



scotas

ROBUST FUEL CELLS

4.1 Final Publishable Summary Report

Table of contents

Executive summary	2
Summary Description of project context and objectives	3
Description of main S&T results/foreground	6
Materials characterization	6
Electrical properties.....	6
Mechanical properties	7
Materials supply	9
Cell development.....	9
Anode layer development.....	9
Anode supported cell development.....	13
Final conclusion on the cell development.....	15
Application relevant testing	17
Sulphur tolerance.....	17
RedOx stability.....	19
Final Assessment Stack test	20
Potential Impact and main dissemination activities and exploitation of results	23
Potential Impact.....	23
Dissemination.....	24
Exploitation	24
Address of public website and relevant contact details	25
Project Website	25
Relevant contact details.....	25

Executive summary

The solid oxide fuel cell (SOFC) is a clean and efficient technology for generation of power, heat and/or cooling. When substituting conventional generating technology, SOFC offers significant reduction in the emissions of CO₂, NO_x and particulate matter. To make the technology more mature for the market, system efficiency lifetime are important parameters. Today system introduced failures are a major reason for insufficient lifetime. For small, a few kW residential combined heat and power supply (m-CHP) three failure mechanisms have been identified, namely loss of fuel, breakdown of the desulfurizer and reformer, which degrade the fuel electrode (anode), when using a state-of-the art nickel cermet. Those failures have to date been addressed at the system level.

The project aims to demonstrate a new type of solid oxide fuel cell (SOFC), based on a ceramic strontium titanate oxide (ST), which addresses the three major failure mechanisms: sulphur tolerance, re-oxidation (RedOx) stability and coking. In this project, the integration of the most promising ST materials into existing cell designs, electrolyte supported and anode supported cells of 100 cm² and 144 cm² size, respectively, have been pursued.

At the early stages of the project, three materials compositions were defined as candidate anode materials, based on suitable electrical conductivity, chemical stability and processing characteristics: A-site modified strontium titanates (lanthanum and calcium substituted strontium titanate (LSCT) and an yttria substituted strontium titanate (SYT)) and one B-site, Niobium modified strontium titanate (STN)). Several kg of powders for the processing development have been produced for each of these materials. Investigations of the electrical and mechanical properties of the porous anode supports revealed that insufficient processing quality control had a clear impact, limiting the mechanical robustness of full anode supported cells at sizes exceeding 25 cm². Thus, priority was given to electrolyte supported cells up to 100 cm², using the various ST materials and with different infiltrated electro catalysts, such as nickel and/or ruthenium together with ceria or gadolinium modified ceria (CGO).

The initial testing showed promising initial performances, but severe degradation over several hundreds of hours. The latter could clearly be attributed to a decrease of the electrochemical activity of the anode. Stable cell performance over several hundreds of hours of operation could be achieved by using Ni/CGO or Ru/CGO as electro catalysts. Ni/CGO and Ru/CGO electro catalyst combinations were then infiltrated into the most promising titanate material, LSCT, and electrolyte supported cells of 100 cm² cells tested for tolerance to sulphur exposure and loss of fuel in 5-cell short stacks operated on pre-reformed pipeline natural gas. Upon sulphur exposure (8 ppm), both types of electrodes showed an initial decrease in performance, which then stabilized for Ru/CGO infiltrated cells. Therefore, at this stage, the cell concept cannot be evaluated as superior to state-of-the-art solid oxide fuel cells in terms of sulphur tolerance. Fuel shut down and subsequent re-oxidation of the fuel electrode, both with and without cooling down the stack temperature, did not affect the cell or stack performance. Thus, **the cell concept is proven to be tolerant towards RedOx cycles**. The RedOx tolerance was finally confirmed in a system test, using a 60 cell stack operated by pipeline natural gas. The resulting power output (AC) was 800 W with an electrical system efficiency of 21 %. This, to the knowledge of the project partners, is the **first demonstration of a ceramic anode based cell in a real solid oxide fuel cell system** and proves the feasibility of the concept.

Summary Description of project context and objectives

The solid oxide fuel cell (SOFC) is a clean and efficient technology for generation of power, heat and/or cooling. When substituting conventional generating technology, SOFC offers significant reduction in the emissions of CO₂, NO_x and particulate matter. While SOFC technology is approaching state-of-the-art, there are still important challenges which must be overcome to successfully commercialise the technology. For small, a few kW residential m-CHP applications three failure mechanisms have been identified, namely loss of fuel, breakdown of the desulfurizer and reformer, which impact the fuel electrode (anode). In order to make the SOFC cells more tolerant and durable, sulphur and coking tolerant and re-oxidation (RedOx) stable cells are required, which are not available based on the state of the art Nickel cermet anodes. Furthermore, replacing carcinogenic nickel and nickel oxide in the fabrication is an important aspect when production in Europe is considered.

An alternative to Ni, resulting from multiple years of European research, is a ceramic oxide namely modified strontium titanate (ST). However, its application in real cells and stacks was not performed prior to this project. Successful demonstration of such a new full ceramic SOFC with superior fuel electrode (anode) robustness towards the above mentioned failures would enable system simplification, which is particularly relevant for small systems, e.g. combined heat and power (CHP).

The project aims to demonstrate a new type of full ceramic solid oxide fuel cell (SOFC), which addresses three major failure mechanisms that, to date, have to be addressed at the system level: sulphur tolerance, RedOx stability and coking. The project includes both the cell development, as well as critical issues related to the operation of micro CHP systems, namely **Start Up/Shut down**(RedOx stability, C tolerance required) and **Grid outage/system failures** (RedOx, sulphur, C-tolerance required). Simplifying the system **reduces statistically based failures** and thus **increases lifetime and decreases costs**. In this way, the project aims to contribute to the following targets in the application area of stationary fuel cells: 45% electrical efficiency, 80% CHP efficiency and increased fuel flexibility. Lifetime targets (40000 h lifetime) and cost competitiveness are not major objectives, but will be considered in the final assessment.

This project thus aims to provide a materials based solution to overcome critical aspects in the operation of small scale SOFC systems particularly in the micro CHP area in a joint approach between materials and processing experts closely together with SOFC cell and stack manufacturers. **Integration of modified strontium titanate as an anode material into the processing routines and cell designs has been the major activity in this project.** The development has from an early stage been targeted towards the technically required dimensions and test conditions for the cells as given by the industrial partners. This is also reflected in the final assessment of the performance of the new cells in **a real 1 kW SOFC system environment.**

The major objectives of this project can be summarised as follows:

- Identifying the most suitable strontium titanate composition for anodes and anode supports
- Integration of these materials into the processing routines and cell designs.
- Testing of the new cells under application relevant conditions
- Identifying performance limitations
- Assessment of results on a system related level

The work in this project has been organised along three materials development lines as illustrated in Figure 1. A-site deficient lanthanum strontium titanates (LST) have been pursued at USTAN, while JUELICH worked on yttrium substituted strontium titanates (YST, an equivalent A-site modified perovskite). DTU Energy Conversion addressed a strontium titanate system modified on the B-site by replacing part of the titanium by of niobium (STN). All three materials have been proven earlier to be physically and chemical compatible with adjacent cell components especially the electrolyte. They can be processed in air and possess in general a high specific electronic conductivity under reducing conditions of the anode as required for an electrode.

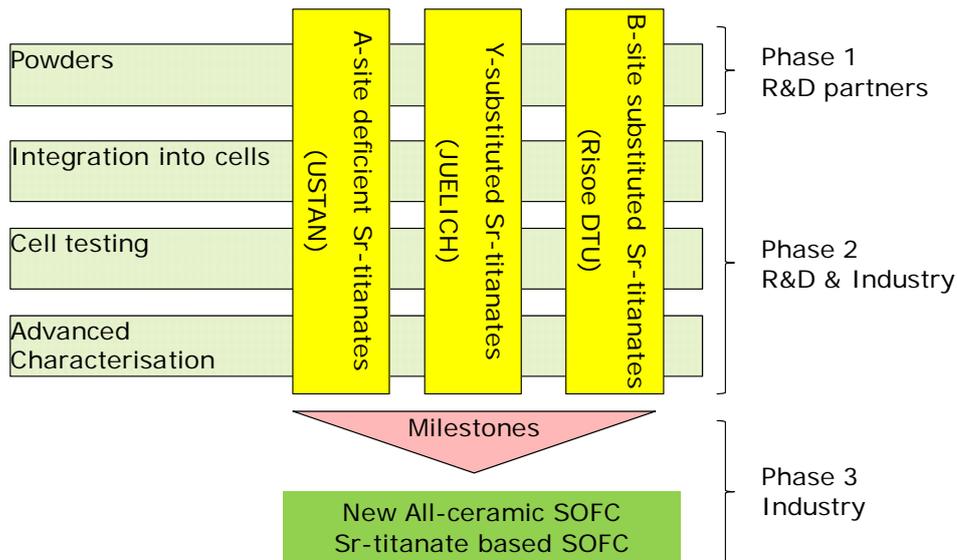


Figure 1 Project approach and organisation of the project

The project was structured to follow the usual steps in the fabrication of ceramic components (as illustrated in Figure 2), starting with materials characterisation and powder development in Workpackage 1, which are used to fabricate the ceramic anode and anode support layers. In Workpackage 2, a large effort has been devoted to the intergration of the ceramic layers into full cells, as regards the compatibility with adjacent layers especially during fabrication but also during operation of the cells.

