



Grant Agreement: 825027

Start date: 01.01.2019

Duration: 3 years

AD ASTRA Deliverable D2.1

"Review of SOC degradation mechanisms and modelling approaches"

Due date of deliverable: M6

Lead Beneficiary: IEES

Nature: Report

Revision	Submission date	Description
0		Original version

Dissemination level (mark with an x the relevant)		
PU	Public	<input checked="" type="checkbox"/>
CO	Confidential, only for members of the consortium (including the Commission Services)	

Acknowledgements: This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation program and Hydrogen Europe.

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Report title: "Review of SOC degradation mechanisms and modelling approaches"	Deliverable No D2.1
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Summary <p>This review aims at presenting the current State of the Art (SotA) in respect to Solid Oxide Cells (SOC) degradation phenomena, mechanisms and modelling approaches. It stresses on the following components evaluated as the most important degradation sources:</p> <ul style="list-style-type: none">• fuel electrode where special attention is given to redox cycling and modification of the Ni network that brings to microstructural changes;• oxygen electrode with accent on Cr poisoning and interconnect protection. <p>The most applied modelling approaches are discussed as well as the efforts towards accelerated stress testing.</p> <p>The main information sources for the preparation of the review are: published literature (mainly papers) and results from previous FCH JU projects correlating with the degradation issues. This information is ensured by AD ASTRA Partners that have participated in those projects.</p> <p>The review will be used as a basis for:</p> <ul style="list-style-type: none">• development of methodology for AD ASTRA Design of Experiments (DoE) which aims at defining successive experimental rounds specifying appropriate combination of testing modality, testing conditions, targeted degradation phenomena and accelerated stress level;• selection of appropriate modelling approaches, modelling tools and validation instruments;• preparation and publication of a Review paper on SOC degradation processes in a High-impact Journal written together with the External experts.	



Key words: SOC, Degradation, Modelling, Fuel Electrode, Oxygen Electrode, Interconnect.



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1. INTRODUCTION

1.1. Description of the deliverable content and purpose

Solid Oxide Cells (SOC) have an important role and hold great promise with their diverse and versatile portfolio in the energy application sector, ensuring opportunities for integration of renewable energy sources into the overall energy system as part of the low carbon economy. However, the scale and scope of the research and market entry agendas for their development and deployment across the spectrum of applications still meets some general barriers, summarized as durability, i.e. resistance to ageing, and costs, which have to be overcome.

Considering the expected useful commercial maintenance-free lifetime of up to 80 000 hours for stationary applications, a challenging objective is to maintain the initial, or close to initial performance for as long as possible. However, the development of long-lasting systems remains still a goal since the degradation is influenced by the multiple factors of the operation conditions. The initial performance degrades over their lifetime due to the effect of use (electrochemical ageing), of time (calendar ageing), of different permanent and/or accidental stress conditions – thermal, current load, mechanical, conditioning, poisoning etc.

Although there are several long term tests which exceed 75 000 hours [1] it should be noted that there is a big difference when testing performed for fundamental studies, usually on button cells and that in pre-commercial studies [2]. The same problems arise in respect to the materials for production of the cells/stacks. The performance behaviour depends not only on the scalability, but also on the selected cell/stack architecture, precision of the measurement instrumentation, geometrical factors, preconditioning, operation conditions, including humidity of the gases etc. Especially for electrochemical testing on cell and stack level there are harmonized protocols [3, 4] which should be followed. Although some differences cannot be avoided, the performance of the research and development following similar experimental approaches will be beneficial for applying results obtained in different laboratories. In the frames of the project ENDURANCE data base for testing and characterization procedures (harmonized where available) was developed with free access [3].

For improvement and optimization of SOC long term performance it is important to identify and quantify the degradation sources and to use them as a base for the development of successful mitigation strategies. However the assess of SOC lifetime is time consuming and thus expensive. Several years are needed for extensive laboratory testing combined with field experiments under actual application conditions. Another challenge is the analysis of the tested cells in respect to the physical failure mechanisms. As the total deterioration achieved during long-term tests is often relatively low Degradation Rate (DR) below 1% / 1000h in Fuel Cell (FC) mode, it is difficult to identify the dominant degradation process. One generalized approach is the combination of the long term testing at constant operating conditions which evaluates the total degradation coming from all the components (anode, cathode, electrolyte, interfaces, barrier layers etc.) with additional electrochemical testing: periodic current-voltage (*i*-*V*) characteristics which give the integral picture of the system to produce electrical energy combined with Electrochemical Impedance Spectroscopy (EIS) in selected working points as embedded technique for in-operando diagnostic monitoring, e.g. status



monitoring, which can evaluate components contribution in the overall degradation. The final stage of this complex study is the post-mortem analysis which visualizes some external degradation effects [5]. Another approach is the performance of dedicated studies of components degradation (anode, cathode, interconnect etc.). However, their behaviour in the cell/stack assembly may strongly differ due to the different operational environment.

Since SOC durability needs sufficient improvement and reliable lifetime prediction, modelling at cell, stack and system level can serve as a powerful prediction and optimization tool. A useful approach is the introduction of “fit-for-purpose” test methodologies, derived from empirical models to address the degradation mechanisms relevant in a variety of real cases. Thus there is a sharp need for further development of sophisticated algorithms and tools for multi-scale assess of performance from cell to system level which, however, cannot avoid the long tests (several years). Obviously they are neither appropriate as information source for further optimization, nor convenient for implementation. The problem solving approach, which is under active development, is the introduction of Accelerated Stress Tests (AST) and sophisticated performance/degradation models to quantify the accelerating impact. They should shorten testing time, while the experimental conditions should activate the same degradation mechanisms as in non-accelerated testing, thus preventing the system from eventual irreversible changes which may bring to false results. Since there are no definite criteria for regulation the level of acceleration, the selection of the acceleration conditions is a critical moment in the procedure.

In AST the life data obtained from the aggravated test conditions are extrapolated to normal operating conditions by means of a model which fits the data to an appropriate life distribution using a life-stress relationship to project the life at normal operating conditions. Since one of the critical factors in AST is that the degradation mechanism should not change on aggravation of the test parameters, it is important to understand the SOC degradation mechanisms at different operating conditions and further to predict such mechanisms developing proper models. Validated with experimental data they act as useful tools for understanding the degradation of SOCs. The next step is to design SOCs with required degradation rate to sustain the operation challenges.

The major factors which influence the degradation of SOCs are temperature, thermal cycling, redox, load cycling and poisoning from fuel contaminants. The effect of those factors on the performance and degradation of different cell components is under intensive studies.

This review aims at presenting the current SotA in respect to SOC degradation phenomena, mechanisms and modelling approaches. It stresses on the following components: fuel electrode, oxygen electrode, interconnects, which have been evaluated as the most important degradation sources (www.ad-astra.eu). Based on this information, in the frames of AD ASTRA project a realistic failure modes picture will be developed and correlated to appropriate models which should be further developed in performance models.

1.2. Deviation from objectives

No deviations are reported from the project objectives for this task and deliverable.

1.3. If relevant: internal property rights

No intellectual property issues are reported. The review is based on published sources.



2. SOC DEGRADATION MECHANISMS AND MODELLING

2.1. Degradation Rate

The requirements for operational stability formulate the parameter “Degradation Rate” [5, 6]. Usually it is defined as the change of a fuel cell performance indicator with time. Most often long term durability tests are performed at constant current load and the decrease of the voltage (for 1000 operation hours) is used for definition of the DR. It can be expressed as [mV kh^{-1}], or with normalized value [% kh^{-1}] [5 - 10]. A linearized average degradation rate for the whole testing time, or segmented one, defining different degradation stages as initial and long term degradation, are applied. The voltage change may be replaced with that of the corresponding Area Specific Resistance (ASR) ($\text{m}\Omega \cdot \text{cm}^2 \cdot \text{kh}^{-1}$) [7, 11, 12]. Obviously to calculate correctly the DR, measurements with high accuracy are needed in which a precise conditioning and high stability of the operating parameters is also necessary (temperature, current, gas flows, hydrogen humidity etc.). The DR currently reported for Solid Oxide Fuel Cells (SOFCs) is below $1\% \cdot \text{kh}^{-1}$. For Solid Oxide Electrolyzers (SOEL) it exceeds $2\% \cdot \text{kh}^{-1}$ [9, 13, 14].

The current target for operation in SOFC mode is about 0.1 % [1, 3, 4, 6, 9] which means that at operating conditions (at constant current corresponding to voltage around 0.8) the voltage decrease should be about 0.8 mV/1000 h. Obviously it is difficult to measure with accuracy the differences for which long term tests are required. Although the problem solving approach is the accelerated stress tests, other approaches for increased sensitivity are of interest. In NEDO Durability project “New Energy and Industrial Technology Development” [15] the target is 90 000 hours and since very small voltage changes should be detected and analysed, the efforts are concentrated on detection of small changes on samples tested for shorter time by application of more precise analytical techniques to identify tiny changes. This approach was developed and approbated in the project ENDURANCE in respect to increased sensitivity in evaluation of the DR [16 - 18]. It is based on analysis of the current-voltage (i - V) curves which are converted into current-differential resistance ($R_d = dU/dI$) dependencies. The DR is determined by the change of the minimum of R_d with time. The increased sensitivity comes from the operation with derivatives.

