Development of 50 kW Class SOFC Systems and Components

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SOFC Joule Project (Contract JOE3-CT95-0015)

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(50 kW Class SOFC)

1. Abstract

This report describes the work performed by Siemens AG, Netherlands Energy Research Foundation, EniTecnologie, ALSTOM Research and Technology Centre, Imperial College, BG Technology and Electricité de France from February 1996 until January 1999 as part of the EC contract JOE3-CT95-0015.

The objective of the Joule project was to develop 50 kW SOFC technology based on the multiple cell array concept of Siemens with a metal separator plate. The existing technology had to be upscaled to bigger stacks and the behaviour of cells and stacks using methane as fuel gas had to be tested and improved.

The 20 kW test facility, developed in the JOE2 project, was finished and two 50 layer stacks were manufactured and operated in this test stand. Using hydrogen and air at 900°C a power output of 7.2 kW was achieved. This test confirmed the feasibility of the chosen assembly concept of parallel-operated stacks and of the corresponding plant concept. The static and dynamic plant behaviour and different components were pre-tested at 850°C for more than 2000 hours with a heated stack dummy. On this basis a concept for the 50 kW class plant, operated with natural gas, was elaborated. Based on 10% pre-reforming of natural gas, as derived from system modelling and cell testing, the design of the pre-reformer as well as of a low temperature desulphurisation device for the 50 kW testing plant was fixed and the components were manufactured. The cell and stack technology including improvements of the sealing technique was validated using smaller stacks.

The size of the active electrode area of one bipolar plate was increased by a factor of 2.8 by assembling an array of nine cells of the size 10x10 cm² with a total electrode area of about 720 cm² per layer. Two four layer stacks of this kind were operated for about 4000 h each, one of them mainly with methane.

The performance of the cells could be improved in such that the power density was nearly doubled, which allowed a reduction of the operating temperature down to 850°C. In two 10,000 h tests degradation rates of the cells below 0.5 %/1000h were demonstrated. Metal stacks showed a degradation of at least 3 %/1000h, measured in 5000 h tests. The difference in degradation between cell and stack was proven to be mainly due to the interface layer formed between nickel grid current collector on the anode side and the bipolar plate material $CrFe5Y_2O_3$1 and counter measures could be demonstrated successfully.

With scandia doped electrolytes together with a double layer anode a power density of about 0.45 W/cm² could be reached at 850°C using methane (S/C = 2) and air.

The termination of the development activities at Siemens in the field of planar SOFC prevented the final demonstration of all these positive results in large stacks within the 50 kW plant.

2.   Partnership

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3.   Objectives of the Project

The objective of this Joule project was to develop 50 kW SOFC technology based on the multiple cell array concept of Siemens with a metal separator plate. The existing technology was intended to be upscaled to bigger stacks delivering a power output of 12.5 kW. At the same time the behaviour of cells and stacks using methane as fuel gas had to be tested and improved. The knowledge gained was to be implemented in a 50 kW component test plant.

Five work packages were defined for the consortium, i.e.:

TASK 1   Re-designing of the multiple array separator plate concept was a work package done by Siemens and ALSTOM. The role of ALSTOM was investigation and development of improved glass-ceramic bonds and assembly methods for SOFC cell arrays into multi-layer stacks, using metallic bipolar plates. The influence of pre-reforming and internal reforming of CH_4 on the stack behaviour was studied using a modelling code available at EniTecnologie.

TASK 2   Design and construction of the 50 kW testing plant was carried out by Siemens. BG Technology and EniTecnologie did the pre-reformer development and the integration of the pre-reformer in the testing plant in collaboration with Siemens. Investigations into the power conditioning requirements for a 100 kW scale SOFC plant were performed by EDF together with ALSTOM.

TASK 3   Manufacturing of ceramic cells, bonding materials and metal separator plates in quantities required by the testing program for the development and demonstration of the proof-of-plant concept was carried out by Siemens (ceramic cells and metal separator plates), ECN (ceramic cells), ALSTOM (bonding materials) and EniTecnologie (cathode powder). Optimisation of the long-term stability of the anode and cathode (materials and microstructure) for the targeted testing conditions (CH_4 and air) was done by ECN. The characterisation of the mechanical strength of the optimised cells both at room temperature (handling and assembly) and at high temperature (start-up and operation) and the elaboration of QA methods were performed by Imperial College.

TASK 4   The assembly of stacks, using the metallic bipolar plate, was carried out by Siemens.

TASK 5   The testing of the different stacks in order to come to the targeted 50 kW test was performed by Siemens. The endurance testing of single cells with optimised materials and the testing of small to medium sized stacks was carried out by ECN in collaboration with the other partners and by Siemens, respectively. The behaviour especially under steam/CH_4 was studied by BG Technology and EniTecnologie.

4.   Scientific and Technical Description of the Project

4.1   Task 1: Design Scale-up of Concept for 12.5 kW

Task 1.1A: Redesign and Upscaling of Separator Plate (Siemens)

During the earlier Joule II project a standard design was elaborated using a 4 x 4 array of 16 cells of the dimensions 5x5 cm² (design 50/16) in one layer.
To improve area utilisation (i.e. ratio of electrode-area to bipolar plate-area) and power output an increase in cell size and bipolar plate dimension was envisaged. This led to an array of nine cells (3 x 3) of the size 10x10 cm² in parallel in one bipolar plate (design 100/9). This means an area utilisation of 56% instead of 38% and a power output of one layer (assuming 0.3 A/cm² at 0.75 V) of 164 W. This is an increase by a factor of 2.8 compared to the design 50/16.
No special measures concerning internal reforming have been implemented because on the one hand results of internal reforming tests and, on the other hand, modelling calculations showed no necessity for significant changes in stack design.

To establish improved assembly concepts with a reduced number of parts, easier assembly, reduced costs and improved reliability, several design concepts have been elaborated as well as the relevant drawings, necessary for manufacturing of test samples. E.g. both sides of the bipolar plate can be coated with glass-ceramics or plasma sprayed ceramics for electrical insulation and to compensate for the thickness of cell and contact layers, which is necessary to reduce the seal thickness to a minimum. First stack tests showed a good behaviour of this design.

Task 1.1B: SOFC stack assembly methods (ALSTOM)

Redesign of the stack seal configuration and the proposal of an alternative method of assembly has resulted in a stack-sealing scheme that should be relatively simple and low cost. The method proposed comprised two stages; applying a glass-ceramic coating to the bipolar plate and an assembly stage in which a single sealing glass layer, deposited in the form of a powder, sealed cell edges and adjacent bipolar plates.

Glass-ceramics for the bipolar plate coatings were developed which have an extremely close thermal expansion match to CrFe5Y ($\Delta\alpha < 3\%$, 25-1000°C). The glass-ceramic bonds displayed sufficiently high electrical resistance to minimise electrical leakage between bipolar plates. No reaction, or other degradation, was evident in bonded samples using these materials that had been thermally aged for 5,000 hours.

A range of glasses was prepared and characterised with the aim of producing an improved stack sealing material. In particular, investigation was made of the crystallisation kinetics of these materials, as slow crystallisation is essential to

maintain a compliant seal that will accommodate volume changes that occur during the prolonged anode reduction heat-treatment.

Task 1.2: Thermodynamics of pre-reforming and internal reforming (ENI)

Using an available modelling code a 50 layer SOFC stack according to the Siemens design was simulated. The single layer of the stack is described as one 16 x 16 cm² cell with 60 channels for anode and cathode sides.

A key feature of the SOFC technology could be the "in situ" reforming of methane in the cell, in order to reduce the cost of a pre-reformer and provide additional cooling of the cell: but in this case, the thermal gradients in the stack could be very high, generating high thermal stresses in the material. A possible solution to this problem is a certain degree of external pre-reforming. Therefore some simulations have been performed varying the degree of pre-reforming to calculate its effect on some important output variables. The pre-reforming reactor is supposed to work at the same temperature of the stream entering the anode compartment of the stack.

The principal achievement of this simulation is that, to meet the requirements on maximum solid temperature without having a too large amount of air, a degree of pre-reforming of 20-50% could be required; which would on the other hand decrease the system efficiency. As alternative, in order to keep pre-reforming low, it should be useful to increase the inlet stream temperatures to the stack (resulting in a temperature difference across the stack between air inlet and outlet of 100 to 150°C instead of 200°C) to increase the minimum solid temperature and to operate with a recycle of the anode stream to reduce the effect of internal reforming.

4.2   Task 2: Design and Construction of 50 kW Testing Plant

Task 2.1: Design of 50 kW Testing Plant (Siemens)

The most important basis for the layout of the 50 kW test stand are the results of the 20 kW test, which was designed and partly manufactured in the Joule II project.