Qualified cells were delivered to Workpackage 3, which addressed the performance evaluation, first to benchmark the cells and, finally to assess the sulphur and re-oxidation tolerance in simulated or real reformat fuels (in this case natural gas, reformed by partial oxidation (POX)). The development of powders, cell fabrication and testing has been an iterative process, based on pre- and post-test analysis in Workpackage 4. In Workpackage 4 also a thorough assessment of the mechanical properties was performed.

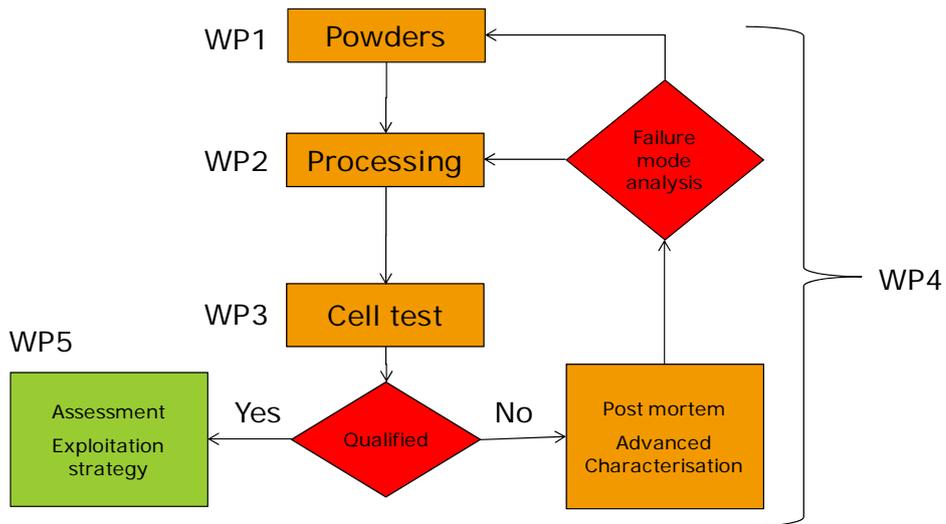


Figure 2: Project organisation and interaction between workpackages.

The responsables for the workpackages have been:

Table 1 SCOTAS-SOFC Work packages and WP leaders

Work package	Title	WP Leader	Participant
WP 0	Management	Dr. Peter Holtappels	Risoe DTU
WP 1	Powders	Prof. John TS Irvine	USTAN
WP 2	Materials Integration	Dr. Frank Tietz	JUELICH
WP 3	Electrochemical Testing	Dr. Jeppe Rass- Hansen	TOFC
WP 4	Advanced Characterization	Dr. Luise Theil Kuhn	Risoe DTU
WP 5	Assessment	Dr. Andreas Mai	HEXIS

Description of main S&T results/foreground

The scientific-technical results of the project are covering mainly three areas:

- Materials properties relevant for the evaluation of the materials, here electrical conductivity and mechanical stability are of most importance
- The development of prototype cells, in particular the upscaling of the cell dimensions
- Application relevant testing, which was performed in short stack configuration using natural gas.
- The performance of prototype cells in a real 1 kW system environment

The main results and achievements are presented in the following along these lines.

Materials characterization

Three specific materials compositions have been identified ($\text{La}_{0.20}\text{Sr}_{0.25}\text{Ca}_{0.45}\text{TiO}_3$ (LSCT_{A-}, USTAN), $\text{Sr}_{0.895}\text{Y}_{0.07}\text{TiO}_3$ (SYT, JUELICH) or $\text{La}_{0.2}\text{Sr}_{0.7}\text{TiO}_3$ (LST, JUELICH), and $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ (STN, DTU Energy Conversion)) within the first 6 month of the project based on previous materials specific investigations by the partners. All materials can be processed in air, have high specific electrical conductivities, which are not affected by re-oxidation. In the course of this project, the materials properties have been investigated as regards the performance of porous layers, in particular their electrical and mechanical properties, which are important for the function of the material as electrodes and electrode supports, respectively.

Electrical properties

The electrical conductivity tests of porous samples are given for STN and LSCT in Figure 3. The conductivities are between 2 and 12 S/cm² and thus significantly lower than conductivity of SoA Ni-cermet anodes (>400 S/cm²). This is important to know, since it requires an adaptation of the current collection from ST based cells.

It should be noted, that values measured for porous structures are more than one order of magnitude lower than specific conductivities measured on dense samples. The reason for this remains unclear since porosity and different pretreatments cannot explain these deviations. The low conductivities could be compensated by appropriate current collectors, thus the origin of the low conductivities was not investigated further in this project.

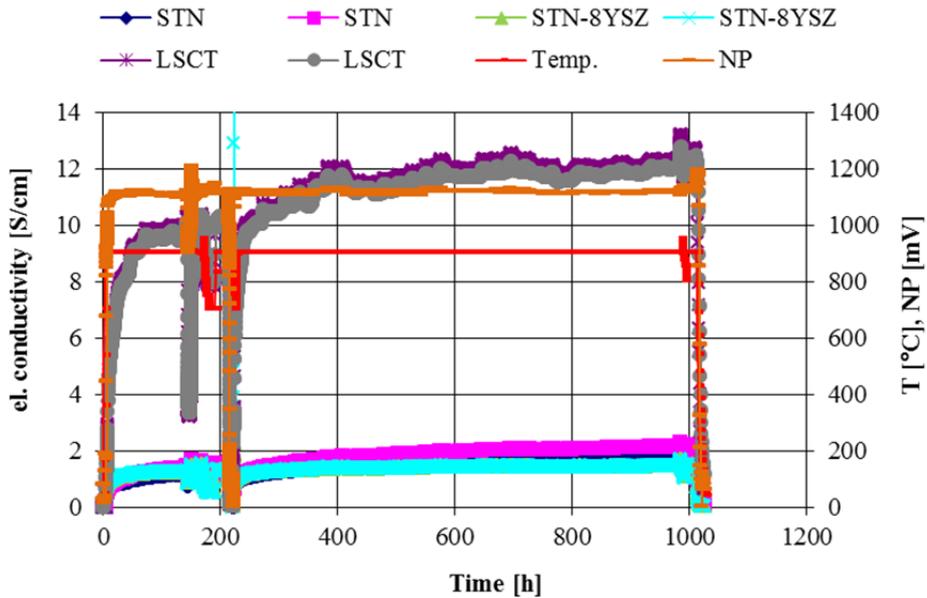


Figure 3 4-point conductivity of STN-based and LSCT thin porous layers in H_2/N_2 atmosphere at $900^\circ C$. Test conditions e.g. temperature (Temp) and Nernst potential (NP) are stable over the whole testing period.

Mechanical properties

The mechanical properties have been assessed for dense and porous samples for all three materials between room temperature and $900^\circ C$. These results have led to a generic model that was found suitable to describe the porosity dependent mechanical properties of all three strontium titanate ceramics, such as Young's Modulus (see Figure 4). The model can thus be used to adapt stack design to the specific strength of the strontium titanate materials when fabricated as porous supports.