To Summarize: Since the operational stability of SOFC is quickly increasing, its experimental evaluation by the parameter DR will become more important, more difficult and less reliable. There are two pathways which may be regarded as problem solving approaches: (i) to introduce accelerated stress tests and (ii) to increase the sensitivity of the methods. Although the second one emerged recently as a concept, the first results are promising and the combined application could be beneficial.

2.2. Degradation studies and modelling approaches on components (fuel and oxygen electrodes and interconnect)

The work on life time improvement needs long term electrochemical tests, which may continue several years, followed by post-mortem analyses for identification and quantitative assessment of the degradation mechanisms in different cell/stack components. It should be noted that significant progress in identification of degradation sources is registered, combined with development of degradation models for faster assessment and acceleration of the optimization steps. Many works are focusing on the phenomena at micro-scale level, since microstructure is regarded as an important optimization parameter in relation to the Triple Phase Boundaries (TFBs) which govern the number of electrocatalytic sites available for reaction and their accessibility by the transport of reactants and products. The experiments are performed on single components as anodes, cathodes, interconnects etc., on cell, or stack level. For extraction of information for the components from cell/stack measurements, EIS and post-mortem analyses are carried out. The picture is more complicated since there is close correlation between phenomena that cause degradation. For



instance the seal tightness and the anode reoxidation are interlinked and it is difficult to evaluate which is the initial degradation source.

The knowledge of the underlying electrode mechanism is an essential condition before considering the modelling of degradation. Continuous microscale modelling which takes into account the electrode microstructural properties as well as the most likely processes occurring therein is essential tool for further development of degradation models for assessment of the complex sources causing the external degradation picture. In this approach, the reactive pathway is divided in a sequence of elementary reactions. For the typical Nickel-Yttria Stabilized Zirconia (Ni-YSZ) fuel electrode, W. Bessler et al. [19, 20] proposed a multiple elementary step based on hydrogen “spillover”, while for the typical mixed-ionic-electronic conductor O₂ electrodes such as (La,Sr)(Co,Fe)O₃ (LSCF), the Adler Lane Steel (ALS) model [21] is generally used to simulate the electrode response in cathodic polarisation. However, there is still need for more sophisticated models that can describe the integrated degradation picture.

A big number of the studies concern improvements in the TPB characterization by nondestructive 3-D imaging and the corresponding modeling approaches for evaluation of the TPB loss. In principle the continuous models consider the homogenised electrode properties that can be computed based on real 3D reconstructions [22]. An advancement in the 3D discrete representation of the heterogeneous structure is developed [23] based on the so-called electrochemical “fin” model. It is applied to a 3-D discrete representation of the heterogeneous structure provided by skeleton-based partitioning. The results on real and artificial structures show that the 3D electrode microstructure is complex, the accessible TPBs are not uniform and the pattern varies depending upon the structure. Connected TPB can be even passivated. In both SOFC/SOEC (solid oxide electrode materials) the combined accessible TPB is mostly affected by each phase separately and the total accessible TPB is largely dominated by the ion conducting phase. This capability to accurately quantify deviations from the ideal case is of relevance for the design of heterogeneous materials.

There are numerous studies (described below) where experimental results are combined with micro-scale continuous modelling. The validation supports the understanding of the governing mechanisms and the influence of the operating conditions. The analysis of the results obtained by different working groups can serve both as a base for further development of the degradation modelling and as a good source for selection of conditions for aggravated tests.

2.2.1. Fuel Electrode

Ni-YSZ cermet is the most commonly employed SOC anode due to its good electrochemical performance and lower price.

Studies of cermet anode

The SOC anode should combine multiple functions, which sometimes oblige contradictory requirements. On the one hand the anode should have both high catalytic activity and suitable electronic conductivity, combined with appropriate porosity. Small particle size of the Ni phase increases the length of the triple phase boundary and thus improves the anode performance. Denser anode structure is in favour of higher mechanical strength. On the other hand in FC mode the anode acts as site for fuel supply and removal of reaction products which influences the concentration polarization and can be controlled by the porosity. Thus, a careful adjustment of the appropriate microstructure should be performed. Ni-YSZ cermet is the most commonly employed SOC anode due to its good electrochemical performance and lower price.

During the manufacturing the anode cermet has a composition YSZ/NiO. The green anode is reduced in pre-operation conditions, when both the final composition Ni/YSZ and microstructure are formed. Thus with the formation of the Ni network the anode layer changes its mass, volume, composition and porosity. The process



is influenced by several parameters: the preparation pre-history of the green sample (YSZ/Ni ratio, pore former, particle size), the technological operations, sintering conditions, reduction regime, etc. which makes this step important for the anode durability, since it ensures the normal start of the system in operation conditions [24 - 27].

The main degradation sources in SOC anodes concern modifications in the Ni network which bring to microstructural changes. During operation Ni-volatilization and Ni particle coarsening occur. Another degradation source is the Ni reoxidation which may be caused by different reasons, some of them unpredictable. The formation of NiO can bring to new degradation processes, or acceleration of existing. In addition to the Ni coarsening which decreases the TPB length, the expansion of the lattice can bring to cracks in the anode and at the interfaces. Thus a big number of the papers are devoted to a deeper insight into the degradation mechanisms caused by changes in the Ni phase microstructure. A relation between the initial powders and the microstructure of the pristine sample with the degradation rate is also studied. Important parameters come from the initial reduction temperature, operating conditions, such as fuel utilization, higher oxygen partial pressure etc. [28 - 31]. Electrochemical testing is combined with post mortem and in situ analyses. The data are used for validation of the models that try to explain the observed phenomena.

A critical review of existing models concerning the H₂/H₂O/Ni/YSZ electrode kinetics is presented in [32]. The use of limited set of data to verify a given model is also discussed as well as strengths of the models.

A new method for performing TPB specific pathway analysis on 3D image data is introduced [33], analyzing the pathway properties of each TPB site in the electrode structure. Two new site specific parameters describing the quality of the TPBs are introduced: (i) the TPB tortuosity, that seeks to quantify the distance from the TPB sites to the source/destination through each phase and (ii) the TPB critical pathway thickness that seeks to quantify the bottleneck width of the pathways to the TPB sites. The new approach is experimentally tested on composite electrodes: YSZ/Ni and LSCF/GDC. It provides valuable microstructural insight.

In [34] a two particle model for degradation analysis of cermet SOFC anodes is developed. The model is based on two main assumptions: (i) the difference in metal particle diameter which is accepted as the driving force for the observed coarsening during long term annealing and (ii) surface diffusion of metal atoms on the particle surface as the dominant diffusion mechanism. Additionally, a function is introduced which considers the limited space for the growth of the nickel particles in the cermet material. The analytical function for the growth kinetics is compared with experimental results for the growth of nickel particles in a Ni-YSZ anode annealed at 1000°C up to 4000 h. The results show that the proposed mechanism - surface diffusion of nickel atoms is fast enough to explain the registered amount of Ni agglomeration in SOFC anodes and is therefore considered to be the dominant mechanism. In [35] degradation phenomena in Ni-cermet samples are evaluated experimentally by measurements of the resistivity increase for 3000 hours at 700°C and 800°C in 80 vol.% H₂O and 20 vol. % H₂. They are related to the change in the microstructure, estimated by image processing and X-ray fluorescence (XRF) analysis carried out for virgin samples and after 300, 1000 and 3000 h of exposure time. The 3D-microstructure is reconstructed using an original spheres packing algorithm. Two processes leading to the Ni-YSZ degradation are detected: Ni-phase particle coarsening and volatilization.

A theoretical model is presented for the evaluation of the performance of an electrode formed by a mixture of electronic conductor/ionic conductor particles having a high *a/d* ratio [36]. A comparison with literature experimental data shows good agreement. The results of the model show that the effects of morphology, i.e. the volumetric composition of the electrode and the dimensions of the particles strongly influence the electrode resistance. The reciprocal electrode resistance reaches a maximum in correspondence to a composition near to the percolation threshold of the electronic conducting phase. The results stress on the importance of obtaining good experimental data of percolation thresholds as well as on better theoretical insight into the critical percolation zones. The model is applied to YSZ/LSM cathodes and YSZ/Ni anodes.



In [37] an improved approach for transmission X-ray microscopy observation of the high-temperature microstructural evolution of Ni-YSZ anode is proposed. The time evolution of a material can be observed. Since the changes of interest in SOC degradation typically occur over long times, it is necessary to evolve the structure outside of the beam. However, when a sample is re-introduced into the Transmission X-ray Microscope (TXM), the resulting images are no longer aligned with the original images, because they are displaced. A new methodology proposes anode micro sample preparation with intervening ex situ ageing steps. The sample is aged at 1050°C for 24 h, in a 5% H₂ / 3% H₂O / 92% Ar gas mixture similar to a typical anode fuel gas. Thus unlike prior studies that compare microstructural differences between different anodes, the proposed three-dimensional measurement directly shows the changes occurring in the same region of an anode, enabling a new understanding of evolutionary processes. The high-temperature (accelerated) ageing for 48 h at 1050°C yields substantial structural changes in the Ni, YSZ and pore networks, including coalescence of Ni particles, leading to a three-fold decrease in three phases.

