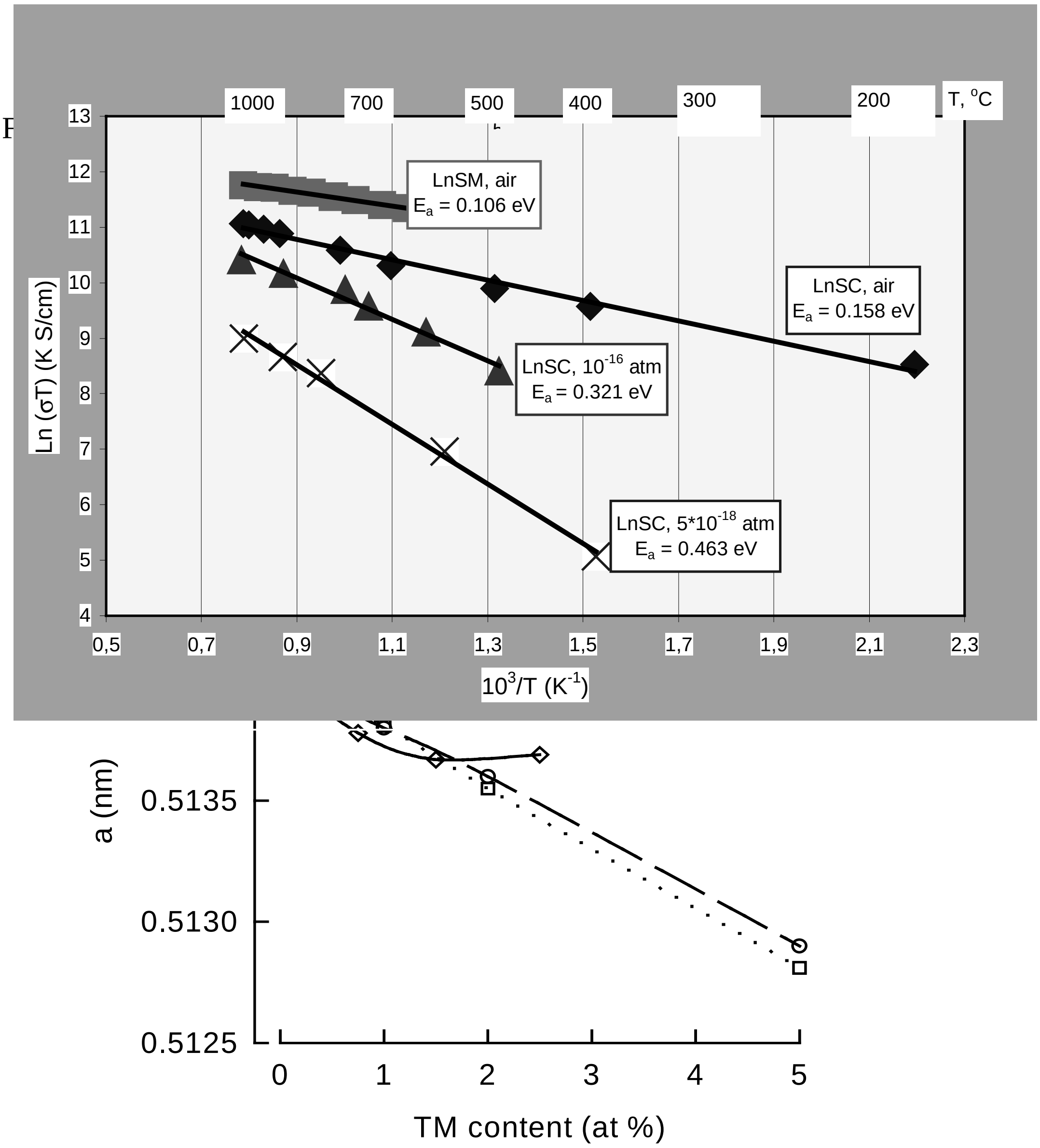

Fig. 2. Cubic lattice parameter for transition metal doped TZ8Y.