The test facility is designed in a manner that 4 stacks can be operated in parallel. The stacks including thermal insulation are placed on a rack of the dimensions 2.8x2.8x2 m³. For good accessibility the thermal insulation is realised by 5 separate units, which can be assembled around the high temperature concrete basement on which up to four stacks can be placed. At the circumference of this basement an electrical heater is installed for heating up the system. The high temperature components as heat exchangers and piping are placed below the stack-platform within the rack area. The cold part of the test facility is mounted on a separate tableau, where all the necessary valves, controllers and measurement devices are placed.

This assembly formed the basis for layout and design of the 50 kW testing plant.

System calculations, varying the amount of pre-reforming, showed, that above a pre-reforming rate of 40% the electrical system efficiency goes down tremendously. This is because of the amount of additional fuel gas needed for the heating of the pre-reformer. Below a pre-reforming rate of 15% the enthalpy of the anode waste gas flow is sufficient to heat up the fuel gas and the pre-reformer without the necessity to heat the pre-reformer by burning the waste gas. Together with results of single cell

testing this let to layout data for the pre-reformer providing a reforming rate of 10%. Based on all these data a flow diagram for a 50 kW testing plant was established and the influence of different operation parameters on the plant design was investigated. Efficiencies, operation range under certain circumstances and lay out parameter for the different components were calculated.

Based on the results of the 20 kW test and the following dummy tests several improvements and changes have been implemented in the plant design.

The detailed control strategy was updated and fixed in a requirement specification for the stored programme computer. The SPC and the relevant documentation was adapted accordingly and the function was checked with the dummy stack operation.

Task 2.2: Construction of 50 kW testing plant (Siemens)

The operation with natural gas requires the humidification of the fuel gas. In a first step the steam generation was realised adapting an available gas pre-heater in combination with a flow controlled liquid pump. This cost-effective assembly is similar to commercial steam generators having the advantage of an easy control of the steam flow over a wide power range. The function was proven in the envisaged range between 5 and 50 kW power output of the plant. In this case the water flow varied between 10 and 80% and the corresponding gas flow was changed by $\pm$ 20% at each water flow to test the influence of flow deviations. Also the dynamic behaviour during start up and load change could be demonstrated successfully.

For reduction of costs and volume there exists a big advantage of plate heat exchangers compared to tube-bundle heat exchangers. Therefore two different types of plate heat exchanger were tested. They allow a much more compact design which results in reduced heat losses and reduced costs. The tests showed that they are suitable in principle, but that several improvements have still to be performed.

Improved thermal insulation, using a micro-porous material instead of ceramic fibres, was installed in the area of piping and heat exchangers. An additional electrical heating device was also implemented in this compartment, to provide the possibility for testing at low partial load to investigate the influence of the heat loss in this area on the plant behaviour.

Task 2.3A: Pre-reformer development and integration (BG)

The task objective was to design and deliver the pre-reforming plant unit. After an initial debate on the balance of external and internal reforming, it was decided to externally reform 10% of the methane and all of the higher hydrocarbons. The finished plant unit incorporates a desulphurisation unit, a catalytic reformer using a BG Technology catalyst, and a heat recovery system.

The operating pressure of the pre-reformer is 1.15 bar, with an inlet temperature of 520°C and an equilibrium outlet temperature of 371°C. The steam:carbon ratio is 2.

A detailed study of available purification processes was performed and specially-formulated carbons were chosen for the removal of sulphur at ambient temperatures. This removed the need for a heat exchanger to pre-heat the gas stream.

The construction of the pre-reforming plant unit has been completed.

Task 2.3B: Selection of methane reforming catalysts (ENI)

In order to select alternative methane reforming catalysts the following companies have been contacted: ICI Katalco, Haldor Topsoe, Procatalyse, UCI, and BASF.
Only BASF suggested catalysts: **G 1-25** and **G 1-25 S**.
Both can operate at temperatures in a range of 600-900°C and can be used at atmospheric and elevated pressures (> 30 bar). They are available in form of rings with a size of 16x16x9 mm and the crushing strength is ~ 35 kg.

Task 2.4A: Power conditioning for a 100 kW scale stack (ALSTOM)

A scheme for the power conditioning circuit topology was derived. This was nominally for a 100 kW_e system but the circuit would be applicable to a range of power ratings from 25 kW_e to 2 MW_e. The power converter requirements are not dissimilar to those for other embedded generators although restrictions on the design and use of the power conditioning will be imposed by the limitations of the SOFC. Further information is required on the performance and limitations of the SOFC in order to specify an optimised power conditioning circuit.

Mathematical models have been developed to represent the behaviour of the planar SOFC stack in order to establish a control philosophy. There is limited practical data against which this model could be compared, however, it appeared to function well and was able to mimic both the results of other models and measured parameters from the planar stack. There were known deficiencies with the model, and various terms were omitted, but care was taken to demonstrate that the effects were negligible.

Time varying simulations using the model have led to the evaluation of a simple control scheme. The control confirms other work that the stack temperature is most significantly affected by airflow and the output by the fuel gas flow. The analysis shows there to be significant cross coupling between these parameters so to improve on the control developed will require an increase in the level of sophistication of the control strategy.

Task 2.4B: Power interface between stack and electrical grid (EDF)

Different stack modelling papers were studied in order to understand the system behaviour of the SOFC under realistic power generation conditions.
The critical point was to create a simplified dynamic model of the SOFC stack that could simulate the behaviour of the fuel cell and the resultant electrical output parameters in response to a load change. This is important, if we are to design a converter and its control that provides good quality electricity to the grid as well as protecting the fuel cell stack.
A SOFC stack macro-model was designed and implemented in the power electronics software 'SABER'. The thermal simulated by the model appears accurate enough for our power converter design needs. Information about the electrical behaviour of

SOFC stack in the time range between 1 to 50 ms was provided by Siemens, based on single cell impedance measurements. The high frequency stack model was extrapolated from these single cell results.

The response of the system (including the power converter) to load steps, grid voltage dips and opening of a phase of electrical grid were investigated, with a parallel adaptation of the control laws. The characteristic time constants were determined.

4.3   Task 3: Manufacture Metal and Ceramic Components

Task 3.1: Manufacture cathode powder (ENI)

During the first year of the project 2500 grams of cathode powder have been synthesised.

Each batch of powder has been checked by XRD, chemical composition and particles size analysis.

As stated in the project the cathode powder was $(La_{0.85}Sr_{0.15})MnO_3$, but because of the change of the cathode powder to improve the performance in air, it was tried to obtain the non stoichiometric composition: $(La_{0.85}Sr_{0.15})_{0.9}MnO_3$.

A cathode powder was obtained that shows the same XRD analysis results than the cathode powder supplied by Siemens as standard. 0.5 kg of this new cathode powder was sent to Siemens and ECN.

Task 3.2: Optimisation of electrodes (ECN)

<u>Anode</u>
Screenprinted anodes were developed in order to reduce manufacturing costs. The performance of the anode was optimised by varying composition, solid content in the screen print paste, sinter temperature and reduction procedure. Cells with screenprinted anodes and double layer cathodes yielded performances of up to 1.1 A/cm² at 700 mV and 950°C in air and hydrogen (ideal test conditions). After evaluation at Siemens the anode AS1 was accepted as being the standard 50 kW anode. It was found that the reduction procedure strongly influences the electrochemical performance of the screenprinted anode. Slow reduction was found to be beneficial for the electrochemical performance of the anode. This behaviour was found both for the screenprinted ECN anodes and also for the screenprinted Siemens anode.

It was established that the addition of small ceramic particles (CeO_2, MgO or GCO) to the anode results in a more stable catalytic activity for the steam reforming. Unfortunately the anodes with small ceramic particles showed a decreasing electrochemical performance with time. Ni/GCO anodes have the advantage of a high and stable catalytic activity for steam reforming of CH_4 but the disadvantage of low lateral conductivity and high degradation rates. To optimise the catalytic activity of the anode in CH_4/H_2O mixtures without losing lateral conductivity a double layer anode AS3, consisting of a Ni-GCO interface layer with a standard Ni-YSZ top layer, was developed. The AS3 anode yielded a performance of 0.67 A/cm² at 700 mV and 850°C under hydrogen (3% H_2O) using a standard double layer cathode (KS1).

Under 10% pre-reformed methane a cell performance of 0.55 A/cm² at 700 mV and 850°C was achieved. Standard ECN, Ni-YSZ anodes only achieve 0.3 A/cm² under the same conditions. There was however reproducibility problems with this new double layer anode, adherence and very close control of layer thickness proved problematical.

Cathode

Two different A-site deficient cathode powders were considered, i.e. powder of Praxair and the Siemens cathode powder. Both types of powder were screenprinted on sintered electrolytes and then co-fired with a screenprinted state-of-the-art anode. The cells were tested in an alumina cell housing with Pt-current collectors using oxygen and air at the cathode side.