In [38] degradation of the Ni-YSZ anode support is tested on single cell at 850°C. The microscopic investigation is carried out by Scanning Electron Microscopy (SEM) image analysis which shows that the cell degradation is related to the coarsening of Ni particles in the anode. A theoretical analysis based on an electrode micromodel is performed for comparison of the variation in performance, expected from particle size change, with the observed data. Comparison of the anode degradation at 750 and 850°C shows [8] that Ni agglomeration is favored at higher temperature. In [39] the anode degradation tests are performed on anode supported solid oxide fuel cell applying different p(H₂O) at constant load (0.75 A/cm²) and temperature (750°C) and monitoring by Impedance Spectroscopy. The anode degradation is described by the equation: RNi,TPB(t) = RNi,0 + ΔR · (1 - exp(-t/τ)). Possible degradation mechanisms are: 1) Ni particle growth and/or 2) Impurity/segregation of species at the triple-phase-boundaries, i.e. blocking the electrochemically active sites in the anode. The proposed degradation mechanisms are:

Testing of cells in steam electrolysis demonstrates the importance of the sealing on the fuel electrode which may prevent from initial passivation in the first few hundred hours of electrolysis [40]. The degradation analyzed by impedance, is found mainly to be caused by increasing polarization resistance associated with the hydrogen electrode (cell voltage degradation of 2% /1000h). The post mortem analysis shows accumulation of impurities in the hydrogen electrode and microstructural changes at the hydrogen electrode-electrolyte interface.

In the frame of FCH JU 2 ENDURANCE and SOPHIA projects, a detailed study of fuel electrode degradation is performed on cell and stack level. Comparative long-term tests are carried out in SOFC and SOEC modes on SOLIDpower cells. The change of Ni particle size/shape and Ni mobility reflects in the loss of Ni percolation which occurs in both SOFC/SOEC modes. By using a multiscale modelling approach, the contribution of the Ni/YSZ electrode in the total degradation for both fuel cell and electrolysis mode is evaluated [41 - 45]. More detailed information about the obtained results is given in the Section 2.4.4.

It is suspected that the steam content in the gas stream could accelerate agglomeration and Ni volatilization resulting in depletion at the electrolyte interface [46 - 48].

Anode reduction/oxidation

The microstructural changes during redox cycling are the primary cause for Ni-YSZ material degradation in both electrochemical performance and mechanical properties. The repeating Ni volume changes are the main cause of this degradation process, damaging the YSZ framework and reducing the TPB density as a consequence of accelerated Ni coarsening. A comprehensive quantification of redox cycling can be achieved by coupling 3D tomography, real-time impedance spectroscopy and mechanical analysis [49]. In [50] the anode degradation analysis is performed on data from medium-term stack testing. The separation of the three anode phases (nickel, yttria-stabilized zirconia and porosity) is obtained by low acceleration voltage



SEM imaging which yields phase proportion, particle size, particle size distribution and a direct measure of triple phase boundary density. The combination of experimental results and modeling allows separating the degradation due to sintering of nickel particles from the total stack degradation. An anode degradation model is proposed for description of the gradual degradation caused by due nickel particle sintering and the concomitant loss of TPB. Fundamental operational and structural parameters of the anode can be used to estimate the TPB length change with time from the degradation rate. It is found that anode degradation occurs principally during the first 500 operating hours. For stack tests carried out over more than 1000 h, anode degradation is responsible for 18 to 41 % of the total degradation depending on initial microstructure.

An original study is carried out [51] correlating real time, in situ spectroscopic observations with electrochemical performance which provides insight into Ni-YSZ anode degradation mechanisms in operational SOFCs under reoxidation conditions. The monitoring of the Ni oxide growth at constant load operating conditions and elimination of the fuel flow is performed with in situ vibrational Raman Scattering. Those conditions bring to large changes of the overpotential. The rate of NiO growth is compared to the cell overpotential and Electrochemical Impedance Spectroscopy data. NiO growth exhibits two distinct steps that match steep jumps in cell overpotential. The results illustrate the dependence of the overpotential on both electrical and ionic conductivity through the cermet anode.

The reduction/oxidation kinetics on Ni/YSZ cermet is studied on dense (no open porosity) two-phase NiO+YSZ samples [52] reduced in a hydrogen-containing environment. The time dependence of the reduced layer thickness at various temperatures is measured. Reoxidation studies are performed on fully reduced anodes reoxidized in air over a temperature range between 650 and 800°C. The kinetics of reduction and reoxidation is described with a theoretical model based on two series kinetic steps: diffusion and interface reaction. It is observed that the reduction kinetics is linear (interface-controlled), while the reoxidation kinetics is nearly parabolic (diffusion-controlled). The kinetics of reduction is thermally activated while the kinetics of reoxidation is essentially independent of temperature. The interface control of the reduction process implies that gas-phase diffusion through porous Ni+YSZ, formed upon reduction of NiO to Ni, is considerably faster than the kinetics of the actual reduction reaction occurring at the interface separating the pristine and the reduced regions, while the diffusion control of the reoxidation process is attributed to slow, gaseous diffusion on account of the very small amount of porosity that remains when Ni reoxidizes to NiO.

In [53] the reduction-oxidation cycling of Ni-based electrodes for solid oxide fuel/electrolysis cells is studied applying improved approach for analysis of the nondestructive 3-D imaging, based on comparison of the sample microstructure before and after exposure to air at 800°C for 45 minutes. Absorption contrast X-ray Nanotomography (XNT) is used. The morphology of the Ni(O) phase is observed to be completely different after reoxidation. The spatial resolution better than 20 nm enables the detection of cracks in the brittle YSZ phase above this dimension. The detrimental effects of the cracks on the effective 3-D transport pathways in the Ni-YSZ anode under polarization is investigated using a skeleton-based discrete representation of the imaged volume and an analytical electrochemical fin model. Topological properties, effective ionic conductivity and polarization resistance are calculated before and after oxidation. The calculations show that cracks in the brittle YSZ phase increase the effective ionic resistivity and polarization resistance in the range of $25 \pm 9\%$ and $12 \pm 5\%$, respectively.

Higher oxygen partial pressure can also cause oxidation-induced Ni anode degradation [28]. The investigation of cell performance at high fuel utilizations simulates situations around the system downstream. When the anode voltage is higher than a voltage threshold, the cell performance is stable. It becomes unstable associated with cell voltage oscillation when anode voltage is around or less than the threshold value. The threshold value is consistent with the anode potential derived from the oxygen partial pressure at the phase boundary at which both Ni and NiO coexist.



2.2.2. Oxygen Electrode

Despite the big number of investigations, the complex, multi-step oxygen reduction reaction continues to be an active field for investigations, since the cathode performance gives a big contribution to the polarization losses. It also degrades under contaminant conditions such as CO₂, H₂O, Cr and S [15, 54, 55]. In addition to the contaminants, important factors which govern the cell performance in respect to the cathode are the operating conditions and basically the temperature and polarization [4, 48, 56]. A series of NEDO projects [15, 56, 57] focus on degradation phenomena on stack level caused by contaminants introduced during the manufacturing process. For the cathode cell Cr poisoning (coming from the steel interconnect) and S impurities are extracted as major degradation sources. In the last NEDO project [57] the accent is on correlation between the cathode polarization and the ohmic losses which is registered and marked as a new viewpoint. The detailed analysis of the cathode degradation reveals that there is a strong need to consider a common degradation mechanism among the Sr volatilization and S poisoning. The Cr poisoning is reviewed in Section 2.2.3.

In [55] the influence of operating temperature and gas conditions (presence of H₂O and CO₂) is studied by EIS in three electrode configuration with the aim to find the corresponding degradation mechanisms. A correlation between the blocking effect of the contaminants and the operating temperature is found. A combination of long term tests and post mortem analysis of experiments performed at different temperatures and current densities show that the cathode degradation dominates at higher current density and lower temperature [4]. Similar results are obtained for operation in humid air with LSM/YSZ composite cathodes [58].

For deeper insight into the cathode reaction behaviour LSCF electrode is reconstructed by XNT [9]. In [59] symmetrical cells tested with two types of LSCF electrode microstructures are studied. A physically based micro-scale electrode model including two reaction pathways is validated using the experimental results based on 3D electrode reconstruction. The model considers an oxidation/reduction at TPBs (surface path) in parallel to an oxygen transfer at the gas/LSCF interface (bulk path). After validation, the model is used to unravel the complex electrode operating mechanisms in electrolysis mode. The simulations show that the transition detected at low anodic polarization is due to a change in the dominant reaction mechanism passing from the bulk to the surface path. The relative contribution of the two pathways is also investigated as a function of temperature. In [60] the LSCF microstructural properties are quantified in a 3D volume and used as input data in a dynamic micro-scale electrochemical model which describes the relation between the microstructure and the impedance response. The numerical tool includes two parallel reaction pathways with an oxygen exchange at the LSCF/gas surface and a charge transfer at the electrode TPB. Electrochemical Impedances are computed in the time domain at OCP, as well as under anodic and cathodic polarizations. Simulations allow the microstructural parameters to be linked to the basic mechanisms of electrode operation according to the electrode polarization.

Another degradation source is the Sr diffusion and segregation of SrZrO₃ at the electrode/electrolyte interface when Sr-based electrodes as the mostly applied LSCF are used. In [9] a set of long-term tests ($t > 1000$ h) is carried out in fuel cell and electrolysis modes on typical Ni-YSZ//YSZ//LSCF-CGO cells. The degradation rates are higher in electrolysis than in fuel cell operation. Post-test analyses have revealed that Sr diffusion and formation of SrZrO₃ at YSZ/CGO interface occur mainly during electrolysis operation. The process is limited in fuel cell mode. This can explain the higher degradation rates in electrolysis mode. For the interpretation of the results a multi-scale model is applied. The simulations show that the electrolysis



operation leads to a strong depletion of oxygen vacancies in the LSCF, while in fuel cell mode an increase in the concentration of oxygen vacancies is expected. The microstructural sensitivity analysis performed on LSCF and LSCF-CGO composite electrodes shows that the composite presents much higher performance especially in anodic polarization.

