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ENHANCING THE LIFETIME OF SOFC STACKS FOR COMBINED HEAT AND POWER APPLICATIONS

SOF-CH

Final report 2007

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RESUME

The objective of this project is the enabling of the Swiss SOFC Consortium, *SOF-CH*, that brings together all the Swiss actors in the field of SOFC, namely the academics, *Empa-HLK*, *EPFL-LENI*, *ETHZ-NIM* and *ZHAW-ICP* (formerly ZHW-CCP) as well as the industries, *Hexis* and *HTceramix*. *SOF-CH*, recognized as a pre-competitive research project by both industries, allows to bundle all the research resources available. It allowed to define 5 work packages, 3 being pre-financed by the *SFOE* in the frame of this preliminary project: WP 1, concentrate on the redox stability of the state of the art anodes in SOFC, WP 2 on the cathode durability and WP 5.1 on the thermo-mechanical properties measurements, simulations and analyses of all components in the stack. The primary objective of *SOF-CH* is the enhancement of the lifetime of SOFC stacks, which is hindering the commercial introduction of the technology. The *SOF-CH* project is thus a key element for establishing the SOFC fuel cell business.

ETHZ-NIM, responsible for WP 1, has engaged since June 2007 a PhD student, Mr. Henning Galinski, working on this subject. A PhD thesis plan has been tentatively made and the student gathered literature data and acquainted himself with microscopic tools such as SEM and TEM. *EPFL-LENI* has engaged a PhD student, Mr. Piedro Tanasini, for WP 2. The student has already performed some experimental work and has made a preliminary thesis plan to be submitted officially at *EPFL* in 2008. In WP 5.1, *Empa-HLK* has made measurements of thermo-mechanical properties of components delivered by *Hexis* (383), and *HTceramix* (250), mainly CTE and Young's modulus, and fed the values to *ZHAW-ICP* and *EPFL-LENI* for simulations. These simulations allowed to visualize the stresses, the pressure distribution and the impact of temperature gradients on the stability within a stack.

This project ended successfully by end of 2007, and is now followed by the *SOF-CH* project financed simultaneously by *swiss*electric research and *SFOE*. This preliminary project was an enabling factor for setting the *SOF-CH* program (5.1 millions CHF of total budget of which 2.1 millions are coming from both funding institutes) but also for launching 2 *CCEM-CH* projects, *Woodgas-SOFC*, and *HTE-CH*. A joint EU project, *SCoReD*, on protective coatings for MICs, has been proposed in 2007 but got only 12.5 points.

Buts du projet

The goal of this project is the establishment of the Swiss SOFC Consortium, ***SOF-CH***, in which the *SFOE* plays the role of enabler. This consortium binds all the Swiss SOFC players from industry (*Hexis AG*, *HTceramix SA*) and academics (*Empa-HLK*, *EPFL-LENI*, *ETHZ-NIM*, *ZHAW-ICP*). The *SOF-CH* project is focusing on **pre-competitive research work**, which will be performed by the universities, with a strong industrial contribution.

This preliminary project is meant to foster this collaboration, establish the technical and coordination means necessary to set the different work packages dealing with enhancing the lifetime issue in the SOFC technology. **5 work packages** (WP), dealing with the most relevant issues of degradation, have been proposed. They are focusing on electrode developments, on thermo-mechanics and simulations tools as both materials and engineering sciences are necessary to analyze the technical challenges and to give appropriate solutions.

The take-off costs for the WP 1, 2 and the financing of WP 5.1 which deal respectively with the redox stability of the anode, the lifetime of the cathode, and the thermo-mechanical properties of the stack components and which serves as a basis for the modelling WP 4 **are covered**. The follow-up of this project is meant to be sustained by a financial contribution from a secondary financial institution.

This project is a key element for establishing the SOFC fuel cell business in Switzerland. It allows to raise the critical mass necessary for the development of SOFC systems in Switzerland. It fits well in the road-map vision of the SOFC industries (see Fig. 1).

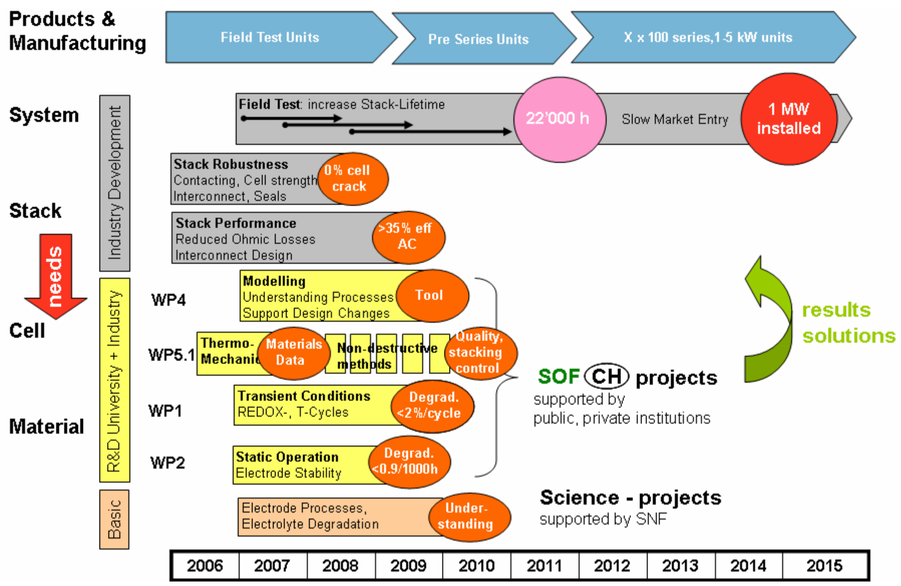

Fig. 1: *Road-Map* for the pre-commercialization of SOFCs in Switzerland. The synergy between the *SOF-CH* and this vision is exposed.

In short, the primarily goals set at the beginning of the project are summarized in the following:

- allow **the take-off of the *SOF-CH* project**;
- **start the WP 1 and 2**
- **finance** the **WP 5.1**
- create a ***SOF-CH* road-map** which sets the basis for the research and development and a business concept for SOFCs in Switzerland
- foresee on these lines **further financing possibilities** for the *SOF-CH* project which spans over the next 3 years.

Travaux effectués et résultats acquis

WP 1 (anode)

Aim : WP 1 is concerned with the redox stability of Ni-based anodes in SOFC stacks.

Goals-milestones: The objective at *ETHZ-NIM* in this Swiss SOFC consortium kick-off project is to recruit a PhD student, and set up the thesis plan.

Work performed: *ETHZ-NIM* has engaged a PhD student, Mr. Henning Galinski, in June 2007. A thesis plan follows the work plan as exposed in the original proposal of *SOF-CH* (*please see the attached ETHZ-NIM full report for a complete picture of the work*).

Summary of the literature search

On the foundation of a general literature survey the fundamental physical phenomena that dominate the degradation of Ni based anodes for solid oxide fuel cells have been identified. Microstructural changes under ideal operating conditions are observed to be due to (i) the coarsening of the metal grains in the metal ceramic composite because the metallic phase is a three dimensionally percolating network of the metal phase in a 3D percolating ceramic matrix intermingled with a 3D percolating pore structure. This system is thermodynamically highly unstable due to its large interfacial area under reducing conditions. The interface between Ni and the ceramic phase is weak due to (ii) bad wetting of metallic Ni on the ceramic. Third factor for degradation under ideal operating conditions is attributed to (iii) the local fuel utilization that might cause surface reactions (carbon deposition), $Ni(OH)_2$ formation or segregation and diffusion of C into the Ni. All this factors lead to a constant decrease in properties of the anode.