The cell performance of the A-site deficient cathodes was similar to the performance of state-of-the-art cathodes. In air performances of $700 \, mA/cm^2$ at 950°C and 700 mV were obtained. Both the Siemens and the Praxair A-site deficient cathodes show performances in air comparable to conventional, stoichiometric cathodes but do not need a long activation period. Maximum cell performance is reached two hours after start-up whereas the stoichiometric cathodes reach maximum performance around 16 hours after start-up.

To improve performance of the cathode under air and lower operation temperature oxygen ion conducting materials were introduced in the cathode. Three compositions were considered: 0% GCO in LSM, 20% G.C.O. in LSM and 50% GCO in LSM. The coarse GCO particles were mixed with the LSM particles and tape cast on sintered electrolytes. The cathode was co-fired with a "state of the art" anode.

The cell performance with the GCO cathode decreased due to decreased lateral conductivity of the cathode. More can be gained, if the loss of electronic conductivity can be avoided by disconnecting cathode interface requirements (electrochemical activity) from current collecting requirement. This was realised by developing double layer cathodes. These composite cathodes were developed based on the Siemens technology using a thin YSZ/LSM layer at the interface with a LSM layer on top, leading to a standard cathode, called KS1.

Many double layer cathodes with varying microstructures were manufactured and evaluated by means of impedance spectroscopy. The following conclusions and recommendations were drawn.
- Ohmic resistance depends on the density of the interface layer.
- Polarisation resistance depends on particle size
- Cathode powder delivered by Praxair was found to be a good alternative for the standard cathode powder manufactured using a mixed oxide route at Siemens and ECN.

Task 3.3A: Manufacturing of 5x5 cm² cells and 10x10 cm² cells (Siemens)

Electrical performance of the cell.

Cathode:
Because the contribution of the so-called mono-layer-cathode to the total cell resistance is about 60% it was the first target to reduce the cathode polarisation. This was done using a screen printing paste out of a mixture of 50% uLSM (substoichiometric LSM) and 50% yttria doped zirconia (8YSZ) using special dispersing agents. After firing this results in fine branches of zirconia within the uLSM connected to the surface of the electrolyte substrate. Since this kind of cathode is targeting in a high lateral resistivity a further coating is necessary acting as a current collector layer. With such kind of double layer cathode consisting of a working and a current collector layer the polarisation resistance could be decreased by a factor of three.

Electrolyte:
Using a double layer cathode the ionic resistance of the electrolyte contributes to about 50% of the total cell resistance. Therefore the further work was concentrated on the improvement of this situation.
Because in the case of scandia doped zirconia the lattice distortion is much less than with yttria, experiments with scandia doping were performed.
The powder for the scandia-doped zirconia (ScSZ) was produced at Siemens and the electrolytes were tape-casted at ECN. The ionic resistance of scandia doped zirconia is excellent in the doping range between 8 and 12 mol-% and is about half of 8YSZ and beyond 10 mol-% scandia content no degradation of the ionic conductivity after ageing was found.

Anode:
Because the mechanical strength of MEAs was lowered by more than a factor of four by the high sintering temperature, necessary for the standard anode, the anode AS1 developed at ECN was transferred to the Siemens pilot plant. So the sintering temperature could be reduced by 100 K. Co-firing of the Siemens standard double layer cathode with this new anode results in cells with comparable electrical performance (about 0.4 A/cm² at 0.7 V; T = 850°C; 50% humidity in the fuel) but much better mechanical stability.

Additional cells have been produced and tested using double layer cathodes and anodes as well as scandia doped zirconia as electrolyte. Current densities of nearly 700 mA (0.7 V) can be attained at 850°C, which is compared to the starting point of the project (total resistivity 1 Ωcm² at 850°C) a factor of three in the performance (resistivity now 0.3 Ωcm²). Concerning ageing no degradation has been detected in the test period of 1000 h.

Mechanical stability of the cell

The mechanical stability is influenced by the mechanical strength of the electrolyte and the cofiring process of the cell.
The mechanical strength of the electrolyte is influenced by the production process of the zirconia tape by a large scale. The standard production in ball mills is leading to a lower strength than attrition milling, which is targeting in finer grains with a narrower

grain size distribution. With the finer grain a more homogeneous slurry can be prepared for the tape casting process and therefore the foil contains less defects, which enhances the mechanical strength. This is confirmed by the σ_o-values measured with the double ring method and evaluated statistically (DIN51110) as well as by the corresponding Weibull coefficients (m).

In addition the mechanical strength can be increased by another 10% by lowering the heating up rate and by an elongation of the dwell time.
All samples tested concerning mechanical strength - also from different sinter batches – follow a nearly ideal Weibull distribution.
After second sintering the Weibull distribution is not deteriorated. Hence, there is a shift in parallel, that means to a smaller fracture load caused by a growth of grains due to additional thermal treatment and probably due to induced tensions caused by loading with alumina plates (different thermal expansion coefficient) during the flattening process.

The parameter, which influences the strength of the cell most, is the co-firing temperature for the burn-in of the electrodes.
Fracture tests by the double-ring method showed that the standard co-firing temperature of electrodes is reducing the mechanical strength of electrolytes (fracture load $\cong$ 80 N) by a factor of four.

As a conclusion the mechanical strength of cells could essentially be increased by the following measures:
• Improvement of milling process of slurry preparation for the tape casting process
• Introduction of ECN anode type AS1 (means reducing the sintering temperature)
• Using partially calcined zirconia in the working layer of the double layer cathode

Because the defect rate in all ceramic material is different from zero a proof-test for electrolytes and cells has been developed in parallel and a corresponding device was manufactured.

Task 3.3B: Manufacturing of metal separator plates with functional layer (Siemens)

For fabricating interconnector (IC) plates for various stacks, as well as the necessary sealing layers, different manufacturing routes were investigated. All production processes were carried out according to a quality assurance handbook, which was established to fulfil the requirements of DIN ISO 9000.

During the project four designs of IC plates, base and top plates and sealing layers were constructed and fabricated. Special attention was paid to the new design with nine cells 10x10 cm² per layer.
In total metal separator plates for a power capacity of 38 kW were manufactured (25 kW in design 50/16, 1 kW in design 100/1, 10 kW in design 100/4, 2 kW in design 100/9).

In order to avoid evaporation of volatile chromium species, coatings were developed for the airside of the IC plate. Meanwhile approximately 200 IC plates and cover-

plates have been coated successfully with the standard material LaSrCrO$_3$ by vacuum plasma spraying.

In terms of cathode contact material powders of the composition LaSrMnCoO$_3$ (LSMC) have been qualified, which replaced the original LaCoO$_3$ (LC) material, because of a better adapted thermal expansion coefficient. Contact materials were processed by wet powder spraying (WPS). The electrical properties (contact resistivity) of the standard material combination (IC coated by LSCr and LSMC in contact with cathode material uLSM) show an acceptable level. Area resistance of less than 30 mΩcm^2 and a low degradation rate can be realised.

Contact resistance measurements have shown that a nickel coating of the anode side of the bipolar plate results in a very low and stable resistance between nickel grid and IC. After some coating trials a manufacturer was found who was able to produce a nickel coating with good adhesion, which was proven by coating 10 plates of the design 100/4.

Task 3.3C: Manufacturing of components (ECN)

The aim of this task is to further integrate and optimise the cell manufacturing routes of both ECN and Siemens.

In close collaboration with Siemens ECN developed tape-casting recipes for scandia doped zirconia electrolytes using powder manufactured at Siemens. A total of sixty sintered and one hundred green scandia doped zirconia electrolytes were manufactured and sent to Siemens for evaluation. Both ECN and Siemens were able to sinter the electrolytes 98% dense. High cell performances were measured at Siemens using these electrolytes.

Following a cell manufacturing protocol exchange between ECN and Siemens it has been demonstrated that ECN was able to reproduce the manufacture of Siemens type cathodes and that Siemens was able to reproduce the manufacture of ECN type AS1 anodes.

As described above the strength of the standard cells was found to be critical for stack testing and therefore efforts were devoted to this aspect. Work was focussed on the optimisation of the electrolyte strength.

Variation of the sintering temperature, time and configuration did not result in a significant increase of the strength of the electrolyte. Sintering of the electrolyte by the standard technique was still found to be the optimum choice.

By examining a large number of ECN electrolytes a correlation was found between the presence of pores and the electrolyte strength and by different measures the number and size of pores could be reduced which resulted in a clearly improved mechanical stability.

Task 3.3D: Evaluation of ceramic component manufacturing with respect to large series production (ECN)

The emphasis of the work within this task is cost-effective manufacturing and product quality and assurance.

The use of alternative green electrolyte tapes (DSM Solufil®) available on a large series production scale has been evaluated by ECN. Using this alternative green tape, flat, dense, 5x5 cm² and 10x10 cm² electrolytes were obtained after sintering in a one step procedure.

By evaluating a number of different sintering plates and configurations, progress has been made concerning reducing the thickness variation and increasing the flatness and yield of up-scaled 10x10 cm² cells manufactured at ECN. Developments for new sintering techniques for electrolytes resulted in an increased sinter capacity by a factor of four. The sinter capacity per furnace was increased from 9 to 40 up-scaled electrolytes per sinter-run.