Diffusion rates of MnO_x in YSZ were measured for both polycrystalline and single crystal YSZ using SIMS and Raman spectroscopy over a wide range of temperatures. The data are presented in Fig. 3. The diffusion rates are about two orders of magnitude larger for the polycrystalline samples than the single crystal i.e. the MnO_x diffusion is much faster along grain boundaries than through the ordered crystal.

To estimate the stability of silica containing sealing glasses the partial pressures of a number of silicon containing species were calculated as a function of oxygen partial pressures based on thermodynamic data from the open literature. Results are shown in Fig. 4. The possible effect of silica on anode performance was investigated, but no significant effect was found as revealed in Fig. 5.

Finally an example of microstructure of a degraded cathode is shown in Fig. 6. The cathode is a double layer cathode with an active cathode layer (C-layer) next to the electrolyte and a cathode current collecting layer (CCC-layer) on top of it. As fabricated both the C- and the CCC-layer are very porous. As seen in Fig. 6 the whole C-layer and parts of the CCC-layer densified during long term testing at 1000°C. Also an accumulation of small pores on the interface between the YSZ and the C-layer is visible in Fig. 6. The changes were only observed on cathodes tested under current load. Samples heat treated at the same temperature and for the same period of time did not show any significant development in microstructure.

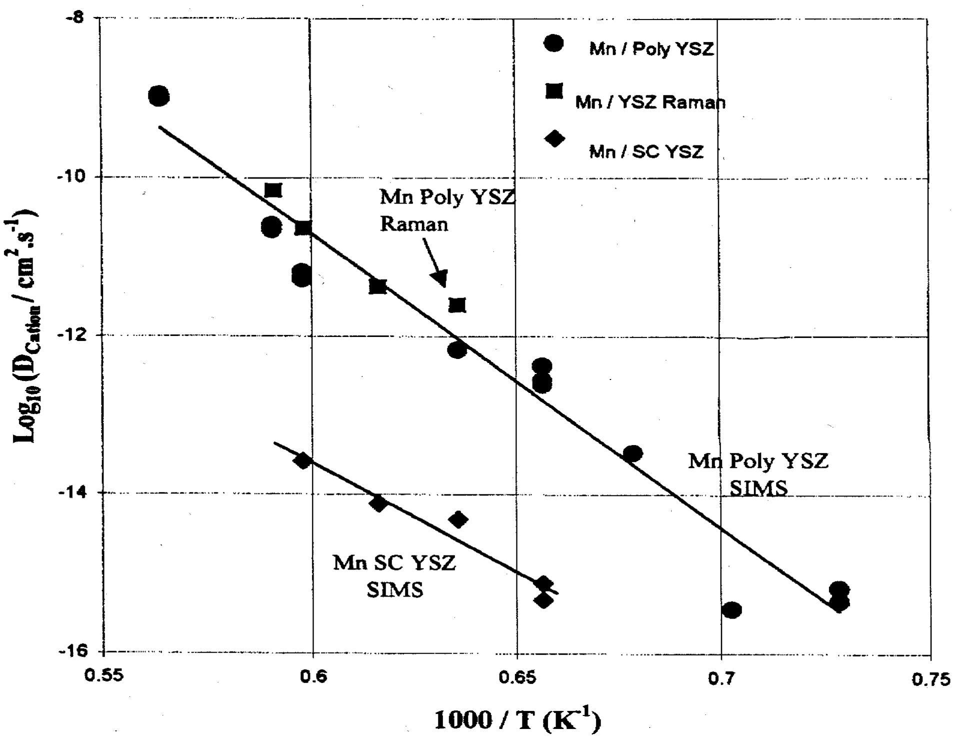

Fig. 3. Diffusion data for MnO_x in YSZ.