Under real operating conditions the disruption of fuel supply due to thermal cycling or system failures can affect the anode's lifetime and performance drastically. From a thermodynamic point of view a disruption of fuel supply means a strong deviation of system's equilibrium conditions. Once the anode is exposed to a critical oxygen partial pressure, the oxidation process forms Ni-oxides on the metal surfaces and might change in the case of a nonstoichiometric ceramic matrix its stoichiometry. The process of oxidation of Ni metal to NiO is accompanied by a volume change of 39.9%. This volume change causes additional tensile stresses on the ceramic network and might locally disrupt its mechanical integrity. The similar applies when reducing again the anode back to normal operation status and the resulting thickness of oxide layers.

Foreseen strategies

There are two strategies that *ETHZ* sees to improve anodes. On the one side one can try to reduce oxidation by doping the metal part of the composite by alloying. On the other hand during operation under H_2 one can try to extend the catalytic active surface area by lowering the conduction band of ceramic matrix via dopants. This means to introduce a mixed electronic/ionic conducting ceramic phase in the cermet. In this case the transition probability for electrons from the Ni-conduction to the ceramics conduction band should be lowered, so that the active surface is not anymore determined by the triple phase boundary (TPB) line but by an area and its adjacent sites.

On the basis of this literature study that explored the basic mechanisms of degradation in porous Ni ceramic anodes, promising concepts to enhance the redox stability of Ni based anodes have been elucidated. Beneficial for reducing Ni oxidation seems to be the modification of NiO with reactive elements like ceria or yttrium. This should hinder the thickness of the oxidation layer in case the anode is cooled down under oxidizing conditions. Another option is to introduce an interlayer between the ceramic and the metal component of the cermet to improve wetting of the metal on the ceramic in order to prevent delamination at the ceramic-metal joints.

Next steps

In the next stage, the work will concentrate onto finding appropriate experimental techniques that provide specific information about the different aging processes. This includes measuring techniques to characterize the interfacial energies between the ceramic and metal (*e.g.* sessile drop method and others) and to characterize interface structures. In addition a method is searched for the characterization of the oxidation process (when Ni/ceramic anodes become NiO/ceramic anodes) *in-situ*.

These techniques should provide information on the different aging processes independently from each other.

WP 2 (cathode)

Aim: WP 2 is concerned with the long term stability of LSM-YSZ cathodes in SOFC stacks.

Goals-milestones: The objective at *EPFL-LENI* in this Swiss SOFC consortium kick-off project is to recruit a PhD student, start training and bibliography, and set up the thesis plan.

Work performed: A candidate student, Mr. Pietro Tanasini, industrial chemist from University of Genoa, was engaged at *EPFL* in 2007. He started the bibliography and received training in the electrochemical test laboratory. Contacts with Materials Science department were made (electron microscopy, powder technology). The candidate was introduced to techniques of EIS, SEM/TEM, all equipments being available at *EPFL.* An extensive thesis plan is now finalized to be presented officially to the doctoral school at EPFL in 2008 (*please see the attached EPFL-LENI full report for a complete picture of the work*).

Literature search

In this first year of thesis work, literature has been reviewed and the usual experimental techniques introduced (cathode paste preparation, screen printing, sintering, single cell assembly, impedance spectroscopy, electron microscopy).

Testing facility

A new sealed test rig based on quartz tubing has been taken in operation. A first symmetrical cell (Pt/0.4 mm YSZ support/Pt) has been mounted (gold ring seals) and tested, theoretical OCV was obtained. Several alternative rigs for testing (symmetrical cells, full cells) will be taken in operation over the next months (with particular attention to avoid influence from Cr poisoning originating from setup metal parts):

- a sealed cell-on-alumina tube test rig will be purchased from *SOFCpower* (Italy) - delivery in January 2008;
- a sealed alumina tube test rig (*Probostat*™) is on order from Norway – delivery in December 2007;
- the current sealless metal flange test rigs (advantageous in the sense that constant pressure is exerted on the current collectors, to avoid contact losses during long term measurement) are being improved (Inconel 602 instead of 600; ceramic coating).

Furthermore, a multi-channel (4) galvanostat has been designed at *EPFL–LEI* and assembled at *EPFL-LENI*. It allows simultaneous operation of 4 cathodes (1 cm^2) on the same anode support half cell, with individual control of current density on each cathode. This bears the great advantages of a gain in test time and of direct comparability of 4 cathodes, since test conditions are strictly identical (anode, temperature, gas flows).

Optimization of the cathode performance

A number of different cathode mixtures (usually 50-50 vol% of LSM and 8YSZ) has been tested in small sized single cells (1 cm^2 active area, metal mesh current collection), generally giving adequate performance (>0.8 V @ 0.5 A/cm^2, and ca. 1 A/cm^2 @ 0.7 V, 800°C). These tests allowed the following observations : the nature of current collection is important (LSC instead of LSM, 0.7 V vs. 0.6 V for 1 A/cm^2), the Zirconia origin and proportion is important (8YSZ from MEL (UK) giving better output than 8YSZ from Tosoh, 1.2 A/cm^2 vs. 1 A/cm^2 @ 0.7 V), replacing 8YSZ by 10ScSZ, however, brought only a small improvement, where it is to be questioned whether this justifies the use of more expensive ScSZ, even when used in small quantities. The regular cathode to date showed -28 μV/h decay (ca. 4%) over 1000 h (800°C) at 1 A/cm^2 in one longer termed test (1400 h). Best performance to date (see Figure 2) was obtained by using powders of high surface area (both for LSM in the composite cathode and for LSC as current collector), reflected in low ohmic drop of 0.07 Ωcm^2 vs. typically >0.1 Ωcm^2, voltage loss attaining -9 μV/h @ 0.5 A/cm^2 at 800°C for the last 2000 h of a 4000 h run, that is ca. -0.9%/1000h. Post mortem analysis of most tests is still required.

Degradation analysis

A systematic test series has been carried out for fixed durations, of 5 identical cells (0, 24, 72, 200 and 1000 h) polarised under identical conditions (850°C, 0.6 A/cm^2). After these fixed polarisation durations, the test will be interrupted and the cells microstructures will be determined quantitatively using SEM and an imaging technique. It will be attempted to link these results to electrochemical modelling efforts, that have been started with the help of Prof. P. Costamagna (*University of Genoa*, IT).

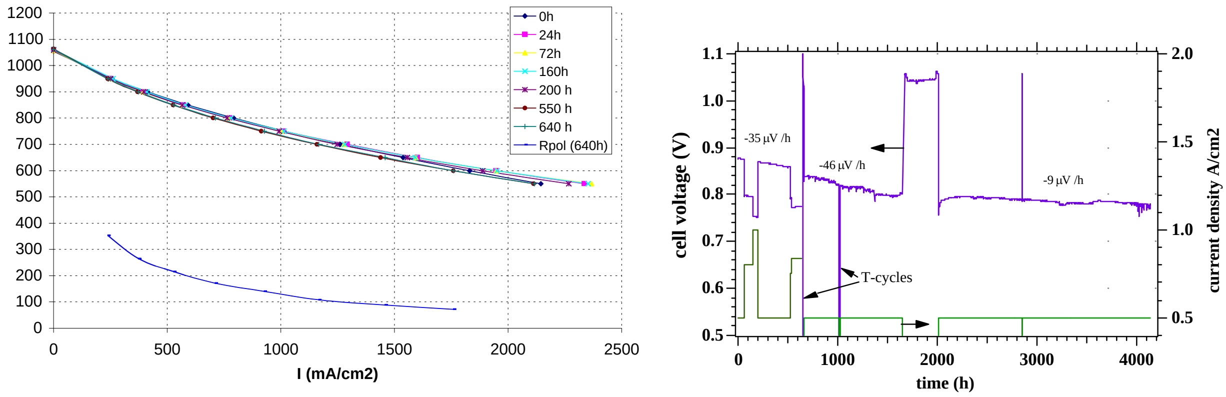

Fig. 2: This particular test combined all best options available to present knowledge. Very high surface area powders of LSM and LSC were used (academic supplier); LSM was mixed in 50-50 vol% ratio with 8YSZ from MEL using the standard paste procedure (terpineol-ethylcellulose). Two thermal cycles were operated after 600 h and 1000 h due to furnace occupation. Highest performance of 1.3 A/cm^2 @ 0.7 V and lowest ohmic drop of 0.07 Ωcm^2 was obtained. At 0.5 A/cm^2, decay was only -9 μV/h for the final 2000 h, which is still -0.9%/1000 h.

