Dato: 30/05/07

PSO-F&U Afslutningsskema

1. Projekttitel	Evaluation and optimization of Danish solid oxide fuel cells – Generation 2.5G and 3G
2. Projektidentifikation	FU 5849
3. Projektperiode (dato, år)	01.04.2005 – 31.03.2007
4. Projektansvarlig virksomhed	Risø DTU
5. Øvrige deltagere	

6. Den underskriftansvarliges underskrift

Dato:……

Navn: ……..

Underskrift: ……..

7. Sammenfatning af projektets formål og de opnåede resultater
(Resumeet må højst fylde 2.000 karakterer. Indhøstede erfaringer og evt. betydelige afvigelser fra de oprindelige projektforventninger kommenteres)

The aim of the project was to provide input for the development of new solid oxide fuel cell (SOFC) generations by detailed electrochemical testing combined with micro structural analysis of the fuel cells.

Durability is a key issue for a successful SOFC technology, together with performance and price. Therefore, it was aimed at gaining a detailed understanding of the underlying degradation mechanisms of 2G and 2.5G cells under technologically relevant and severe ('accelerated') operating conditions by continuing the comprehensive long-term testing combined with subsequent micro structural analysis.

SOFCs are known to be flexible with respect to the useable fuels. Within the project the usability of biomass derived fuels and ammonia was to be demonstrated.

Within the project a comprehensive cell testing program was accomplished, accompanied by microscopic analysis. More than 100 tests of cells were initialized. About 60000 hours (or almost 7 years) were dedicated to long-term testing to study durability and identify degradation paths.

One of the main achievements in the project period was the support of the break through in development of 2.5G (and 2.xG) cells showing excellent performance and good long-term stability. This achievement was possible by combined effort of cell and manufacturing development, cell testing, and cell characterization by microscopy.

Furthermore, degradation paths were identified on a fundamental level through cell testing, micro structural analysis and with the help of thermodynamic modeling. As a result, the currently most developed cell generation 2G was significantly improved with respect to long-term stability under severe operating conditions and performance as well.

The application of a variety of fuels was demonstrated successfully by using ammonia, simulated biosyngas of gasified biomass, and simulated reforming gas of ethanol reforming.

The development of design and manufacturing of 3G cells was significantly moved forward by the knowledge gained in cell testing and microscopic analysis.

8. Abstract *(Skal fylde ca. 1.000 karakterer. Der lægges vægt på resultater, der har international interesse)*

One of the main achievements in the project period was the break through in development of 2.5G (and 2.xG) cells with excellent, internationally competitive performance and good long-term stability.

Furthermore, a better, detailed understanding of degradation paths was gained through cell testing, micro structural analysis and with the help of thermodynamic modeling. Using this knowledge, the currently most developed cell generation 2G was significantly improved with respect to long-term stability under severe operating conditions and performance as well.

The application of a variety of fuels was demonstrated successfully. Specifically, ammonia, simulated biosyngas of gasified biomass, and simulated reforming gas of ethanol reforming was tested in long-term tests with good performances and stabilities.

The development of metal supported, 3G cells was significantly moved forward by the knowledge gained in cell testing and microscopic analysis. As a result, alternative approaches to cell manufacturing have been developed, and at least two new cell designs have appeared.

9. Resultatanvendelse, forretningsstrategi, offentliggørelse og formidling *(Realiserede og mulige resultatanvendelser omtales, sammen med en kort beskrivelse af forretningsstrategien. Publikationer, rapporter, artikler samt indlæg om projektet ved møder og konferencer oplyses)*

The results were presented at conferences and communicated in international journals. The possibilities for a patent are currently investigated.

10. Finansieringsoversigt		
Oversigten er ikke et projektregnskab. Projektregnskabet udformes (og revisorpåtegnes for private) i overensstemmelse med gældende Regler for udførelse af PSO-F&U projekter og indsendes separat	**Totale projekt-omkost-ninger**	**Heraf PSOtilskud**
Lønomkostninger	5.276.735	5.276.735
Overhead	5.659.082	1.055.347
Apparater, udstyr, materialer	625.594	625.594
Eksterne ydelser	587.507	587.507
Rejser og ophold	58.096	58.096
Andet (OH øvrige udgifter)	0	254.240
Samlede faktiske omkostninger og PSO-tilskud	12.207.014	7.857.519
Eventuelle indtægter og restanlægsværdi	0	0
Projektets reelle udgifter og PSO-tilskud	12.207.014	7.857.519

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May 2007

Resumé

Evaluation and optimization of Danish solid oxide fuel cells – Generation 2.5G and 3G

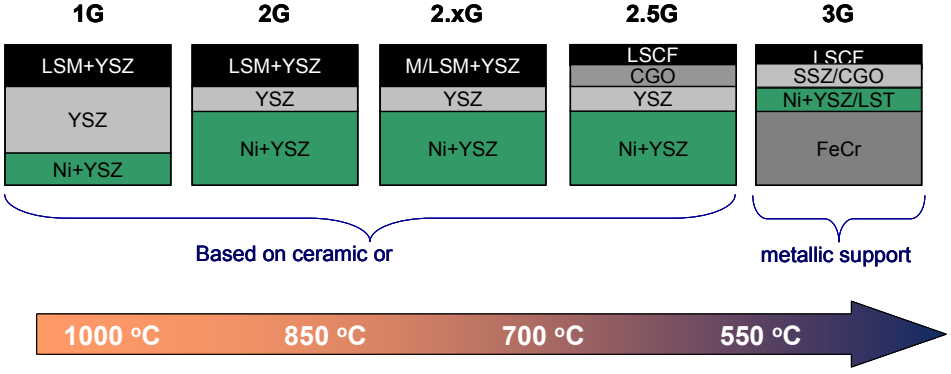
PSO-Eltra Project 5849

April 1, 2005 to March 31, 2007

Introduction

The aim of the project was to provide input for the development of new solid oxide fuel cell (SOFC) generations by detailed electrochemical testing combined with micro structural analysis of the fuel cells. Furthermore, the long-term stability and degradation behavior was studied with the aim to understand degradation mechanisms and thereby give profound input to improve the long-term stability of the fuel cells under technologically relevant conditions using a variety of fuels.

The currently most developed cell generation is the 2G cell (see Illustration below), which is produced in the pre-pilot facility at Risø. The optimal operating temperatures are around 800 to 850 °C. New cell generations (2.5G and 3G, see Illustration), allow a decrease of the working temperature to ~700 °C and ~500 °C, respectively, at the same or improved performance. The advantages of these cell generations are a drastic reduction of the prize and an expected higher durability and lifetime.



Results

Cell development: 2.5G cells

Cells of the generation 2.5G are composed of the same half cell (anode support, active anode and electrolyte) as 2G cells. The limiting cell component of 2G cells at operating temperatures of 750 °C and below is the cathode. A new composite cathode (lanthanum strontium cobaltite ferrite – LSCF/ cerium gadolinium oxide – CGO) is expected to have lower resistances at these temperatures. In the current project, 2.5G cells received from the development were tested with respect to electrochemical properties (resistance contributions) and micro structure. A large number of 2.5G cells with varying composition and manufacturing parameters were tested. A breakthrough was achieved regarding the understanding of the main correlation between the micro structure and performance. Based on this understanding, a fine-tuning of the electrochemical properties of 2.5 G cells is now possible and area specific resistance as low as 13 Ωcm^2 at 750 °C (vs. 0.41 Ωcm^2 for 2G cells) have been obtained. At lower temperatures, the performance improvement is even more significant (see Fig. 1).

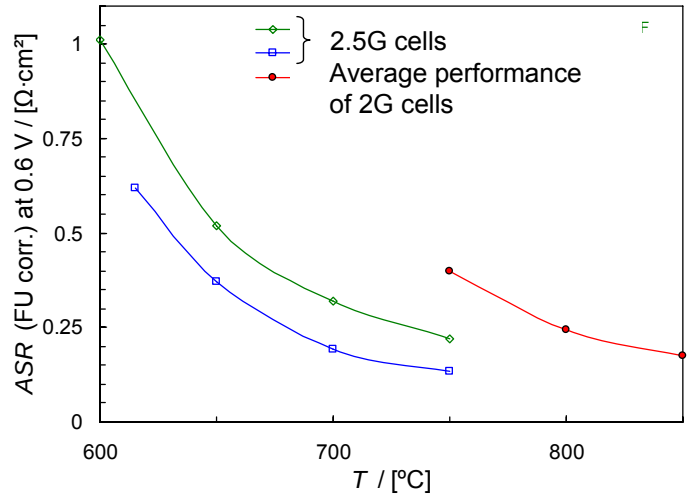


Fig. 1 Area specific resistances (corr. for fuel utilization) as function of temperature obtained on a standard 2G cell and two versions of 2.5G cells with slightly different compositions

Durability

Durability is a key issue for a successful SOFC technology, together with performance and price. An extensive test program was carried out on 2G and 2.5G cells. Whereas the latter studies were aimed at improving the stability by optimization of the cell composition and structure, the long-term testing of 2G cells focussed on a detailed understanding of degradation mechanisms, applicability of a variety of fuels derived from fossil and alternative sources, and to provide ideas for the improvement of the durability based on profound knowledge of degradation mechanisms.

Severe operating conditions affecting either mainly the cathode or the anode were identified. Accordingly, higher temperatures facilitate anode degradation that proceeds fast, within a few hundred hours. By developing and using advanced microscopic methods and test of model anodes, the coarsening of percolating Ni-particles in the anode was evaluated and correlated to testing conditions/degradation rates.

Operating the fuel cells at lower temperatures (750 °C) and high current density (0.75 A/cm^2) affects the cathode significantly. A continuous degradation proceeds over the whole testing duration. Detailed insight in the micro structural changes induced by operation was gained by a combination of micro structural analysis and comprehensive electrochemical characterization. During operation, changes in the cathode/ electrolyte interface occur. Specifically, the attachment of LSM particles from the cathode to the electrolyte is weakened. At the same time, foreign, isolating phases are formed. Although these processes are restricted to the interface region, they lead to a significant loss of performance. They are highly dependent on the oxygen partial pressure on the interface. When working in pure oxygen instead of air, these degradation mechanisms were completely suppressed. This knowledge was used together with thermodynamic calculation to suggest a modification of the cathode in 2G cells that makes them significantly more stable (see Fig. 2).

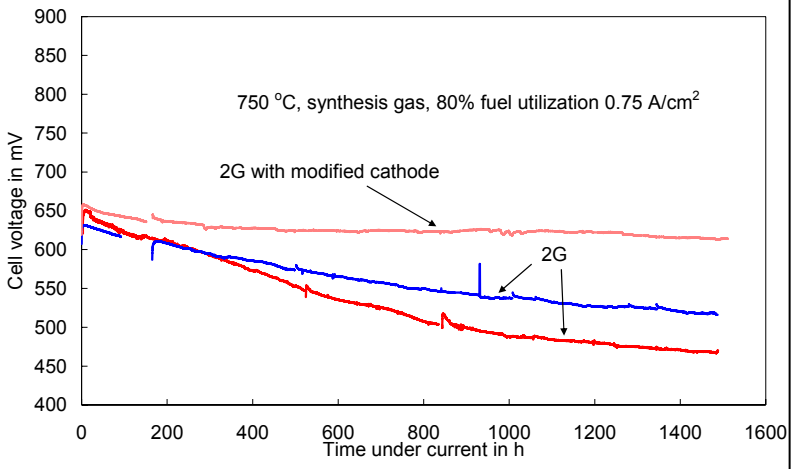


Fig. 2 Long-term tests of 2G cells and the best 2G cell with improved cathode at 750 °C, 0.75 A/cm^2, synthesis gas at the anode side with a fuel utilization of 80%

The flexibility of SOFCs with respect to fuels is often mentioned. One aim of the current project was to demonstrate the durability of SOFCs using bio-derived fuels and ammonia.