In consultation with Siemens, ECN invested in a production type screenprint machine for large series production of ceramic components. Siemens also purchased the same type of machine in order to keep the manufacturing routes of both ECN and Siemens well tuned to each other. For large series production new laboratories were installed.

Task 3.3E: Manufacture class-ceramic bonds (ALSTOM)

A method of applying glass-ceramic coatings of a specified thickness and over a well-defined area to CrFe5Y bipolar plates has been devised. Such coatings form part of the planar SOFC seal assembly and also provide electrical insulation between the overlapping edges of neighbouring bipolar plates. The coating method which uses conventional ceramics processing techniques is suitable for volume production and should be low cost.

The method developed is based on the application of tape-cast glass powder to the bipolar plates which on firing produces a dense glass-ceramic coating. By evaluating a range of glass-ceramic materials and process parameters, including binder formulations and sintering conditions the coating thickness and flatness of coated bipolar plates could be controlled to the tight tolerances necessary for stack assembly. The materials used in the process are environmentally benign and the ability to recycle the tapes should ensure their efficient use.

Task 3.4: Mechanical testing and quality assurance of cell components (IC)

The objective of this task is to provide data and understanding of key mechanical properties of cell components that can then be used to ensure and improve individual component quality and hence the mechanical reliability of stacks.

Elastic modulus, Toughness and Fast Fracture of YSZ Electrolytes

Young's modulus, E, shear modulus, G, and Poisson's ratio of circular disc specimens of tape-cast YSZ electrolyte were measured at 25°C and partly at 900°C by different measures. The results are summarised in the following table:

Measurement technique	Elastic properties		
	E (GPa)	G (GPa)	Poisson's ratio (ν)
IET (20°C)	216.2 ±4.5	82.2 ±1.8	0.315
Slope (20°C)	233.7 ±10.5	--	" "
Slope (900°C)	163.5 ±13.1	--	0.315
IET (900°C)*	152.0	--	" "

(*) The value of E was obtained by reducing E (IET) in proportion to the measured reduction in E (slope) with temperature (30% at 900°C).

The biaxial flexure strength at both 25°C and 900°C was measured using the ring-on-ring loading configuration. The flexural strength of each specimen was calculated using the large deflection solutions to the elastic analysis of deformation of the specimens. The elastic analysis was carried out using finite element modelling (FEM). The following table lists the average flexure strength and the Weibull parameters for YSZ tape-cast specimens. The room temperature Weibull strength (~446 MPa) was found to be about 36% higher than the Weibull strength at 900°C (~282 MPa).

Test temperature	Average strength, σ_{avg} (MPa)	Weibull strength, σ_o (MPa)	Modulus (m)	Sample number
20°C	415.9 ±70	445.7	6.7	34
900°C	265.2 ±38.6	281.5	8.0	20

The measurements revealed an average strength of about 416 MPa at 25°C and 265 MPa at 900°C. These values are much greater than the values reported previously for similar electrolytes (by approximately 70% for the room temperature strength). Investigation by scanning electron microscopy (SEM) of the fracture surfaces suggested that the unusually high average strength of these samples be due to their small defect size (of the order of a few microns) and low porosity (< 2%).

The fracture toughness of the tape cast electrolyte was measured at 25°C using the double torsion geometry with rectangular specimens (25 mm in width and 50 mm in length). An initial crack was introduced near the loaded edge of the specimen by indentation cracking. Fast crack growth from the indentation crack was then studied at different constant displacement rates. The average value (of at least 5 measurements on different specimens) of K_{Ic} was 1.58 ± 0.12 MPa m$^{0.5}$ at room temperature and 1.02 ± 0.05 MPa m$^{0.5}$ at 900°C.

A value of 2.5 MPa m$^{0.5}$ is typical of a polycrystalline ceramic having equi-axed grains. This indicates that the high flexural strength of the present electrolytes is due to the absence of large flaws and not to an inherently tough microstructure.

SEM examination of fracture surfaces of specimens after strength measurement revealed that fracture initiated at defects in the tensile surface. The defect that initiated fracture of the weakest specimen (failure stress 240 MPa) was an approximately semicircular depression 35 microns deep. Applying the theory to the strongest specimen (failure stress 520 MPa) implies a critical defect size of only 7 microns, which is consistent with the observed defect size.

The fracture loads under the biaxial flexure of the square plates of symmetrical cells (5x5 cm²) with the stacking sequence of NiO-YSZ-NiO and LSM-YSZ-LSM were measured at 25°C using the ring-on-ring.
The test results revealed an average fracture load of 32.3 N for YSZ, 35.1 N for NiO-YSZ-NiO, and 14.0 N for LSM-YSZ-LSM. It is apparent from the figures given for fracture loads of YSZ and MEAs that the cathode (LSM) is responsible for lowering the strength of cells. Also the Weibull modulus of the LSM coated samples is about 37% of the value from the uncoated YSZ (n = 6.14). This suggests that the cathode coating induces a strong broadening of the size distribution of critical defects on the uncoated YSZ.

Slow Crack Growth in Electrolyte
Subcritical crack growth was investigated by the load relaxation method, measured in a modified test rig.
The crack velocity, v, measured at 25°C and 900°C is a function of applied stress intensity, K_I. In the subcritical region the relationship

$$v = A K_I^n$$

is obeyed with a value of n of approximately 20 at 25°C and 2.6 at 900°C. The large difference between the two n values indicates that the dependence of v on K_I in the subcritical region at 900°C is much lower than that at 25°C. The v - K_I suggest that the stress concentrations within the cells should be kept small enough to provide $K_I < K_0 = 0.5$ MPa.m$^{0.5}$ for the SOFC operations at 900°C and $K_I < K_o = 0.7$ at room temperature.

Failure Modes of Seals
The stresses experienced by the seals are the summation of residual stresses and applied operational stresses. The residual stresses arise mainly from differences in thermal expansion between the sealing material and the components being sealed when the temperature is different from the effective temperature at which the seal was fabricated in a stress-free state.
With an improved test configuration the fracture of all the fifteen samples representing the Siemens standard assembly was found to initiate from the singularity points where the shear stress is maximised, suggesting that the symmetrical test configuration provides the conditions to achieve a pure shear loading of the lap joint, and that the origin of failure in the joint can be predicted by the current FEM model developed for the simulation of the test.
The apparent shear strength of the seal was expressed as the applied load at failure per unit area of seal. The average apparent shear strength was measured to be 83.4 MPa, the Weibull characteristic strength was 89.5 MPa and the Weibull modulus was 6.4.

Lifetime Prediction and QA

The mean strength of the first batch of electrolyte plates measured in this project was considerably larger than those measured in earlier projects. The study of the fracture process, described above, demonstrated that standard brittle fracture theory was suitable for these materials and that their toughness was quite low. Therefore the high strength must have been due to the absence of large defects. The application of fracture theory also enabled the critical defect size to be predicted and this was found to be consistent with the size of processing defects found in the samples. This knowledge was then used by the electrolyte manufacturers to improve the manufacturing process so as to reduce the incidence of manufacturing defects above approximately 20 µm in size. As a result the high mean strengths were obtained on a routine basis and the reliability was improved, as reflected in a higher Weibull modulus.

The effects of slow crack growth in the electrolyte could be clarified. It can be seen that slow crack growth can be taken into account approximately by down-rating the mean strength by about 25%.

4.4   Task 4: Assembly of Stacks

Task 4: Assembly of stacks (Siemens)

The mounting of stacks was performed according to a standard process procedure. Stacks were assembled in four large and eight smaller test facilities. The following quantity of stacks have been prepared:

Stack design 50/16   24 stacks with 2 layers, 8 stacks between 5 and 50 layers
Stack design 100/1   36 short stacks with two layers
Stack design 100/9   2 stacks with four layers

All necessary parts, as bipolar plates, cells, insulating ceramic frames and glass foils were quality tested before the assembly in the test stand.
Several special assemblies of all stack designs were prepared in order to find out reasons for the observed cracking of cells.
After the tests all stacks were disassembled and especially the top- and base-plates were refurbished for further stack tests.

4.5   Task 5: Testing of Cells and Stacks

Task 5.1A: Optimisation of cells for IR and micro-modelling (ENI)

Electrochemical characterisation: fuel – hydrogen

The first period of activity revealed that the use of a nickel grid as current collector on the anode side instead of a platinum grid results in a great improvement of the anode stability, which implies a great improvement of cells working life. Probably, as

suggested by Siemens, at the operating temperature (950°C) and in presence of steam, the platinum grid represents a catalyst for the $Ni(OH)_2$ formation. This is a very volatile component; so nickel anode material gets lost with the fuel stream when platinum grids are used. With nickel grid this nickel hydroxide formation decreases and the anode structure is more stable.