Effect of the current density

Current density was varied to assess cathode stability as a function of this parameter, all other cell conditions (anode, temperature, gas flows) remained constant. Theses tests are on going but reveal different cell behaviours (see Figure 3).

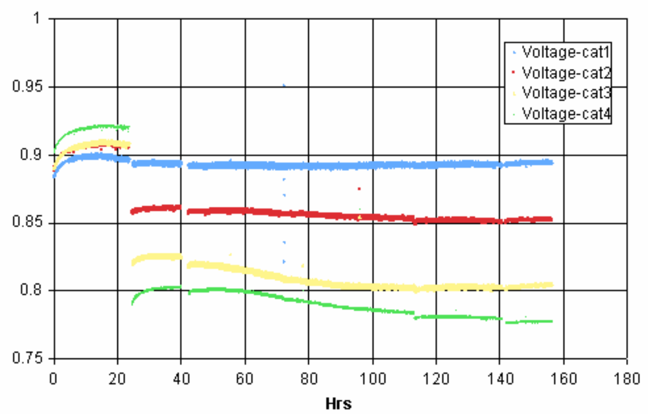

Fig. 3: Current density effect on the cell degradation.

Chemical stability

Reaction couple tests (LSM-YSZ, LSM-ScSZ, LSM-GDC, 850°C, 1500 h) are ongoing. A sealed single cell test rig has been constructed and validated; other test rig options are under evaluation. A multi-cathode test rig has been taken in operation allowing to simultaneously characterize 4 cathodes (with individual galvanostatic control) for parameter variation and optimisation.

WP 5.1 (thermo-mechanics and simulation)

Aim: WP 5.1 is concerned with mechanical integrity of cells within stacks during operation. It aims at investigating mechanical stresses induced into the various components of the stack under different operation conditions. In general, internal stresses are induced by external forces, mismatch of the thermal expansion coefficients of different stack components as well as by a non-homogeneous distribution of the stack temperature. Once a critical stress level is reached, this can cause cell fracture which almost certainly leads to the complete failure of the affected cell.

This package foresees the measurement at *Empa-HLK* of the mechanical properties of stack components made available by the 2 manufacturers, *Hexis* and *HTceramix*. These properties, basically the

CTE and the Young's modulus, are meant to be integrated into simulation tools to visualize and predict the thermo-mechanical behavior within the stack.

Goals-milestones:

- *Hexis* provides samples to *Empa-HLK* for testing.
- *HTceramix* provides components to *Empa-HLK* for testing.
- *EPFL-LENI* models the thermo-mechanical properties of *HTceramix* stack.
- *ZHAW-ICP* models the thermo-mechanical properties of *Hexis* stack

Work performed:

- *Hexis* has delivered all samples (383) to *Empa-HLK* as foreseen by the contract. *Empa-HLK* has performed all the measurements and fed them to *ZHAW-ICP* who is developing simulation tools for the visualization and prediction of the thermo-mechanical properties of the stack (see hereafter a short presentation of the status of the work at *ZHAW-ICP*). *Empa-HLK* delivered a full report on all measured data to *Hexis* and *ZHAW-ICP*.

- *HTceramix* has elaborated and tested different processing routes for the production of the required samples. The technical challenge and effort to produce samples compatible for the requirements of precise property measurements of all materials listed in the initial test matrix was underestimated; as conclusion, the provision of samples was limited to the ones judged most critical. Following samples have been provided: NiO/YSZ, Ni/YSZ, NiO/YSZ (20% coarse), Ni/YSZ (20% coarse) for CTE coefficient measurement and determination of E moduli, NiO/YSZ, NiO/YSZ (20% coarse) and NiO/YSZ (modified NiO route) for bi-axial strength measurements and determination of Weibull module. Additional test samples became available at a very late stage only. The samples delivered on time have been used at *Empa-HLK* for measurement and determination CTE coefficients, E-moduli and bi-axial strength. The raw data has been provided to *EPFL-LENI*. Due to the sub-optimal quality of the test samples, Finite Element calculation was necessary to adjust the measured values; the corresponding models have been elaborated at *EPFL-LENI* (see hereafter a short presentation of the status of the work at *EPFL-LENI*).

In order to increase the benefits of the generated data and results, a Workshop on the thermo-mechanical stability of components was hold at *Empa-HLK* on December 5, with participants from *HTceramix, EPFL-LENI* and *Empa-HLK*. The workshop contributed greatly to the understanding of the mutual needs, *i.e.* compliance of test samples to test equipment, need of data for simulation, and final objective of work program in order to increase life-time of stacks.

Empa-HLK delivered a full report on all measured data to *EPFL-LENI* and *HTceramix*.

Status at EPFL-LENI (please see EPFL-LENI full report for a complete picture of the work)

Two one-dimensional models taken from literature [1; 2] were implemented at *EPFL-LENI* to assess residual stresses in anode-supported cells. The 2 approaches were implemented in *gPROMS*. The models however strongly rely on the accuracy of the material mechanical data. Small variations can lead to strongly different stress profiles – switch from compressive to tensile, depending on temperature. The data provided by *Empa-HLK* are being processed to compute real probabilities of survival.

As a guideline, Table 1 lists the required data to exploit all the capabilities of the models developed at *EPFL-LENII* within the frame of this project. Some are within the test matrix of *EMPA-HLK/HTceramix*, others might be complemented in the future. It is paramount to realize that such work currently leads to a qualitative representation of the phenomena induced by the residual and thermal stresses; a quantitative study requires more data.

Table 1: Required data to exploit the current capabilities of the models.

		Layer thickness [m]	Reduction strain %	Zero stress temperature [K]	Young's Modulus [GPa]	Coefficient of Thermal Expansion *10-6 [K-1]	Characteristic Strength [MPa]	Weibull modulus*	Porosity
Support	(NiO-YSZ)	at RT	f(T,n)	T	f(T,n)	f(T,n)	at RT, f(n)	at RT, f(n)	at RT
		at RT	f(T,n)	T	f(T,n)	f(T,n)	at T operation, f(n)	at T operation, f(n)	at RT
	(Ni-YSZ)	-	f(T,n)	T	f(T,n)	f(T,n)	at RT, f(n)	at RT, f(n)	at RT
		-	f(T,n)	T	f(T,n)	f(T,n)	at T operation, f(n)	at T operation, f(n)	at RT
Layer	(Material)	at RT	-	T	f(T,n)	f(T,n)	at RT, f(n)	at RT, f(n)	at RT
		-	-	-	-	-	at T operation, f(n)	at T operation, f(n)	at RT

The thermal stresses in a cell were simulated in a three-dimensional *FEM* model by combining a finite difference method - *gPROMS* - to a finite-element software - *ABAQUS*. The first carried out the thermo-mechanical simulations while the structural analysis was performed in the latter. *MATLAB* routines were used to pass the temperature field between both tools. Different operating conditions were simulated as listed in Table 2.