Biomass can be converted by a number of established technologies, e.g. gasification to biosyngas, anaerobic digestion to methane, and fermentation to ethanol. It was shown that the obtained carbon containing fuels can be used directly; here the SOFC anode acts as catalyst converting all hydrocarbons to CO and hydrogen with steam. Long-term tests were performed on model mixtures representing biosyngas derived from wood chips. A model mixture representing ethanol reforming gas was used as fuel in another long-term test. The degradation rates were similar to other tests with a synthesis gas derived from methane reforming under similar testing conditions (see Fig. 3). The feasibility of using such fuel was thus demonstrated. In the forthcoming time, the effect of minor components in the biosyngas on the SOFC performance will be studied.

In addition to biomass derived fuels, ammonia is an interesting fuel, because it has a high energy density (comparable to methanol), good storage/transport properties, and there is no carbon involved in the fuel cell process. It was found that ammonia is only cracked on the SOFC anode, where after the hydrogen is electrochemically converted as usual.

A long-term test in ammonia at 850 °C over 1500 h has shown that pure ammonia can be used as fuel on a generation 2G cell with a slightly larger degradation rate compared to tests in synthesis gas (see Fig. 3).

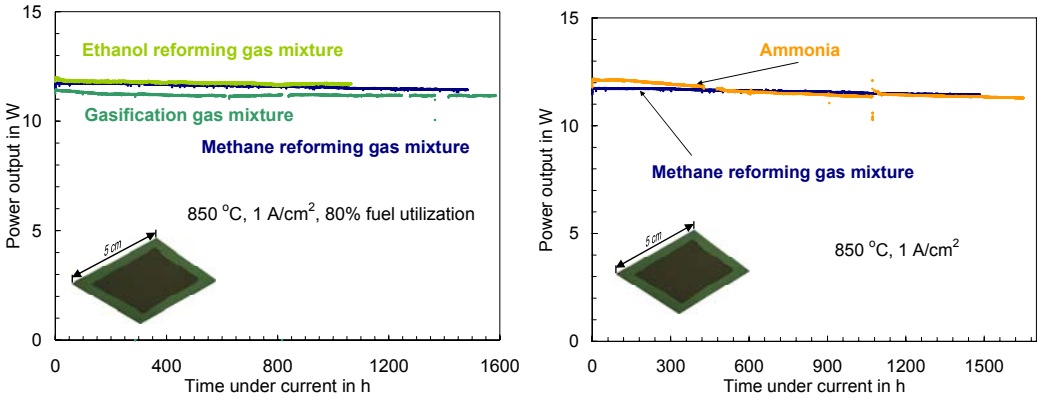


Fig. 3 Long term tests using model mixtures of methane reforming, ethanol reforming, biosyngas obtained by wood chips gasification, and ammonia

Cell development: 3G cells

A series of cells with a nickel-metal containing anode layer were made and selected cells were tested. It was found that the nickel-metal in the anode (the fuel electrode) mixes with iron and chromium from the stainless steel support under manufacturing.

Part of the testing work carried out during this project evaluated the extent and type of problems arising as a result of this mixing (alloying) of the metals in the cell, and their dependence on the manufacturing temperature. It was shown that both performance and in particular stability was heavily influenced by alloying and its consequences. As a result of these studies, alternative approaches to cell manufacturing have been developed, and at least two new cell designs have appeared. These new cells have already demonstrated much improved stability compared to the old cell design, although the performance is still relatively poor compared to 2G cells. New 3G cells with an alternative catalytic (metal oxide) material in the anode have also been manufactured and tested successfully.

Summary

Within the project a comprehensive cell testing program was accomplished, accompanied by microscopic analysis. More than 100 tests of cells were initialized. About 60000 hours (or almost 7 years) were dedicated to long-term testing to study durability and identify degradation paths.

One of the main achievements in the project period was the support of the break through in development of 2.5G (and 2.xG) cells showing excellent performance and good long-term stability. This achievement was possible by combined effort of cell and manufacturing development, cell testing, and cell characterization by microscopy (the lasts two issues financed by the present project).

Furthermore, a better, detailed understanding of degradation paths was gained through cell testing, micro structural analysis and with the help of thermodynamic modeling (financed by this project and a EU-project). As a result, the currently most developed cell generation 2G was significantly improved with respect to long-term stability under severe operating conditions.

The application of a variety of fuels was demonstrated successfully. Specifically, ammonia, simulated biosyngas of gasified biomass, and simulated reforming gas of ethanol reforming was tested in long-term tests with good performances and stabilities.

The development of design and manufacturing of 3G cells was significantly moved forward by the knowledge gained in cell testing and microscopic analysis.

The results of the project were presented at international conferences and published in high-ranking scientific journals.

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May 2007

Final Report

Evaluation and optimization of Danish solid oxide fuel cells – Generation 2.5G and 3G

PSO-Eltra Project 5849

April 1, 2005 to March 31, 2007

Table of contents

Introduction

The current project has been part of the combined effort to establish a Danish solid oxide fuel cell (SOFC) technology. Specifically the aim of the project was to provide input for the development of new cell generations by detailed electrochemical testing combined with micro structural analysis of the cells. Furthermore, the long-term stability and degradation behavior was studied with the aim to establish degradation mechanisms and thereby give profound input to improve the long-term stability under technologically relevant conditions using a variety of fuels.

The currently most developed cell generation is the 2G cell (see Fig. 1), which is reproducibly produced in the pre-pilot facility at Risø at a capacity of over 12000 12 x 12 cm^2 cells per year. The optimal operating temperatures are around 800 to 850 ^oC. New cell generations (2.5G and 3G, see Fig. 1), allow a decrease of the working temperature from to 700 ^oC and 500 ^oC, respectively, at the same or improved performance. The advantages of these cell generations are a drastic reduction of the prize and an expected higher durability and lifetime.

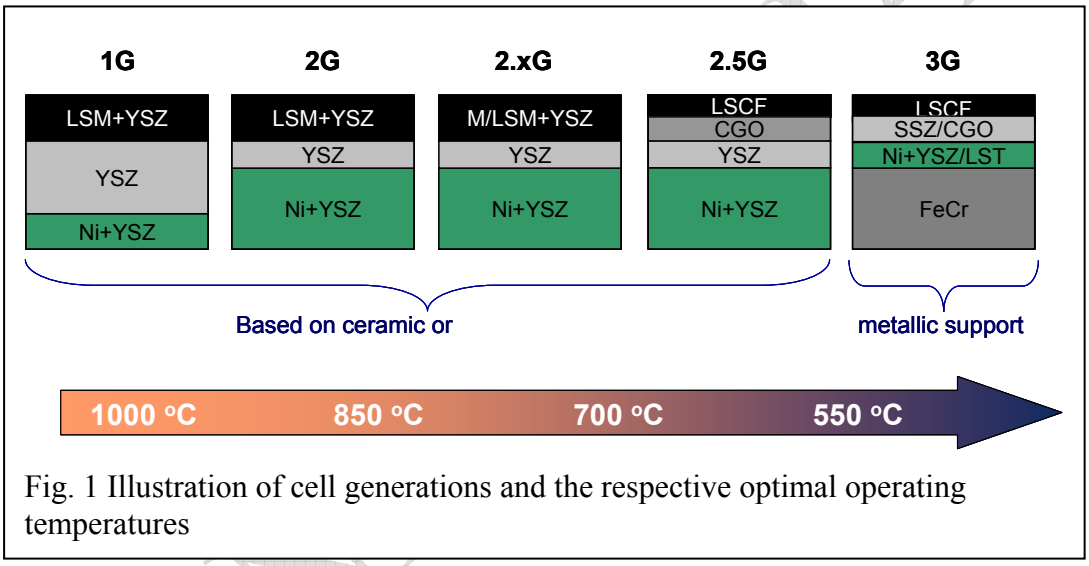

Fig. 1 Illustration of cell generations and the respective optimal operating temperatures

The following issues were addressed and the outcome is reported here:

(1) Development of 2.5G cells

Within the project, the development of 2.5G cells was to be supported by cell testing input, both regarding performance and long-term stability. Thus, focus was on the detailed electrochemical characterization of cells and study of the micro structure in order to understand the relation between performance and structure initially and during/after long-term testing. It was expected that the pre-pilot production of 2.5G cells will be achieved within the project period.

(2) Long-term stability and degradation mechanisms

Durability is a key issue for a successful SOFC technology, together with performance and price. Therefore, it was aimed at understanding of the underlying degradation mechanisms of 2G and 2.5G cells under technologically relevant and severe (‘accelerated’) operating conditions by continuing the comprehensive long-term testing combined with subsequent micro structural analysis.

(3) Alternative fuels for the use in SOFCs

SOFCs are known to be flexible with respect to the useable fuels. Within the project the usability of biomass derived fuels and ammonia was to be demonstrated.

(4) Development of 3G cells

Metal supported SOFCs are considered the optimal option for operating temperatures around 600 ^{o}C, not only in Danmark but also in other leading SOFC development laboratories throughout the world. The development of this cell generation was expected to be supported significantly by cell testing.

Results and Discussion

(1) Development of 2.5G cells

Cells of the generation 2.5G cells are composed of the same half cell (anode support, active anode and electrolyte) as 2G cells. The limiting component of 2G cells at operating temperatures of 750 ^{o}C and below is the cathode. A new composite cathode (lanthanum strontium cobaltite ferrite – LSCF/ cerium gadolinium oxide – CGO) is expected to have lower resistances at these temperatures. As the cathode material can react with the electrolyte of the 2G half-cell (YSZ), a barrier layer has to be applied in between these two components.

As only the cathode material was modified compared to the well-known 2G cells, no large problems in establishing 2.5G cells were expected. It turned out, however, that just substituting the 2G by the 2.5G cathode was not sufficient. Understanding the performance and finding / manufacturing the optimal micro structure proved to be more challenging

The project could continue using the achievements of the previous PSO project 5302, where first 2.5G cells made in the lab were tested and a good performance was shown. However, the degradation rate was too fast. In the current project, more 2.5G cells received from the development were tested with respect to electrochemical properties (resistance contributions) and micro structure. In total 28 tests were performed. In order to obtain the required understanding and 2.5G cells with the anticipated properties, cells with different chemical compositions, varied manufacturing parameters and methods for application of barrier layer and cathode were tested. Selected cells were subjected to microscopy before and after testing.

It was found that the cathode thickness beyond values of 10-20 µm had a large effect on the cathode polarization resistance, i.e. the resistance towards reactions at the cathode (Fig. 2), a finding which is different from 2G cells. With increasing thickness towards 20 µm, the resistance decreased. With the knowledge of this correlation, a new processing method to apply the cathode was chosen and established: screen printing, as the anticipated thicknesses exceeded the feasibility limits for sprayed cathodes. Besides the cathode thickness, an understanding of the optimal micro structure in the cathode was gained.