Using auxiliary probes on the electrodes it could be shown that the anode contact resistance of a cell with platinum grid increases steeply while the resistance with a nickel grid is almost constant.

This measurement fits very well with the morphological and structural analysis carried out on the anode, which reveals that an amount (10-14 atomic %) of nickel near the grid contact interface is lost; moreover the investigations carried out on the anode platinum grid show a diffusion of nickel anode material into the grid. These results and the formation of $Ni(OH)_2$ can probably explain the increase of the anode-grid resistance observed during the electrical tests.

Structural analysis of anode and cathode materials before and after testing, related to 5x5 cm² cells supplied by Siemens, was performed. Anode layer material shows YSZ and Nickel crystalline phases with standard crystallographic parameters, while all cathode layers show a regular strontium-doped lanthanum manganite (LSM) perowskite-type phase and a segregated impurity La_2O_3 -like phase.

A significant sintering phenomenon of the nickel particles with increasing testing period was observed. For the cathode a more regular thickness was measured; pore size and form factor distribution are broader than on the anode layer. Surface and electrolyte/cathode interface regions seem to be denser than the central part of the layer. By acoustic C-Scan images of the anode and the cathode interfaces a damage area fraction was evaluated.

IR methane characterisation

With Siemens 2.4.1 type cells (single layer cathode) constant current tests and I-V tests were performed.

During the long term testing the outlet gases at the anode side were analysed with a gas chromatograph gauged to detect N_2, H_2, CH_4, CO and CO_2.

The gas analysis revealed an almost constant behaviour with the following outlet gas composition:

- N_2 0 - 0.3 % vol
- CH_4 0 % vol
- CO 28 ± 3 % vol
- H_2 69 ± 3 % vol
- CO_2 3 ± 0.3 % vol

I-V curves of the Siemens 2.5.1 type cells (double layer cathode) with different fuels measured at 850 °C fit very well with results of the other partners (Siemens, ECN).

The constant current test with methane as fuel and a S/C of 2 was performed at 200 mA/cm² at an initial voltage of 0.8 V.

At 1700 h the cell performance decreased. An oxidation of the anode using air was performed in order to recover anode performance (probably oxidation of carbon, formed during methane feeding, occurred). During this operation the temperature was kept at 850°C.

The reduction step was very fast in this second case: the open circuit voltage reached a high value (about 1.2 V) in a few minutes, then the cell was fed with methane plus steam again and showed a stable behaviour.

After 3200 h the cell voltage declined sharply; the outlet flow check revealed a large leakage problem. The test was stopped and cracking of the cell was confirmed.

Relation of IR (Internal Reforming) performances and anode reduction procedure

The aim of this work was to confirm the relation between reduction procedure and electrical performance of the cells in the IR mode. In order to confirm first results, a large number of anode material samples and complete cells was investigated using different techniques.

The main results of this analysis reveal that during the fast reduction procedure both nickel and zirconia particles agglomerate and, mainly for nickel grains, a spherical and smooth shape was detected.
This anode structure was retained after the re-oxidation and new reduction steps.
In the Siemens reduction case small particles of zirconia and nickel according to the initial cermet structure are present more markedly, if compared with the fast procedure anode.

In the fast reduction case the IR tests did not give any result: after the change of fuel from hydrogen to methane (S/C = 2) no stable open circuit voltage was measured and a complete failure of the cell was detected after two hours of constant load current.
In the Siemens reduction procedure the behaviour of the cell in the IR mode was stable and allowed to perform i-V and impedance measurements during the constant current tests.
Considering the model presented here it means that the degradation process mainly affects the anode-electrolyte interface, if a fast reduction is performed. This behaviour is detected only in the IR mode.

Task 5.1B: Single cell characterisation (IR) (ECN)

The anodes optimised in task 3.2 were tested using methane steam mixtures as fuel.

The IR-SOFC single cell tests were carried out in an alumina cell housing. Nickel grids were used as anode current collectors. Under IR conditions the converted fraction of methane is small near the inlet, and therefore the e.m.f. and current density are low in that region. A large electrode surface area is necessary to obtain a realistic picture of the electrochemical performance. An electrode surface of 80 cm² was therefore chosen. The catalytic activity for the reforming reaction was determined by analysis of the anode exhaust gases in a gas chromatograph. The catalytic activity is most conveniently expressed in terms of an effective rate constant k, which is obtained by assuming that at each position along the anode gas channels the reforming rate is given by:

$$r = k \cdot \left(pCH_4 - \frac{pH_2^3 \cdot pCO}{pH_2O \cdot K_r} \right),$$

where the pX are partial gas pressures which vary with the distance from the anode inlet, and K_r is the equilibrium constant of the steam reforming reaction. The rate constant k is expressed in mol/s.bar.m² and depends on the temperature. The electrochemical measurements were performed with air at the cathode and methane/steam with S/C = 2 at the anode. The anode flow rate was chosen in a way that it would correspond to the flow in the first cell of a series of four in a stack operated at 80% fuel utilisation and at a current density of 0.4 A/cm².

Model calculations

Model calculations have been carried out for an IR-SOFC single cell to determine the optimum range for the rate of the reforming reaction. It was concluded that:

- At isothermal conditions the only effect of the catalytic activity for the reforming reaction is on the cell performance and is due to the effect on the e.m.f. There is a rather strict lower limit to the catalytic activity, but no upper limit. However, beyond a given catalytic activity there is no further improvement of the performance. The minimum catalytic activity corresponds to an effective *k*-value of 0.1 mol/s.bar.m².

- In the case of adiabatic cells the present model calculations can only give semi-quantitative results. At adiabatic conditions there is an optimum range for the catalytic activity for the reforming reaction. The lower limit is now determined by the maximum temperature that is attained in the cell as well as by the cell performance. The upper limit is mostly determined by the thermal gradients that occur.

- High thermal conductivity or high air ratios will result in a more even temperature distribution. In such cases the lower limit is more strict than the upper limit. In the case of low thermal conductivity or low air ratios larger gradients arise over the cell and the upper limit to the catalytic activity is more strict, the optimum range moves to lower catalytic activities.

- With effective *k*-values at 850°C between 0.1-0.4 mol/s.bar.m² thermal stresses in the order of 120-170 MPa have been calculated whereas the strength of the cells is in the range 200 - 300 MPa.

TEST RESULTS

- The performance using CH_4/H_2O as a fuel with AS1/8YSZ/KS1 cells sintered at the standard temperature is better than with cells sintered at increased temperature.

- The catalytic activity for the steam reforming reaction on AS1 anodes is in the range suited for operation under CH_4/H_2O with an activation energy of 35 – 48 kJ/mol.

- The stability of the catalytic activity of AS1 anodes for the reforming reaction is not optimal and seems sensitive to changes in the gas composition

- The catalytic activity of the standard ECN Ni-YSZ and especially the ECN double layer anode seems to be in the upper range of what can be accepted for a stack at "Siemens" conditions.

Task 5.1C: Study of anode working conditions in steam/methane (BG)

The main objectives of this task were to investigate the various important issues in IR-SOFC operation including:

1) the operation and performance of half-cells and single cells in methane/steam
2) the development of a kinetic model of the reforming reaction in OCV conditions
3) the investigation of carbon deposition.

Cells were supplied by the partners and tests were performed to investigate the influence of various operating parameters such as the amount of pre-reforming, flowrate, steam:methane ratio, oxidation factor (amount of simulated electrochemical oxygen in the gas mixture), temperature and the effect of the shift reaction on the rate of reforming/activity of the anode. The main conclusion was that the rate of reforming was not only dependent on methane and steam concentrations but also on the concentration of hydrogen. This was confirmed with a more-controlled set of tubular reactor tests. The cells appeared to be more stable the higher the amount of pre-reforming. The activity of the anode was very dependent on the reduction procedure.

Reliable kinetic data is required for stack modelling in order to optimise the system for internal reforming. Ternary gas compositions were investigated systematically in a tubular reactor in order to investigate the influences of temperature and the concentrations of steam, methane and hydrogen. The reaction was found to be first order in methane. There was a strong negative effect of steam and a weaker positive effect of hydrogen. The temperature dependence of the rate was non-Arrhenius.

These tubular reactor experiments were extended to full gas compositions, which were described in terms of system related parameters. From this a rate equation was deduced.

The results were qualitatively explained by the findings from the ternary gas study. The reforming rate showed a maximum as the amount of pre-reforming was increased. Increasing the oxidation factor decreased the rate and there was a small effect of the steam:methane ratio on the rate.

Carbon deposition on SOFC anodes was investigated using Thermogravimetric Analysis (TG) and also using a differential pressure (dP) reactor. The TG results showed that equilibrium constants for Boudouard and methane decomposition carbon on SOFC anodes were similar to those based on graphite. The dP reactor tests on a Siemens anode were generally consistent with this.