Table 2: Operating conditions taken into account for the simulations.

	Flow configuration	Analysis type	Fuel
OCV full load	Co	Steady-state	TPOx NG
OCV full load	Counter	Steady-state	TPOx NG
Operation at full load	Co	Steady-state	TPOx NG
Operation at full load	Counter	Steady-state	TPOx NG
Operation at part load	Co	Steady-state	TPOx NG
Operation at part load	Counter	Steady-state	TPOx NG
Shutdown	Co	Dynamic	TPOx NG
Shutdown	Counter	Dynamic	TPOx NG
Severe	Co	Steady-state	internal SMR
Severe	Counter	Steady-state	Internal SMR

Determination of thermo-mechanical properties of cell materials

As for the work done at *ZHAW-ICP*, it was necessary to extract the right values of the strength using non-linear *FEA*.

Validation of the models

The final choice of elements for the three-dimensional model and the accuracy of the one-dimensional model were quickly tested on a benchmark against solid elements.

Results

The main results are as follows:

- The one-dimensional model can simulate the residual stresses with a very good accuracy. Its use is not limited to the room temperature case, but can be extended to operation if the temperature distribution remains quite homogenous, *i.e.* the contribution of the residual stresses is dominant. It is obviously not able to compute the variation of the stresses at the edge.
- The loading of the cell did not induce an increase of the stresses. Actually, the probability of survival is higher. Failure may however occur, since the stresses at the fuel side turn from compressive to tensile. In particular, a poor manufacturing process can induce defects at this particular location. The failure criterion does not consider such problems.
- The differences induced by different reduction temperature were found to be small, but visible. It is critical to keep in mind that the choice for the values for the simulations was quite empirical due to the lack of data. An additional strain of 0.1% is a major contribution to the total strain. Its value and temperature dependence should be known with accuracy. The same applies for the variation of the CTE of the oxidized and reduced anode support. Much more efforts should be done in this direction. This comment is obvious since the anode is the supporting layer in the cells considered in the present study. Thermal cycles are very critical cases.
- The dynamic simulation did not appear as critical. Indeed, the conditions during a cooling with preheated air are far from a thermal shock.
- Industrials are usually interested in knowing if the cell will fail during a particular operating point or sequence. The highest stresses occur at room temperature. Results from *Empa-HLK*

indicate that both strength and Weibull modulus of oxidized samples do not vary significantly with temperature. Thus the critical case is room temperature. However, once again, this simple analysis does not yet consider the temperature dependence of both CTE and Young modulus. Furthermore, the data for reduced anode material at operating temperature cannot currently be measured, whereas it is the key value. The YSZ is the most studied of all layers. Nevertheless, large variations exist between the measured values reported by the different research groups.

- A particular issue in simulating stresses in SOFC is the very broad temperature range. In contrast to thermo-electrochemical modeling, where only the operating temperature is of interest and can be decoupled from the other ones to some extent, an accurate modeling of the stresses depends on both material properties of all the layers within the whole temperature range - sintering to considered temperature - and phenomena during particular manufacturing processes - reduction, assembly.

Some examples of what has been obtained are given in Figures 4-6.

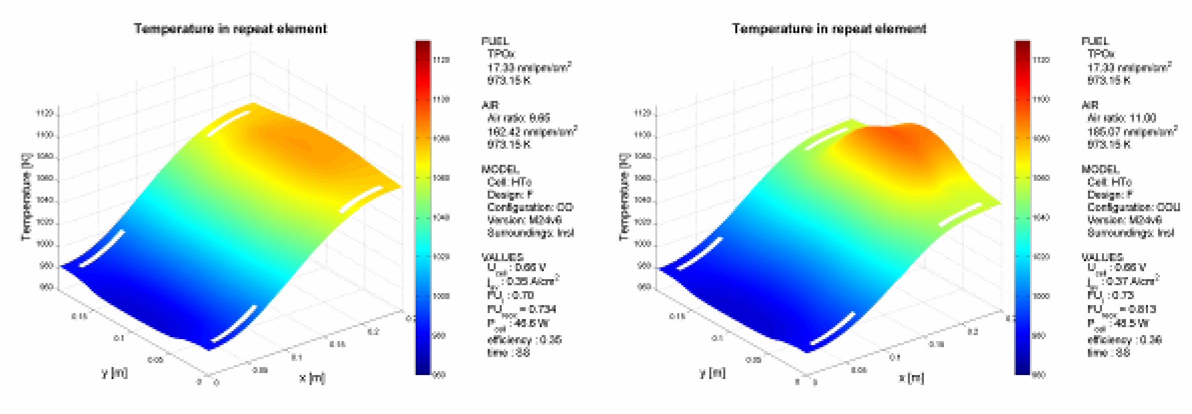

Fig. 4: Temperature profile at full load in a co-flow configuration (left) and a counter-flow configuration (right). As imported in *ABACUS*.

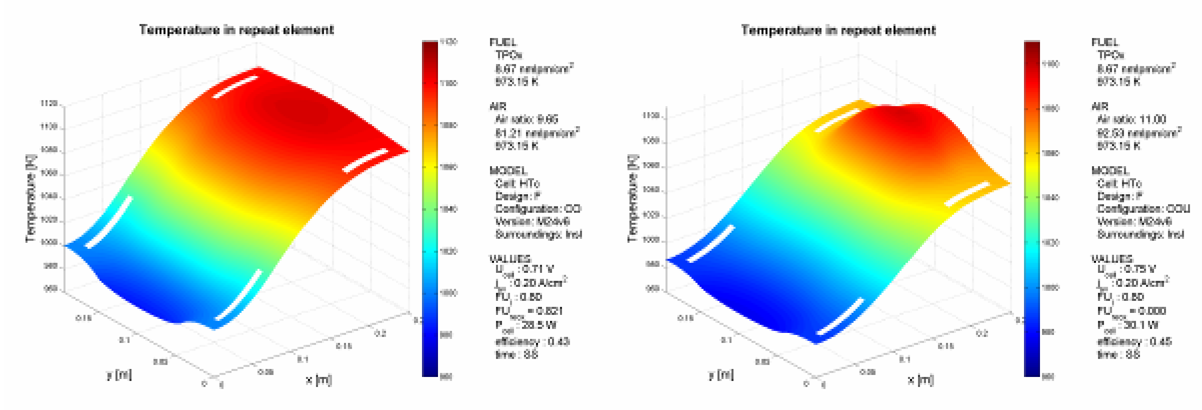

Fig. 5: Temperature profile at part load in a co-flow configuration (left) and a counter-flow configuration (right). As imported in *ABACUS*.

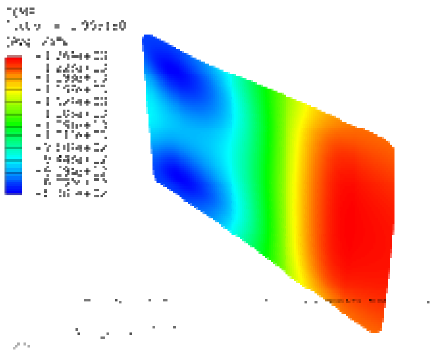

Fig. 6: Temperature profile during severe conditions (as imported in *ABACUS*).