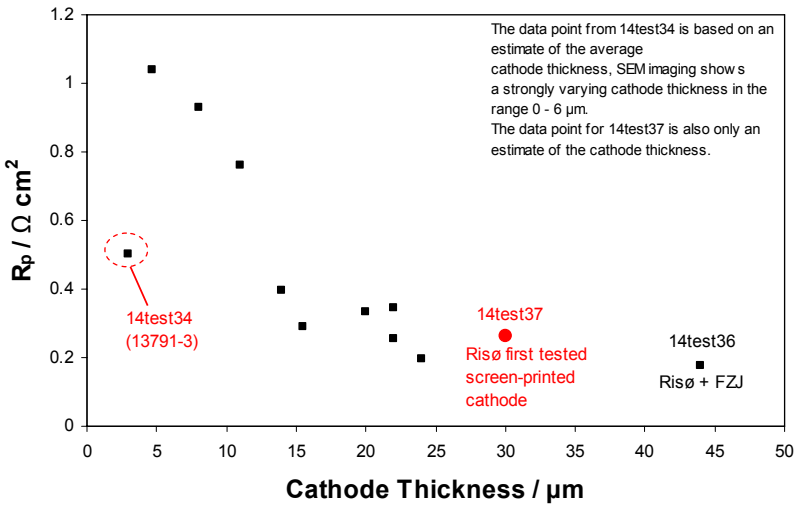

Fig. 2 Correlation between cathode thickness and resistance, manufacturing parameters were different for the cells, one cell (14test36) was a joint production by Risø and Forschungszentrum Juelich (Germany)

By screen printing the cathodes and varying the manufacturing parameters aiming at obtaining the anticipated micro structure, a breakthrough in 2.5G development was achieved. A further fine-tuning of the electrochemical properties of 2.5 G cells was thereby possible and a series of 2.5G cells was produced and delivered to partners in other projects. Although the number of tested equal 2.5G cells is not sufficient yet, a variation of performance within 20% is realistic to expect. In Fig. 3, the excellent performance of 2.5G cells is demonstrated. Area specific resistance as low as 0.13 Ωcm^2 at 750 ^oC (vs. 0.41 Ωcm^2 for 2G cells) have been obtained. At lower temperatures, the

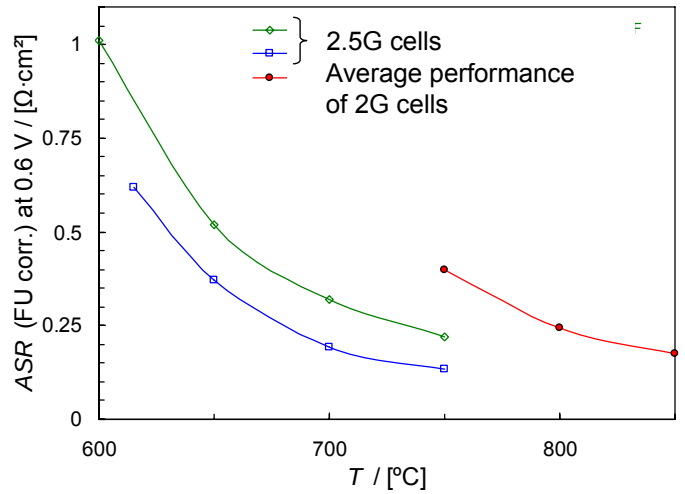

Fig. 3 Area specific resistances (corr. for fuel utilization) as function of temperature obtained on a standard 2G cell and two versions of 2.5G cells with slightly different compositions

performance improvement is even more significant. Small series of 2.5G cells are being manufactured.

(2) Long-term stability and degradation mechanisms

An extensive test program with respect to durability was carried out on 2G and 2.5G cells. Whereas the latter studies were aimed at improving the stability by optimization of the cell composition and structure, the long-term testing of 2G cells focussed on a detailed understanding of degradation mechanisms and to provide ideas for the improvement of the durability based on profound knowledge of degradation mechanisms.

Cathode degradation mechanism of 2G cells

Severe operating conditions affecting either mainly the cathode or the anode were found. Accordingly, higher temperatures facilitate anode degradation that proceeds fast, within a few hundred hours. Operating the fuel cells at lower temperatures (750 ^{o}C) and high current density (0.75 A/cm^2) affects the cathode more significantly. A continuous degradation proceeds over the whole testing duration. Detailed insight in the micro structural changes induced by operation was gained by a combination of micro structural analysis, comprehensive electrochemical characterization in different gasses, and thermodynamic modeling (the latter was financed by other projects).

Knowing that the cathode/electrolyte interface was the weak region regarding long-term stability under severe operating conditions, attempts to strengthen this interface by variation of the manufacturing parameters were undertaken. Indeed, a slight increase of stability was achieved by these measures, however at the expanse of the initial performance (see Fig. 4).

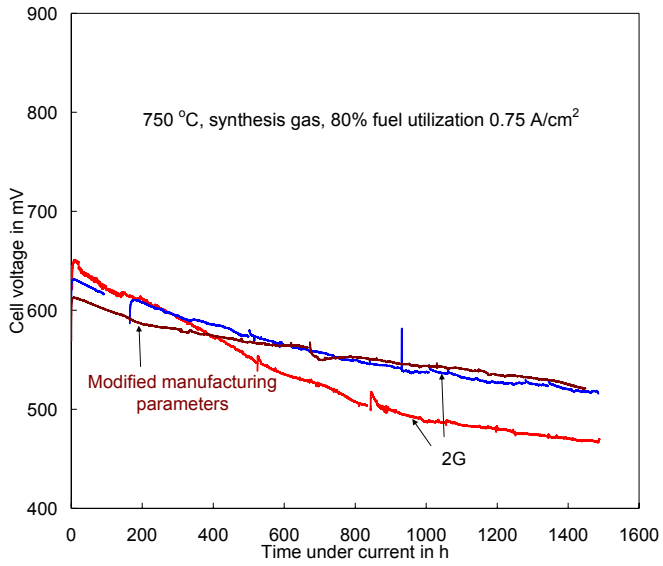

Fig. 4 Long-term tests of 2G cells and a 2G with slightly improved stability (brown) at 750 ^{o}C, synthesis gas, fuel utilization 80%

Valuable information about the detailed degradation mechanisms at the cathode were gained by performing long-term tests in oxygen instead of air as cathode gas. It was observed that the cell degradation could be stopped after an initial degradation within the first few hundred hours when testing in oxygen (see Fig. 5). The cells were characterized by impedance spectroscopy before, during, and after test and the contributions from cathode, anode, and serial resistances were determined using a model developed in a previous project (see Fig. 6).

Accordingly both the serial and cathode resistances increased significantly after test in air, but remained the same after test in oxygen. The resistances attributed to the anode increased similarly after both tests, in air and oxygen. From previous studies it is known that changes of the micro structure are often difficult to trace, even if the cells degraded significantly during test. It is thus valuable to have a preliminary idea about the regions where the changes occur with high probability.

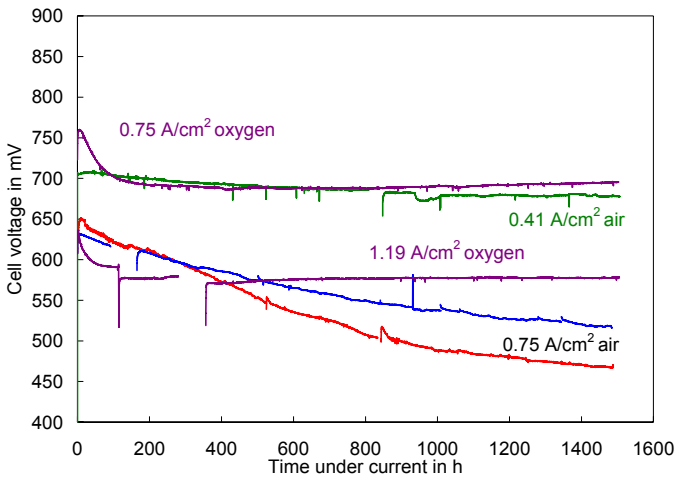

Fig. 5 Long-term tests of 2G cells at 750 °C, synthesis gas, fuel utilization 80% in air or oxygen (purple) at the cathode side at different current loads

Post test microscopic analysis was therefore performed with focus on the cathode/electrolyte region. The cathode was removed and the imprints of it left on the electrolyte surface were investigated. Clear craters, which were contact regions of LSM particles on YSZ, were identified on the not tested cell (Fig. 7 and 8). These sharp craters were still present in the cell after test in oxygen, however, became flatter and smaller after test in air (see Fig. 7 and 8). In addition, small nano-sized particles of a new phase appeared (see Fig 8). It was concluded that the attachment of LSM particles from the cathode to the electrolyte was weakened during testing in air. At the same time, foreign, isolating phases were formed. The weakening of contact and formation of nano-sized particles of foreign phases are illustrated in Fig. 9. Although these processes are restricted to the interface region, they lead to a significant loss of performance. They are highly dependent on the oxygen partial pressure on the interface.

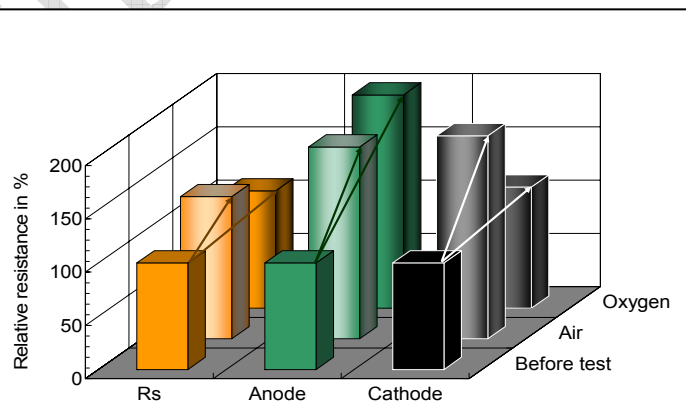

Fig. 6 Relative changes of area specific resistance contributions after test in air or oxygen at 0.75 A/cm^2 and 750 °C

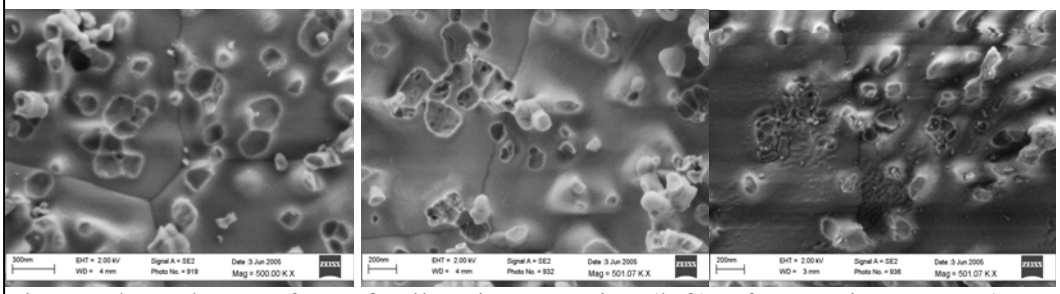

Fig. 7. Electrolyte surface of cells prior to testing (left), after test in oxygen (center) or air (right) after removal of the cathode studied by high resolution SEM

Apart from the micro structural analysis, these effects can be observed using impedance spectroscopy and result in a simultaneous increase of the serial and cathode polarization resistance. When working in pure oxygen instead of air, these degradation mechanisms are completely suppressed.

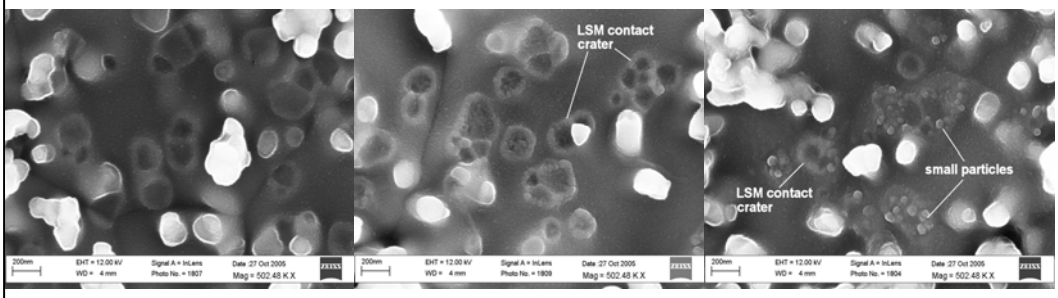

Fig. 8 High resolution SEM images showing the craters on the cathode/electrolyte interface of cells tested in different cathode atmosphere, reference cell (left), pure oxygen (center), and air (right). These images were taken by an in-lens secondary detector at an accelerating voltage of 12 kV. The samples' surface was carbon-coated

By thermodynamic modeling, the nature of and driving forces for the formation of foreign phases were determined.

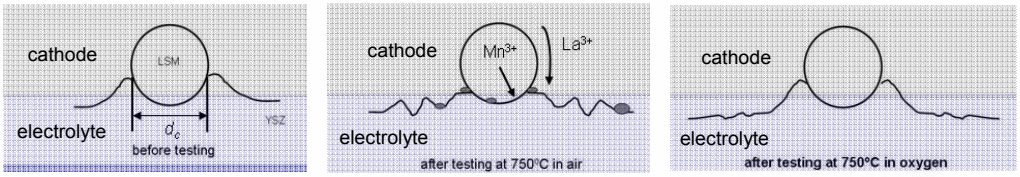

Fig. 9 Illustration of the loss of contact area between an LSM particle from the cathode and the YSZ electrolyte and the formation of nanosized, isolating particles during test in air compared to before testing and test in oxygen

Based on this knowledge, the cathode of 2G cells was modified aiming at a stabilization of the cathode/electrolyte interface, i.e. the suppression of detachments and formation of foreign phases. Indeed, a significant improvement of the long-term stability compared to standard 2G cells was achieved (see Fig. 10). After an initial degradation, the cell voltage remained constant as anticipated. Moreover, the electrode (polarization resistance) of these cells was lower than on 2G cells as measured by impedance spectroscopy (see Fig. 11). Therefore an improvement of the performance was achieved as well (although the modification procedure did not yield

cells with reproducible performance yet). The cell manufacture will now be optimized.