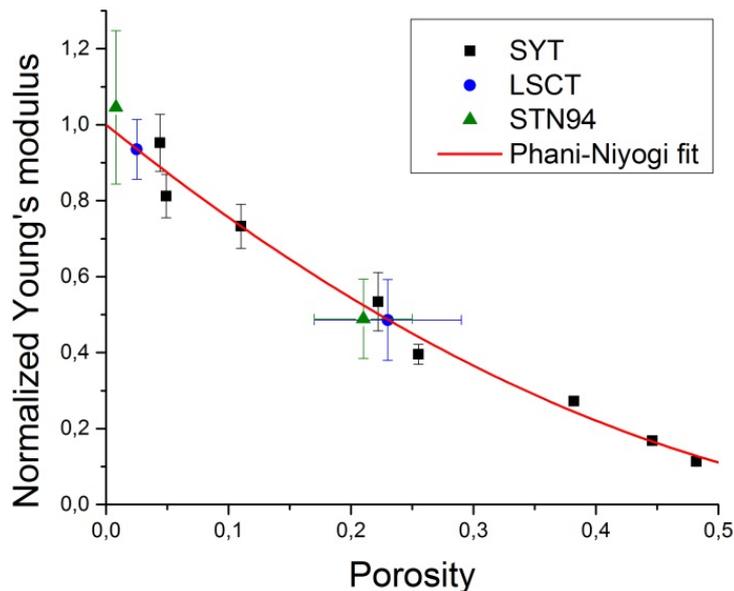


Figure 4 Young's modulus – porosity dependency in normalized form for SYT, LSCT and STN material.

The resilience, e.g. the ability of a material to absorb elastic deformation, was determined from porosity normalized Young’s moduli and strength measurements. The results for the various STs are compared to Ni cermet in Figure 5 and Figure 6 for room temperature and at 800 °C, respectively. All materials investigated within this project revealed a similar resilience, which is in fact similar to the weakest reported Ni-YSZ cermet, whereas the strongest Ni-YSZ composite has an about 20 times higher value at both room temperature and 800 °C. An additionally produced SYT-3YSZ composite yielded the highest resilience among the investigated materials despite the fact that some large defects were found in the specimens. This indicates a clear a clear potential for improvement through better control of the ceramic processing.

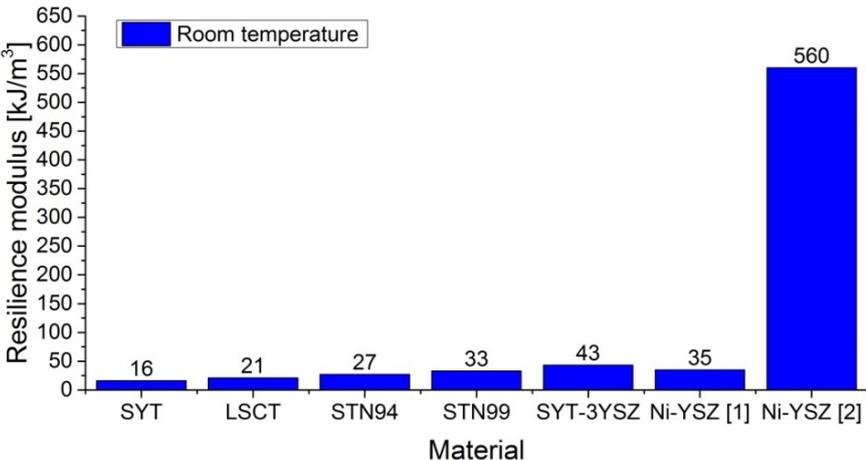


Figure 5 Room temperature resilience of the materials investigated within SCOTAS project.

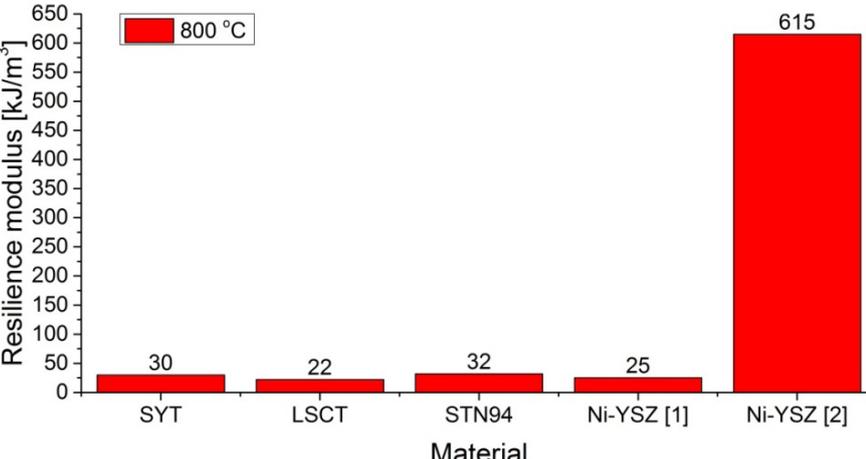


Figure 6 Resilience modulus of the materials at 800 °C.

Materials supply

The development of larger cells required significant amounts of ceramic powders with suitable characteristics for the processing. While in house produced powders have been used in the beginning, commercially available powders were aimed for in the later course of the project.

Several materials suppliers have been compared to in-house produced powders. All commercial materials needed refinement and thus have not been assessed superior to the in-house produced powders. This clearly indicates the need to develop a materials supply chain for powders with desired properties if larger amounts are needed.

Cell development

Based on the mechanical and electrical properties of the porous layers, it has been concluded that all materials have a potential as anode materials while for the anode substrates LSCT and SYT have been selected based on their electronic conductivity and advanced development state, respectively. However, the still relatively low electrical conductivity might impose some challenges on the cell and stack design.

Anode layer development

The anode layer is the layer in direct contact to the solid electrolyte and thus the place where the conversion of the fuel in the electrode takes place. The anode developed in this project consists of a porous strontium titanate layer, which is infiltrated with a solution containing catalytically active elements. Upon drying and decomposition ceramic and/or metallic nanostructured particles are formed on the ST surface. The concept is illustrated in Figure 7.

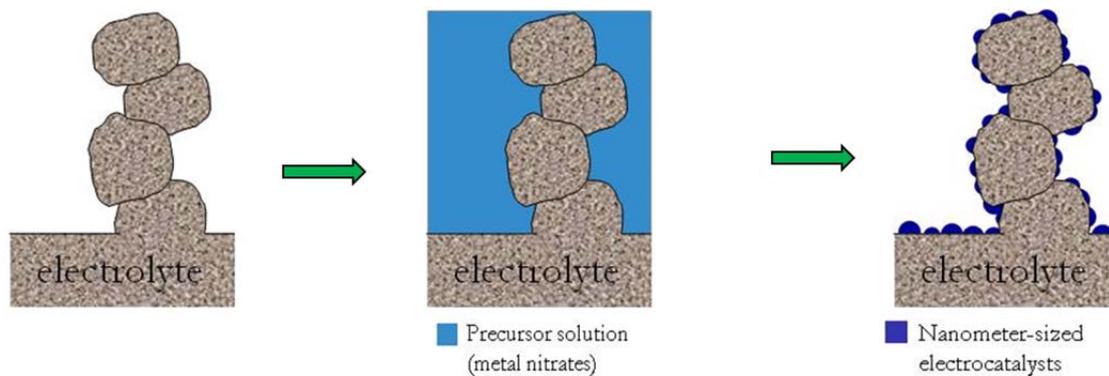


Figure 7 Concept of infiltrated electrodes

Figure 8 shows an representative image of the infiltrated layer before and after testing for a SYT based electrode. After preparation a fine nano sized layer of Ni and ceria uniformly covers the SYT surface. After initial operation of the anode, the structure changes by forming discrete and isolated electro catalysts particles of larger size (approx. 50 nm). These structures have been observed after short time testing and also after longer test periods, which indicates that this distribution is formed during an initial operation period and remains stable for several hundreds of hours.