Status of ZHAW-ICP (please see ZHAW-ICP full report for a complete picture of the work)

For the thermo-mechanical stress-analysis of the *Hexis* SOFC-stack, the following 3D and 2D rotational-symmetric FE-models have been developed and used at *ZHAW-ICP*:

- 3D Thermo-mechanical-flow FE-model of a repeat-unit of the Hexis stack
- 2D rotational-symmetric mechanical FE-model of a cell mounted in a ring-ring device
- 2D rotational-symmetric thermo-mechanical FE-model of a cell
- 3D thermo-mechanical FE-model of a cell
- 3D mechanical FE-model of a repeat-unit (cell + interconnect)
- 2D rotational-symmetric thermo-mechanical FE-model of a stack

For all calculations, the in-house multi-physics FE-code *Seses* (www.icp.zhaw.ch/seses) was used. The following points were tackled.

Determination of thermo-mechanical properties of cell materials

At the beginning of the project, it has been a major challenge to accurately determine temperature-dependent Young's modulus data as well as thermal-expansion coefficients (CTEs) for all cells components, *i.e.* for the anode- and cathode-layers as well as for the electrolyte material. This is because the very brittle and fragile structure of SOFCs causse a large variability and large uncertainties in the experimental characterization of their thermo-mechanical properties. The data at high temperatures shows huge variations. Similar variations have been obtained from CTE-measurements of different electrode-layers. Fortunately, for both Young's modulus and CTE-data, plausibility checks can be made.

Thermo-mechanical stresses induced by local temperature-gradients

A 3D thermo-mechanical-flow FE-model of a repeat-unit of the *Hexis* stack has been developed. As shown in Figure 7, for symmetry reasons, only 1/8 of the repeat-unit needs to be taken into account. This model is used to investigate how non-homogeneous stack temperatures cause locally induced mechanical stresses in different cell-components. Since in the model, the main characteristics of the metallic interconnect (MIC) geometry have been parameterized, it is ideal for MIC-design optimizations.

Figure 8 shows for example the temperatures of a cell mounted in a repeat-unit of the *Hexis* SOFC-stack for two different operation conditions. In OCV-mode, all heat is supplied from the post-combustion zones located at the perimeter of the stack. Consequently, the coolest temperatures occur in the center (where the fuel entry is located) and at the air-inlet channel (at the perimeter). In contrast, under full-load operation, much of the heat is released on the cells close to the fuel gas inlet, shifting the maximum temperature from the outside to the inside of the stack.

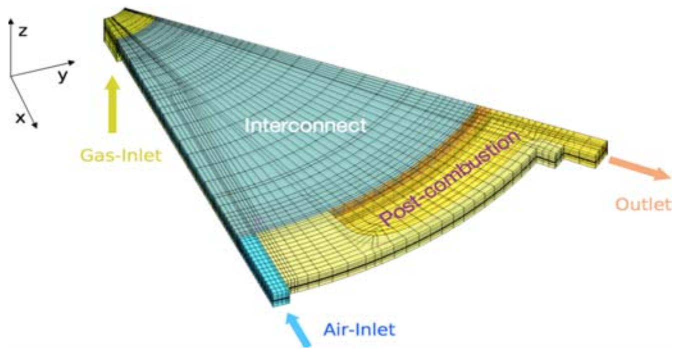

Fig. 7: 3D thermo-mechanical-flow-model to obtain the flow and temperature distribution within a single repeat-unit and to calculate the stresses caused by local temperature-gradients.

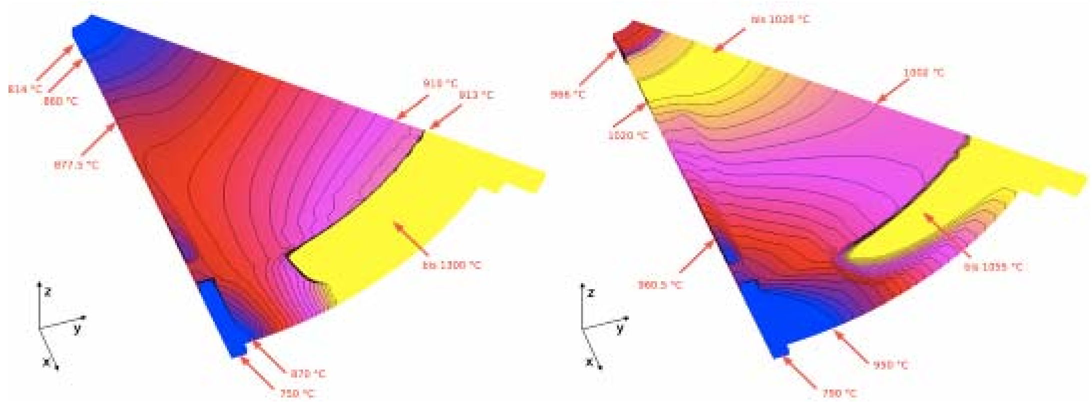

Fig. 8: Temperatures of a cell mounted in a repeat-unit of the *Hexis* SOFC-stack under OCV-conditions (left) and full-load-conditions (right). The highest temperatures are indicated in yellow, the lowest in blue

Figure 9 shows the maximum principal stresses resulting from the temperature-profiles presented in Figure 8. Under OCV-conditions, the highest tensile stresses occur in the center near the fuel inlet, whereas in full-load mode, the highest tensile loads occur near the air inlet at the stack perimeter. These results clearly indicate the importance of the heat-exchanger and insulation components surrounding the stack. When the temperatures of the gas-streams entering the stack deviate from the average stack temperature too much, this is a major source for thermo-mechanical stresses exerted to different cell components. By making sensitivity analyses, this model allowed to propose some optimization routes to reduce these thermal stresses.

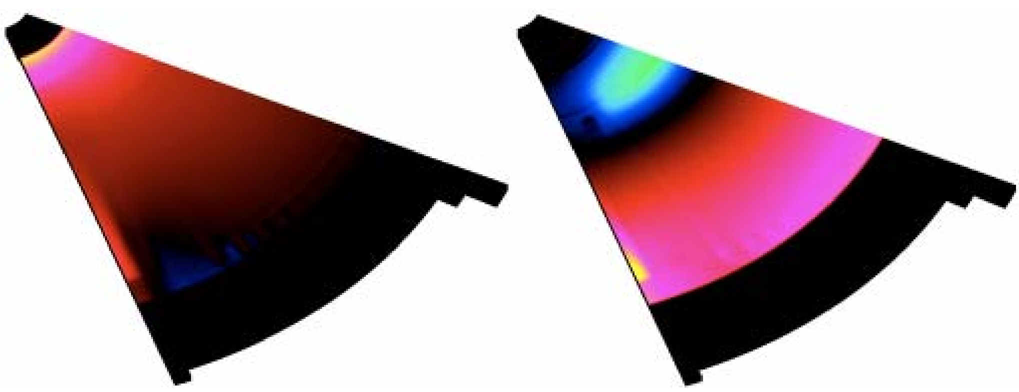

Fig. 9: Maximum principal stresses of a cell mounted in a repeat-unit of the *Hexis* SOFC-stack under OCV-conditions (left) and full-load-conditions (right). The highest stresses are indicated in yellow, stress-free zones are shown in black and compressive stresses in blue and green.

External mounting and force-distribution in the Hexis SOFC-stack

Besides thermally induced stresses as caused by CTE-mismatch and local temperature-gradients, external forces induced by the stack mounting play an important role. In addition, these external forces have a strong influence on the sealing tightness of the SOFC-stack. The idea is to perform model-based optimizations of the stack-mounting and the interconnect-design to ensure a homogenous force-distribution as well as a gas-tight system. Once the effective mechanical stack properties are known, they can be used to calculate the stresses and deformations of the whole stack in a simple rotational-symmetric configuration.