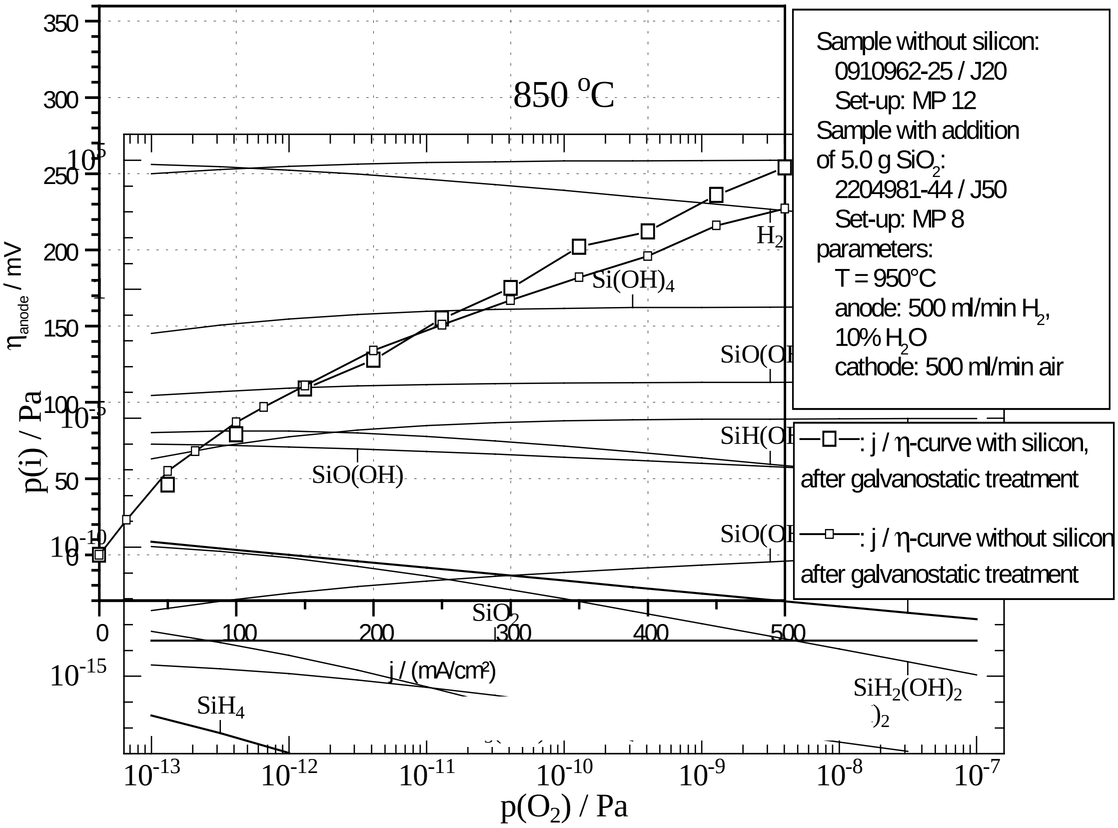

Fig. 4. Partial pressure of Si containing species over $SiO_2^{(Quarz)}$ in a humid atmosphere at 850°C and different oxygen partial pressures.

Fig. 5. Current/potential curves of hydrogen oxidation with and without addition of SiO_2, T = 950°C, H_2/H_2O = 90/10