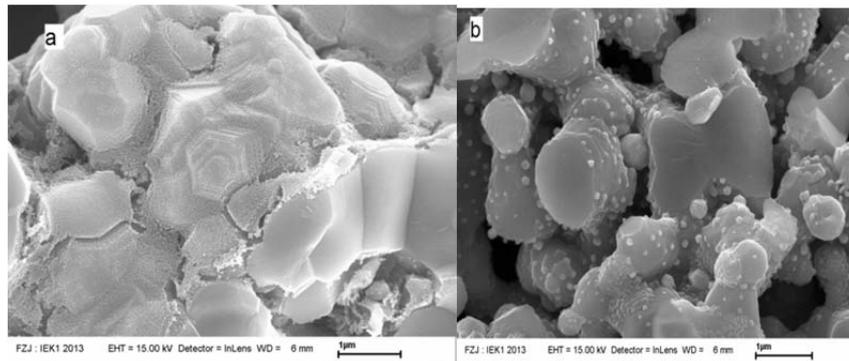


Figure 8 SYT electrode with Ni/ ceria infiltrated catalysts a) before testing b) after testing

The infiltrated electro catalysts were clearly identified to determine the electro catalytic activity. Non-infiltrated ST backbones had low activity towards hydrogen oxidation reflected in area specific resistances (ASR) of up to 100 Ohm cm². By using a composite of the ST and the electrolyte material, the activity could slightly be enhanced (10 Ohm cm²), but is still much lower compared to nickel cermet based anodes. By infiltrating nickel and ceria as electro catalysts into the ST backbone, the activity is comparable to conventional SOFC anodes (ASR around 0.1 Ohm cm² at 850 C). Thus, porous ST layers with infiltrated electro catalysts have been the main development line for the anode layer in both anode supported and electrolyte supported cells.

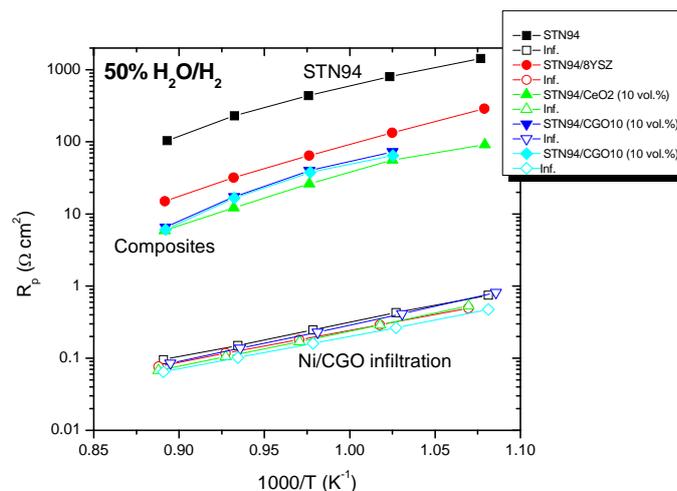


Figure 9 Comparison of symmetrical cell performance of STN either as pure material, as composite with YSZ and with infiltrated Ni/CGO electro catalysts.

Benchmarking of anode layers with infiltrated electro catalysts on button cells and 25 cm² sized cells indicated that initial power output of 0.5 W/cm² can easily be achieved by using Ni together with ceria or Gd-modified ceria as electro catalyst. However, most cells experienced a severe degradation during the first hundreds hours of testing, clearly attributed to the electrode activity, and thus to the infiltrate. In order to investigate the influence of the backbone (pure STN or composite STN/YSZ electrolyte) and nature of the infiltrate and the pretreatment of the cells on the longterm stability, a detailed study was performed by using STN based anode layers. No clear correlation to the backbone composition could be made. Various pretreatments including high temperature conditioning and gas cleaning did not improve the high degradation rate of 300-500 mV/kh of full cells. Hot gas cleaning, known to improve cell stability by removing residual inorganic impurities, did not change the degradation rate either (Figure 10).

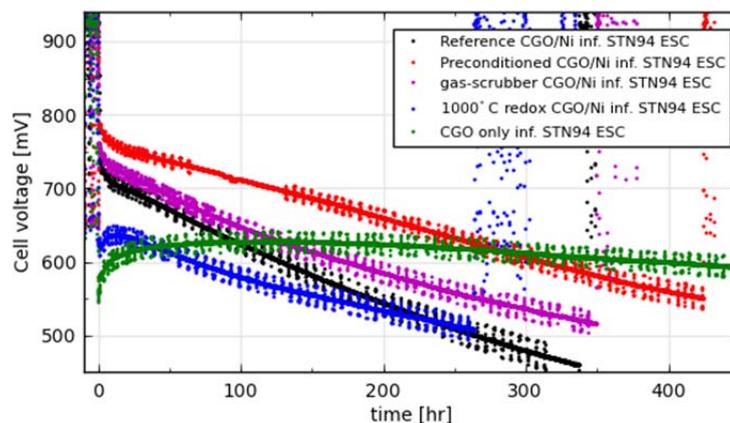


Figure 10 Long-term degradation of STN full cells with either gas cleaning or different pre treatments

The first improvement towards long-term stability was observed when only CGO without Ni as electro catalyst was infiltrated into STN backbones. Cells showed a sufficiently low degradation rate of 50 mV/khs, however on the expense of cell performance in terms of power output. This result points to the metallic component in the infiltrate being responsible for the degradation. Thus, alternative electro catalysts, including Ru, Pd, Pt with and without CGO have been screened first on button cells and promising candidates have subsequently been tested on full 25 cm² sized cells. Figure 11 compares the best performing electro catalysts Ru/CGO with Ni/CGO and CGO alone. Significantly higher cell voltage at similar loading of the cells could be achieved (870 mV for Ru/CGO compared to 750 mV initial cell voltage in case of Ni/CGO @125 mA/cm²)

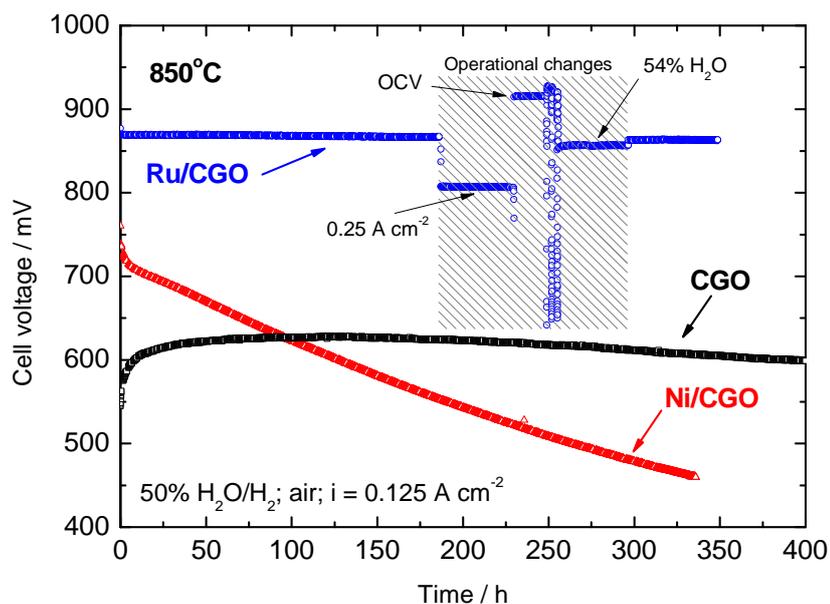


Figure 11 long-term stability of STN full cells with different infiltrates.

Pre- and post-test analysis has been extensively carried out in Workpackage 4 to identify the performance limiting parameters in the newly developed cells. Based on the fact described before that the initial structural change of the infiltrate from a homogenous coverage to more isolated catalyst particles did not change upon long-term operation, this is unlikely to explain the observed steady state degradation during several hundreds of hours of constant operation.

A more detailed analysis of the Ni/CGO/STN system, including model experiments performed on powders indicated two features 1) a separation of Ni and CGO and 2) a change in the CGO surface structure on an atomic scale, namely reconstruction from a highly faceted to a more blurred surface structure after long-term exposure to a hydrogen/water atmosphere. In order to understand the metal catalyst/oxide support interactions, a literature study was made and revealed additional possible processes occurring on an atomic scale, such as particle coverage and cation interdiffusion, as possible origins for the degradation. These processes can be slow but severely affecting the electrode performance and thus might explain the observed long term degradation of STN backbones infiltrated with Ni/CGO due to weak metal support interactions.

Stable electro catalyst nano-structured are in contrast predicted for Ru as the metal element in combination with ceria. Here matching crystal structures and orientations lead to a strong metal support interaction, which is most probably the reason for the observed superior long term stability of the Ru-CGO infiltrate. This indicates that indeed long-term stable electrodes with infiltrated nano structured catalysts can be prepared by appropriate choice of elements and controlling the interface structure.