In [61] the cathode degradation phenomena are investigated on SOFC stack tested at 780°C for 3000 h. Post mortem comparative analysis with pristine cell performed by XRD, Raman spectroscopy, SEM-WDX and STEM-EDX shows that diffusion takes place at the barrier layer/cathode interface and the barrier layer/electrolyte interface where insulating phases and solid solutions are registered at both interfaces in both the pristine and the tested cell. This result confirms the importance of the preparation stage. When composite cathodes are used the electronic conductivity is also an optimization factor.

In [62] the focus is on the engineering of the composite cathode. A relation between porosity, current collector thickness and interconnect coverage is demonstrated as well as the need for interrelated optimization, since changes in one of the microstructural or geometrical parameters affect the transport of oxygen, of ions and electrons, i.e. all aspects of the coupled reaction-transport processes should be considered for optimization of the cathode.

2.2.3. Interconnect/Cathode

Cromium Poisoning

Chromium poisoning is well known degradation source which comes from the stainless steel interconnects which contain Cr. Their oxidation causes increase of the interconnect resistance and formation of volatile Cr species. Thus SOFCs using chromia-forming alloy interconnect need tolerance towards Cr deposition and poisoning. Volatile Cr species are generated over the chromia scale, poisoning the cathodes such as $(La,Sr)MnO_3$ (LSM) and $(La,Sr)(Co,Fe)O_3$ (LSCF) and causing a rapid degradation of the cell performance [63]. Additionally depletion of Cr in thin interconnects leads to destructive break-away oxidation [64]. To prevent the Cr evaporation protective coatings with low electric resistivity and high chemical stability should be used to inhibit its evaporation. Their function is to hinder both oxidation and chromium migration from the substrate steels. The difficulty in the modelling approaches arises from the wide range of testing conditions and the influence of the gas atmosphere. Usually *ex situ* characterization methods of protective coatings involve chromium evaporation measurements, ASR measurements and long-term exposure tests [64]. In [65] a precursor numerical model with respect to the oxidation and evaporation kinetics of the steel, based on the oxidation behaviour studies of an uncoated ferritic stainless steel interconnect for a supposed SOFC system operating at 850°C, is developed. The model is able to predict the weight gain of the samples upon oxidation, the oxide film thickness, the volatilization of chromium and the useable lifetime of interconnects based on chromium depletion calculations. Mixed Mn-Co spinels characterized by high conductivity values and good thermal expansion compatibility with ferritic stainless steels, are used as protective coating materials. In [66] the effect of Fe, Cu and simultaneous Fe+Cu doping of Mn-Co spinels is studied. A multiple doping approach is proposed as an effective strategy to design cobaltite materials properly tailored for application. The effect of Cu on $LaFeO_3$ is studied in [67] based on comparative analysis of coatings with and without copper. The dual phase Cu- $LaFe_2O_3$ seems to be more promising. For simulation of real SOFC cell, ASR and Cr-barrier properties of the coated steel are simultaneously evaluated on a special set up. The coating with Cu is more promising. Chromium deposition at SOFC cathodes is most likely dominated by the chemical reduction of high valence Cr species, facilitated by the nucleation agents on the electrode and electrolyte surface and/or at the electrode/electrolyte interface [63].



In principle Cr rich compounds deposit on the most electrochemically active sites which decreases the TPB points. They are observed where the cathode, electrolyte and oxygen gas come at common locations [68]. In [69] $(\text{Mn,Cr})_2\text{O}_3$ is detected in the LSM cathode.

The surface segregation and migration of cationic species plays a critical role in the Cr deposition. Although the stress is on the electrodes and electrolyte, the sealant is also polluted which introduces other degradation sources. In [70] the analysis of a sealant/interconnect from the inlet and outlet manifolds of a stack operated at 750°C for 4000 h shows that the sealant exposed to the outgoing air is significantly polluted by chromium.

To summarize: Modelling approaches on components are powerful tool for accelerated optimization and decrease of the experimental volume and time. Although the final degradation result is the decrease of the Triple Phase Boundaries length which is closely related to the microstructure and which governs the number of electrocatalytic sites available for reaction, the knowledge of the main degradation mechanisms is essential. New approaches for extraction of more detailed and direct experimental information are under intensive development. A promising pathway is the TPB characterization by non-destructive 3-D imaging followed by modelling of the TPB loss. The validation which is based on experimentally determined parameter (TPB) supports the understanding of the governing mechanisms and the influence of the operating conditions.

2.3. Degradation studies and modelling approaches on cell/stack level

If we are looking at the total degradation of the cell/stack operating at constant conditions, it can be presented as the sum of the contributions coming from the main components (electrodes, electrolyte, interconnect, their interfaces) [4]. SOFCs can be examined also from point of view of: electrochemical generator in respect of electrochemical reactions at continuum level; heat and mass exchanger in a perspective of fluid dynamics and transport phenomena; chemical reactor in viewpoints of chemical reactions depending on fuel composition and heat effects associated with the electrochemical conversion [71]. This includes special attention on mass transport, heat transport, charge transport, reaction mechanisms etc. In addition when the experiments and the modelling are based on separate study of the component under investigation, the influence of the other components is vanishing. In the previous sections different degradation phenomena, mechanisms and modelling approaches (mainly modelling on microscale) were presented. However, there can be overlapping of the contribution of different processes (some of them accelerating). That is why the general goal is to go deeply (by experimental procedure and modelling) in the degradation behaviour of a specific component/part in the cell/stack [4] and to find the relation between degradation and operating conditions, including failures [72]. This general approach can ensure degradation prediction based on architecture and operating conditions, for which experiments on cell/stack level at different operation conditions are important. Since the numerical results of a computation are only an approximation of the real world conditions and considering that convergence is not sufficient, experimental validation is a necessary step in the development of the computational models [73, 74], which should be introduced in the modelling approach. In [75, 76] a 3-D model for the simulation of planar FC performance is developed, successfully validated for MCFCs and extended to SOFC technology applications. The model is based on physical principles and its core is a semi-empirical electro-kinetic relationship which has to be tuned thanks to an experimental parameter identification. The cell plane is divided in an optimized number of sub-cells, where local mass, energy, charge and momentum balances are applied and thermodynamic-kinetic properties are calculated. The model allows the calculation of the main chemical-physical variables characterising the FC operation. Different working conditions can be simulated. For simulation of both stack and auxiliaries (balance of plant components) a dynamic lumped model is introduced [77]. It has a limited number of parameters which are identified by experimental data.



Obviously, in respect to the predictive modelling of the complicated SOFC system, a multiscale approach is necessary [71] which can combine microscale and macroscale modelling. For instance, Continuum electrochemical models are commonly used when the electrical current density, the cell voltage and the heat production are considered. Continuum electrochemistry models can be used to determine effects of various designs and operating parameters on the generated power, maximum cell temperature, fuel conversion efficiency, stresses caused by temperature gradients and the effects of thermal expansion. The performance of a particular electrode under different operating conditions can be calculated, but sufficient information on how an electrode with different microstructure will perform cannot be calculated with the macroscale models, i.e. for the electrode design and optimization microscale modelling is needed.

In [78] a multiscale approach is developed, where the microscale electrochemical model (Lattice-Boltzmann algorithm) calculates the performance of the porous electrode material based on material structure at the microstructure level, distribution of reaction surfaces, and transport of oxygen ions through the material. The microscale electrochemistry modelling is used to calculate the overall fuel cell current-voltage relation, which is then used as input to the macroscale calculations, where the current density, cell voltage and heat production are calculated.

A critical review of the SotA multiscale models applied in SOFC can be found in [71], where it is marked that the challenge for the future is to develop approaches for multiscale multi-physics modeling considering coupling of fluid flow, heat transfer, species transport, electrochemical kinetics and also reforming kinetics (when hydrocarbon fuels are used).

In order to assign the degradation behaviour of a given cell with the final goal to predict its total lifetime in a justified manner, it is important to perform extensive testing and characterization which however, should give information about a specific part of it, or even a specific process. This should be performed at different operation conditions and transformed into a model. In this way the life time can be predicted for different operating conditions. The experimental data are also necessary for model validation. This requirement makes testing of different degradation sources more valuable when the experiments are performed in cell/stack level and the influence of the operating parameters registered for the SOC components. Electrochemical Impedance Spectroscopy is a powerful tool for this separation.

In [8] the long term testing on cell level combining electrochemical testing with post test analysis is performed for extracting information about the behaviour of the two electrodes at different temperatures and current density. The integrated result gives lower degradation rate at higher temperature, even at high current density. The extraction for the two electrodes shows domination of the cathode degradation at higher current density and lower temperature and of the anode – at higher temperature which brings to the conclusion that the anode degradation is less detrimental to the cell performance than the cathode one for a range of operating conditions. Similar approach (based on EIS) is applied in [79] for separation of the anode, cathode and electrolyte degradation as a function of the temperature, which, however, produces different side effects - introduction of other accelerated degradation processes as poisoning, carbon deposition etc., or enhanced temporal performance as improved contacts.