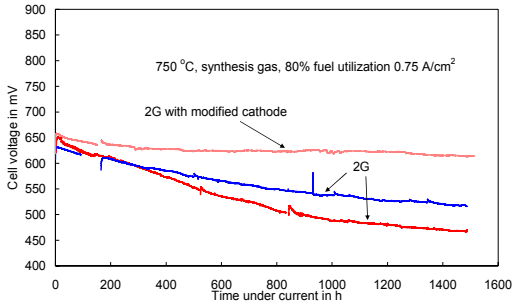

Fig. 10 Long-term test of 2G cells and the best 2G cell with improved cathode at 750 °C, 0.75 A/cm², synthesis gas at the anode side with a fuel utilization of 80%

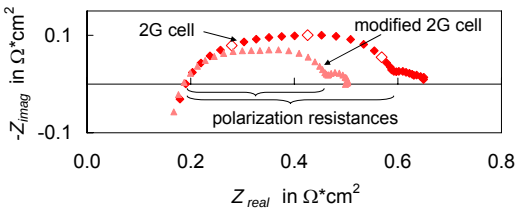

Fig. 11 Impedance spectra of 2G cell and cell with improve cathode at 750 °C, 25% humidification

Cathode degradation of 2G cells in humidified air

There is a strong interest in more knowledge about the stability / degradation behavior of 2G cells in humidified air, which could be found in potential application areas. A drying of air is expensive and a certain tolerance against humidity could improve the competitiveness of the SOFC technology. A number of tests were performed using mostly a water bottle to humidify the air on the way to the cathode. In that way, ca. 4% humidification is obtained.

An initial cell test (see Fig. 12) showed that the introduction of humidity under current load was immediately followed by a drop of the cell voltage and an accelerated degradation afterwards. After removal of the humidification, the cell voltage jumped up again and the degradation rate seemed to slow down. Later, even higher degrees of humidity were introduced and the cell degradation was thereby accelerated. After this first observation, that humidification indeed affected the stability, more systematic studies were initiated where the humidification of the cathode gas was started in the initial period of the long-term test (see Fig. 13). At the moment, it is only clear that humidification affects the

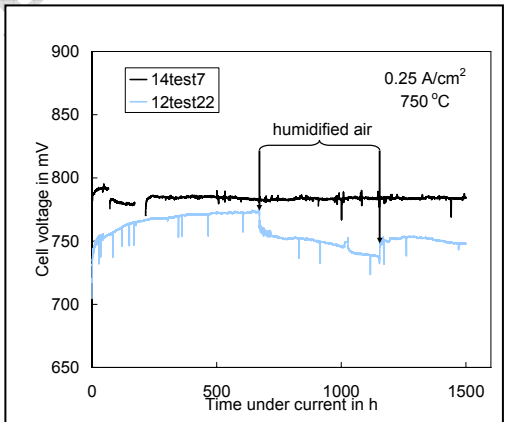

Fig. 12 Long-term tests at 750 °C with dry air and with periods using humidification of air

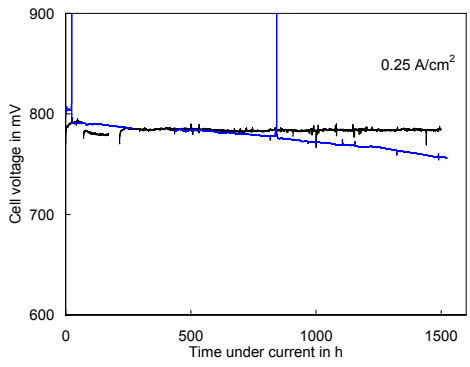

Fig. 13 Long-term tests at 750 °C with dry air and using humidification of air

durability. However, more studies are necessary to investigate the dependency of degradation as function of operating parameters and to identify the underlying mechanisms.

Anode degradation of 2G cells

The anode of 2G cells is composed of nickel (Ni) and Yttria-stabilized Zirconia (YSZ). At the relatively high operation temperature, the metallic Ni phase tends to sinter and coarsen. In addition, Ni particles can 'disappear' from (are transported out of) the anode. Since Ni is responsible both for transportation of electrons from the anode-electrolyte interface and the catalytic oxidation of the fuel gas at the interface, it is important to understand the process of Ni coarsening.

In the anode (fuel electrode) fuel gas (e.g. hydrogen) is oxidized to water

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$.

Therefore, the anode will inevitably be subjected to high concentrations of water at operating conditions. It is also of interest to maximize the utilization of the fuel gas, leading to water concentrations of up to 80-90%.

In this project, anode materials similar to what is found in technological cells were treated in carefully controlled high temperature atmospheres with varying concentrations of water/fuel gas. During this treatment the electrical conductivity was measured in-situ, and after treatment the microstructural changes were studied by a variety of microscopic techniques (optical microscopy, scanning and transmission electron microscopy and focused ion beam). In addition, already tested cells were subjected to the same microscopic studies.

A low-voltage scanning electron microscopy (SEM) technique has been developed, using a microscope (Zeiss Supra 35) at Risø, equipped with a field-emission gun. With this technique it was made possible to attain contrast between Ni and YSZ and contrast between percolating (conducting) and non-percolating Ni (see Fig. 14). Such a distinction is extremely useful to evaluate changes upon testing and relate the found effects to operating parameters and degradation rates.

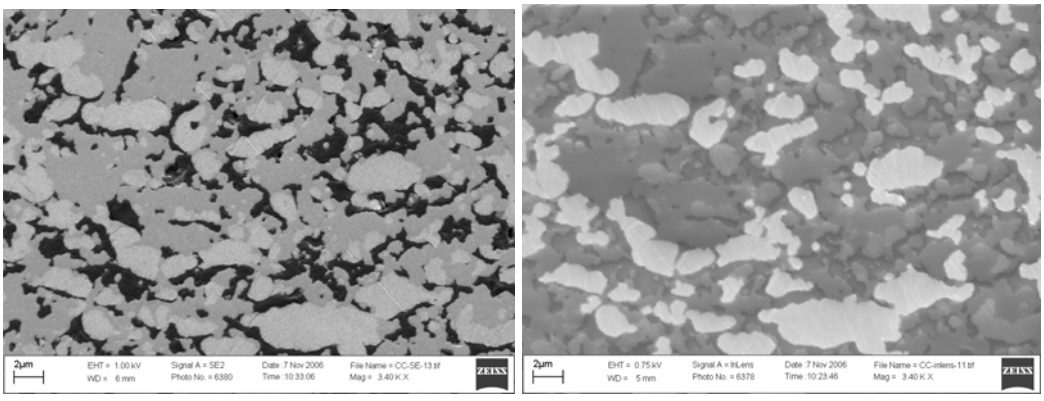

Fig. 14 Left: Image recorded by use of a low voltage and the lateral SE detector. The bright phase is Ni, the grey phase is YSZ and the dark phase is pores. Right: Image recorded by use of low voltage and the inlens SE detector. The bright phase is percolating Ni and the dark phase is non-percolating Ni and non-conducting phases

Until recently, all microstructural parameters measured for SOFC electrode microstructures are based on 2-dimensional images of sample cross-sections. 3D information of long-term tested fuel cells can be expected to result in a better understanding of microstructural changes and degradation mechanisms during operation. Three dimensional analysis of the Ni-YSZ anode by use of dual beam FIB-SEM is a way to acquire microstructural information on the nanometer scale from a limited sample volume. Since composite SOFC electrodes are very much depending on not only particles sizes and size distributions, but also interconnectivity between and within the different phases, high resolution 3D reconstruction is a very interesting technique to apply. In this study, a FIB-SEM was used to attain three-dimensional data on a Ni-YSZ anode from a long-term tested cell (2 years of operation under relatively severe conditions) initiating a collaboration with Dr. Eric Wachsman and Danijel Gostovic (ph.d. student), at the Department of Materials Science and Engineering, University of Florida. The FIB-SEM work was performed at the Major Analytical Instrument Center (MAIC), University of Florida.

Preliminary results on two samples from a cell tested over two years comprise e.g. Ni-phase distribution as a function of distance to the anode/electrolyte interface, specific surface area for the sample and for the each specific phase (i.e. Ni and YSZ). These results are not possible to achieve from 2D measurements, since no relevant assumptions for the third dimension do exist. From the obtained results, clear differences are seen between the tested cell and the reference cell with respect to Ni distribution in the anode (see Fig. 15).

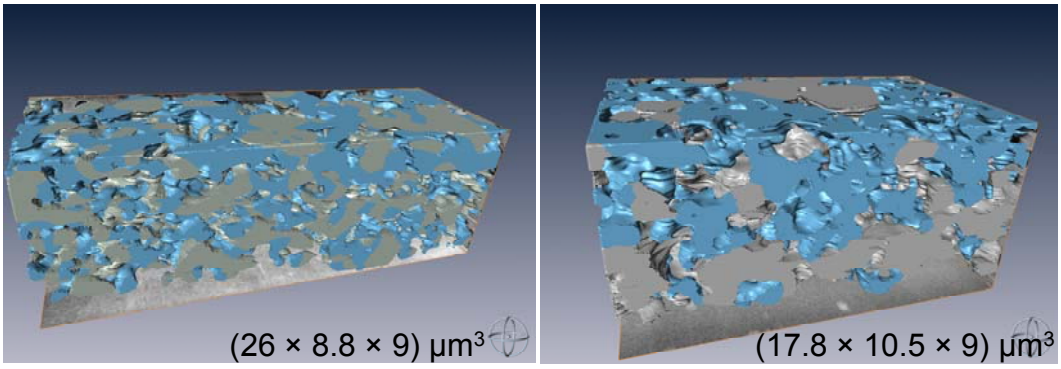

Fig. 15 3D visualization of image stack, performed in 3D software Amira, Blue phase: pores, grey phase: nickel, transparent: YSZ, left: reference cell, right: cell after two years testing

Degradation of 2.5G cells

A successful cell has to prove good performance and stability at the same time. First 2.5G cell versions showed excellent performances, however, degraded also very rapidly (one example shown in Fig. 16). A long-term test matrix was therefore needed to study the effects of for example chemical composition, calcination and sintering temperatures, layer thicknesses, application methods etc on the durability. Over the project period, ten long-term tests of 2.5G cells over 1500 hours were initiated and an improvement of the durability under severe degradation conditions was achieved. The newly developed 2.5G cells showed excellent performances at temperatures around 750 ^{o}C and lower (the anticipated temperature range) and good long-term stability (see Fig. 16).

The degradation mechanisms on the 2.5G cathodes have not yet been sufficiently studied as most testing work within the project period was aimed at improving the cells. However, first tests on the best 2.5G cells suggest that degradation paths might involve similar processes as on 2G cells.