Task 5.2A: Long term testing of optimised cells (ECN)

Endurance behaviour under hydrogen

Small scale cells (2x2 cm²)

Using nickel current collectors a standard tape cast cell (standard cell in beginning 1996) showed no degradation during 2500 h of testing at 80% fuel utilisation.

An AS1/KS1 cell was tested for 14000 h with 50% humidified hydrogen at the anode, air at the cathode, 300 mA/cm² and 850°C. In the first 500 h the cell improved. After this period the cell degraded at a rate of < 8 µΩcm²/h over a period of 7500 h. After 7500 h the cell started to improve again. The cell is still running and has now been tested for > 15000 h and is back at the original value as when the test commenced.

Upscaled 10x10 cm² cells
The endurance behaviour of an upscaled AS1/KS1 cell, measured at 850°C and 300 mA/cm² over a period of 1000 h proved the successful upscaling of this type of cell. The performance under hydrogen and air was slightly higher than the performance of the small-scale cell, probably due to edge effect in the small-scale cells.

Three cell stacks of up-scaled cells
The endurance behaviour of upscaled AS1/KS1 cells was measured at 850°C in three cell stacks delivered by Siemens.
As a consequence of the post test analysis of a first stack test with high degradation rate the nickel grids of the top-two layers of the second stack were very carefully spot-welded to the separator plates and the number of spots was increased, whereas the nickel grids of the bottom cell were kept "as received". An extra voltage probe was attached to the nickel grids of the bottom cell in order to determine the voltage loss over the contacts between the nickel grids and the separator.
After start-up the average cell performance was 360 mA/cm² at 700 mV (60.5 Watt) at a cell temperature of 850°C. The stack was tested for 4950 h. During the first 100 h the voltage drop between the nickel grids and the separator plate of the bottom cell increased dramatically from 20 to 250 mV (0.85 Ω.cm²) and became nearly stable after this period. Due to this voltage loss the performance of the bottom cell became 250 mV lower than the performance of the top two cells. Overall the average degradation rate over the last 4500 h was about 5 % V-cell/1000h.
It was demonstrated that the degradation of Siemens stacks was for the main part caused by corrosion of the contacts between anode current collector and the bipolar plate material.

Endurance behaviour under methane

Small scale cells (2x2 cm²)
A small scale AS1/KS1 was operated with CH_4/H_2O mixtures for about 4800 h at 850°C. This cell showed an increasing cell performance, which was 300 mA/cm² at 0.73 V at the end of the test. This increasing cell performance was due to an increased effective reforming rate constant k. The converted fraction of methane was 50%.

Upscaled 10x10 cm² cells
Modelling of stacks and system calculations at EniTecnologie, BG and Siemens showed that 10% pre-reforming of the CH_4 was beneficial for the temperature distribution in the stack without significant loss of electrical efficiency in the system. An upscaled AS1/KS1 cell was therefore tested in alumina housing with 10% pre-

reformed methane as a fuel. The performance was initially unstable due to variations in the rate of the reforming reaction. After an initial rapid decrease of cell voltage and "OCV", the cell started to improve. The cell was tested for 1600 h showing nearly no degradation.

A 10x10 cm² cell with a double layer anode consisting of a Ni/GCO active layer and a standard Ni-YSZ upper layer was tested at 850°C with 10% pre-reformed methane and a steam to carbon ratio of 2 for more than 2000 h (the test had to be stopped because of power failure). The cell voltage as well as the OCV (i.e. reform rate) were quite stable, and the performance was very good (0.83 V @ 0.3 A/cm²). The degradation over the whole testing period under methane was 16 μΩcm²/h, although this increased after 1000 h (33 μΩcm²/h between 1000 - 2200 h), due to a slightly decreasing OCV. The conversion, however, remained 100%, so a reduction in the reform rate could not be measured.

Three cell stacks of up-scaled cells
As in the case of the stack test with hydrogen the spot welding of the nickel grids to the separator plate was improved for the third 3-cell stack in metal housing. Based on the experience of testing upscaled AS1/KS1 the stack was fuelled with 10% pre-reformed CH_4/H_2O (steam to carbon ratio of 2). The stack was tested for 4000 h and showed less than 1% degradation per 1000 h over the last 3500 h. The standard Ni/YSZ anode in the 3-cell stack showed a decrease of the reform rate, corresponding to a decrease of the effective rate constant from 0.3 to 0.12 mol/s.bar.m² during the 4000 h of testing. Towards the end of the test the conversion was 80%. Unfortunately the test was terminated due to a power failure.

A second three-cell stack was started with 10% pre-reformed methane at the anode. Upscaled 10x10 cm² cells with a modified double layer anode with improved adherence to the electrolyte were used. Similar to single cell testing the performance of the stack under 10% pre-reformed methane was very high (78 Watt, 700 mV per layer at 465 mA/cm² and 850°C) but also similar to single cells, the stack degraded rapidly.

Task 5.3: Testing of stacks (Siemens)

Single cell measurements

Long-term testing of cells
A long-term test of two cells with ECN-type anodes was performed for 10000 h. These cells were operated at 850°C with 50% H_2 and 50% steam and a constant current density of 0.3 A/cm² at a starting cell voltage of about 750 mV. The performance of both cells reached a maximum after about 1500 h of operation and then decreased slightly during the next 8500 h. The total degradation rate was 0.2 resp. 0.4 %/1000h.

Detailed analysis of impedance measurements, of in plane resistance of the electrodes and EDX investigations revealed the following results (valid for ceramic housings):
• cell degradation is mainly due to contributions of anode and cathode and less due to degradation of contacts

- a reversible response of the cathode polarisation on load was found (activation under load and deactivation under open circuit)
- there is strong evidence that the main part of degradation between 7000 and 10000 h is due to contamination of the cathode / electrolyte interface by platinum evaporation from the cathode current collector, which is not valid for real stack operation

<u>Methane operation of cells</u>

After a long-term test under methane and total internal reforming (S/C = 2) with a single cell, performed for 2100 h, the anode of the cell showed a white stripe along the edge at the fuel inlet side. Microscopic and EDX analysis revealed a pronounced loss of Ni in this area and resistance measurements showed missing electronic conductivity. As this phenomenon was also observed with anodes after flushing with the same type of gas outside of a cell, it is concluded, that it is only due to the gas atmosphere and that it is not a primary effect of current flow. As with an addition of 10% hydrogen to the methane water vapour mixture the nickel loss could be suppressed, it is concluded that this is also the case when the anode is fed with partly pre-reformed methane.

Several further tests have been performed with methane (S/C = 2) and hydrogen/steam as fuel gas to investigate the behaviour under different conditions.
I-V curves starting at the same OCV showed that in any case the performance of the cells tested with hydrogen and with methane was similar. Differences are mainly due to the cooling of the cells caused by the high reforming rates of the anodes, measured to be about 30 K. A cell with scandia doped electrolyte with double layer anode reached current densities of 0.7 A/cm² at 850°C and 650 mV, fed with methane with and without a content of 10% of hydrogen (simulated pre-reforming) at moderate flow rates (corresponding to a methane excess flow rate of about three).

Examination of special aspects

In the first several hundred hours normally no degradation but an improvement of cell performance was observed. It was evident that different effects (degradation of the anode and improvement of the cathode) may compensate each other so that the overall performance seems to be stable. This complicated behaviour of different components of the MEA also depends on the operating temperature. The target to separate these long-term effects is now achieved by analysing impedance spectra at definite running times of a cell. Thus it is possible to separate contributions due to anode, cathode and ohmic parts of the cell.

As could be shown by impedance spectroscopy, all short-stack experiments using metal interconnector plates (with and without protective layers) suffer from the fact that the serial (ohmic) resistance is rather high compared to measurements in ceramic housings.
Tests with special samples showed a rapid increase of the resistance, strongly dependent on temperature, caused by a reaction zone formed between nickel and chromium under presence of water vapour. To avoid this reaction different protective layers deposited on the bipolar plate were investigated. The most stable behaviour was gained using a nickel coating, which promises a lifetime of 40000 h staying below the target value of 10 mΩcm².

Short-Stack Tests

To test new variants of sealant and isolation layers several short-stack tests have been performed. Short-stack tests with CrFe5Y interconnector plates coated with LSCr showed that it is possible to decrease or even block the diffusion of chromium and the formation of chromium oxide on the interconnector surface.

Different methods of stack assembly were investigated in order to devise a simpler and cheaper design. Two approaches to replace the expensive spinel insulating frame with coatings applied directly to the bipolar plate were investigated: plasma sprayed ceramic coatings and glass ceramic coatings, developed by ALSTOM. Both methods gave sufficient gas tightness and high electrical resistance in tests operated in excess of 2000 hours.

Tests using a screenprinted glass sealant, which was a modification of the standard glass, showed a highly improved chemical stability in combination with a good sealing behaviour.