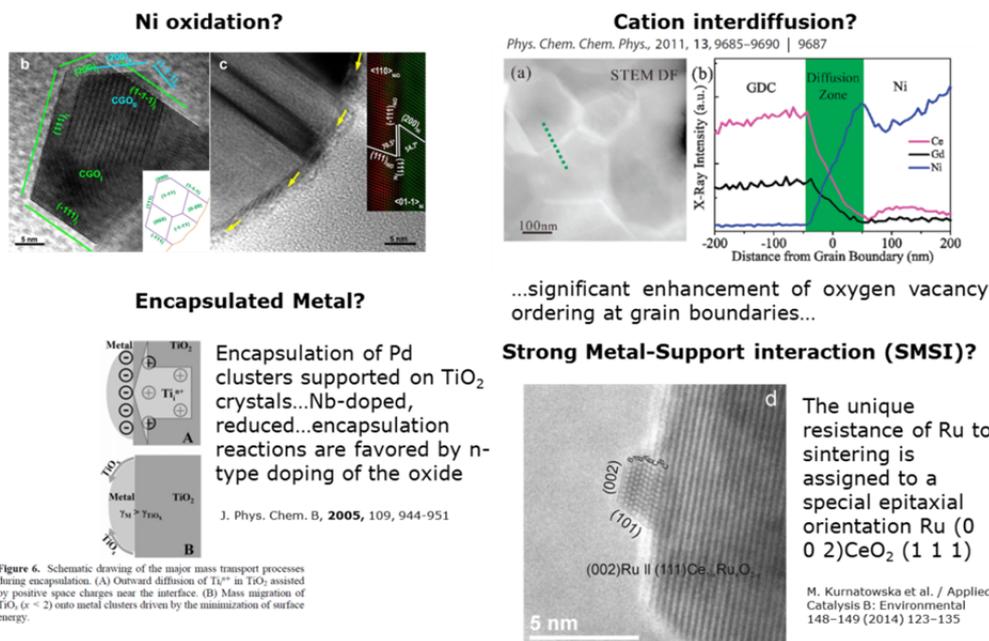


Figure 12 possible long-term degradation mechanisms: 1) Ni-Oxidation was indicated to cause a de-faceting of the CGO surface which might affect oxygen exchange and fuel oxidation (studies within this project on powder mixtures as model samples, 2) encapsulation and 3) cation interdiffusion both are alternative mechanisms that can reduce oxygen exchange and fuel oxidation. 4) Strong metal support interactions recently identified for Ru-ceria can explain the superior stability of the Ru-CGO sample.

Anode supported cell development

The development of anode supported cells (ASC) focussed mainly on two ST compositions, SYT and LSCT for both the anode and the support layer. The development started from button cell level up to the targeted cell sizes of 144 cm².

SYT based ASCs with Ni/CGO infiltration were fabricated as 25 cm² sized cells for single cell testing.. The first tests showed initial ASRs between 0.4 and 0.7 Ωcm². The power output was 0.3 Wcm² at 0.7 V cell voltage. It should be noted that the open circuit voltage (OCV) was significantly lower than the theoretical value, however the reason has not yet been fully identified. Interdiffusion of Ti into the YSZ electrolyte is known to occur and could introduce some level of electronic conductivity into the electrolyte. The measured oxygen increase in the fuel compartment is, however, rather high assuming an oxygen ion flux through the mixed conducting electrolyte.

SYT based anode supported cells of 144 cm² size have been iteratively developed for testing in a short stack (e.g. 10 cell stack configuration). The general experience with larger SYT cells prepared by warm pressing showed clearly that mechanical robustness as required for the TOFC stack design could not be achieved. Remaining stresses in the materials caused cell cracking either during preparation, stack assembly or start up. Despite cells have been quality assured with respect to waviness, handling stability and gas tightness prior to delivery, and also survived a mechanically demanding laser cutting prior to the stack assembly, these failures have often been observed as the last step in the experimental set up. The fractography analysis from WP4 indicated that most likely remaining stresses from the fabrication and pre-reduction process, e.g. incomplete reduction in correlation with structural in homogeneities most likely caused the cell

failures. Thus, optimization of the production and conditioning process of SYT based cells are still necessary for this type of material, e.g. by tape casting instead of warm pressing.

LSCT anode supports have been developed based on aqueous tape casting. On button cells power output exceeding 0.6 W/cm^2 in hydrogen at 800 C was achieved indicating a promising performance and justifying the further upscaling of the cells in terms of cell size.

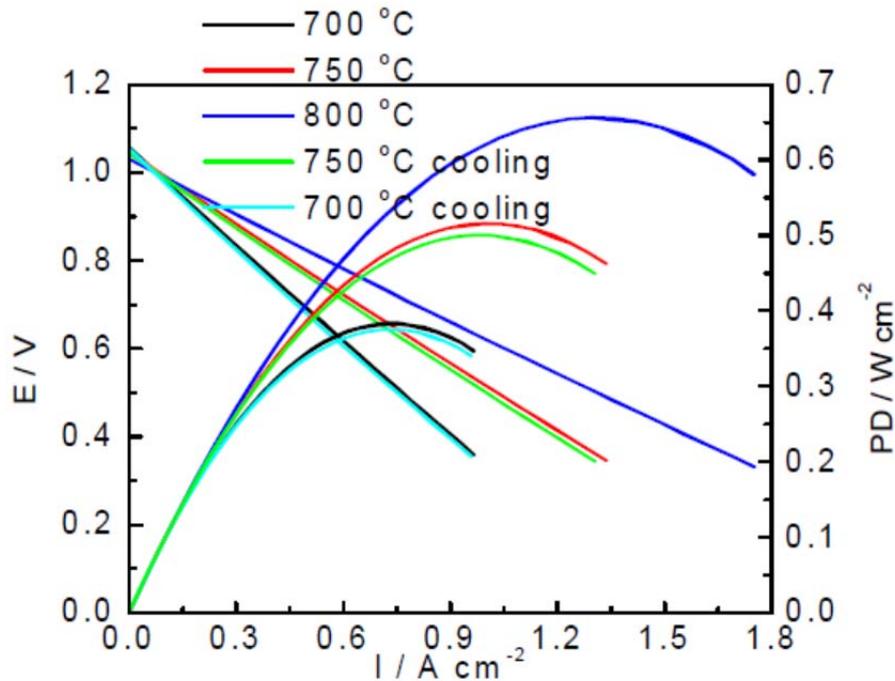


Figure 13 Anode supported LSCT cell with CeO_2 and Ni as infiltrates. Tested in humidified H_2 (3% H_2O)

The development of larger LSCT anode supported cells, was pursued in a joint effort between partners. A commercial batch of LSCT powder was used and recipes transferred from laboratory to pilot line processing equipment. Adaptation of the recipe to the new powder characteristics and facilities needed more time than available for this task. Finally, tape casted anode support anode and electrolyte layers could be successfully fabricated, and mechanically robust half-cells of 25 cm^2 produced by methods known to be upscalable to 144 cm^2 . Due to time restrictions towards the end of the project, these cells could not be tested anymore within the project period. This has to be pursued in a separate project.

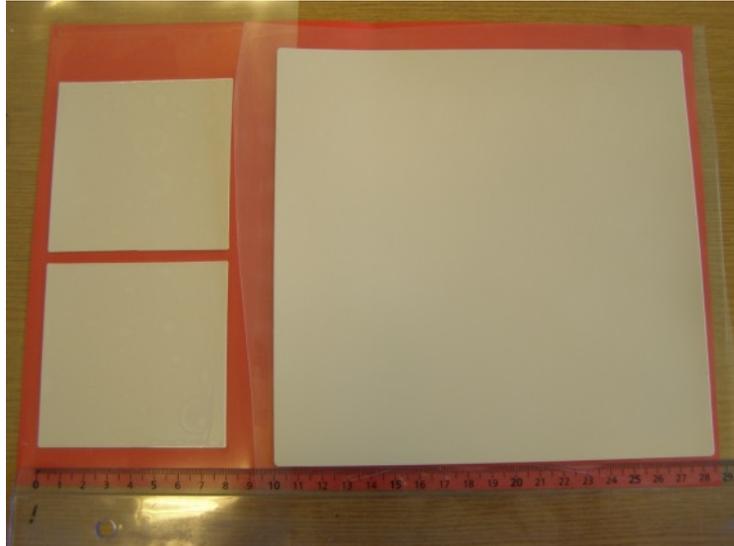


Figure 14 13*13 cm² LSCT cells jointly prepared by USTAN (formulation) and DTU Energy Conversion (equipment + electrolyte layer).

Final conclusion on the cell development

In summary, the project made good progress towards the development of electrolyte supported cells, while anode supported cells could not finally be assessed.

