# Endurance Mid Term Report Executive Summary

## Introduction

The project aims at developing reliable predictive models to estimate a long-term (i.e. > 20 kh) performance and probability of failure of SOFC stacks based on existing materials and design from the industrial partners. This goal can be achieved by an increased awareness of the phenomena occurring inside a cell and in the whole set of components of a stack during operation (i.e. start up, working, stand by, shut down processes).
Therefore the project is structured on three main working plans defined as Loops: during the 1st. Loop the investigation was performed on SoA operated stacks and samples in order to refine the protocols, find out the main issues on materials, interaction at the interfaces, relationships between the operation and the materials evolution; during the actually running Iterative Loops, new designed samples representative of the most critical areas of the stack are tested and studied post-experiment in parallel with segmented short stacks operating in order to feed with fresh and reliable data the modelling experts for the needed refining process; the Validation Process is the third and last Loop, started at month 18 and actually focused on the preparation of the test benches suitable to operate improved stacks and samples.
The investigations performed during the first Loop have been carried out by means of post-experiment methods comparing simplified characterization techniques with powerful high resolution ones in order to check the detection limits of the phenomena under investigation.
At the same time electrochemical investigation by means of EIS have been carried out to set a reference on SoA cells/stacks and refine the deconvolution methods. This brought to an improved understanding of the outputs of such technique and to new applications as the redox response of single anodes and the evolution of metal-glass-metal samples.
New parameters, useful to determine the EWOS and to find mitigation of counter strategies by IATA (to be started during the second half of the project), have been identified and ready to be tested.
The identification of new degradation issues allowed to design new samples geometry for laboratory tests currently running in the iterative Loops that are meant to focus on the main problems of materials evolutions and interactions leading to stack performances degradation.
Some counteractions are already under investigation to mitigate the detected stack degradation and failure sources.
The first set of results on this Loop has been additionally used to feed the electrochemical and thermomechanical models achieving higher resolutions and a more accurate predictability of the phenomena occurring at the stack level.
During the first part of the reporting period a design and implementation of the Internal web site as a Web Library & Data Bank has been performed. The introduction of the Book of Samples, Handbook of Experiments, and the Knowledge Pool improved the knowledge management in the consortium.
Several meetings and workshops have been organized promoting the communication among the partners which led to an increase of the commitment and to the complementarity of the partner activities.
Several educational activities promoted the dissemination section of the project. Science festivals participation, development of a serious game, a videoclip, the participation to local radio programs and the publication of articles on a national newspaper had the aim to raise awareness,

inform and educate the community reaching out to different age groups in the most appreciated method for each of them.
This summary reports, for each WP, the main outputs, deviations from the DoW and brief conclusions about the activities carried out in the first half of the project.
A complete description of the objectives and the results achieved in the period M1-M18 is exposed in the full report (annex).

## WP2 Materials & Manufacturing

The activities within this work package were dealing with:
1) manufacture of reference materials, both tested and untested, in order to obtain thorough understanding about the performance of stacks currently produced by SOLIDpower.
2) development and manufacture of slightly adapted materials for the GDC barrier layer and for the glass seal to investigate if stack degradation can be further mitigated.

The produced materials and samples have been distributed within the consortium for further testing and post mortem analysis.
All requests for materials were fulfilled in time. This was due to strong interaction with WPs 3, 4, 6 and correct anticipation of the project partners mentioned in the DoW, i.e. SP, MTEC and SCHOTT. Additionally, the involvement of other partners (i.e. DLR and UNIGE) that possessed specific expertise and infrastructure allowed to accomplish specific tasks in a more effective way.

| Strength | Weaknesses |
|---|---|
| -All requests for materials were fulfilled in time<br>-Strong interaction with WPs 3, 4, 6. | -Late fulfilment of new materials may delay the validation process. |

## WP3 Experiments Design & Results Synthesis

One of the main goals of WP3 is to deal with the organization of samples and experiments. In a first stage, decisions were taken based on state of the art knowledge coming from previous projects and state of the art literature. In a second phase, the observations on the particular generated samples are used for further decisions for organizing experimental work in the consortium.
In order to optimize resources, the main goal has been the harmonization of two aspects: the technological capacities of the members and the collection of the phenomena with a highest impact in the stack performance. In an initial step, the technical capabilities from different partners were assessed in order to determine the consortium capabilities and conceive the most convenient distribution of efforts. By other side, a compilation of bibliography dealing with degradation in SOFCs was organized as a functions of different phenomena affecting different parts of the stack. Simultaneously, the knowledge arisen from previous projects (Robanode and SofcLife) and particular experience from different groups was collected. Different mechanisms (modes) were arranged in a table, including information about potential causes, probability of occurrence, severity and possibility of recovery. After active internal discussions, the modes where ranked using a modulating factor that accounts for the relevance in the particular state of the art technology considered in ENDURANCE project. This *Degradation Modes and Effects Analysis* (DMEA) was one of the goals compromised in WT3.1.