Stack Tests

To find out the best combination of protective and contacting layer on the cathode side, which on the one hand influences the contact resistance and on the other hand the chromium evaporation, 12 short stacks were tested between 1000 and 5000 h. Fife of them showed a degradation between 1 and 2%/1000h in the first 1000 h. One was operated for 5000 h with a degradation of about 3%/1000h, influenced by several equipment failures. The used functional layers (lanthanum chromate as protective layer and LSMC as contact layer) showed a very promising behaviour. So this material combination was used as standard for further tests.

With several 2 layer stacks with 16 cells (5x5 cm²) per layer the reasons for the problems arisen during the 20 kW test were investigated. It could be analysed that, under special circumstances and at temperatures above 900°C, arsenic in the sealing glass used (a commercially available glass containing ~0.5 weight % arsenic as a refining agent) reacts with hydrogen to form gaseous AsH_3. Bubbles of AsH_3 in the glass caused it to flow into, and block, the gas supply channels. This caused destruction of the cells which had insufficient gas supply. Several measures, such as reduction of the operation temperature and changes in the geometry of the seal were implemented to avoid this failure, simultaneously improvements in the sealing glass itself were also investigated.

A 10 layer stack of the type 50/16 was operated for 7100 h at 300 mA/cm² including four thermal cycles down to room temperature. Twice the stack was removed from the furnace and stored without any weight for several weeks in the lab. Afterwards the stack was prepared once more for an electrical test in the same test stand and was operated with the prior conditions. The stack showed nearly the same performance as prior to the corresponding thermal cycle. This test validated the strategy to fabricate and run the stacks in a smaller test unit and then to assemble several of these stacks, connected in parallel, in a larger test facility. This is valid despite a non-optimised seal and low mechanical strength of the cells. The total degradation rate of the stack was about 6.5 %/1000h. Final measurements proved

that this degradation was mainly caused by the contact resistance between Ni-grid and bipolar plate, which can be greatly improved in future by implementing e.g. a Ni-coating on the surface of the bipolar plate.

Two stack tests were performed to approve the new design 100/9 (each layer containing 9 cells of the size 10x10 cm²) and to test a new, large steam generating system for methane operation in a test stand, suitable up to 25 kW. One of them was operated for more than 3500 h with methane, without visible degradation during operation with stable conditions. These tests revealed no severe problems either with the new stack design incorporating nine large cells per layer or with methane operation.

Task 5.4: Testing of 50 kW module (Siemens)

The 20 kW test facility was put into operation using two stacks connected electrically in parallel, each consisting of 50 layers. The operation temperature of the stacks was 900°C. During the measurement of a first current/voltage characteristic using hydrogen and air the two stacks behaved very similarly concerning temperature distribution, voltage and current (the current of each stack was recorded individually). A power output of 7.2 kW could be achieved at a fuel utilisation of 30% and an air utilisation of 50%. During the following measurements (with oxygen instead of air) the stack resistance increased in such a way that the test had to be stopped.

This first operation of the test facility has proven, that all components of the test stand operated well and that the assembly concept of parallel-operated stacks is feasible. The problems inside the stack were found to be because of the instability of the sealing glass used. This problem has now been solved as could be shown by several tests in small stacks, discussed earlier.

For continuation of operation of the test facility independent of the stack development, a heated stack dummy was designed and manufactured. Using this dummy, the test facility was operated for more than 2000 h at temperatures between 800 and 900°C without significant failures. The control system (stored programme computer, SPC) fulfilled the requirements and performed automatic control as well as safety monitoring. Auto-thermal operation of the system is possible at thermal loads of at least 6 kW at stack temperatures between 820°C and 950°C, which is a clear improvement compared to the first assembly. The total heat loss of the system is about 4.5 kW at a stack temperature of 850°C. This was made possible by replacing the ceramic fibre insulation material in the piping area by a micro-porous material.
The static and dynamic behaviour of the system was investigated under various conditions to enable the adaptation of characteristics and parameters of stack and plant control. It was found, that the system needs 1 h (at 15 kW) up to 10 h (at 6 kW) to reach thermally stable behaviour. Rapid load changes from 7.8 kW to 15 kW and vice versa with a frequency of 5 minutes result in a very smooth temperature change.

5.   Results and Conclusions

OPTIMISATION OF ELECTRODES (Siemens, ECN)

- The sensitivity of the cathode to load changes was significantly reduced by using A-site deficient LSM as the cathode powder
- Double layer cathodes were developed in order to optimise the performance of the cathode in air.
- A double layer anode was developed to optimise the catalytic activity for steam reforming of methane without losing lateral conductivity (0.55 A/cm^2 at 700 mV and 850°C whereas standard AS1 anodes only achieve 0.33 A/cm^2) Further optimisation in terms of adherence, stability and reproducibility is necessary.

MANUFACTURING OF COMPONENTS (Siemens, ECN, EniTechnologie, ALSTOM)

- The strength of sintered electrolytes was increased by optimising electrolyte tapes.
- The strength of cells was optimised by reducing the sintering temperature and the quality was improved by inventing a proof test.
- The manufacturing routes of both ECN and Siemens were evaluated and integrated. As a result of the integration of the manufacturing routes the ECN AS1 anode and the Siemens cathode were accepted as the standard 50 kW electrodes.
- New laboratories for large series production were installed at ECN. Standard cells and cell components were manufactured in this facility according to the request of Siemens.
- In close collaboration with Siemens, ECN developed tape-casting recipes for scandia doped zirconia electrolytes using powder manufactured at Siemens. Both ECN and Siemens were able to sinter the electrolytes 98% dense.
- Bipolar plates and components with 4 and 9 cells per layer can be manufactured
- A method of applying glass-ceramic coatings of a specified thickness and over a well-defined area to CrFe5Y bipolar plates has been developed by ALSTOM. Such coatings form part of the planar SOFC seal assembly and also provide electrical insulation between the overlapping edges of neighbouring bipolar plates.
- The glass-ceramic coating method uses conventional ceramics processing techniques, is suitable for volume production and should be low cost. The materials used in the process are environmentally benign and the ability to recycle the tapes should ensure their efficient use.

IR SOFC SINGLE CELL TESTING (ECN, EniTechnologie, BG Technology)

- The catalytic activity for the steam reforming reaction on AS1 anodes is in the range suited for operation under CH_4/H_2O mixtures
- The stability of the catalytic activity of AS1 anodes for the steam reforming reaction is not optimal, and seems sensitive to changes in the gas composition.
- The catalytic activity of the standard ECN Ni-YSZ and especially the ECN double layer anode seems to be in the upper range of what can be accepted for a Siemens stack configuration.
- Carbon deposition on SOFC anode materials and steam reforming catalysts is in line with traditional wisdom given in the literature.

- Equilibrium constants for carbon formation are lower for the catalyst materials studied than those assuming graphite carbon.
- The observed equilibrium constants offer no scope for reduction of the amount of steam added in the feed of SOFCs operating above 800°C.

ENDURANCE BEHAVIOUR UNDER H₂ (Siemens, ECN, EniTechnologie)

- The upscaled AS1/KS1 cell yields under hydrogen/water vapour and air very stable (slightly improving) performance over a period of 1000 h. This behaviour is comparable to the behaviour of small-scale cells. The voltage degradation over a period of 10000 h is below 0.5 %/1000h
- The initial performance of a three cell stacks is comparable to the performance of the upscaled cells tested in an alumina cell housing.
- The degradation rate of a 50 W stack under hydrogen and air was too high (5 %/1000h instead of the aim: 1 %/1000h), but the invention of an additional contact layer on the anode side of the interconnect will clearly improve this.

ENDURANCE BEHAVIOUR UNDER METHANE (Siemens, ECN, EniTechnologie)

- The use of pure CH_4/H_2O mixtures as fuel seems to lead to degradation in the form of a loss of lateral conductivity, which corresponds to a loss of nickel at the cell inlet, also observed. This effect can be avoided by using 10% pre-reformed methane.
- A quick reduction process is critical for the performances of the cell.
- A platinum grid on the anode side instead of a nickel grid increases the degradation of the anode by a large degree.
- The catalytic activity for the reforming reaction is not stable. The trend seems to be that, after initial deactivation of the Ni-surface, the catalytic activity slowly increases, resulting in a net improvement of the performance. The origin of this effect needs further investigation.
- A 3-cell stack operated with 10% pre-reformed CH_4/H_2O showed a degradation of < 1 %/1000h over 4000 h, which was a major goal in the project.
- Using double layer anodes (AS3) a 3-cell stack operated with 10% pre-reformed CH_4/H_2O yielded 0.32 W/cm^2 at 850°C, which is higher than the target power density of the project.
- A cell with scandia doped electrolyte with double layer anode reached current densities of 0.7 A/cm² at 850°C and 650 mV (0.45 W/cm²).