Stable and performing electrolyte supported cells have been achieved by using STN and Ru/CGO as electro catalysts on LSCT and STN backbones (see Table 2). SYT based cells showed a comparable power output, however, the degradation was still too high for consideration of these cells for short stack tests. Due to the low electronic conductivity of the porous STN layer, particular attention had to be paid on the current collection from the anode on larger, e.g. 25 cm² sized cells. Unfortunately, suitable current collectors were not compatible with the targeted short stack design initial cell tests

In conclusion LSCT based cells infiltrated with Ni/CGO or Ru/CGO were considered the most promising cells for the application relevant testing of short stack testing regarding the sulphur and RedOx tolerance.

Table 2 Overview of cell development

TABLE IV. Overview of cell development						
	LSCT		YST	STN		Ni-Cermet reference
Max power / Wcm ⁻²	0.2	0.12	0.3	0.5	0.5	
Voltage degradation [mV/kh]	400	Not evaluated Appears similar to STN-Ru/CGO	175	375-500	45	3.5
Cell geometry	5 cell stack	5 cell stack	25 cm ² cell	25cm ²	25cm ²	100cm ²
Test conditions	CPOX 80% fuel utilisation	CPOX	4% H ₂ in H ₂ O	H ₂ / 50% steam	H ₂ / 50% steam	CPOX
Temperature [°C]	950	850	850	850	850	900
Infiltrate	Ni/CeO ₂	Ni/CGO Ru/CGO	Ni	Ni-CGO	Ru/CGO	None
Comment	High degradation	suitable for SCO tolerance testing	Possible leaks or electronic short-circuit through the electrolyte	Au/Pt current collector needed	Au/Pt current collector needed	
Cell type	ESC	ESC	ASC	ESC	ESC	ESC

Application relevant testing

Sulphur tolerance

In order to evaluate the sulphur tolerance of the new cells, it was important to know more in detail the impact of sulphur on SoA Ni-cermet based cells. Thus, a study was performed investigating the impact of sulphur on anode supported Ni-YSZ based cells operated on reformed natural gas. Figure 15 illustrates the effect of sulphur on cell voltage when running at 60% fuel utilisation and a current density of $140\text{mA}/\text{cm}^2$. At around 10 ppmv sulphur the cell voltage is so low that there is a potential risk of re-oxidizing the anode and resulting stack failure.

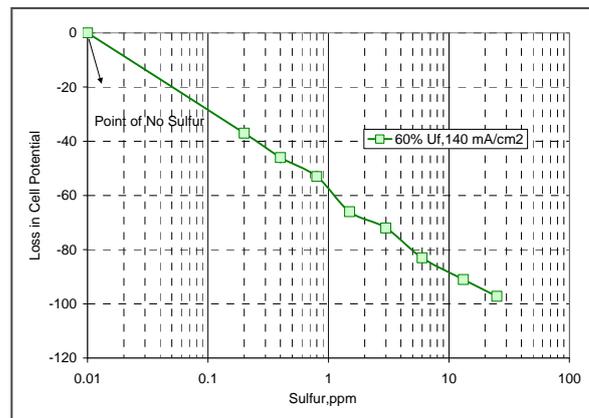


Figure 15 Loss in cell potential for a stack running on a CPO gas at 60% fuel utilization and a current density of $140\text{mA}/\text{cm}^2$ at sulphur levels from 0-25 ppmv.

The reason is that the reaction rate of the water-gas shift reaction (WGS) reaction is significantly decreased by sulphur. This is due to sulphur covering the Ni surface and thereby decreasing the catalytic activity. The effect is reversible, so removing sulphur from the fuel will slowly regenerate a clean nickel surface and cell voltage will increase back to a level as before introducing sulphur. Figure 16 below illustrates this phenomenon. The figure shows the dry gas exhaust and the resulting Nernst potential from test with a CPO gas after running shortly at 300 ppmv sulphur.

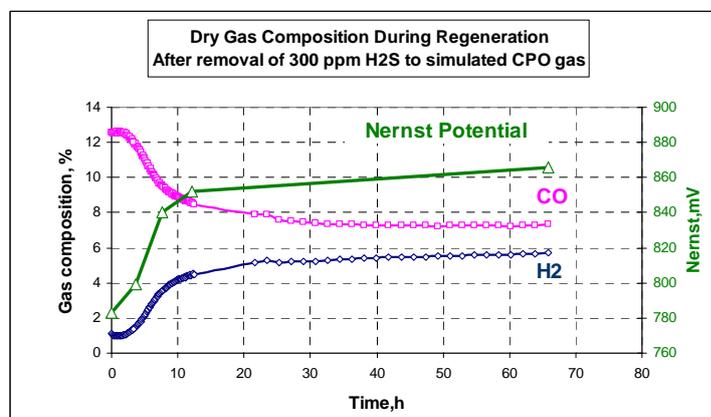


Figure 16 Exit gas measurements and corresponding Nernst potential calculation after removing sulphur from a stack test.

As a consequence of this analysis it was decided to address the sulphur exposure as much as possible in reformat gas mixtures (H_2 , CO , CO_2 , H_2O ration corresponding to POX reformed natural gas). Hydrogen alone is not considered an industrial relevant fuel. Furthermore, the fuel utilization should exceed the hydrogen content, in order to map the impact of sulphur on the water gas shift reaction in the ceramic anodes.

As regards the sulphur tolerance of the optimized LSCT cells, Figure 17 shows the exposure to sulphur for a short stack of LSCT Ni-CGO cells while

Figure 18 shows the data for a similar cell but with Ru-CGO as electro catalyst. Both types of cells show a decrease in cell potential upon bypassing the desulphurizer. The cell performance could be recovered after 4 hours of exposure on Ni/CGO infiltrated cells. Longterm exposure of Ru/CGO infiltrated cells resulted in a partial recovery, indicating also irreversible changes in some of the cells.

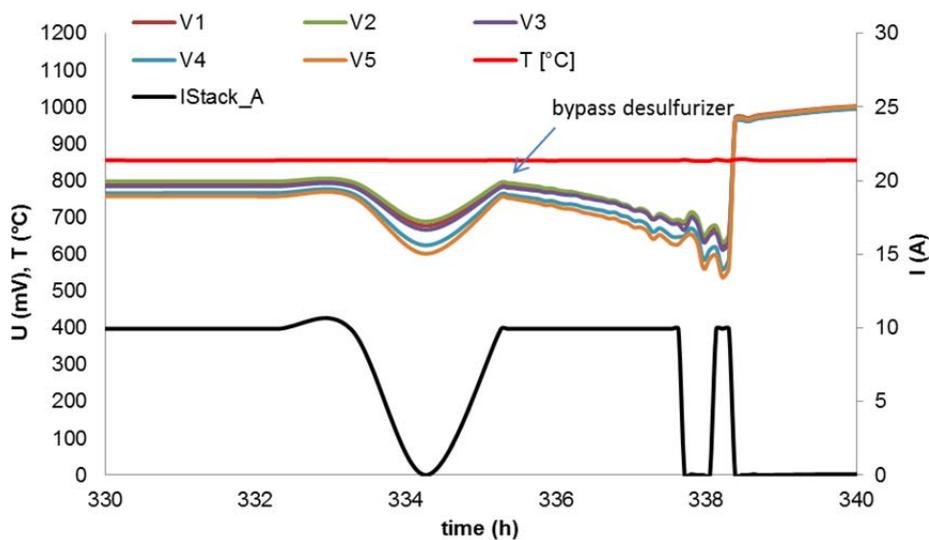


Figure 17 LSCT with Ni/CGO infiltrate, S-Exposure: 850°C, 4 g/h Natural gas per cell, CPOX, air: 1000 g/h per stack, about 8 ppm sulphur must specify backbone it is not clear which