At the light of this information, a set of samples was designed and distributed to the different partners for the analysis. The characterization was focused on the particular degradation phenomena highlighted in the DMEA. These samples consisted in different pieces coming from stacks operated under real conditions during 3700h. The regions of interest included interconnect, seals, and cell portions from different regions in order to determine possible influences of gas composition and temperature. Reference non degraded samples were also delivered for comparison. Observations carried out in different laboratories were harmonized, when convenient. The lists of samples and protocols have been included in the Book of Samples and Handbook of Experiments developed in WP8.
The first set of outcomes provided a basis for the generation of new samples to be tested and analyzed in the frame of the project. After exposing and discussing the results, the most likely occurring phenomena (the so called *minima phenomena*) and the variables affecting them were determined. A set of four experiments where planned and the appropriate samples where defined taking into account the particular needs of every involved partner.
Finally, related parallel activity has been carried out consisting on the generation of Early Warning Output signals from the state of the art data. On this task, evidences of degradation at an early stage have been searched. Intensive Active Tests and Analysis (IATA) procedures have been applied in order to get evidences of anode degradation. Also the evolution of seals can be induced from variation of the impedance between interconnects.

| Strength | Weaknesses |
|---|---|
| -Technical capabilities from different partners were assessed in order to conceive the most convenient distribution of effort<br>-First set of outcomes provided a basis for the generation of new samples<br>-Generation of Early Warning Output signals from the state of the art data. | -Frequent meetings with WP 4, 5, 6, 7 are needed to keep consistent the action. |

## WP4 Macro&Micro tests and data generation

The activities within this work package were dealing with:
1) construction/adaptation of test rigs by several partners in the consortium to carry out tests on micro-samples and macro-samples under near real life and under accelerated conditions
2) execution of NRL and accelerated tests
3) definition of protocols for sample management and transfer.

Measurements on micro-samples at IEES revealed, among others, that within the normal stack operating limits the anode reduction conditions affect the anode reduction kinetics, anode electrical response and anode permeability. Long term tests at CEA under steady-state conditions showed that the cell degradation rate at a fixed fuel utilization does not vary significantly within the expected stack temperature boundaries, while accelerated thermal cycling tests revealed that the cell degradation due to thermal cycling is limited.
Measurements on macro-samples at HTc and short stacks at SP using reference materials were performed as well. The tests were carried out for at least 1000 h under steady-state conditions. Accelerated conditions were avoided as it was thought to risk failure of the materials, which could

have led to considerable delay in the project. Nevertheless, the materials were considered useful, and were distributed for analysis to provide a baseline for materials improvement to further mitigate their degradation.
The results obtained on micro-samples, macro-samples and short stacks were found to provide vital input for the development and verification of the predictive models developed in WP 6.
Protocols for sample management and transfer have been developed and were recorded in the Handbook of Experiments provided by WP 8.

| Strength | Weaknesses |
|---|---|
| -The results obtained on micro/macro samples and short stacks provided vital input for development and verification, in WP6, of predictive models<br>-Development of protocols for samples management and transfer. | -Time consuming experiments<br>-In case of failure, the experiments have to be repeated with consequent delay. |

## WP5 Advanced sample analyses

The advanced sample analyses were focused on segmented stacks and short stacks after ageing. In the latter case parts of the macro samples were considered as micro samples. Pristine Anode Supported Cells were also studied as reference in order to investigate their initial state.
The objectives of the studies were, after careful dismantling of the specimens, to collect data on materials evolution and mutual interaction during operation. The investigations concerned the bulk properties of the cells materials and the microstructural characterizations of the interphases (new phases formed by chemical reactivity). Moreover, several interfaces between adjacent layers were carefully studied.
The strengths of this WP were to gather the results obtained using several *different and complementary tools*, offered by the different partners. Then, following extensive exchanges among them, strong scientific conclusions could be given at M18.
All parts of the stacks are closely related and affecting each other. The elevated temperature, long operating time and the applied polarization resulted the main parameters responsible of the investigated degradation phenomena.
Regarding the anode side, partial nickel depletion was evidenced during the reduction step. Moreover, the nickel grains coarsening occurring during operation may be promoted by the current load.
On the cathodic side, strontium diffuses from the LSCF through the GDC barrier layer to the electrolyte. Resistive phases are formed at the interface, leading to an electrochemical deactivation of the cathode. Cerium is partly diffusing from the barrier layer towards the YSZ electrolyte.
The gas sealant is affected by elements coming from the interconnect, mainly Cr, Mn and Fe, and prone to become porous due to cation evaporation. Moreover, an increase of the glass sealant crystallinity is observed, lowering the mechanical strength of the cells.
Many pollutants were evidenced in different parts of the cell. After a careful examination, excluding those coming from the interconnect (Cr, Mn, Fe), mainly Ca, Ba, Sr and S have been taken under control.