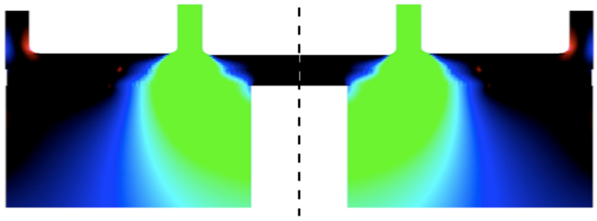

Fig. 10: Axial stress-distribution near the top of the *Hexis* SOFC-stack. Compressive forces are indicated in green and blue, tensile forces in red. Stress-free zones are shown in black.

Figure 10 shows as example the distribution of axial stresses near the top of the *Hexis* SOFC-stack. One sees that this specific mounting-design (in combination with the particular interconnect-design) causes a rather uneven force-distribution which might be a source for gas-leakages, especially at the stack perimeter, where compressive forces are low. To solve this problem, the model has been used to compare different designs for the stack-mounting with each other.

Influence of cracks on the mechanical integrity of the electrolyte material

In electrolyte-supported SOFCs such as the one used in the *Hexis*-system, cracks in the electrodes might be an important mechanism by which the electrolyte material is weakened. Such cracks occur during manufacturing, handling and operation. A 3D thermo-mechanical FE-model has been developed to analyze this effect. As shown in Figure 11, the model contains two artificially introduced cracks in the radial and azimuthal directions. The picture to the right shows a typical stress-distribution in the vicinity of a crack. One sees that the highest tensile stresses (indicated in yellow) occur right at the electrode-electrolyte interface. This clearly demonstrates the crack-induced weakening effect the electrodes can have on the electrolyte.

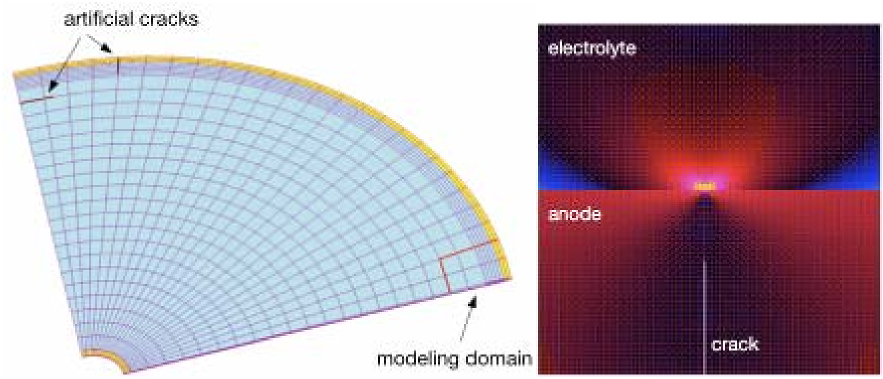

Fig. 11: 3D FE-model of a cell with artificially introduced cracks in the radial and azimuthal directions. The FE-grid is shown on the left and the picture on the right shows the calculated stresses around a crack near the interface between the electrode and the electrolyte.

In a further step, the influence of different crack-populations on the cell stresses and cell deflections have been analyzed. Figure 12 shows the typical deflection of a newly manufactured cell at room temperature. The predicted shape agrees well with experimental observations. This is an impressive example of how the employed models can be used to identify microscopic phenomena that that can hardly be understood solely by experimental methods.

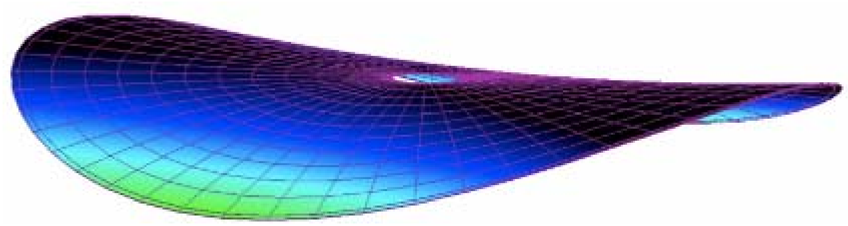

Fig. 12: Prediction of the deflection-behavior of a cell as a combination of its thermo-mechanical material properties and a certain distribution of electrode-cracks.

Collaboration nationale

This project allowed to foster and revive the collaborations between all the Swiss SOFC community. Collaboration of the research institute is more regular among them as well as with the industrial partners in terms of data exchange, sample supply and reporting (see Figure 13).

With the momentum created by the present project, an application for the financing of the ***SOF-CH*** in the order of 2.1 millions CHF over the next 3 years has received approval from swiss*electric* research and *SFOE*. The project started officially on the 1st of August 2007. The contracts with *SFOE* have already been signed, and a contract with swiss*electric* research is being at present finalised.

The *SOF-CH* acted further as an enabler as it allowed to receive funding for a *CCEM-CH* project, the ***Wood-gas-SOFC***, binding the competences of *Empa-HLK*, *EPFL-LENI*, *Hexis*, *HTceramix* and *PSI-LEM* (*CPM, TPE*). This project is aiming to address the impact of the hazardous components released in wood gasification on SOFC stacks.

Similarly, another *CCEM-CH* project, the ***HTE-CH***, has been deposited in October and is awaiting approval. This project binds the competences of *Empa-HLK and Empa-H&E*, *EPFL-LENI and EPFL-LPI*, *Hexis*, *HTceramix*, *Insultech AG*, and *PSI-STL*. And is aiming to study the production of H_2 by means of high temperature electrolysis using solid oxide electrolysis cells (reverse SOFC) using the heat derived from nuclear or solar power.

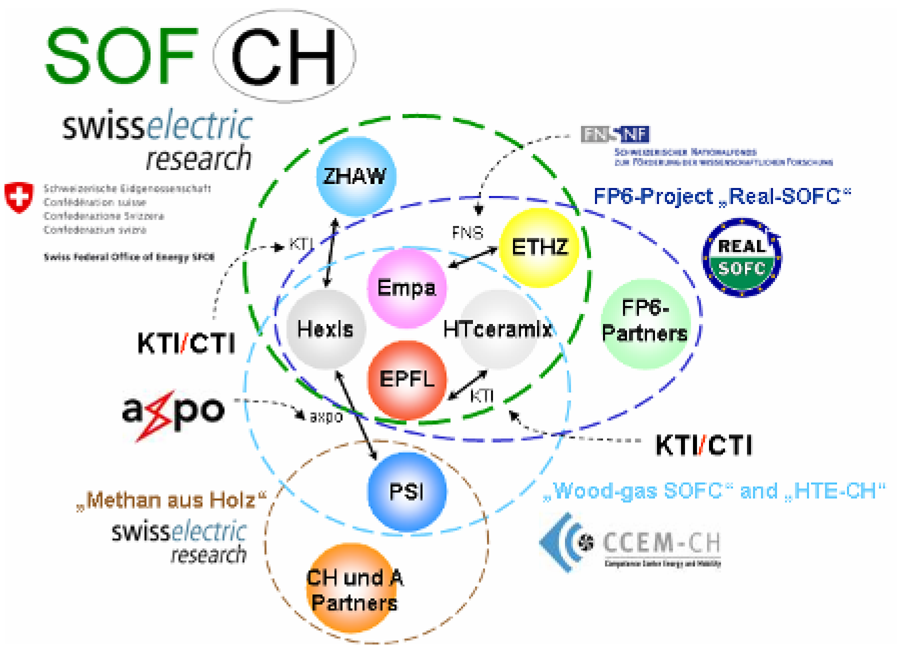

Fig. 13: Collaboration network within the *SOF-CH* and the links to other on-going projects. The "*Wood-gas SOFC*" project is tangent to another industrial project aiming to produce methane out of wood.