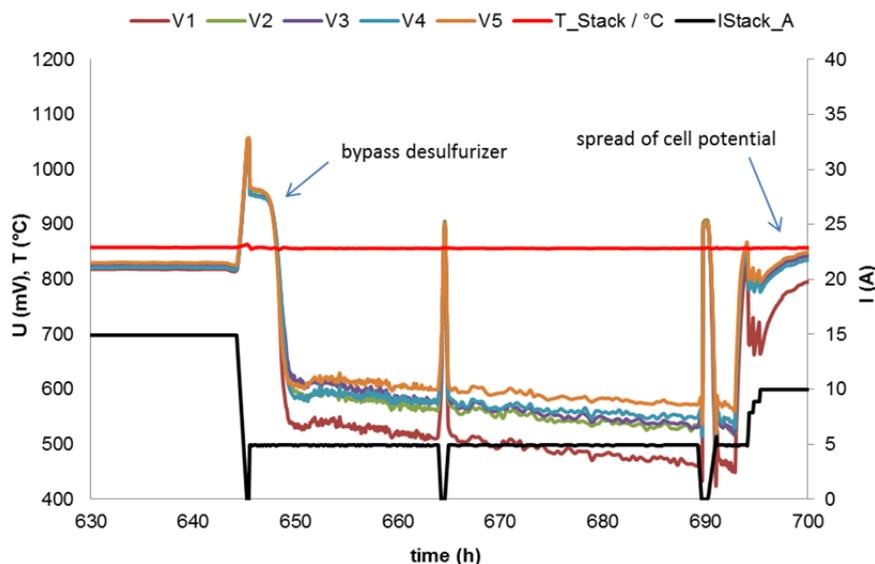


Figure 18 LSCT Ru-CGO: S-Exposure: 850°C, 4 g/h Natural gas per cell, CPOX, air: 1000 g/h per stack, about 8 ppm sulphur

From those results, it appears evident that with respect to sulphur tolerance the use of infiltrated Ni or Ru-CGO electro catalysts does not show superior performance compared to Ni-Cermet based anodes. This was also indicated from preliminary S-exposure tests on STN 94 single cells using hydrogen as fuel. Thus, the concept is not assessed to be superior as regards sulphur tolerance when using these nano structured electro catalysts. In contrast, preliminary tests performed on STN cells using CGO as electro catalyst only, show an improvement of the anode activity, however on the expenses of overall performance. Since the concept is flexible as regards the choice of electro catalysts, more suitable materials might become available and could be integrated into the ceramic backbone.

RedOx stability

As regards the tolerance to re-oxidation, it was evident already from button cell tests that the ST based electrodes are tolerant to RedOx cycling and even improvement of cell performance on button cells have frequently been observed.

RedOx cycling by real fuel cut-offs, also including thermal cycling, has been performed as part of the short stack tests using LSCT cells infiltrated with either Ni/CGO or Ru/CGO. Figure 19 shows the time dependence of the individual cells of a LSCT Ni-CGO short stack. No change in cell performance is observed. Also RedOx cycling in conjunction with thermo cycling did not affect the cell's performance (Figure 20).

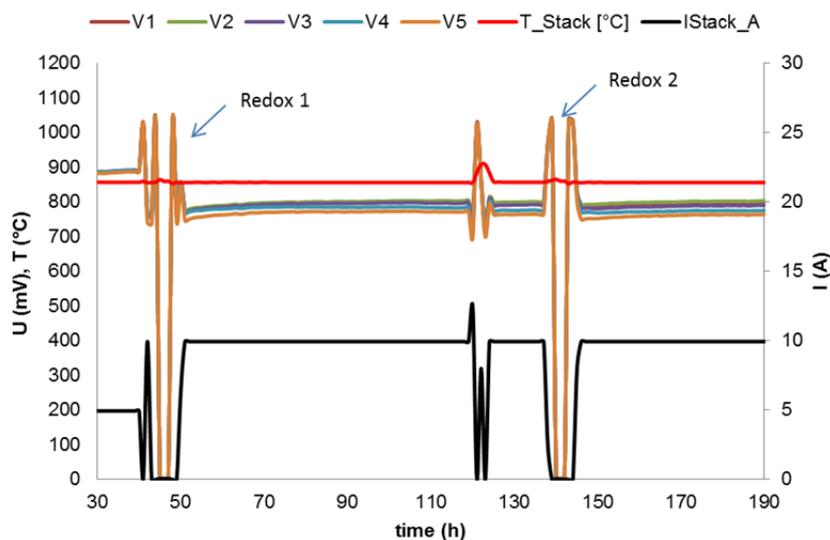


Figure 19 LSCT Ni-CGO: RedOx-cycles: 850°C, 4 g/h Natural gas per cell, CPOX, air: 1000 g/h per stack

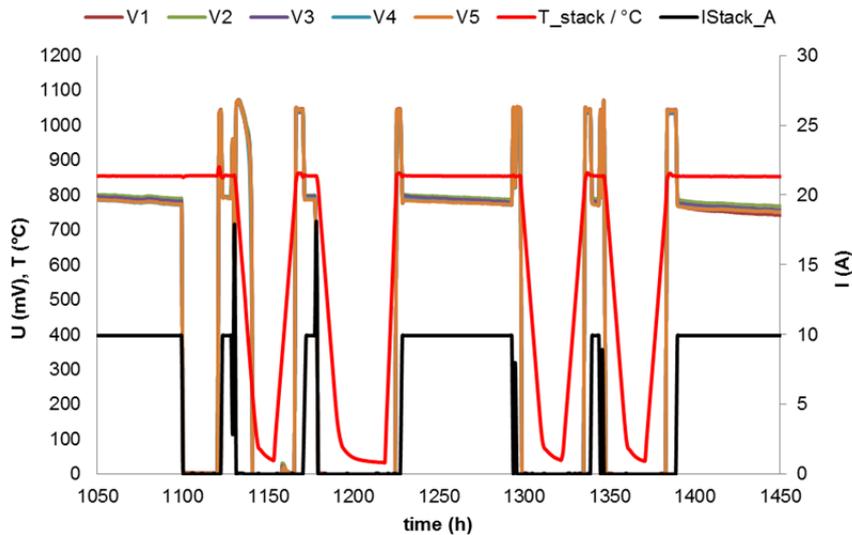


Figure 20 LSCT Ni-CGO: Thermo-RedOx-cycles: 850°C, 4 g/h Natural gas per cell, CPOX, air: 1000 g/h per stack

Summarizing the results from the testing of LSCT based cells RedOx tolerance is confirmed on short stack level for electrolyte supported cells using LSCT as backbone materials and Ni and or Ru as metal infiltrates. For all other ST based cells RedOx tolerance is confirmed on 25 cm² sized cells as well as on button cell and component level. Thus, it is concluded that a superior RedOx stability compared to Ni-Cermet electrodes is demonstrated with the ceramic anodes based on strontium titanate backbones.

Final Assessment Stack test

As a final proof of the full ceramic cell concept, a 1 kW stack with 60 LSCT Ni-CGO infiltrated cells was assembled to investigate the behavior of the new type of cells in an established stack/system environment.

For the cell fabrication, a laboratory recipe was transferred to the automated Hexis screen-printing line. Due to time and materials restrictions, an iterative adaptation of the recipe to the HEXIS screen-printing line could not be made. However, even though not optimized in microstructure, a low but reproducible performance of the cells was demonstrated.

The HEXIS Galileo System test reached an initial power output of 800 W, at a fuel utilization of 60 % and a resulting system efficiency of 21 %. The individual cell power output was significantly lower compared to results from the cell and short stack tests, but reproducible and stable for all cells within the first 3 days. The subsequent degradation of the stack was analyzed by following 6 individual clusters, each comprised of 10 cells. Central clusters being at much higher temperatures than outer clusters ($dT > 100$ °C) degraded more rapidly, indicating that the stability of the cells is largely affected by the operation temperature. Such large temperature gradients as observed with the ST based cells have not been observed in the case of Ni-cermet based stacks. The higher center temperatures are most likely related to higher ohmic losses arising from a lower electronic conductivity in ST based anodes combined with a reduced anode thickness (10-15 micron).

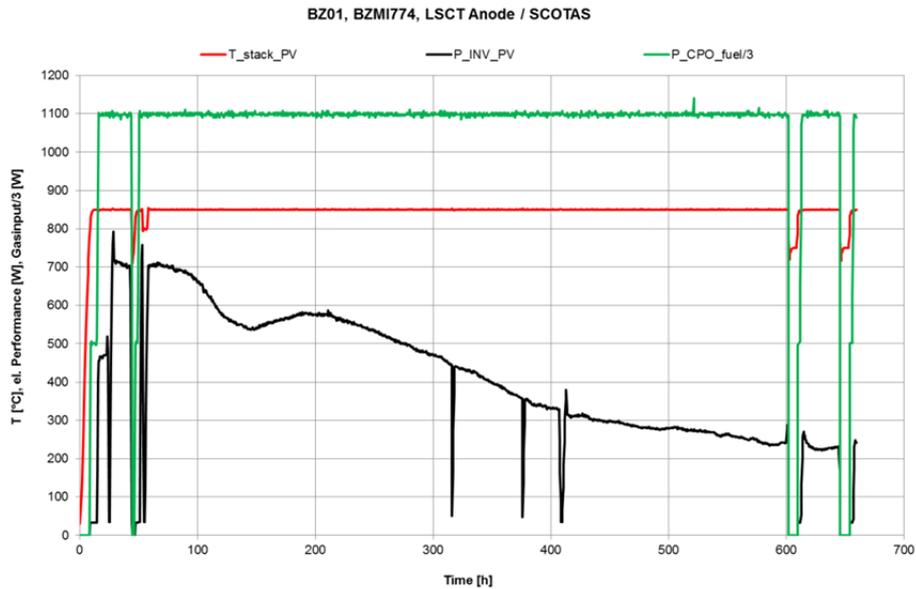


Figure 21 1 kW system test running Sept 6th to Oct 9th 2013 at HEXIS.