In [80] 180 durability tests for degradation studies of single components (electrodes and electrolyte) in cells as a function of the operating conditions (temperature, current density, steam in the fuel, fuel utilization) are performed. The separation is based on comparison of the ASR of pristine and degraded cell which is split on contributions from the different components. The dominating increase of the ASR is found to come from the fuel electrode which is strongly influenced by the overall steam content. The experiments in [81, 82] aim at selection of optimal operation profiles for accelerated stress tests.

In [83] the effect of hydrogen and air temperature on the temperature distribution in a planar SOFC with two architectures – anode supported and electrolyte supported, is examined with 2D mathematical model. For description of the temperature distribution, coupling of mass and energy transport phenomena with



electrochemistry is applied. The studied parameters are: hydrogen and air temperature values and cell geometry. The finite differences method is applied for numerical calculations of the equations governing the system. The temperature distribution in each domain of the SOFC is calculated by the 2D mathematical model. The results (predictions) give the temperature distribution, i.e. the different heat effect depending on the temperatures of the two gas flows. In [79, 83] simulations of the degradation caused by interconnect corrosion, loss of ionic conductivity, nickel particle growth, Cr contamination and formation of insulating phases on the cathode are performed. An electrochemical model [79] and a two-dimensional model of the cell and interconnection system are used. The conclusions are that the cathode largely contributes to the degradation. The local overpotential predominantly governs chromium contamination, which can promote the formation of insulating phases as operation proceeds. The local electronic current density has comparatively weak direct influence on the degradation. Qualitative agreement with experimental data from the literature is achieved, without dedicated adjustments of the parameters.

In [84] a physics-based procedure combining experiments and multi-physics numerical simulations is developed for overall analysis of SOFCs operational diagnostics and performance predictions. In this procedure, essential information for the fuel cell is extracted first by utilizing empirical polarization analysis in conjunction with experiments and refined by multi-physics numerical simulations via simultaneous analysis and calibration of polarization curve and impedance behaviour. The performance at different utilization cases and operating currents is also predicted to confirm the accuracy of the proposed model. It is demonstrated that, with the present electrochemical model, three air/fuel flow conditions are needed to produce a set of complete data for better understanding of the processes occurring within SOFCs. After calibration against button cell experiments, the methodology can be used to assess performance of planar cell without further calibration. The proposed methodology accelerates the calibration process and improves the efficiency of design and diagnostics.

Recently several higher-level modelling approaches are under investigation, which allows faster assessment of the complex phenomena causing macroscopic performance degradation. In [85] a lumped modelling approach (i.e. no spatial distribution of the main variables within the cells/stack is described) is used to develop a dynamic SOFC system model applied for diagnostic purposes. In [86] a Remaining Useful Lifetime (RUL) estimation algorithm based on fast modelling of physical degradation of the electrochemical surface area of a PEMFC is developed. Although related to a different technology, this work suitably describes the approach through which the development of a proper RUL estimator for real-time uses can be performed. Thus in [87] a control algorithm design to improve lifetime based on the RUL estimator described in the previous work is proposed. This approach helps linking the main variables affecting degradation for the definition of suitable control strategies.

Data driven approaches (i.e. black-box models) are also adopted, such as neural networks [88], multilinear regressions [89], and others. These works provide the modelling basis on which degradation models and, thus, lifetime prediction tools for performance model can be built.

For operational control diagnosis tools are developed to avoid premature degradation of the fuel cell. The main task of this fault diagnosis is to evaluate the deviation of the current state from the normal behaviour of the fuel cell, by detecting the hazardous states. The State of Health (SoH) has to be identified by diagnosing these faulty modes. To reach this goal, several stages have to be followed as: data acquisition, data treatment and fault detection. A correlation between degradation phenomena and fault detection has to be introduced for which the modelling approach can be used. In [69] a review on SOFC degradation phenomena and corresponding fault detection methodologies is given. An analysis of the gap in the literature is also performed. In [90, 91] a hybrid model (Multiple Model Prognostic Approach) that combines operational points databases with signal-based methods is introduced. It uses a specific structure, where a supervisor manages multiple sub models related to operation points or intervals and saves operation point/interval related data from the databases referring to the operation point model. The sub models have signal based



tools to analyse their data. They investigate the data and the change of operation. The supervisor uses the future current profile and the results of the operation point models to estimate the Remaining Useful Lifetime.

In [92] on-line experimental validation of a model-based diagnostic algorithm applied to a precommercial SOFC system is introduced. The proposed algorithm exploits a Fault Signature Matrix based on a Fault Tree Analysis and improved through fault simulations. The algorithm is characterized on the considered system and validated by means of experimental induction of faulty states in controlled conditions.

To summarize: The total degradation of the cell/stack operating at constant conditions can be presented as the sum of the contributions coming from the main components (electrodes, electrolyte, interconnect, their interfaces). In this configuration the degradation studies of the components are more accurate since they are closer to real operating conditions. However, a complication may come from correlation between different phenomena occurring in the system, i.e. some degradation processes and mechanisms may be interlinked which can hide the initial degradation source and mechanism. For this purpose, a big number of tests should be performed in different operating conditions. The analysis of the results from the literature shows that for reduction of the experimental volume and time an algorithm for elimination of the induced degradation caused by the connectivity of the cell/stack components performance is needed in addition to the accelerated testing. One possibility is the preliminary artificial aging of selected component which will ensure reliable information about the influence of its degradation on the total behaviour of the cell/stack in conditions of accelerated stress testing.

In respect to the predictive modelling of the complicated SOFC system a multiscale approach which combines microscale and macroscale modelling is necessary. Continuum electrochemical models can be used to determine the effect of various designs and operating parameters on the generated power, maximum cell temperature, fuel conversion efficiency, stresses caused by temperature gradients, effects of thermal expansion. For the electrode design and optimization microscale modelling is needed, since it will ensure information about the influence of the microstructure on the SOFC system performance.

2.4. Degradation studies and modelling approaches in recent FCH JU projects

This Section includes short summary of several FCH JU projects related to the topic of this review. They give a common vision of the goals, applied approaches and obtained results, which draws the pathway for further development, currently expected from AD ASTRA. The short descriptions are prepared by members of AD ASTRA that participated in the corresponding projects.

2.4.1. New all-European high-performance stack: design for mass production NELLHY (GA 621222) (info from ENEA)

This project combines European know-how in single cells, coatings, sealing, and stack design to produce a novel 1 kW SOFC stack of unprecedented performance, together with the proof of concept of a 10 kW SOFC stack. The main goal of the project is to optimize each specific key component or aspect of the production chain of SOFC stacks in order to achieve high efficiencies and high yield of productions while lowering the production cost.

Cell manufacturing and characterization

The development of single cell manufacturing processes was carried out, improving material formulations and modernizing equipment to achieve the lowest scrap rates possible maintaining the highest standards for cell quality, performance and reliability. Thus the project target of 95 % effective yield was achieved and surpassed, reaching 96 %. ENEA supported the cell development process by conceiving and realizing a highly



innovative set-up for locally resolved, in-depth, in-operando electrochemical characterization of produced cells.

Interconnect manufacturing and characterization

The design of the interconnect plate was improved, as well as tailored to selected mass-manufacturing processes. An incompatibility was found between the hydroforming process (which shapes the interconnects by high-pressure water moulding) and the interconnect material, which showed early-stage tarnishing due to the highly reactive cobalt in the coating. Extensive material combinations (of substrate and coating) with in-depth analysis of their behaviour in stack-relevant environment were investigated, leading to radical new insights (self-healing properties as well as unforeseen diffusion phenomena: the lower operating temperature of Elcogen stacks is favourable for the use of cheaper materials, but the formation of the passivation (oxide) layer on the interconnect air side is also slowed down, which ultimately worsens the resistance to corrosion if material combinations are not tailored carefully). Manufacturing line of interconnects was optimized achieving over 99 % yield rates. The bottleneck in this process however remains the welding of different layers of extremely thin, shaped plate, where 96 % of yield was nevertheless achieved, but process times are slow.

Three steel grades with increasing Cr content from 18 to 22 - 24 wt. % were tested in combination with the Sandvik Materials Technologies pre-coating Ce/Co technology. Both uncoated and Ce/Co coated steel samples were prepared and analysed. The steel grades used in the project and their chemical composition are reported in the following Table 1. To be noted that steel Outokumpu 4622 is not a commercial steel grade.

A special set-up for conducting the dual atmosphere exposure tests with multiple samples was designed and then realized by ENEA. In some cases, a conventional single fuel cell test system was also used for continuously monitoring the ASR during the dual atmosphere exposure. The tests were conducted at 650°C for up to 1000 h feeding the air-side of the samples with humid air (3 % H₂O). Two different fuel gases were used: humid hydrogen (3 % H₂O) and simulated syngas (5CH₄-5CO-27CO₂-18H₂-44H₂O). Temperature profile program used for the dual atmosphere tests is reported in Fig. 1 (left).

Breakaway oxidation with formation of thick hematite layers covering the entire sample surface was invariably observed on the air-side of the all uncoated steel grades, under both hydrogen or syngas fuel conditions. However, thicker hematite scales formed in presence of humid H₂ at the fuel-side, indicating that the 97H₂-3H₂O condition promotes a more aggressive and accelerated dual atm. effect on the steel interconnect degradation behaviour.

Fig. 1 (right) reports an example of XRD spectra of the air-side of uncoated Crofer 22 APU and K41/441 steel samples tested under hydrogen fuel gas condition. Absolute predominance of hematite phase present on both the steel surfaces is evident.