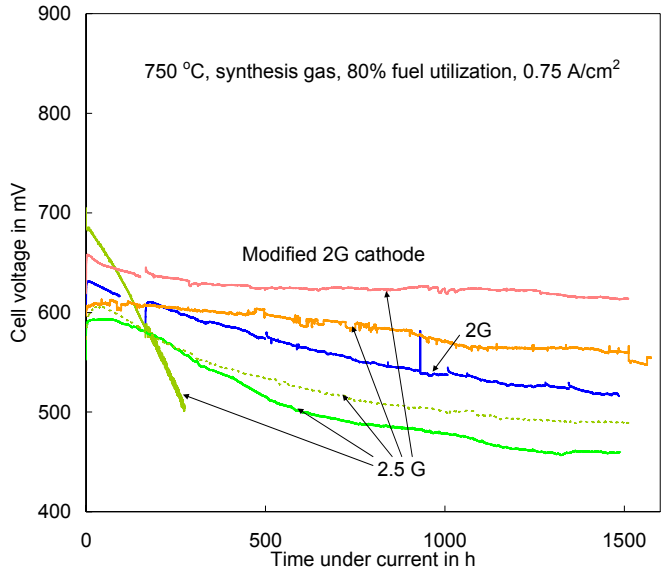

Fig. 16 Selection of long-term tests of 2G and 2.5G cells. An improvement of the stability of the cells was achieved from the rapidly degrading first cells (light green) to the ones with at least as good stability as 2G cells

(3) Alternative fuels for the use in SOFCs

The flexibility of SOFCs with respect to useable fuels is often mentioned among the advantages of this type of fuel cell. The current energy supply system is still mainly based on conventional – fossil - fuels. There are, however, a number of environmental, political, and economic driving forces towards more sustainability such as the limited natural resources, the increasing prices of fossil fuels, environmental impacts, and the security of energy supply. Here the use of fuels derived from sustainable sources (alternative fuels), for example from biomass conversion (see Fig. 17), is an attractive option. Such fuels rise of course new challenges due to their variety and variation of compositions. Carbon containing fuels, for example derived from biomass by anaerobic digestion, are converted to CO and hydrogen when passing over

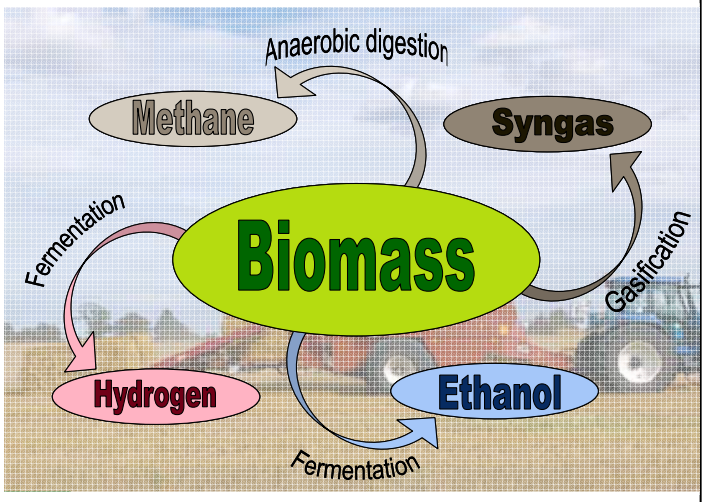

Fig. 17 Selection of known processes to provide biomass derived fuels

the SOFC anode by reforming with steam. That was shown by analysing the gas composition entering and leaving the anode compartment of a SOFC (see Fig. 18). CO and hydrogen in turn are electrochemically converted to carbon dioxide and water producing electrical power and heat. The aim with testing such fuels was to demonstrate the performance and stability of 2G cells.

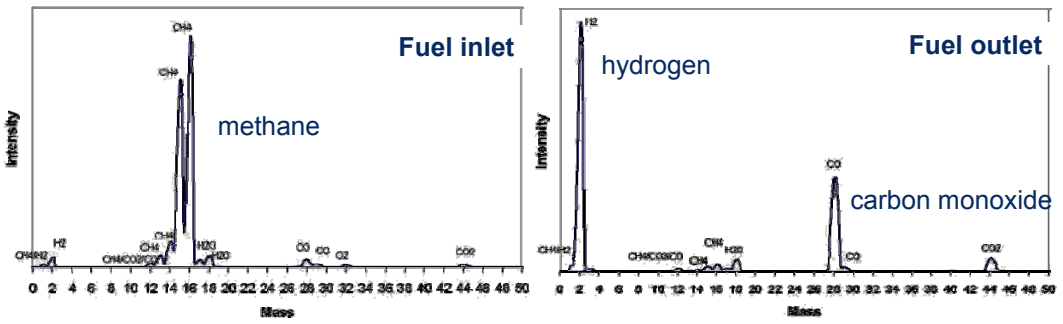

Fig. 18 Gas analysis of a mixture of methane and steam entering the anode (left). At the outlet, these are almost completely converted to hydrogen and CO (right)

Gasification of biomass, for example organic domestic waste, is an interesting process to accomplish a sustainable energy production. The product of such gasification contains mainly hydrogen, CO, CO_2 and water (biosyngas). The composition is of course depending on the source of the biomass. One test was performed with a simulated gasification gas by using a composition presented in the literature for the gasification of wood chips (PhD thesis A. Norheim, Trondheim 2006, Norway).

Furthermore, a model mixture representing ethanol reforming gas was used as fuel in another long-term test. The degradation rates in both tests were similar to other tests with a synthesis gas derived from methane reforming under similar testing conditions (Fig 19). The feasibility of using such fuel was thus demonstrated. In the forthcoming time, the effect of minor components in the biosyngas on the SOFC performance will be studied.

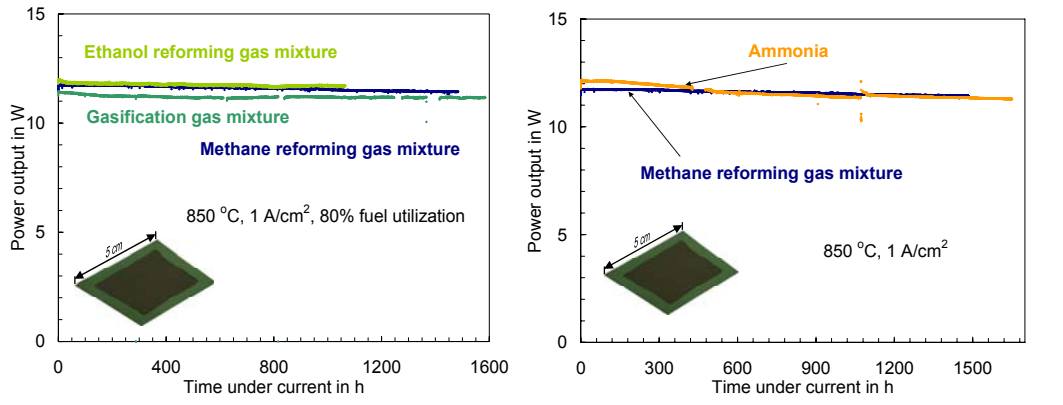

Fig. 19 Long term tests using model mixtures of methane reforming, ethanol reforming, biosyngas obtained by wood chips gasification, and ammonia

In addition to biomass derived fuels, ammonia is an interesting fuel, because it has a high energy density (comparable to methanol), good storage/transport properties, and there is no carbon involved in the fuel cell process. In addition, ammonia technology

has been established all over the world and producers are interested in exploring new fields of applications.

At the testing temperatures of 750-850 °C, ammonia decomposes into nitrogen and hydrogen and the thermodynamic equilibrium is almost completely on the side of the two gasses. It was found by gas analysis that ammonia is only cracked on the SOFC anode, where after the hydrogen reacts as usual (see Fig. 20).

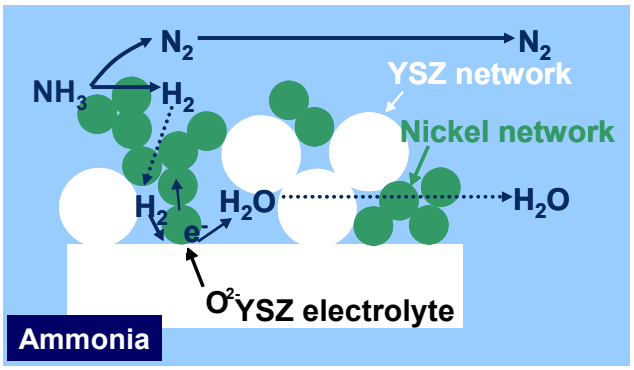

Fig. 20 Illustration of how ammonia is cracked over the SOFC anode and the formed hydrogen converted with oxygen ions from the cathode

A long-term test in ammonia at 850 °C over 1500 h has shown that pure ammonia can be used as fuel on a generation 2G cell with a slightly larger degradation rate compared to tests in synthesis gas (see Fig. 19). Degradation processes affect anode and serial resistance of the cell in particular as concluded from analysis of impedance spectra.

(4) Development of 3G cells

3G cells (see Fig. 1) are based on a metallic (stainless steel), structural support that allows a very thin anode layer, electrolyte, and cathode layer to be deposited on top of it. The respective thickness of these layers is in the range 10 – 25 µm, roughly corresponding to one fifth to half of the thickness of a human hair. These layers would be too thin and too brittle to be handled if they were not supported on top of a relatively rigid structure.

A number of button cells that were manufactured using different conditions were tested. The electrolyte compositions were varied and the electrolyte thickness ranged from 15 – 20 µm for all cells. Furthermore, different application methods for the cathodes were used (screen printing, lamination). A special test setup was used for these small cells (see Fig. 21).

The foremost aim with the testing of 3G cells was to assign electrolyte tightness and stability under open circuit voltage (OCV - no current load applied). Furthermore, the total area specific resistance (ASR) was determined and a deconvolution of resistance contributions from the cell components by impedance spectroscopy was attempted.

Even though the manufacturing conditions (apart from sintering time and temperature) were not identical for the set of cells compared here, an overall trend concerning the sintering time and sintering temperature used for the cell manufacture and the performance and stability of the cells was found (see Fig. 22).

The studies in combination with pre-test and post-test microscopy showed furthermore that the first 3G cells experienced extensive alloying/mixing of metals between cell support and anode layer (Ni, Cr, and Fe). Apart from effects on the performance, also expansion and electrolyte rupture were the result.

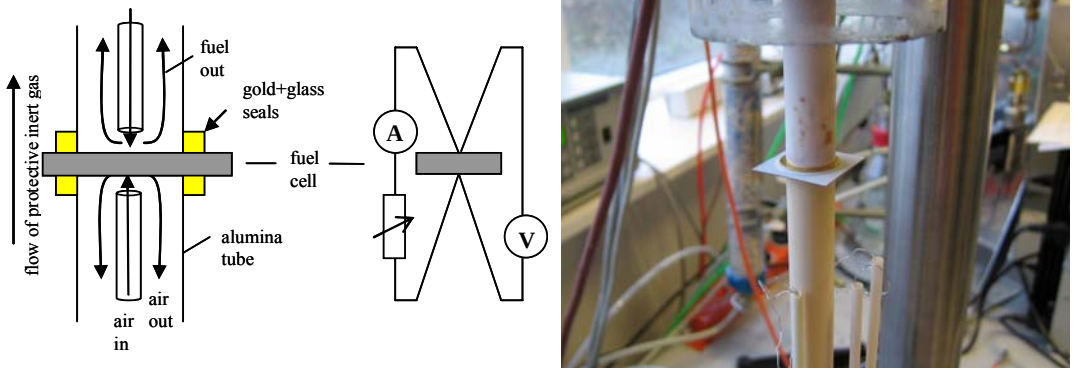

Fig. 21 Schematic(left) and picture (right) of 3-atmosphere rig for the test of button cells

In order to avoid this problem, 3G cells with new designs have been manufactured and tested.

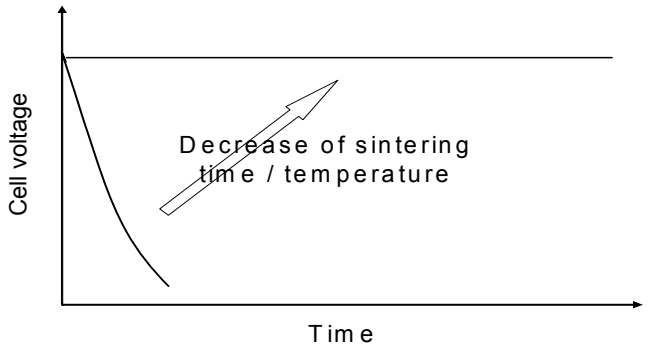

Fig. 22 Schematic performance (cell voltage) of 3G cells, from first to later versions – A horizontal line at high cell voltage is the aim

One of these cells showed a remarkable stability (best stability ever observed for a 3G cell to date) during the whole test, where the cell was left at OCV at five different temperatures in the interval 650 – 840 ºC for a period of 24 h up to ca 100 h per temperature. Impedance spectra were recorded in the beginning and at the end of each period. The gas tightness of the cell was investigated initially at 650 ºC by varying the *p*O2 on the cathode side (air – oxygen changes) and a response near the theoretically predicted was observed (ca. 30 mV change in cell voltage), indicating a reasonably gastight cell. The corresponding oxygen leak currents were calculated from the cell voltage observed initially at each temperature and was found to be in the range 0.2 – 0.6 A cm^{-2} corresponding to an oxygen leak of ca 2%. After spending approximately 100 h at 850 ºC the oxygen leak was unchanged within the experimental error.