MECHANICAL PROPERTIES OF YSZ AND MEAs (IMPERIAL COLLEGE)

- Elastic modulus, strength and toughness of the electrolyte has been measured at 25 and 900°C. Toughness is low at 25 and 900°C and is best measured using the double torsion method.
- Measurements of fracture of symmetrical MEAs has shown that the cathode is responsible for lowering the strength of MEAs.
- Susceptibility to slow crack growth at 25°C in air has been characterised. There is some slow crack growth with a velocity that varies as approximately the 20th power of applied stress intensity. There appears to be a threshold stress intensity below which there is no slow crack growth.
- Measurements made at 900°C in air have shown that the slow crack growth takes place with a velocity that varies as approximately the 2.6[th] power of applied stress intensity under these conditions, which are relevant to the cathode side.

- The effects of slow crack growth can be approximated by a 20% reduction in long term strength
- The standard strength test is not suitable for reliability prediction because the volume of material under stress is too small. A proof test procedure, which has a much larger stressed volume, was developed.
- The defects responsible for electrolyte fracture have been revealed. By reducing the number and severity of these defects (through better control of tape casting conditions) the electrolyte producers have increased the strength and reliability of the electrolyte foils.

FAILURE MODES OF SEALS (IMPERIAL COLLEGE)
- A new test configuration for fracture strength of the reference Siemens seal has been devised and evaluated, that minimises the opening mode stresses. This gives a high mean apparent shear strength of about 80 MPa.

STACK DESIGN, MANUFACTURING AND TEST (Siemens, ALSTOM)
- A new assembly concept with fewer parts and a replacement of ceramic frames by glass-ceramic coatings was devised and tested successfully in short stacks
- A range of glass-ceramics with extremely close thermal expansion matching to CrFe5Y ($\Delta\alpha$ < 3%, 25-1000°C) has been developed.
- A new stack design (type 100/9) with increased plate and cell size was designed manufactured and tested successfully
- Stack operation including four temperature cycles down to room temperature and two times removal from the furnace could be demonstrated successfully. This shows that it is possible to test stacks in the laboratory before integrating them into the plant.

PLANT DESIGN, MANUFACTURING AND TEST (Siemens, BG Technology, EDF)
- Below a pre-reforming rate of 15% the enthalpy of the anode waste gas flow is sufficient to heat up the fuel gas and the pre-reformer without the necessity to heat the pre-reformer by burning the waste gas
- 10% pre-reforming is a good compromise between requirements for stable stack operation and high plant efficiency
- The first operation of the plant showed the basic functioning of the plant concept
- Based on dummy tests the components and control concept could be improved
- Pre-reformer and desulphuriser for the 50 kW plant is available
- Alternative high temperature heat exchangers are available

6.   Exploitation Plans and Anticipated Benefits

The calculated efficiencies for SOFC plants in the whole range from 100 kW up to more than 100 MW are 15% to 20% higher than conventional plants. So the benefits are less fuel consumption and less exhaust gases. Per generated kWh a SOFC power plant emits significantly less CO_2 and no SO_x, ozone or CO. Due to lower process temperatures compared to direct combustion, NO_x emissions are also significantly lower (one to two orders of magnitude). Since the processes that take place in a fuel cell are electrochemical reactions, ideally there would be no moving parts to generate noise and vibration. In practice however, pumps, blowers, transformers and other auxiliary devices are generally required. Despite this, fuel cells operate much more quietly and smoothly than most other power-generating devices and should require less maintenance. Fuel cells are as safe as coal-, oil- and natural gas-burning central power stations.

These advantages provide a market potential, which is envisaged first in co-generation of electrical power and heat in the range between 100 kW and 10 MW, where the installed power per year is about 500 MW (Europe 1998).

The bigger market in the future will be the electrical power generation in decentralised plants. The installed power in Europe in 1996 in the range between 0.1 and 10 MW is about 3.4 GW in the case of gas-motor power plants and 1.1 GW with gas-turbines. In the year 2010 a market for gas-motors will be in the range of 5.2 GW/a and for gas-turbines 2.2 GW/a. About 10% of this market, which means about 500 MW/a can be taken over by fuel cells, if the specific prices of all systems are in the same range. This means a market volume of about 500 MECU per year will be available for the manufacturers of fuel cell systems. Because of the specific advantages of the SOFC, especially the very high electrical efficiency, the SOFC is in a good position to take over the major part of this fuel cell market. Because of the predicted growth of this market the fuel cell volume can be doubled until the year 2020, which means a market volume of 1 Billion ECU per year.

Siemens power generation group is one of the worlds leading companies in the field of power generation, working on nearly all types of power plants. Therefore the SOFC technology belongs to the core business of the company.
As a result of the integration of Westinghouse Power Corporation into Siemens, the more advanced tubular SOFC design now also belongs to Siemens. Based on this design it is thought that the market entrance can be realised several years earlier as with the planar design. To keep this chance Siemens decided to terminate the planar development and to focus on tubular. The exploitation of planar technology is not foreseen in the next years, but it is seen as an alternative in the future. Therefore a new consortium is planned (without Siemens), which shall use the knowledge gained within this programme and continue the planar development.

At ECN investments are being made and preparations are being undertaken in order to move manufacturing of SOFC cells out of the laboratory. The aim at ECN is to establish what could be considered a pre-pilot plant cell manufacturing facility within a short time scale. This cell manufacturing facility would be a commercial

organisation operating in close collaboration with ECN but operating outside of the organisational structure. As a first step towards this goal ECN has contracted Arthur D. Little and Boer and Croon to asses the market potential of SOFC and to draw up a business plan for manufacturing of ceramic fuel cell components.

ENI is the major Gas and Oil Company in Italy and is involved in sale and distribution of natural gas. The fuel cell, fuelled with natural gas, appears to be a good opportunity to grow the gas business.
EniTecnologie is the corporate research of ENI and is interested to monitor the technological development where a potential business has been foreseen.
In the current project ENI plays an active role to give end user specification and to support the technological needs with his competencies and testing facilities.

ALSTOM is among the world-leaders in the manufacture and supply of power generation systems and transmission and distribution equipment. As such, ALSTOM recognizes that ongoing deregulation and liberalization of global electricity markets will lead to an increasing demand for distributed generation and co-generation. ALSTOM is committed to fuel cell technology as one of the key solutions to this expanding market.

ALSTOM has recently formed a joint venture company with Ballard Power Systems of Canada which aims to market proton exchange membrane fuel cell (PEMFC) systems for small-scale CHP and distributed generation markets. ALSTOM regards the development of SOFC technology as complementary to this activity. The operating characteristics of the SOFC will make it more applicable to higher power ratings and applications where the high grade waste heat can be utilised, either for co-generation or advanced gas turbine combined cycles.

It is clear that the environmental benefits alone will not sell fuel cells; they must be competitive with conventional plant. Cost studies by ALSTOM and other partners within the consortium demonstrate that, long-term, planar SOFC is the most likely to reach commercial targets. ALSTOM will, therefore, seek to further develop planar SOFC, where appropriate, exploiting IPR generated within the completed project.

BG plc is one of the world's major energy companies, with expertise at every stage of the gas chain - from exploration through production to infrastructure management and gas marketing. It is active in the UK through its subsidiary Transco, which owns and operates the UK's onshore gas transportation and storage network. Business around the world is divided between BG International and Production, and BG International Downstream. BG Technology provides research and development for the whole BG group.

BG International Downstream is involved in major power generation projects, examples being in Northern Ireland, in the Philippines (a 1500 MW power station) and in Argentina. However, as an international energy company, BG recognises that the power generation business worldwide is undergoing major changes. De-regulation and the opening of markets to competition are likely to lead to a move

away from large central power stations towards an increase in embedded, and dispersed power generation and co-generation (both combined heat-and-power, and combined cooling-and-power). The driving forces for such changes are both environmental and fiscal. With natural gas being the most widely available fossil fuel well into the next century, BG believes that significant business opportunities exist therefore in gas-fuelled industrial or commercial co-generation. Fuel cells have an important role to play in these businesses. As a company, BG will benefit partly by maintaining the market for gas in the power generation business, but mainly by taking an equity stake in a fuel cell commercialisation partnership.

BG Technology will seek to exploit the IPR generated within the present project, preferably in collaboration with the existing partners. However, it also recognises that some of the exploitable results may also be used by other companies, working on SOFC and also other fuel cell technologies.

EDF is one of the world's leading electrical utilities with increasing activities in distributed generation. Fuel cells could play an important future role in the means of power production used by EDF.

Within the framework of this programme, the R&D division has worked on the design of a power converter based on IGBT devices, which is optimised for the constraints of a SOFC stack and the demands of the electrical grid.
The control command instructions for the power converter results from instructions for the grid or the stack.
These results can be used to build a power converter for SOFC systems taking into account the constraints brought by the end user. They will be capitalised in future work on interfacing SOFC systems to the electrical grid.
The potential application of this design is the construction of IGBT converters for SOFC systems. The end user of this result is the converter manufacturer and SOFC systems integrator.

Several of the partners are interested in participating in the new consortium to continue the development of planar SOFC towards a demonstration plant.