Following the conclusions obtained at this stage of the project, several mitigation ways were suggested. Among them, the following four seem particularly important to consider regarding:
1) the Ni depletion and coarsening phenomena
2) the optimization of the GDC barrier layer in order to mitigate the strontium diffusion
3) the preparation of up to 10 new glass formulations
4) the preparation of YSZ coated interconnect as base for the application of the glass-ceramic sealant.
The exchange of information, the amount and quality of results obtained during this short period revealed the strength of the consortium despite several non-disclosure obligations provided by the industrial partner regarding some procedures and parts of the cells and stacks.

| Strength | Weaknesses |
|---|---|
| -Exploitation of different and complementary tools for the investigations on samples<br>-Achievements of solid conclusions at M18<br>-Identification of several mitigation strategies. | -A delay from WP 4 is reflected on bad timing of results. |

## WP6 Predictive Modelling

UNIPI, CEA and EPFL have developed during M1-18 a set of numerical tools comprising dynamic and steady-state models, based on continuum or discrete formulations ranging from the micro-scale of electrode features to the macro-scale of the stack to identify the factors that limit the initial and long-term performance of SOLIDpower stacks. Electrochemical and thermomechanical aspects have been addressed. The models are physically-based, to capture the interactions between the degradation phenomena, the possible changes in regimes and failure modes, depending upon the stack history.

The understanding of the electrochemical behavior of SOLIDpower cells available at the start of the project has been improved significantly. Model-based analysis of EIS data from a segmented-cell experiment enabled the identification of 7 processes in the spectra. The remaining uncertainty on three of them, mainly related to the LSCF/GDC/YSZ interfaces, is the subject of ongoing efforts. Sensitivity analysis has showed that the model can detect alterations in the model parameters that cause a decrease of the cell voltage in the range of 1%. This capability is promising for EWOS. Regimes in the reaction pathways in the composite LSCF-GDC cathode have been identified. Under SOFC stack operation, the charge transfer at TPBs is the predominant mechanism. This important results informs on (i) the possibility for improvements of the microstructure, (ii) the measurements to perform in WP5 to identify the possible causes of degradation and (iii) the relevant assumptions for stack level continuum models.

The electrode models have been implemented in stack models and completed with degradation phenomena. The calibrated stack model could predict the initial performance of SOLIDpower stacks within 10 mV over a large range of operating conditions. Degradation patterns observed in the experiments could be predicted, in terms of magnitude and characteristic time. However, the evolution of the spatial distribution of the degradation measured in segmented-cell experiments

could not be captured in full details. A reason is the limited sensitivity of continuum models to localized material alterations. New developments have been therefore initiated to retrieve information beyond that conveyed by averaged standard metric and topological properties. The efforts have been placed first on the cell materials for which 3-D imaging data from WP5 became available at M14.

FEM stress analysis of the Ni-YSZ microstructure predicts the increase of the risks of microcracking of YSZ upon thermal cycling. The quantification of the detrimental effects requires electrode discrete modeling (electrochemical performance) and stack thermo-mechanical analyses (external loading conditions), which have been performed in parallel. The framework developed here is relevant for the study of local contaminations or morphological changes as well. The capability of models based on a 3-D discrete representation of electrode microstructures have been tested using the dataset from a same Ni-YSZ sample imaged before and after reoxidation. The 3-D simulations of the polarization resistance are in line with EIS measurements (0.07 $\Omega \cdot cm^2$ and 0.05-0.08 $\Omega$ $cm^2$) and the effects of local alterations can be detected and quantified. The related developments for the stack thermo-mechanical analyses are (i) the fabrication of two setups for the measurement of the creep and strength properties of SOLIDpower materials at high temperature and in controlled atmosphere and (ii) a 3-D contact model of the SOLIDpower stack. Cycles comprising stack fabrication and qualification, followed by combined long-term operation and thermal cycling have been simulated. The decrease of the contact pressure over the active area is amplified during combined thermal cycling and aging and is potentially critical for the electrical contact. This confirms the need for models to study the effects of the operation history on the failure modes.