Collaboration internationale

Some outcomes of this project are expected to be presented in the frame of the European *Real-SOFC* program as well as in international conferences. This will allow to trigger interests and will serve as basis for future European collaborations.

For the WP 2, coaching of Mr. Tanasini's thesis has been obtained from the *University of Genoa* (Italy) by Prof. Paola Costamagna. *Risø National Laboratory* (Denmark) has hosted Mr. Tanasini for 2 months student internship from October till beginning of December 2007 as part of an exchange program in the frame of the European *Real-SOFC* project involving all the Swiss SOFC partners; the topic of investigation is the influence of humidity (0-20% steam) on the performance and stability of the LSM-YSZ cathode. Other interactions have taken place through visiting scientists active in cathode research at *EPFL-GGEC* and *EPFL-LENI*, Dr. Cécile Lalanne from *CNRS Bordeaux* (F) on nickelate cathodes, Dr. Lars Hildebrandt from *KTH Stockholm* (nickelates) and Dr. Cristina Saez Jiminez (*University of Madrid*, LSM-YSZ), who each stayed for periods of 3-4 months at *EPFL* during 2007.

On the European level, a joint application binding *Hexis*, *HTceramix*, *EPFL-LENI* and European academic as well as industrial partners have been proposed by *Hexis* and deposited to the EU commission under the lead of *Forschung Zentrum Jülich* (*FZJ*). The project, ***SCoReD***, dealing with protective coating on MICs, collected only 12.5 points so that the chances to see the project funded are quite low.

Évaluation de l'année 2007 et perspectives pour 2008

WP 1 (anode)

Aim of the project is to reveal, in accordance with the experimental analysis of *Hexis* Ni-YSZ anodes and alternative anodes, the fundamental physical processes controlling the single steps of anode degradation. Targeted is to propose, on the grounds of a developed model for degradation in Ni based anodes, concepts to overcome or mitigate common degradation effects.

Within the framework of the project started at the 1.June 2007, deliverables, which are subdivided in three working packages (WP), and milestones (M) have been defined. Figure 14 shows the time scheduling for the different working packages. Consistent with the agenda an extended literature review of redox-stability and degradation of state-of-the-art Ni-YSZ, with special focus on effects for long-term degradation an redox-stability and their improvement, has been performed.

In the next period, the work will concentrate onto finding appropriate experimental techniques that provide specific information about the different aging processes. This includes measuring techniques to characterize the interfacial energies between the ceramic and metal (*e.g.* sessile drop method) and to characterize interfacial structures. In addition a method is searched for the characterization of the oxidation process.

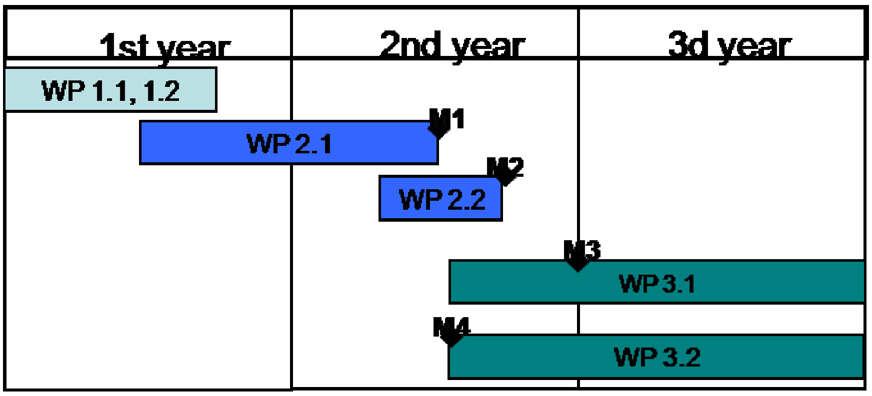

Fig. 14: WP 1 project road-map showing the different periods and the expected milestones.

Work packages (WP):

<u>WP 1: Literature analysis of redox-stability and degradation of state-of-the-art Ni-YSZ anodes:</u>

WP 1.1: Literature study on long-term degradation and redox-stability of Ni-YSZ anode.

WP 1.2: Literature study on improvement of redox-stability of Ni-YSZ anode.

<u>WP 2: Degradation and redox stability of *Hexis* Ni-YSZ anodes:</u>

WP 2.1: Microstructure analysis of *Hexis* Ni-YSZ anodes prior to redox cycling and post-mortem.

WP 2.2: Model for the redox-degradation of Ni-YSZ anodes is developed.

<u>WP 3: Improved redox stable anodes:</u>

WP 3.1: Experiments on alternative redox stable anodes towards Ni-YSZ.

WP 3.2: Experiments to improve redox-stability of Ni-YSZ anodes

<u>Milestones (M):</u>

M1: Model for the redox-degradation of Ni-YSZ anodes proposed.

M2: Microstructure changes through redoxcycling of Hexis anodes characterized.

M3: Alternative anodes are identified.

M4: Experiments to improve redox-stability of Ni-YSZ anodes are proposed.

WP 2 (cathode)

This one-year *SFOE* kick-off project has given an excellent start to the PhD thesis work on cathodes. Literature has been reviewed, training with the usual techniques has been given and first systematic studies initiated.

In the follow-up work in 2008, carried out within the *SOF-CH* project, quantification of the cathode microstructure will be undertaken, the paste rheology finalised, the sealed cell test bench mounted at *EPFL-GGEC*, and electrochemical modelling implemented with Prof. Costamagna. Test series as defined in the submitted proposal (see Figure 15), as part of the thesis plan, will be carried out.

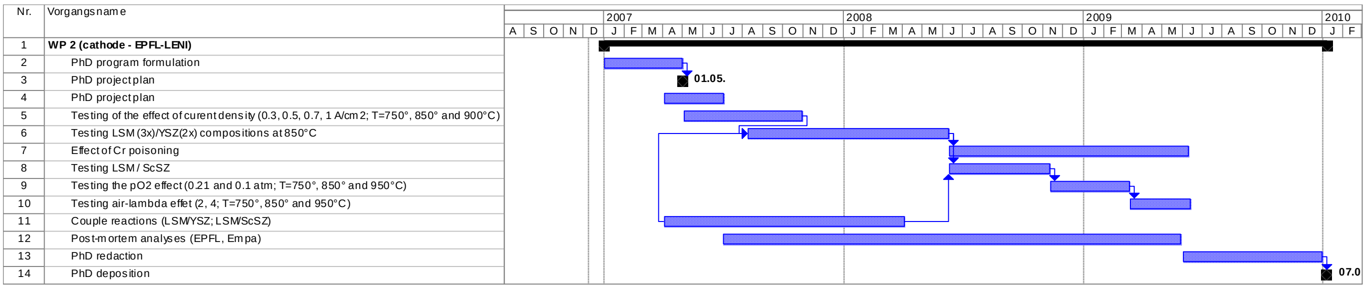

Fig. 15 : WP 2 project road-map showing the different periods.