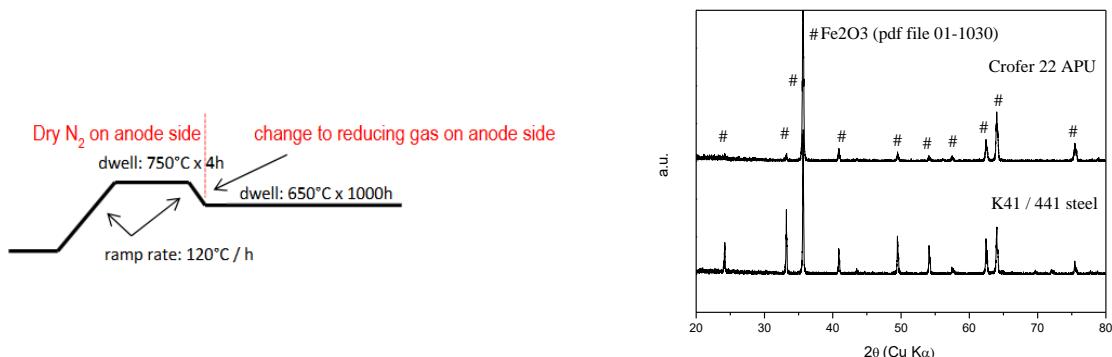


Fig. 1. Dual atmosphere tests (left) and XRD spectra (right) of the air-side of uncoated Crofer 22 APU and K41/441 steel samples tested under hydrogen fuel gas condition.



Evaluation of coated steel samples was performed using only the more aggressive 97H₂-3H₂O gas condition. Results indicated that Ce/Co coatings improved to a large extent the resistance to Fe breakaway corrosion allowing the formation of only sporadic Fe oxide nodule attacks. The positive barrier effect of the coating appeared to improve in combination with the Cr content of the underlying steel substrate. In fact, localized attack by Fe nodules was completely absent on the Ce/Co coated Crofer 22 APU steel, whereas several nodule attacks were found on the K41/441 steel sample. A few nodules, but less than in the case of K41/441 steel, were also observed on the surface of Outokumpu 4622 steel, which is the steel with an intermediate Cr content between K41/441 and Crofer 22 APU.

The chosen aggressive conditions allowed also to highlight the presence of some degradation effects also on the coated surface of Crofer 22 APU steel. The degradation consisted in an evident outward Fe diffusion through the Ce/Co coating suggesting thus the Cr content of the steel is an important factor that may retard the Fe nodule attack on Ce/Co coatings, but not avoiding it completely.

Seal manufacturing and characterization

A breakthrough sealing material was formulated, that combines the high-temperature resistance and excellent sealing properties. This new formulation, patented during the NELLHI project under the name CL87, has been successfully tested to assess different application means, including glass coating and design optimisation to reduce the number of manufacturing steps required as well as improve manageability of the finished, cut seals.

Finally, all the developments above were put together in the high-performance stack that gives the name to the project. This entailed much design optimisation of interconnects and seals, assembly and conditioning procedures, stack characterization protocol definitions and testing, deconvolution of the ultimate compound stack performance into the contributions of each component. Numerous stacks were tested in several conditions, yielding comprehensive data for the assessment of the progress achieved in the successive stack generations.

Stack manufacturing and characterization

Even though the objectives of NELLHY project were mostly related to the mass manufacturing optimization, several tests were carried out in order to assess the reliability of the produced stacks coming from the modified production chain. To reach this goal, stack durability for thermocycles was tested. Testing has been carried out in three phases: thermocycles down to 300°C (TC 1 - 5), thermocycles down to 50°C (TC 6 - 8), and complete removal of the stack from the test system (TC 9) and reinstallation, repeating phase 1 (TC 10 - 14). During the thermal cycles, a mixture of 1/1 H₂/N₂ was supplied to the anode while air was supplied to the cathode. Heating and cooling rates were 60 K/h. The leakage level and the polarization of the stack were tested after each thermal cycle. Test conditions for the polarization measurement were: fuel flow rate (H₂) = 0.52 IN/min/cell and (N₂) = 0.52 IN/min/cell, flow rate (air) = 2.2 IN/min/cell, furnace temperature = 650°C, current ramp rate = 1 A/min, maximum current 30 A. At 30 A, the stack voltage was let to stabilize for 60 min in order to determine degradation after which current was ramped back to 0 A. Stack voltage was allowed to stabilize after the polarization measurement for 60 min after which open circuit voltage was recorded in order to analyse the leakage level. The leakage level was calculated by using the Nernst equation which reveals the ratio between hydrogen and steam. As the leakage can be determined from the open circuit voltage and that is increasing during thermocycles, leakage value is decreasing in thermocycles. The leakage value was below 0.4 % during the 14 thermal cycles. The degradation was determined from the stack voltage measured at 30 A after each thermal cycle and then compared to the voltage before the thermal cycles that was 908 mV. After 10 thermal cycles, stack voltage was decreased 0.6 % compared to the initial value.

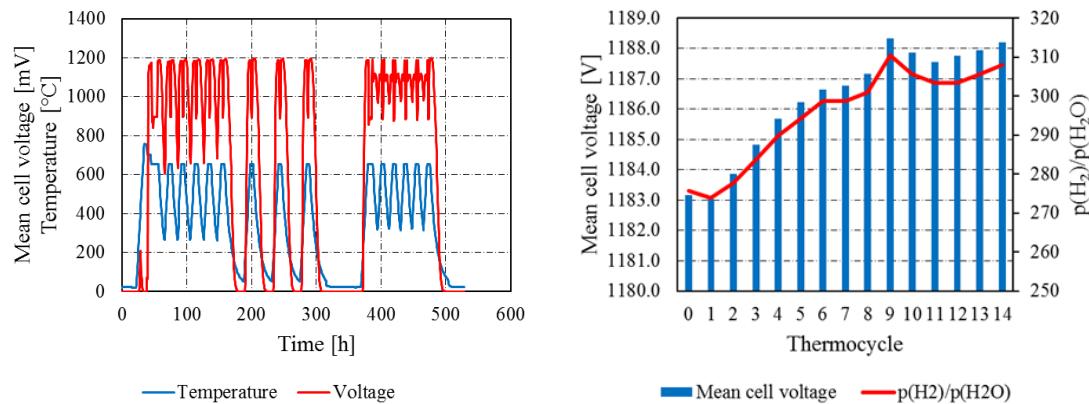


Fig. 2. Thermal cycle test (left), open circuit voltage and ratio of H₂ and H₂O in the anode as function of thermal cycles (right).

The durability of the stacks was tested for five different stack types, employing different combination of interconnect materials and coatings. Several thousand hour tests were conducted. Stack degradation was determined between 20 - 1100 hours as a linear fitting to the voltage data resulting in degradation value of 0.9 % /1000 hours. After a thermal cycle conducted at 1100 hours, voltage decay rate increased to 1.8 % /1000 hours for the remaining test period. Post mortem investigation showed that the measured degradation was mainly ascribable to modifications within the interconnect structure, pointing out the role of temperature, and its variations, as a key parameter to accelerate degradation phenomena.

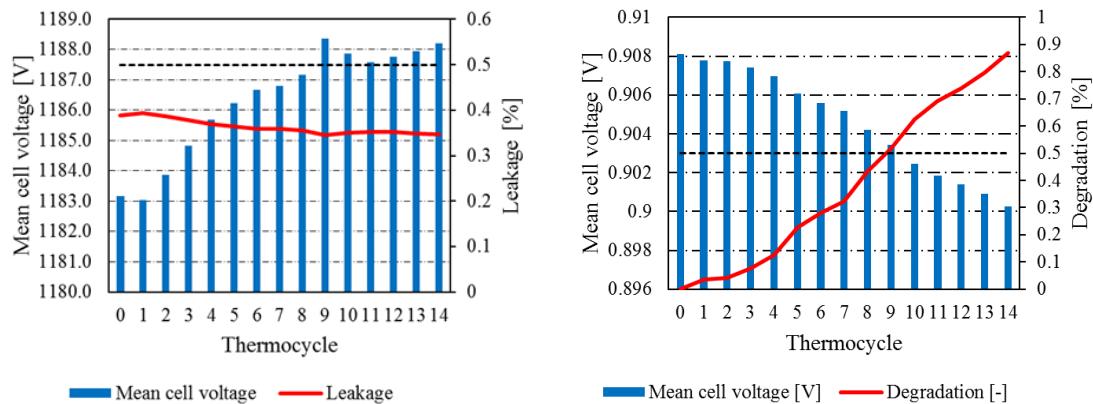


Fig. 3. Oxygen leakage to anode and open circuit voltage as function of thermal cycles (left), mean cell voltage and relative voltage change as a function of thermal cycles (right).

2.4.2. Increasing penetration of renewable power, alternative fuels and grid flexibility by cross-vector electrochemical processes BALANCE (GA 731224) (Info from ENEA)

The main goal of the BALANCE is to gather leading research centres in Europe in the domain of SOE and SOFC to collaborate and accelerate the development of European Reversible Solid Oxide Cell (RSOC) technology. To achieve this goal, the project foresees a number of activities concerning the improvement of RSOC overall system efficiency in both fuel cell and electrolysis modes, leading to the demonstration of a 6 kWe RSOC module with improved performances and enhanced durability.