| Strength | Weaknesses |
|---|---|
| -Identification of a model that can detect parameters which could decrease the cell voltage of 1%<br>-The model developed could predict the initial performances of SP stacks within 10mV over a large range of operating conditions. | -Limited sensitivity of continuum models to localized material alterations. |

## WP7 Statistical Validation Experiments

The work package started in Month 18, however a minor activity was started a little earlier by the DLR, leading partner of the WP7. The activity concerned the preparation of the set up for the improved segmented cell to be tested during the Statistical Validation Loop.
In preparation of the planning of the activities in the work package a questionnaire collecting information on the samples (micro-samples, stacks) and the test procedures (scope of test, purpose of test method, sample size, number of samples, description of test method, test duration post-treatment of samples and expected output) has been sent to all partners involved. The questionnaires filled in by all partners have been evaluated and the information is used to set up the test programme in the coming weeks. During a project meeting which took place on September 15 in Genoa next steps for starting the activities in WP 7 have been discussed.

Conclusion and outlook
Six stacks from SP will be delivered to three partners (UNIGE, EPFL, DLR) to be tested at identical operational conditions. Furthermore, accelerated tests for statistical validation of the recognitions achieved during the project are performed at the micro-level to be able to cover the whole spectrum of interphases and phenomena affecting the performance of the stack. The aim is to validate the acceleration models of WP6 and the efficiency of counter strategies triggered by EWOS and to refine them. A control of the validity of the acceleration protocol will be made by comparing the results of the micro-samples with the corresponding stacks.

| Strength | Weaknesses |
|---|---|
| -Collection of information about samples and testing procedures among the partners in order to plan the testing activity in the validation loop<br>-Early preparation of the setup. | -Some of the test benches are still under construction. |

## WP8 Communication and Dissemination

The main goals of WP8 in the first reporting period (months 1-18) were:

1) To organize quickly a friendly for the partners system for gathering and safely storing consortium results, achievements and virtual products (testing procedures, protocols, experimental results etc.);
2) To ensure a friendly access to the accumulated intellectual resources and thus to support the development of the project exploitation plan;
3) To plan, organize and support targeted (Industry, Scientific Community, General Public) dissemination of the project results, extending the "lab-to-public" applying new and original tools.

The project website has been planned to serve as an important and integral tool in the project's online communication strategy, combining an engaging external section and a restricted access internal section – a virtual “hub” for project information and pooling of partner resources.
During the first part of the reporting period a design and implementation of the Internal web site as a Web Library & Data Bank has been performed. It includes **three Databases** with access to the consortium members.
**Book of Samples (BoS) –** a database for samples creation and shipment, for collection of testing and characterization results and their analysis. Thus BoS ensures information about the current status of all project samples.
**Hanbook of Experiments (HoE) -** a database for collecting and storing testing procedures and protocols (existing or developed during the implementation of the project).
**Knowledge Pool (KP) –** a database for storing publications and materials relevant to the project.

Although separated in different tasks, in the first part of the project implementation the Exploitation and Dissemination activities were structured and developed in parallel.
**External web site (www.durablepower.eu)** - one of the strong exploitation and dissemination tools, structured to ensure illustrative presentation of project advancements and other useful for the stakeholders information and materials. The most informative part is the INFO CENTER, where there is already rich information on exploitation and dissemination activities (iCREATE childrens'

workshops; Festival of Science in Genoa; the first public presentation of the educational game "The lost Colony").

**Serious Game**: a special product has been proposed as deliverable with long term impact – the Serious Game "The Lost Colony", aiming at transferring knowledge related to fuel cells to young people - pupils, students and young researchers.

**Publications and conference participations**: 9 publications and 18 presentations at scientific events.

For the reporting period two milestones and three deliverables have been prepared and delivered. The planned activities were performed in volume and quality. The web site should be updated more frequently.

| Strength | Weaknesses |
|---|---|
| -Realization of an external website, a serious game and dissemination activities as exploitation tools<br>-Implementation of the Book of Samples, Handbook of Experiments and Knowledge Pool as useful tools available for all the partners in the consortium. These tools allow an effective management of the samples and knowledge. | -The website has not been periodically updated. |