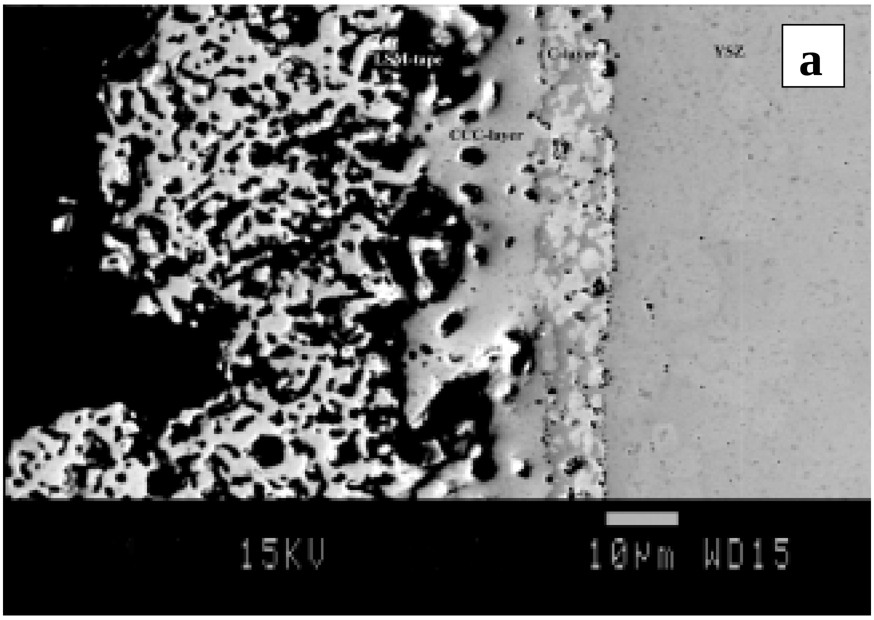

Fig. 6. Backscattered electron image of a cathode, which is tested with current load. The C-layer is dense with pores less than 1µm in size at the interface between the CCC-layer and the C-layer and between the C-layer and the electrolyte.

6. Conclusion

The objectives of the project were reached in almost all aspects, and a large amount of valuable information has been generated. With respect to durability, cells showed low performance losses during thermal cycling (0.01%/cycle) and the degradation rate was below 1% per 1000h up to 300mA/cm^2. It was shown that operation temperature was not a main parameter in controlling the degradation rate. Most important was the current density, which grossly affected the durability of both the anode and the cathode. Also the fuel utilisation proved to be of significant importance for the anode durability. The contacts between cell and metallic interconnect were improved, but further improvements are necessary, and tests have to be done over longer periods 1000 -2000h. Cost calculations showed that the objectives of the project are not sufficient for commercialisation of SOFC technology. A further lowering of both degradation rate and ASR, i.e. increasing of power density, W/cm^2, is necessary.

7. List of project publications

1. M. Juhl, S. Primdahl and M. Mogensen, "Characterisation of composite SOFC cathodes by impedance spectroscopy", in *Proc. 17th Intl. Symposium on Materials Science: High Temperature Electrochemistry: Ceramics and Metals*, Editors: F.W. Poulsen, N. Bonanos, S. Linderoth, M. Mogensen and B. Zachau-Christiansen, Risø Nat.Lab., Roskilde, Denmark 1996, p. 295.
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5. S. Primdahl and M. Mogensen, "Durability and Thermal Cycling of Ni/YSZ Cermet Anodes for SOFC. Submitted to *J. Appl. Electrochem.*
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10. R. Weiss, D. Peck, M. Miller and K. Hilpert, "Volatility of Chromium from Interconnect Material, Proc. 17th Intl. Symposium on Materials Science: *High Temperature Electrochemistry: Ceramics and Metals.* Editors: F.W. Poulsen, N. Bonanos, S. Linderoth, M. Mogensen and B. Zachau-Christensen. Risø Nat. Lab. Roskilde, Denmark 1996, p. 479.

11. N. Lahl, K. Singh, L. Singheiser, D. Bahadur and K. Hilpert, "Crystallisation Kinetics in AO-Al_2O_3-SiO_2-B_2O_3 Glasses", (A=Ba,Ca,Mg), submitted to *J. Mat. Sci.*
12. N. Lahl, L. Singheiser, K. Hilpert, K. Singh, D. Bahadur, "Aluminosilicate glass ceramics as sealant in SOFC stacks", Solid Oxide Fuel Cells (SOFC VI), Electrochem. Soc. Proc. Vol. 99-19, pp. 1057-1066.
13. N. Lahl, "Untersuchungen zur chemischen Kompatibilität zwischen Glasloten und den Komponenten der Hochtemperatur-Brenstoffzelle", Report of the Research Center Jülich, Jül-3663, Jülich 1999.
14. J. Divisek, J.W. Erning, U. Stimming and K. Wippermann, "Der Einfluss der Betriebsbedingungen von SOFC-Anoden auf die Kinetik der Wasserstoffoxidation", GDCh-Monographie Bd 14: *Elektrochemische Reaktionstechnik und Synthese*: *Von den Grundlagen bis zur industriellen Anwendung*, Ed. J. Russow a.o. GDCh, Frankfurt (1999), ISBN 3-924763-74-7, pp. 285-292.
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