Impedance spectra recorded at 650 ºC in the beginning and at the end of the test are displayed in Fig. 23. Both the serial and the polarisation resistances increased by a factor of three during the test. Post-test analysis needs to be carried out to help explain the observed changes. Possible origins of the change in R_s and R_p observed here are corrosion of the support, delamination, and Ni grain growth. The results show that there is still a large effort needed to obtain 3G cells with sufficient performance and stability.

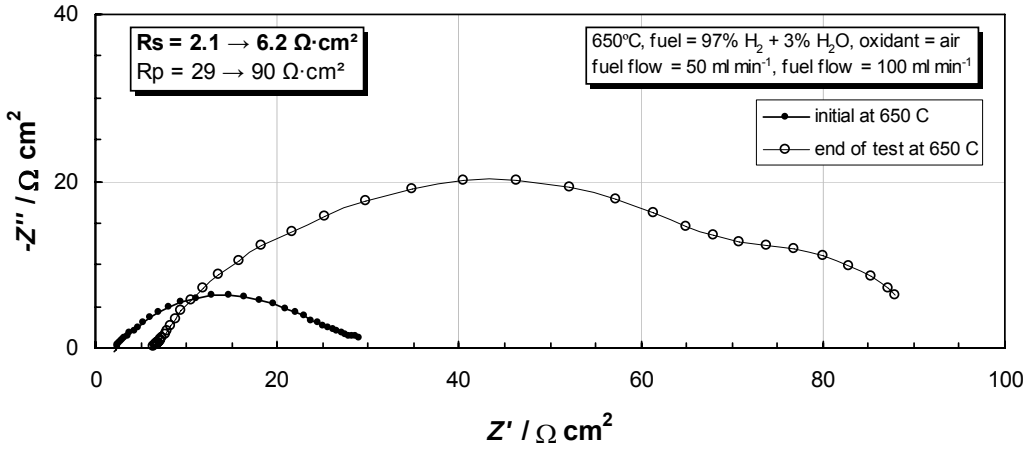

Fig. 23 Impedance spectra recorded at open-circuit voltage at 650 ºC. Both the serial resistance and the polarisation resistance increases by a factor of three during the test

Summary

One of the main achievements in the project period was the break through in development of 2.5G (and 2.xG) cells with excellent performance and good long-term stability. This achievement was possible by combined effort of cell and manufacturing development, cell testing, and cell characterization by microscopy (the last two finances by the present project).

Furthermore, a better, detailed understanding of degradation paths was gained through cell testing, micro structural analysis and with the help of thermodynamic modeling. As a result, the currently most developed cell generation 2G was significantly improved with respect to long-term stability under severe operating conditions. Furthermore, also an improvement of the performance was achieved.

The application of a variety of fuels was demonstrated successfully. Specifically, ammonia, simulated biosyngas of gasified biomass, and simulated reforming gas of ethanol reforming was tested on 2G cells in long-term tests with good performances and stabilities.

The development of design and manufacturing of 3G cells was significantly moved forward by the knowledge gained in cell testing and microscopic analysis. As a result of the 3G studies, alternative approaches to cell manufacturing have been developed, and at least two new cell designs have appeared. These new cells have already demonstrated much improved stability compared to the old cell design, although the performance is still relatively poor compared to 2G cells. New 3G cells with an alternative catalytic (metal oxide) material in the anode have also been manufactured and tested successfully.

List of papers, contributions to conferences, and other reports

Articles

- A . Hagen, R. Barfod, P.V. Hendriksen, Y.-L. Liu, S.Ramousse

  Degradation of anode supported SOFCs as a function of temperature and current load

  J. Electrochem. Soc. 153(6) (2006) A1165-A1171.

- R. Barfod, M. Mogensen, T. Klemensø, A. Hagen, Y.-L. Liu, P.V. Hendriksen

  Detailed characterization of anode supported SOFCs by impedance spectroscopy

  J. Electrochem. Soc., 154 (2007) B371-B378.

- R. Barfod, A. Hagen, S. Ramousse, P.V. Hendriksen, M. Mogensen

  Break Down of Losses in Thin Electrolyte SOFCs

  Fuel Cells 6(2) (2006) 141-145.

- A. Hagen, M. Menon, S. Ramousse, P.H. Larsen, R. Barfod, P.V. Hendriksen

  Properties and Performance of SOFC Cells Produced on a Pre-Pilot Plant Scale

  Fuel Cells 6(2) (2006) 146-150.

- K. Thydén, R. Barfod, Y.L. Liu

  Degradation of conductivity and microstructure under thermal and current load in Ni-YSZ cermets for SOFC anodes

  Adv. Sci. Technol. 45 (2006) 1483-1488.

- S. Koch, P.V. Hendriksen, M. Mogensen, Y.L. Liu, N. Dekker, B. Rietveld, B. de Haart, F. Tietz

  Solid oxide fuel cell performance under severe operating conditions

  Fuel Cells 6 (2006) 130-136.

- D. Lybye, Y.L. Liu,

  A study of complex effects of alumina addition on conductivity of stabilised zirconia

  J. Eur. Ceram. Soc. 26 (2006) 599-604.

Oral presentations

- A. Hagen, Y.L. Liu, R. Barfod, and P.V. Hendriksen

  Anode Supported Solid Oxide Fuel Cells – Deconvolution of Degradation into Cathode and Anode Contributions

  10th Int. Symp. SOFC, Nara, 06/2007, to be given

- A. Hagen, R. Barfod, P.V. Hendriksen, Y.-L. Liu, S. Ramousse

  Effect of operational parameters on long-term stability of SOFCs

9th Int. Symp. SOFC, Quebec, 05/2005

- R. Barfod, M. Mogensen, T. Klemensø, A. Hagen, Y.-L. Liu, P. V. Hendriksen

  Break down of losses in thin electrolyte SOFCs

  9th Int. Symp. SOFC, Quebec, 05/2005

- Y.L. Liu

  Microstructure degradation of 2G cells

  Risø-Topsoe meeting, 25 Sept 2006.

- Y.L. Liu, L.Theil Kuhn

  Interface and Nano-Analysis for Solid Oxide Fuel Cells

  Risø-DTU meeting on Electron Microscopy, 24 Jan 2007.

- J.B. Bilde-Sørensen, K. Thydén, Y.L. Liu, Y.L.

  Characterization of Ni-YSZ cermets by low-voltage scanning electron microscopy

  Risø-DTU meeting on Electron Microscopy, 24 Jan 2007.

- K. Thydén

  Characterization of Ni-YSZ cermets by low voltage SEM (or How to distinguish Ni from YSZ without an X-ray spectrometer)

  Thermo Fisher scientific microanalysis Nordic users meeting, Risø (DK), 17 Jan 2007.

- K. Thydén, R. Barfod, R. Y.L. Liu

  Degradation of conductivity and microstructure under thermal and current load in Ni-YSZ cermets for SOFC anodes

  CIMTEC 2006 - International conferences on modern materials and technologies; 11. International ceramics congress, Acireale (IT), 4-9 Jun 2006.

Poster presentations

- J. Hjelm, M. Søgaard, M. Wandel, M. Menon, M. Mogensen, A. Hagen

  Electrochemical Impedance Studies of SOFC Cathodes

  10th Int. Symp. on SOFCs, Nara, 06/2007, to be given

- Y.L. Liu,K. Thydén, J.B. Bilde-Sørensen

  Visualization of percolating Ni grains in Ni/YSZ composites, at low voltage in a FE-SEM

  Microscience 2006, London (GB), 27-29 Jun 2006.

Conference proceedings

- J. Hjelm, M. Søgaard, M. Wandel, M. Menon, M. Mogensen, A. Hagen

  Electrochemical Impedance Studies of SOFC Cathodes

Proceedings of the 10th Int. Symp. on SOFCs, Nara, Japan, 2007.

- Hagen, Y.L. Liu, R. Barfod, and P.V. Hendriksen

  Anode Supported Solid Oxide Fuel Cells – Deconvolution of Degradation into Cathode and Anode Contributions

  Proceedings of the 10th Int. Symp. on SOFCs, Nara, Japan, 2007.

- R. Barfod, A. Hagen, S. Ramousse, P. V. Hendriksen

  Degradation mechanisms of SOFCs operated at high current density

  Proceedings of 26th Risø Int. Symp. on Materials Science 2005, Roskilde, Denmark, 2005.

- Hagen, R. Barfod, P.V. Hendriksen, Y.-L. Liu, S. Ramousse

  Effect of operational conditions on long-term stability of SOFCs

  Proceedings of the 9th Int. Symp. on SOFCs, Quebec, Canada, 2005.

- R. Barfod, M. Mogensen, T. Klemensø, A. Hagen, Y.-L. Liu, P.V. Hendriksen

  Detailed characterization of anode supported SOFCs by impedance spectroscopy

  Proceedings of the 9th Int. Symp. on SOFCs, Quebec, Canada, 2005.

Reports

- Internal status reports and BC notes
- Contributions to Topsøe/Risø monthly Newsletters

Anke Hagen
Risø National Laboratory
Fuel Cells and Solid State Chemistry Department

Project 5849: Evaluation and optimization of Danish solid oxide fuel cells – Generations 2.5G and 3G

Report on milestone

Activity: Cell development of 2.5G cells

Milestone 1a) Definition of 2.5G standard cell

Cells of generation 2.5G are composed of the same half-cell (anode support, active anode, and electrolyte) as the currently best developed generation 2G cells. The cathode, however, contains another material (lanthanum strontium ferrite cobaltite – LSFC in 2.5G vs. lanthanum strontium manganite – LSM in 2G). In order to prevent reactions between the new cathode and the electrolyte, application of a barrier layer in between is necessary. The 2.5G cells are a milestone on the way towards 3G cells. The same cathodes will be used in that new generation, while the support will be a metallic one (not ceramic as in 2G and 2.5G). The aim with these developments is to decrease the working temperature of the solid oxide fuel cell from ~850 to 700 ^{o}C and further down. The current project provides input from cell testing to the materials development and cell processing.

A successful cell has to prove good performance and stability at the same time. First 2.5G cell versions showed excellent performances, however, degraded also very rapidly (one example shown in Fig. 1). As a result of many testing-development cycles, an optimum between performance and stability was now found (improved stability under very harsh operating conditions, Fig. 1). A pre-pilot production of the first two series of 2.5G cells was initiated.

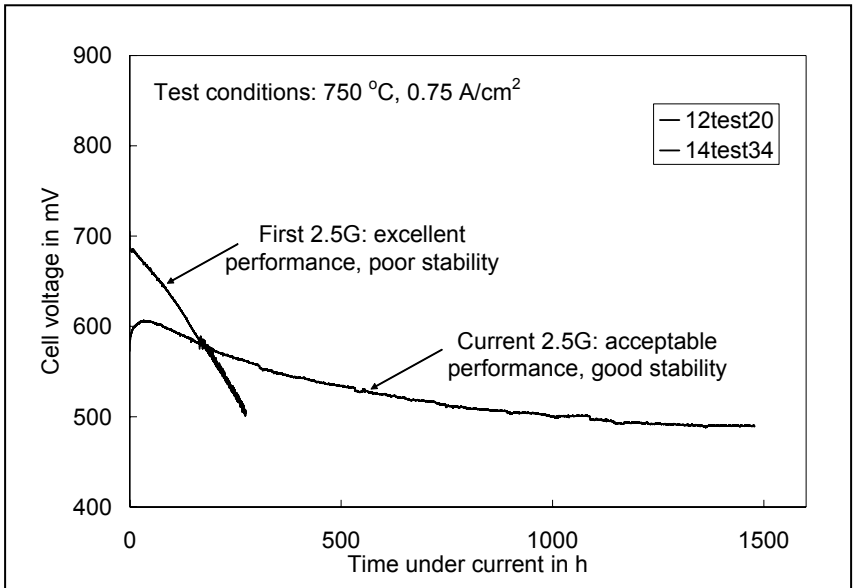

Fig. 1 Long-term stability of 2.5G cells (two examples)

Project 5849: Evaluation and optimization of Danish solid oxide fuel cells – Generations 2.5G and 3G

Report on milestone

Activity: Cell development and manufacturing of 2.5G cells

Milestone 2a) Reproducibility of 2.5G cell performance within 20%

2.5G cells are now produced by spraying and co-sintering of the 2G half cell (anode support, active anode, electrolyte) with the barrier layer of CGO. Subsequently, the 2.5G cathode (a LSCF composite) is screen printed.