WP 5.1 (thermo-mechanics)

Summary and outlook at EPFL-LENI

This study is a preliminary work, which addresses only part of the issues. It is already clear that key data will not be available at the end of the project. Nevertheless, it was very profitable from both the modeling and experimental point of view:

1. Models were developed and could lead to set requirements on material data. The combined effect of thermal and residual stresses was well observed. The influences and possibilities of additional layers clearly appeared as well. Interesting phenomena due to reduction were observed.
2. The quality of the data from *EMPA-HLK* is by far superior to the data previously available. The final processing has not yet been completed by *EPFL-LENI*, exceeding the scope of this current project (included in the part supported by s*wisselectric research*). This is a very good starting point.
3. Additional measurements of materials properties will further strengthen the accuracy of the models. It is strongly suggested to measure the additional samples available from *HTceramix* by *Empa-HLK* in a follow up project in 2008 and to integrate those values in the models by *EPFL-LENI*. As the initial communication delays have been overcome by now, it is expected that the continuation of this joint effort will be efficient and contribute significantly to progress in the field.

Summary and outlook at ZHAW-ICP

In 2006, *Hexis*, *Empa-HLK* (Jakob Kübler) and *Empa-MMS* (Prof. Eduardo Mazza) and *ZHAW-ICP* with support from *NM Numerical Modelling GmbH*, Thalwil, started their joined efforts to investigate the thermo-mechanical behavior of the *Hexis* SOFC-stack. The close collaboration between system developers, modeling experts, and material scientists was crucial and gave substantial insight into the different phenomena by which cell-breakage occurs. Based on this understanding, several new concepts have been developed and further refined by model-based parameter optimizations. They show promise to significantly lower the levels of thermo-mechanical stresses induced in the cells. Specifically, the following results have been obtained:

1. Temperature-dependent Young's modulus for the electrolyte and the different electrode-layers have been obtained from correlating the FE-model for the ring-ring setup with force-versus-deformation curves measured at *Empa-HLK*. The obtained values at high temperatures show huge variations. However, these variations could be substantially reduced by checking its consistency and plausibility when used to predict cell-deflections at different temperatures and comparing them with experimental data. Still, it would be desirable to get more accurate Young's modulus data at high temperatures – especially for the electrolyte, which is the supporting cell-layer in the *Hexis* cell.

2. The situation is similar concerning the determination of temperature-dependent CTE-data. Here as well, the data – especially for the anodes – showed huge variations, however this time at lower temperatures. By making the above mentioned plausibility checks and by comparing the obtained results with literature data (e.g. F. Tietz, *Ionics*, vol. 5, pp. 129 – 139, 1999 and F. Tietz et al., *Solid State Ionics*, vol. 177, pp. 1753 – 1756, 2006) the variations could be reduced. Still, it would be desirable to get more accurate CTE-data especially for the anodes, which are mainly responsible for the residual stresses induced in the electrolyte.

3. The low-temperature Weibull-data determined at *Empa-HLK* provides statistically sound information about the stress-levels that can cause cell fracture. To obtain information about stress-levels that are critical at high temperatures, the low-temperature data was extrapolated based on literature information and experience by our partners at *Empa-HLK*. It became obvious that both stresses caused by CTE-mismatch of adjacent layers as well as those caused by local temperature-gradients are within the critical range. Clearly, improvements are necessary both on the cell- and the system-design. To perform the required parameter-optimizations, the FE-models mentioned in the "employed models" section have proven to be powerful. However, the development of new concepts for the cell- and system-design is still ongoing and will probably extend to midyear of 2008. To further improve on the available pool of material data, it would be useful to have Weibull-statistics also available at high temperatures.

4. The thermo-mechanical FE-analysis of the whole *Hexis*-stack and its mounting showed that the uniformity of the stresses throughout the stack strongly depends on the mounting- and the MIC-design. A uniform distribution of compressive stresses throughout the stack is critical for good contacting of the different stack-layers as well as for minimal leakage-losses, especially at the inner and outer stack-boundaries. By using model-based optimizations, new concepts have been developed to improve the mounting- and the MIC-design.

However, as has become obvious during the last months, certain thermo-mechanical phenomena are tightly linked with the manufacturing process, the system dynamics and operations modes such as redox- and thermo-cycles. The latter leads to various degradation phenomena which in turn influences the mechanical integrity of the cells. Therefore, *Hexis* and *ZHAW-ICP* plan to carry out a number of further investigations within the *SOF-CH*-project:

1. Thermo-mechanical analysis of the manufacturing process of the cells.
2. Continued thermo-mechanical analysis of different operations conditions including the system dynamics
3. Continued optimization of the MIC-design and the stack-mounting to reach a more homogeneous stress distribution and to reduce gas-leakages.
4. Extend thermo-mechanical models to include the impact of degradation phenomena such as redox- and thermo-cycles.

Budget

The status of the budget is shown in the following table (Table 3).

Table 3: Summary of the budget

Partner	WP 1 anode	WP 2 cathode	WP 5.1 thermo-mechanics	road-map coordination	Total project budget	Planned budget till end 2006	milestone reached %	money to distribute 06	money to distribute 07	Rest at end of project
ETHZ	55'000				55'000	50'000	50	25000	25000	5'000
EPFL		49'250			49'250	44'250	80	35400	8850	5'000
Empa/Hexis			97'500	10'000	107'500	102'500	100	102500	0	5'000
Empa/HTceramix			88'250		88'250	83'250	70	58275	24975	5'000
					300'000	**280'000**		221175	58825	**20'000**

102'500.- this sum has already been released to *Empa-HLK*, *ZHAW-ICP* and *Hexis*;

83'250.- this sum has already been released to *Empa-HLK*;

44'250.- this sum has already been released to *EPFL-LENI*;

50'000.- this sum has already been released to *ETHZ-NIM*.

The financial reports summary is given in Table 4. The financial report of *EPFL-LENI* is missing, being only available in the 3rd week of December.

Table 4: Summary of the financial reports. na (not available) due to non-delivery.

Institution	WP	Period	Salaries	Durable equipment	Consumables	Travel	Other	Total expenditure	Budget for the period of report	Balance
Empa-HLK	5.1		145750	0	10'000	0	0	155750	155750	0
EPFL-LENI	2 & 5.1		na	na	na	na	na	na	64'250	64'250
ETHZ-NIM	1	1.6.2007-31.12.2007	29'281	0	0	0	195.7	29'477	55'000	25'523
ZHAW-ICP	5.1	2006-2007	17'580	0	0	0	0	17'580	15'000	-2'580
Hexis coordination		1.7.2006- 31.4.2007	26'936	0	0	0	0	26936	10'000	-16936
							Total	229743	**300'000**	70'257

The project is as such terminated and has fulfilled the goals initially set, as discussed above. It is followed by the *SOF-CH*, co-funded by *swisselectric* research and *SFOE*. The rest money of 20'000.- can be released and distributed to all the academic partners following the chart (Table 3).

Références

[1] C. H. Hsueh, ***Thermal stresses in elastic multilayer systems***, Thin Solid Films, 418, p. 182-188, 2002.

[2] J. Malzbender, ***The use of theories to determine mechanical and thermal stresses in*** *monolithic, coated and multilayered materials with stress-dependent elastic modulus or gradient in elastic modulus exemplified for thermal barrier coatings*, Surface & Coatings Technology, 186, 416-422, 2004.

[3] F. Tietz, Ionics, Vol. 5, p. 129-139, 1999.

[4] F. Tietz et al., Solid State Ionics, Vol. 177, p. 1753-1756, 2006.

Annexes

- A more detailed report for WP 1 from *ETHZ-NIM*

- A more detailed report for WP 2 from *EPFL-LENI*

- A more detailed report for WP 5.1 from *ZHW-CCP*

- A more detailed report for WP 5.1 from *EPFL-LENI*

- The *SOF-CH* road-map

- Curriculum Vitae of the 3 PhD students involved in this project