The analysis of the stack test indicates that due to different electronic and thermal conductivities of the full ceramic cells, the cell and stack designs needs to be adapted in order to make full advantage of the new type of cells. This holds for electrolyte supported cells, but is considered even more important for anode supported cell designs, if demonstrated successfully.

All in all, especially the electrolyte supported cells with the LSCT based anodes showed promising results in terms of performance, RedOx- and thermo-cycling Also the usability in a complete system could be demonstrated. This system delivered 800 W DC power, **which is to our knowledge the highest published power output of an SOFC with fully-ceramic anodes. Thus, more robust SOFC systems towards fuel outage can be fabricated by integrating a strontium titanate based anode into the cell design. Based on the present results a use of this anode type for commercial use seems to be feasible on mid-term.**

Another advantage of this type of anode is still believed to be the potential for sulphur tolerance which would drastically reduce the cost of the fuel cell unit and increase the robustness. Although an improvement of the sulphur tolerance could be seen when Ru was used instead of Ni, a 100 % tolerance towards sulphur could not be achieved within this project. Here the concept of infiltrated electro catalysts into porous ceramic ST backbones provides the flexibility to explore other, better suited materials as electro catalysts.

The overall objective of the project has been to provide a materials based solution to mitigate know system failures. In the following table the expected impact stated in the project proposal is finally assessed based on the project results.

Table 3 Expected impact and final assessment

	Ni-based anode	SCOTAS anode	Concluding Advantages	Expected Impact	Final Assessment
Thermal expansion coefficient	Higher than other stack components	Close to other stack components (zirconia electrolyte, metallic interconnect)	Reduced thermal stresses, high robustness against thermal cycling and high heating rates	Highly robust system, increased lifetime, simplified operation strategy	Achieved No thermal stresses identified for STN and LSCT
Chemical expansion during RedOx-cycling	Large expansion due to oxidation/reduction Ni ↔ NiO	Negligible chemical expansion	High-robustness against RedOx-cycles, start-stop-cycles	Highly robust system increased lifetime, simplified operation strategy	Achieved, all ST materials are proven to be RedOx stable. Thus a more robust system and increased lifetime as regards fuel outage is possible.
Sulphur tolerance	Sulphur contents in natural gas (few ppm) lead to significant degradation	Sulphur tolerant	No desulphurisation of natural gas and other fuels necessary	Reduced system costs and maintenance (saving 0.01 – 0.02 € per kWh)	No clear advantage identified with Ni and Ru as electro catalysts Oxide electro catalysts might be an option but need to be explored
Coking tolerance	Coking intolerant, coking leads to metal-dusting of the nickel → cell failure	Coking tolerant	Operation regimes, where coking occurs, can be tolerated for a limited time	Simplified operation strategy, heating up with gas possible	Not assessed in detail Expected to depend on the catalyst choice

Potential Impact and main dissemination activities and exploitation of results

Potential Impact

The overall evaluation of the project results proves the feasibility of a novel electrode concept based on a ceramic backbone and using infiltrated nano-particles as electrocatalysts. The cells are re-oxidation tolerant and thus can withstand typical fuel cut offs in micro-CHP systems. A candidate backbone material has been identified and the concept allows for more and improved electro catalysts combinations. Therefore, this novel cell concept presents the needed flexibility for further tailoring of both sulphur and coking tolerances, but is not limited to these. The unique feature of this cell concept is that the electrochemical performance is de-coupled from the structural support and electrical current pick-up. This fact is expected to facilitate accelerated electrode development, since compatibility requirements with adjacent cell materials are significantly reduced. Thus, faster development and more innovation cycles for the next generation of SOFCs can be envisaged at this point.

Based on the promising stability towards re-oxidation, the ceramic anode is considered particularly suited for small scale applications, e.g. up to several kilowatt electrical power. In this context, also smaller systems operating on other hydrocarbon based fuels e.g. Methanol and Ethanol or Dimethylether become interesting applications, e.g. for remote power below 1 kW.

However, there is still some R&D necessary so that the anodes can compete with the state-of-the-art Ni-cermet anodes. One conclusion from this project is that with the current development level only electrolyte supported cell design is possible. If the RedOx stable ceramic anodes should be disseminated to anode supported designs – which would be desirable from a performance point of view – further development is needed on cell and materials levels possibly in parallel with stack design modifications. Unless these problems are solved, ST based anodes supports do not appear as an option for low temperature operation by using thin, supported electrolytes.

As regards a further implementation of such a new cell concept, a supply chain for the strontium titanate powder has to be developed. Another aspect to be addressed is to tailor the anode fabrication process for industrial use. With respect to that the use of infiltration is not state of the art. The infiltrated electro catalyst clearly affects the initial performance (including an initial performance loss), however, long-term stability seem to be influenced by catalyst support interactions on a nano scale or even below. Thus, further understanding and especially control of the infiltrate structure in porous anode backbone structures is a remaining development task.

A wider socio economic impact is expected by implementing the new anode layer into SOFC designs. An environmental aspect is the replacement of Ni as major material in the anode and especially the anode support by a potentially more environmentally benign strontium titanate ceramic. Even though the focus of the ceramic alternative is most likely the anode layer, a wider application of these novel SOFCs will significantly reduce the amount of carcinogenic Ni, NiO during cell fabrication by replacing it by a more environmentally friendly ceramic as a major material in the fuel electrode. Since no supply chain for the material exists to date, this needs to be established.

A further beneficial environmental impact is considered through the development of water based tape casting for the fabrication of the ceramic anode support. Such a fabrication process will reduce the amount of solvents in the fabrication process, which is advantageous not only for the production process itself but also reduces solvent capture and regeneration effort and thus installation effort and

energy consumption in the production line. The development of the water based tape casting for this particular material has the potential to be transferred to other materials.

Dissemination

The project results have been communicated at several conferences and published in respective proceedings and peer reviewed scientific journals. One PhD thesis on the thermo-mechanical properties of ST ceramics arised from the project. Thus the main dissemination addressed the respective scientific community. The project has further been presented in International Innovation, an open access journal worldwide informing decision makers, stakeholders and politicians about ongoing R&D activities. Other dissemination included the presentation of the project at FCH JU organised workshops and Review Days. For more details on the publications from this project, see the publication list as part of the Final Report.

Exploitation

The project has achieved its objective to demonstrate a new type of Solid Oxide fuel cells. At this stage, however, further R&D is needed to commercialise the new type of cells. Especially, upscaling of the manufacturing of electrolyte supported cells, in particular the infiltration process, and development of a supply chain for suitable ceramic powders are considered the most important steps forward. Based on the present results a use of this type of anode for commercial use seems to be feasible on mid-term.

The results are also of interest other EU –FCH JU funded projects, e.g. METSAP and utilized therein. Information exchange is facilitated by project partners active participating in both projects.

The current project has resulted in new knowledge on ceramic titanate anodes and supports as well as significantly improved knowledge on state of the art Ni/YSZ anode. The results are also important for the further development of solid oxide cells for solid oxide fuel cells by the project partners. These results can be used to make a more precise definition of the requirements specification of a new anode thereby enhancing the probability of success for such a development. More general understanding has also been generated in the following areas:

- Water based tapecasting
- Knowledge to stabilize nano structured electrodes
- Knowledge on mechanical properties of porous ceramic structures

This new knowledge is expected to be taken up by other disciplines through the projects publications.

Address of public website and relevant contact details

Project Website

A brief project description including the Deliverables classified “public” can be found on the project website:

www.scotas-sofc.eu

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