There have not yet been sufficient test of the same cells in order to assign the reproducibility. However, the first few tests let expect a standard deviation of the area specific resistance within 20% and thus the achievement of the milestone.

Anke Hagen
Risø National Laboratory
Fuel Cells and Solid State Chemistry Department

Project 5849: Evaluation and optimization of Danish solid oxide fuel cells – Generations 2.5G and 3G

Report on milestone

Activity: Cell development and manufacturing of 2.5G cells

Milestone 2b) Distribution of losses on a 2.5G cell

In the past months, intensive testing of 2.5G cells, having the same half-cell (anode support, active anode, and electrolyte) as the currently best developed generation 2G cells and a different cathode (lanthanum strontium ferrite cobaltite – LSFC plus a barrier layer between electrolyte and cathode), was carried out. The general composition of the cells as been frozen. However, when producing a lager number of cells with the most promising characteristics, the anticipated performances could not be accomplished.

The milestone was supposed to report on results of a detailed electrochemical characterization of 2.5G cells with the aim to deconvolute the total resistance into single contributions from cathode, (barrier layer), anode, and electrolyte. A final assignment is not possible at this point. However, a fundamental correlation was discovered, which is different from the cathodes (LSM) in 2G cells.

The cathode thickness beyond values of 10-20 µm has a large effect on the cathode polarization resistance, i.e. the resistance towards reactions at the cathode (Fig. 1). With increasing thickness, the resistance decreased. With the knowledge of this correlation, a new processing method to apply the cathode was chosen: screen printing, as the anticipated thicknesses exceed the limits for sprayed cathodes. The results of testing such a cell were promising (red: 14test37 in Fig. 1) and cells with screen printed cathodes will be used as basis for producing a larger number.

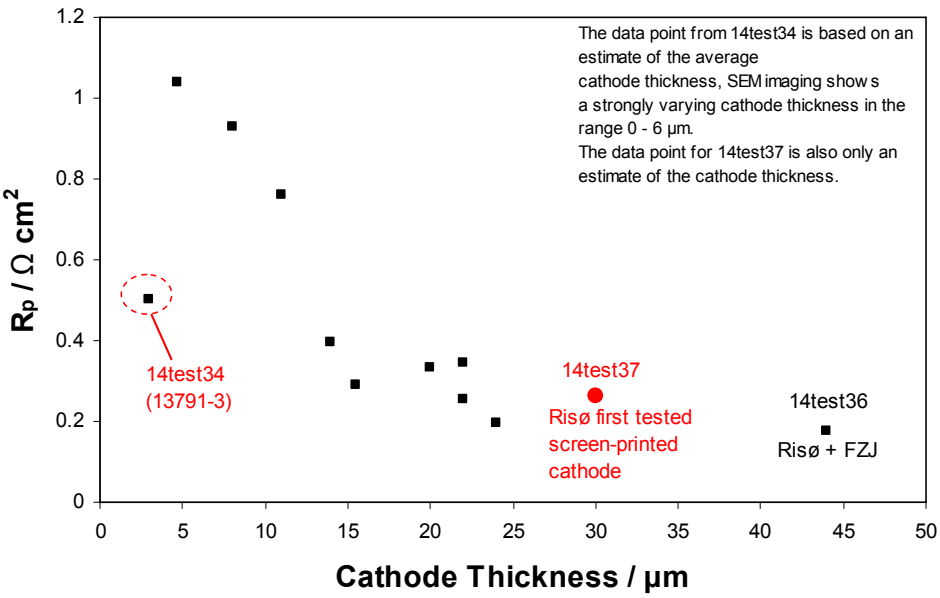

Fig. 1 Correlation between cathode thickness and resistance, manufacturing parameters were different for the cells, one cell (14test36) was a joint production by Risø and Forschungszentrum Juelich (Germany)

Anke Hagen
Forskningscenter Risø
Afdelingen for Materialeforskning

Projekt PSO-F&U 2005, Projektnummer 5849 – Rapport milepæl

Aktivitet: Langtidsholdbarhed og ældningsmekanismer (3) i tidsplanen)

Milepæl 3a) Model for degradering af 2G-celler opstillet

Formålet med undersøgelsen var at evaluere langtidsholdbarheden og at opstille en model over degraderingen som funktion af driftsbetingelser. Testene er blevet udført over 1500 timer og temperatur, strømtræk, brændsel blev varieret.

Den samlede celleydelse set som funktion af testtiden er summen af mange delprocesser, såsom aktivering og degradering på katode- og på anodesiden.

Degraderingshastigheden blev defineret som linear funktion (differens i cellespænding divideret med tid) og beregnet for alle test (se Fig. 1). Idet der tydeligt kan ses, at degraderingsmekanismer skifter med tiden, er værdierne blevet beregnet efter 300 og 1500 timers testtid og relateret til driftsbetingelserne (temperatur, strømtræk).

Det kan konstateres, at degraderingshastigheden stiger med højere polarisering (dvs. 'belastning') af cellen. Forskellige degraderingsprocesser dominerer under forskellige driftsbetingelser. Anodedegraderingen formodes at foregår hurtigere, inden for de første ~300 timers test. Ved lavere driftstemperaturer og høj strømtræk, er katodeprocesser (specielt vedhæftning mellem katode og elektrolyt) formentlig det mest afgørende årsag til den samlede degradering.

Generelt set viser cellerne en høj langtidsstabilitet under teknologisk relevante betingelser, f.eks. udgør degraderingen kun 2%/1000 timer ved 850 ^{o}C og 1W/cm^2 effekttæthed, hvilket svarer til teknologisk set skrappe driftsbetingelser.

Flere igangværende studier vil undersøge mere detaljeret, hvordan degraderingen fordeler sig over cellekomponenterne katode og anode og hvilke degraderingsmekanismer der dominerer under hvilke driftsbetingelser.

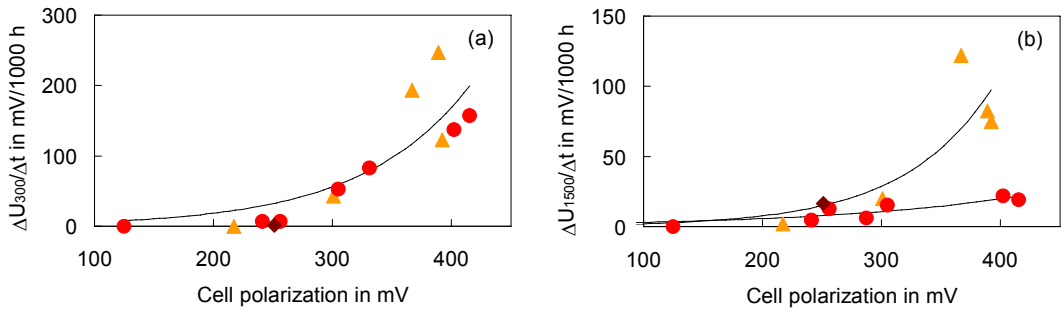

Fig. 1 Degraderingshastighed som funktion af cellepolarisering ved 750 (trekanter), 850 (cirkler) og 950 (firkant) ^{o}C beregnet efter 300 (a) og 1500 (b) timers test

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Project 5849: Evaluation and optimization of Danish solid oxide fuel cells – Generations 2.5G and 3G

Report on milestone

Activity: Durability and degradation mechanisms of 2G cells

Milestone 3b) Degradation under accelerated testing conditions

High current load at 750 ^{o}C

The degradation of anode supported cells was studied over 1500 h as function of cell polarization either in air or oxygen on the cathode. Based on impedance analysis, contributions of anode and cathode to the increase of total resistance were assigned. Accordingly, the degradation rates of the cathode were significantly smaller when testing in oxygen compared to air at the cathode. Microstructural analysis at the cathode/electrolyte interface carried out after removal of the LSM cathode showed sharp craters on the electrolyte surface prior to the testing; imprints left from the LSM particles. After testing in air, these crates flattened out, indicating a decreased three phase boundary length. In addition, the formation of foreign phases was observed. Both findings explain a weaker adhesion of the LSM cathode to the electrolyte as found earlier. These degradation processes did not occur when the tests were carried out in pure oxygen. Based on this result, it was possible to make the cathode more stable (see Fig. 1).

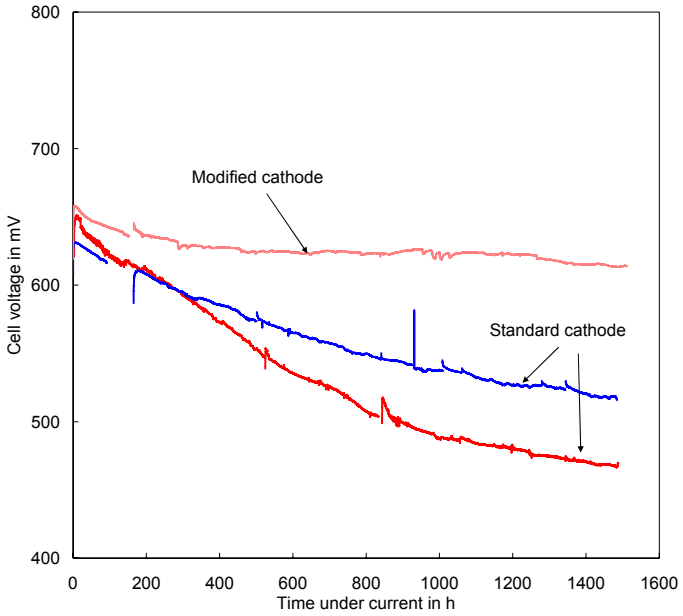

Fig. 1 Long-term test of 2G cells and 2 cells with improved cathode at 750 °C, 0.75 A/cm^2, synthesis gas at the anode side with a fuel utilization of 75%

Periodically changing current load

Technologically relevant conditions include change of the power output, i.e. non-steady state conditions. Tests were performed at 750 and 850 °C. While the degradation rate was not much affected by the changing instead of a constant current load at 750 °C, it was significantly larger during tests at 850 °C. At both temperatures, however, the anode seems to be more vulnerable to a changing current and shows a more pronounced degradation compared to a constant current over periods of 1500 hours testing. A possible way to minimize this effect could be a careful adjustment of the fuel flows and fuel utilizations, which must be within certain levels under all operating conditions.

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Activity: Long-term stability and degradation mechanisms

Milestone 3c) Ten 1500 hour long-term tests on 2.5G cells performed

Since the start of the current project, ten 1500 hour long-term tests were initiated on 2.5G cells. Additional seven 1500 hour long-term tests were performed on 2G cells with improved cathode (generation 2.xG cells).

The degradation studies were done on different versions of 2.5G cells in order to optimize manufacture and composition to achieve good performance combined with good stability (see selection of results in Fig. 1). In addition, the operating temperature and current densities were varied. There was a clear improvement of the stability from the first tested 21.5G cells (dark green in Fig. 1) to recently manufactured versions (orange and magenta in Fig. 1).