Concerning the decrease of performances related to RSOC operation, the project has identified the principal degradation phenomena, mainly related to high current density operation, which causes severe damage at the air electrode/electrolyte interface related to high internal O₂ partial pressure, and thermomechanical stress due to the different thermal behaviour in SOFC (exothermic) and SOE (exothermic, thermoneutral or endothermic, depending on the operating point) modes, that in turn leads to a loss in the percolation of the Ni particles at the fuel electrode.

To tackle these issues, the project foresees the development of modified cells, with respect to standard Ni-YSZ/YSZ/CGO/LSC cells, where Ni based anodes will be replaced by titanate based anodes, with enhanced performances, and nanostructured infiltrated cathodes (Fig. 4, 5), that have demonstrated to be more resistant to the delamination phenomena related to the high current density operation in SOE mode.

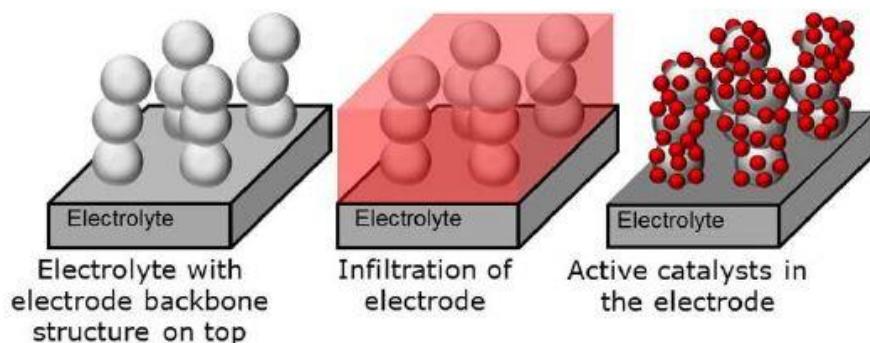


Fig. 4. Concept of infiltrated electrodes.

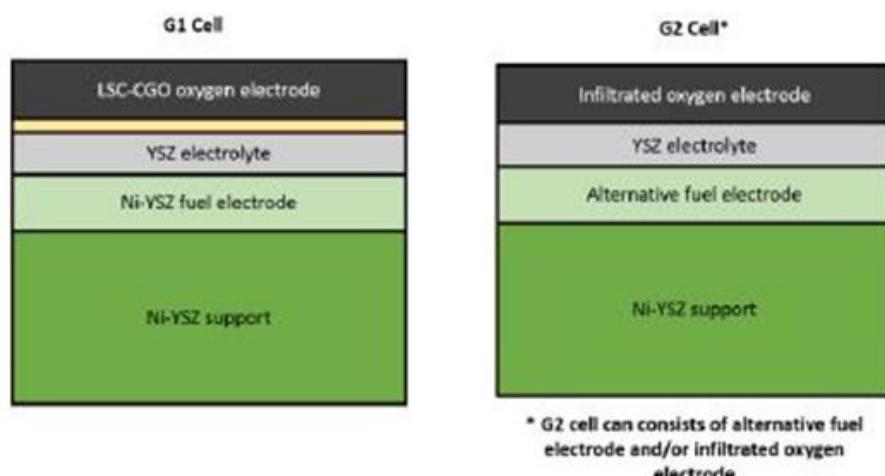


Fig. 5. SotA cells (G1) and optimised cells (G2).

The performances and the degradation rate, related to current density and temperature variations, will be addressed by means of the following experimental campaign (Fig. 6), which foresees several numbers of SOFC/SOEC cycles at different operating conditions, monitoring the performance and the degradation by means of polarization curves and electrochemical impedance spectroscopy.

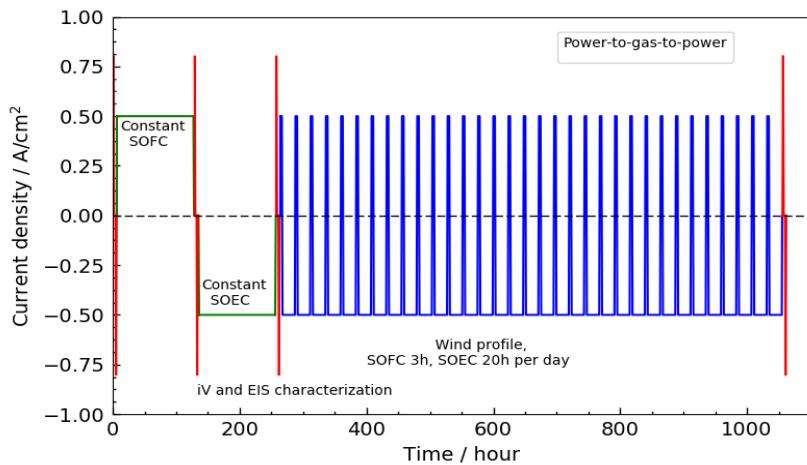


Fig. 6. Operating profile for cell testing.

The targets that the project aims to achieve are resumed in Table 1.

Table 1. BALANCE Targets.

Parameter	SotA	Project target
ASR on cell level	0.2 Ω·cm ² , 800°C in SOE, 1A/cm ² 0.15 Ω·cm ² , 800°C in SOFC	0.2 Ω·cm ² , 700°C in SOE, 1.25 A/cm ² 0.15 Ω·cm ² , 700°C in SOFC
Targeted temperature reduction and increased current density will be achieved by		
<ul style="list-style-type: none">Using alternative electrode materials and nanostructured electrodes.Strengthening the electrode-electrolyte interface using optimised cell architecture.		
Degradation rate	0.5 % /1000 h, 800°C in SOE, 1A/cm ² 0.5 %/1000 h, 800°C in SOFC	< 0.5 % /1000 h, 700°C in SOE, 1.25 A/cm ² < 0.5 %/1000 h, 700°C in SOFC
Improvements in the degradation rate will be realised by systematically addressing the identified critical test parameters and cell components that control the degradation phenomena.		

2.4.3. Enhanced Durability Materials for Advanced Stacks of New Solid Oxide Fuel Cells ENDURANCE (GA 621207) (Info from IEES)

The aim of ENDURANCE project is to contribute to an increased understanding and awareness of the degradation phenomena occurring in real SOFC stacks by: (i) descriptive and predictive models based on real experiments; (II) improvement/development of new materials; (iii) implementation of Failure Mode and Effect Analysis with data achieved from specifically detailed experiments.

Based on post mortem and electrochemical analysis of stacks with 15 000 h operation preliminary Failure Mode and Effect Analysis was performed with degree of importance of every degradation source. In the end of the project, based on the experimental results, the Analysis was updated. The implementation combined



experiments on both button cell, cell and stack level. Electrochemical methods (U/t; i/V curves and EIS), and a big number of characterization approaches, including 3D reconstructions by X-ray tomography, were used.

Thermo-electrochemical and mechanical models were developed for improving the understanding and prediction of SOFC stack degradation based on experimental results performed in the project. The model scales span from the characteristic size of the material phases in the electrodes to that of the stack. Both thermo-electrochemical and thermo-mechanical aspects were investigated. The developed frameworks were integrated, i.e. continuum micro-models developed for phenomena analyses were implemented in full details up to the stack scale.

The dynamic effects and Ni coarsening were studied using 3-D imaging (XNT and FIB-SEM/EDX serial sectioning). The evolution of all the electrode parameters such as the Triple Phase Boundaries lines (TPBIs) or the phase tortuosity factors were measured on the 3D volumes.

The microstructural analyses have shown that the Ni volume fraction remains unaffected by the operation confirming that the Ni volatilization followed by its condensation is very limited in the applied experimental conditions. Nevertheless, the Ni phase size distribution is shifted towards bigger particle diameters indicating a significant Ni coarsening upon operation. As expected, the process is associated to a significant loss of active TPBs. It is also correlated with a strong decrease of the Ni/gas specific surface area, while the one between Ni and YSZ is not changed upon operation. This result points out that the ceramic backbone limits the Ni sintering in the cermet preventing any massive Ni agglomeration to occur in operation. When considering similar conditions of steam partial pressure and current density, the rate of Ni coarsening is independent on the H₂ electrode polarization in fuel cell or electrolysis mode. However, the growth of the Ni particle size is thermally activated resulting in a higher material ageing at higher temperature.

In order to simulate the Ni agglomeration, a classical power-law sintering model was adjusted on the evolution of the mean particle size and density of TPB. A rather high exponent (n=8) was necessary to fit accurately the evolution of the microstructural parameters. Such value reflects the inhibiting effect of the YSZ backbone on the Ni sintering and could also be consistent with a mechanism controlled by surface diffusion. The adjusted law describing the TPB decrease over the time was implemented in multi-scale modelling framework to compute the loss in cell performances. The microstructural change in the H₂ electrode causes about 30% of the total degradation (experimentally observed) in fuel cell mode and about 20 - 25 % in electrolysis mode at 850°C after 1000 - 2000 h.

For the oxygen electrode, SEM-EDX, TEM-EDX, X-ray μfluorescence and μdiffraction techniques were employed to investigate the phase reactivity in the region of the CGO barrier layer. The characterizations have revealed that Sr diffusion across the barrier layer and formation of SrZrO₃ occur mainly during electrolysis operation, whereas the process is very limited in fuel cell mode. As a consequence in the tested conditions, LSCF destabilization does not participate to the degradation of cell performances during fuel cell operation. However, the SrZrO₃ formation, which was clearly highlighted after the electrolysis tests, could be related to the highest degradation rates recorded in this operating mode. The post-test analyses have also confirmed a diffusion and an accumulation of Co in the region of barrier layer which is concomitant with the formation of SrZrO₃. The formation of these Co-rich segregates in the porous structure of the barrier layer in contact with SrZrO₃ grains have been identified as cobalt-ferrite type compound.