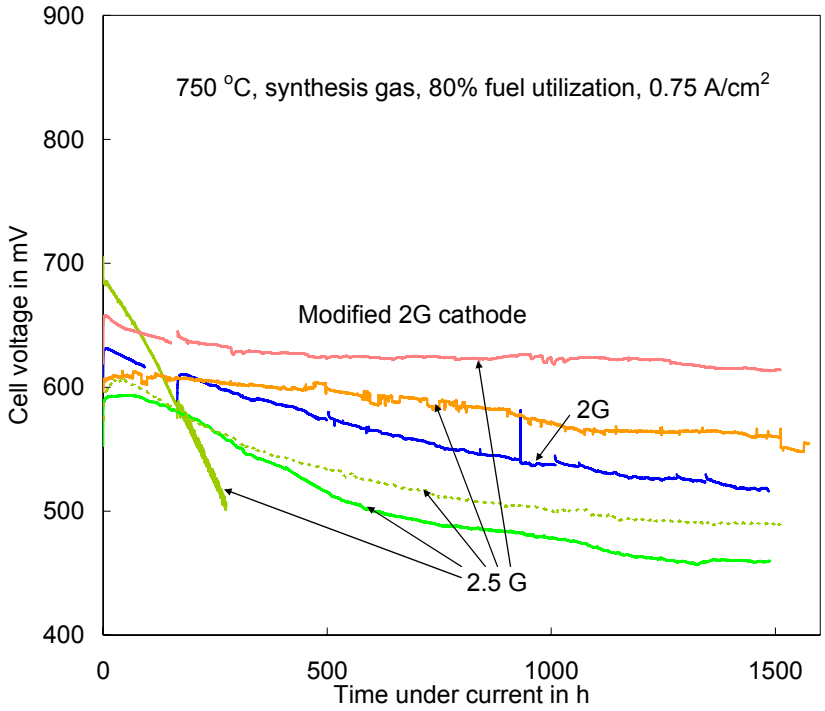

Fig. 1 Long term tests on 2.5G cells under technologically relevant conditions

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Activity: Long-term stability and degradation mechanisms

Milestone 3d) and 3e) Degradation mechanisms for 2G and 2.5G cells

Based on a large test matrix performed on 2G cells, dominating degradation mechanisms were identified. Under severe operating conditions for the cathode part of the cell (lower temperature, high current load), detailed insight in the micro structural changes induced by operation was gained by a combination of micro structural analysis and detailed electrochemical characterization (see below). This knowledge together with thermodynamic calculation has led to a modification procedure that makes 2G cathodes more stable.

The mechanisms on the 2.5G cathodes have not yet been sufficiently studied. Most testing work within the project period was aimed at improving the cells. However, first tests on the best 2.5G cells suggest that degradation paths are similar as on 2G cells.

During operation, changes in the cathode/ electrolyte interface occur. Specifically, the attachment of LSM particles from the cathode to the electrolyte is weakened. At the same time, foreign, isolating phases are formed (see illustration in Fig. 1). Although these processes are strictly confined within the interface region, they lead to a significant loss of performance. They are highly dependent on the oxygen partial pressure on the interface. When working in pure oxygen instead of air, these degradation mechanisms are completely suppressed.

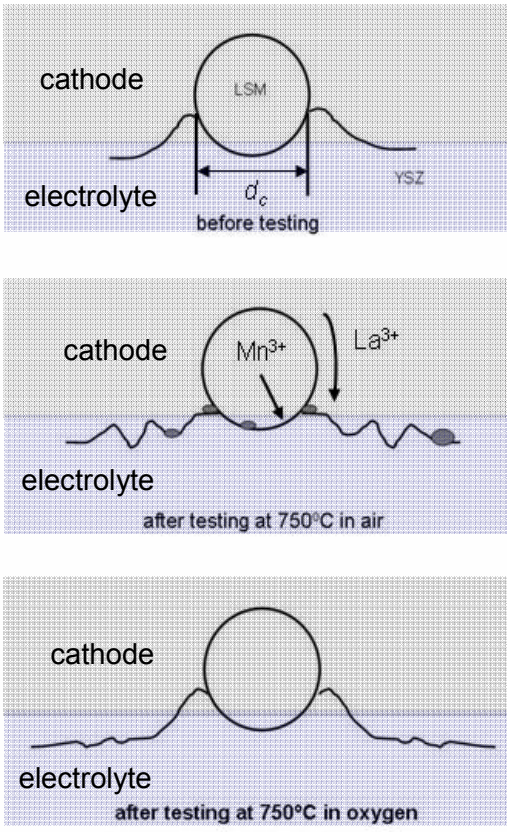

Fig. 1 Illustration of the loss of contact area between an LSM particle from the cathode and the YSZ electrolyte and the formation of nanosized, isolating particles during test in air compared to

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Activity: Alternative fuels

Milestone 4b) Test with ammonia fuel performed

Ammonia is an interesting fuel for fuel cells, because it has a high energy density (comparable to methanol), good storage/transport properties, and there is no carbon involved in the fuel cell process. In addition, ammonia producers are interested in exploring new fields of applications.

At the testing temperatures of 750-850 ^{o}C, ammonia decomposes into nitrogen and hydrogen and the thermodynamic equilibrium is completely on the side of the two gasses. A catalyst might be necessary to speed up the slow cracking reaction, but nickel in the anode could act as a mild catalyst for that reaction.

A long-term test in ammonia at 850 ^{o}C over 1500 h has shown that pure ammonia can be used as fuel on a generation 2G cell with a slightly larger degradation rate compared to tests in synthesis gas. Degradation processes affect anode and serial resistance of the cell in particular as concluded from analysis of impedance spectra.

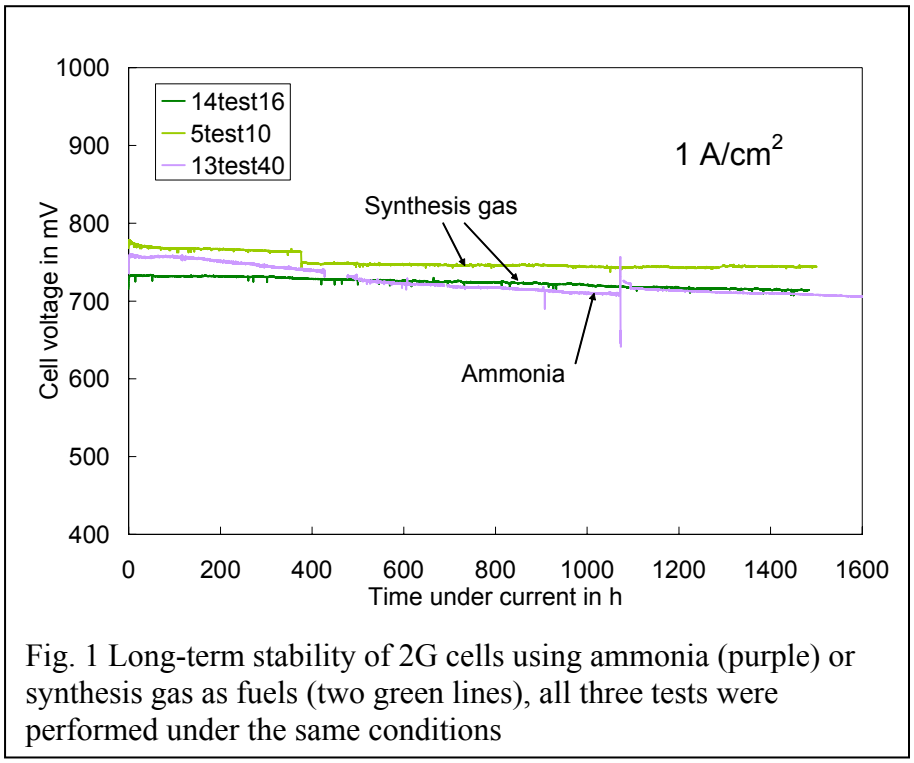

Fig. 1 Long-term stability of 2G cells using ammonia (purple) or synthesis gas as fuels (two green lines), all three tests were performed under the same conditions

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Activity: Alternative fuels

Milestone 4c) Simulated gasification gas as fuel

As SOFCs are known to be flexible with respect to the fuel, one aim was to demonstrate the long-term durability for the use of alternative fuels. Gasification of biomass, for example organic domestic waste, is an interesting process to accomplish a sustainable energy production. The product of such gasification contains mainly hydrogen, CO, CO_2 and water. The composition is of course depending on the source of the biomass. One test was performed with a simulated gasification gas by using a composition presented in the literature for the gasification of wood chips (PhD thesis A. Norheim, Trondheim 2006, Norway).

The degradation rate was similar to other tests with a synthesis gas derived from methane reforming under similar testing conditions (see Fig. 1). The feasibility of using such fuel was thus demonstrated. It is of course necessary to perform tests in a real mixture, also containing the relevant impurities in the fuel.

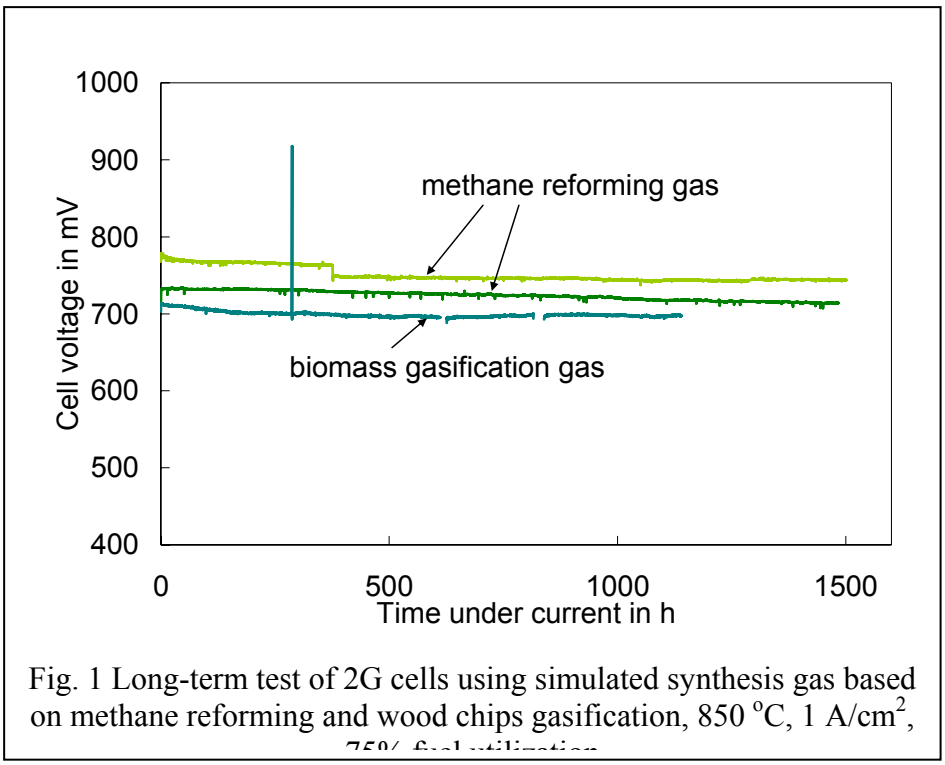

Fig. 1 Long-term test of 2G cells using simulated synthesis gas based on methane reforming and wood chips gasification, 850 °C, 1 A/cm^2, 75% fuel utilization

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Activity: Cell development of 3G cells

Milestone 5a) Test of first 3G cells performed

The development of metal supported cells of generation 3G has been a huge challenge because it includes working with new materials and processing methods. The first cells with specifications good enough to be tested could only be made in a small size (~1cm^2). After further developments, also 5 x 5 cm^2 large cells could be made successfully. Both versions of cells were subjected to cell testing in the current project. A detailed analysis of performance was undertaken in order to understand the electrochemical behavior and to support further development by input from cell testing.

In Fig. 1, the improvement obtained so far on performance and stability from the very first 3G cells to later ones is schematically shown. A correlation between sintering time – sintering temperature, and cell stability was found.

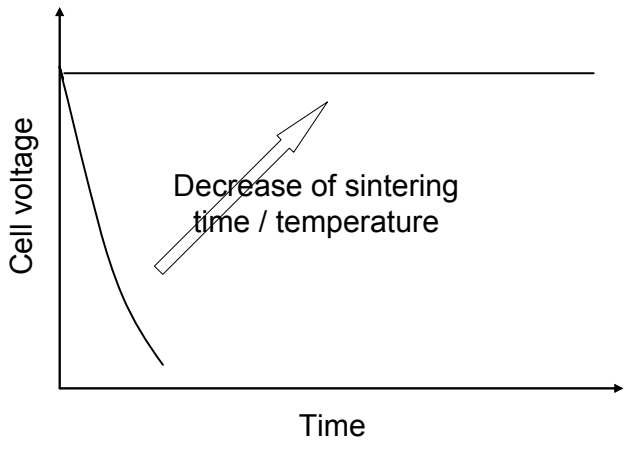

Fig. 1 Schematic performance (cell voltage) of 3G cells, from first 3G to later versions – A horizontal line at high cell voltage is the aim