A continuum model for LSCF-based electrode was developed to interpret the role of the cell operating mode on the LSCF destabilization mechanism. The computed distribution of vacancies within the electrode is strongly dependent on the electrode polarization. Under cathodic (anodic) current, the amount of vacancies in the perovskite is increased (decreased). Therefore, the deviation from stoichiometry tends to zero under anodic current, which drives the precipitation of SrO. This would explain why X-ray and 2-D electron microscopy show a formation of SrZrO₃ phase much more pronounced in SOEC mode than in SOFC mode. The detrimental effect of the SrZrO₃ inclusions on the conductivity of the YSZ/GDC interface was quantified



by 3-D time lapse finite-element transport analyses using FIB-SEM/EDX dataset. The quantitative morphological measurements of SrZrO₃ detected at the interface suggested a mild degradation during SOFC operation, though much less pronounced than in SOEC mode. The conductivity degradation due to the sole presence of the SrZrO₃ inclusions predicted by finite-element simulations remained also mild (linear relative increase reaching 4 % after 4700 h).

The continuum composite electrode models developed for analysis at the micro-scale were also coupled to CFD for thermo-electrochemical simulations of the SOLIDpower stack design. The developed degradation laws described above were complemented with semi-empirical relationships for the degradation of the YSZ electrolyte and anode scaffold from the literature, and metal interconnect (MIC) oxidation model. The degradation measured in short-stack testing could be captured. The capability of segmented-cell tests to access local information, i.e. evolution of the spatial distribution, allowed an in-depth examination of the model predictions. The anode degradation model based on percolation theory could predict the overall decrease in performance, but differences in the spatial evolution of the degradation were observed, showcasing potential improvements for the future.

Combining testing, characterization and modelling, improvements in the barrier layer (evaluated as critical by the Effect Analysis), were obtained. Several approaches for densification were tested – Pulsed Laser Deposition (PLD), highly active sintering aids and impregnation methods to further increase the density of screen printed layers. The best ones were proposed for introduction in the technology (PLD deposition of GDC and GDC doped with MgO).

New glass sealing with improved properties - composition with improved long-term behaviour during operation, with no pore formation, due to boron volatilization and formation of barium chromate that could give rise to spallation in respect to introduction of contaminations, was also developed. The thermal expansion coefficient of the glass was matching to the interconnect steel with good thermal stability at maximum SOFC operating temperature. The standard test procedure comprised ageing time, polarization test, and dual gas test on micro samples evaluated accordingly. The evaluations showed that the diffusion barrier made out of YSZ between metal and glass sealing could successfully prevent ion migration. Additionally, it was found that the wetting and, consequently, the adhesion of the glass on the YSZ coating/metal is better than on the non-coated metal. Thus, it is recommended to apply a barrier coating on the SOFC interconnect steel plate.

Original studies were devoted to the variety of interfaces in which the interconnect, its protective coating and the sealant were used. They reproduced the real conditions in the stack.

2.4.4. Steel Coatings for Reducing Degradation in SOFC SCORED2:0 (GA 325331) (Info from EPFL)

SCORED 2:0 aims to further elaborate on the production of coated steel components showing markedly improved properties with regard to chromium release, electrical resistivity and scale growth. The focus is on choosing optimised combinations of protective layer materials with different steel qualities (including low-cost options) and analysing the influence, practicality and cost of different methods of coating, as well as understanding which factors influence the efficacy of such coatings.

The short summary is focused on degradation issues from the interconnects materials.

Testing/characterization methods

The parameter used for evaluation of the degradation is the Area Specific Resistance (ASR) = (voltage difference/current applied).contact surface ($\Omega \cdot \text{cm}^2$)



- Area Specific Resistance

ASR is measured on small samples of 1 cm² contact area for 1000 hours at 700°C which was considered the least amount of time needed to achieve a stabilization of the measurements. The degradation of the samples was quantified comparing the ASR values at 1000 hours. The precise description of the method and the testing protocols are given in [93, 94]. All the combinations of interconnect materials tested are summarized in Table 2.

The results from ASR indicate that dense coatings, such as those deposited via Physical Vapor Deposition (PVD) or Atmospheric Plasma Spray (APS) provide the lowest ohmic losses and that small coating composition is relevant just if the coating is not dense.

The threshold to define an acceptable degradation value is set at 0.05 Ω.cm². Other results are reported in [95 - 97].

Table 2. List of material combinations tested as small samples in the FCH JU project SCORED2:0.

Coating Method	BATCH 1		BATCH 2		BATCH 3		BATCH 4		BATCH 5	
	Coating	Steel	Coating	Steel	Coating	Steel	Coating	Steel	Coating	Steel
ALD	MCO	Crof 22 H K41 SS HT		MCF	Crof 22 H K41 SS HT		Ce + MCO	Crof 22 H K41 SS HT		
					Crof 22 H K41 SS HT					
APS	MCO	K41 SS HT	SAME COATING COMPOSITIONS AS BATCH 1 WITH NITRIDED SUBSTRATES	MCF	Crof 22 H K41 SS HT		MCFC	Crof 22 H K41 SS HT		
					Crof 22 H K41 SS HT			Crof 22 H K41 SS HT		
PVD	MCO	K41 SS HT		MCF	Crof 22 H K41 SS HT		MCFC	Crof 22 H K41 SS HT		
					Crof 22 H K41 SS HT			Crof 22 H K41 SS HT		
WPS 1	MCO	K41 SS HT		MCF	Crof 22 H K41 SS HT		MCFC	Crof 22 H K41 SS HT		
					Crof 22 H K41 SS HT			Crof 22 H K41 SS HT		
WPS 2	MCO	K41 SS HT		MCF	Crof 22 H K41 SS HT		MCFC	Crof 22 H K41 SS HT		
					Crof 22 H K41 SS HT			Crof 22 H K41 SS HT		
PVD	CeCo	SS HT								

- Voltage degradation over time V(t) (V)

The measurements were performed on short stacks (6 single repeat units) containing different interconnects. Table 3 summarizes the types of interconnect tested.



Table 3. List of interconnect tested in the FCH JU project SCORED2:0.

	Steel substrate	Nitriding	Coating	Deposition tech.
STACK A	K41	NO	MCF	WPS
STACK A	K41	YES	MCO	WPS
STACK A	K41	NO	MCO	WPS
STACK B	K41	NO	MCF	APS
STACK B	K41	YES	MCO	APS
STACK B	K41	NO	MCO	WPS
STACK C	K41	NO	MCF	PVD
STACK C	K41	NO	MCO	PVD
STACK C	K41	NO	MCO	WPS

$$\text{The degradation} = [(\text{voltage}@10000\text{h} - \text{voltage}@1000\text{h})/\text{voltage}@1000\text{h}/9000 \text{ hours}] * 100 \quad (\% \text{ kh}^{-1})$$

The Single Repeating Unit (SRU) is considered successful if the degradation rates are below 0.5 %. In this case as well the SRU units PVD coating showed the best performances.

- SEM observations

Both the small samples that underwent ASR testing and the interconnects in the stack were embedded in resin, cut and polished in order to observe the cross sections. The main searched information was the amount of Cr that migrates from the steel substrate into the contacting perovskite material.

The degradation threshold was 1 at. % of chromium inside the perovskite materials, i.e. if in the contacting material the percentage of chromium found was more than 1 at. % the solution was considered not suitable for SOFC application. In this case as well, the PVD and APS coatings were always successful. On the other hand, the porous coatings succeeded if the sintering process had a reducing atmosphere step.

No accelerated testing was produced in the project.

Inputs regarding modeling

The modelling was performed by the University of Birmingham [98].

2.4.5. Generic Diagnosis Instrument for SOFC Systems (GA 245128) (Info from EIFER) GENIUS modelling

GENIUS is aiming at developing a generic diagnosis instrument for improving SOFC systems reliability in order to advance their commercial deployment. It is focused on introduction of specific diagnostic methods for determination the actual state of the stacks in real-time and optimization of the control actions and degradation prevention capabilities.



The residual based approach (the system is modelled from the experimental results and the residuals between experimental and predicted values are calculated) and the pattern recognition approach (indicators are extracted from the signal and directly classified according to their mathematical behaviour) were applied. Within the GENIUS project, grey box model, black box model, signal/pattern recognition based algorithms as well as classification model based on neural network were developed and tested on both small stack and real commercial systems, where modifications have been performed on the hardware for fault simulations. In the project, several stack and systems from VTT (Technical Research Centre of Finland), TopSoE, Hexis, Wärtsilä, EBZ have been characterized in order to provide data to develop and validate the algorithms.

For example, the European Institute for Energy Research (EIFER) performed test on the Galileo N1000 system manufactured by Hexis. Before the validation tests, two test rounds were carried out on the same system but the stack was replaced before starting the second round. The first round lasted for approximately 3200 hours and a complete Design of Experiment (DoE) test plan (21 operating conditions) was achieved, including EIS and polarization characterizations. The second test round also lasted around 3300 hours in the similar conditions than the first round except that 52 steady-state operating conditions were completed. Successively, for the diagnosis tool validation phase, a set of procedures was designed to experimentally mimic specific faults on the Hexis Galileo 1000N system, to study the system behaviour under specific fault conditions.

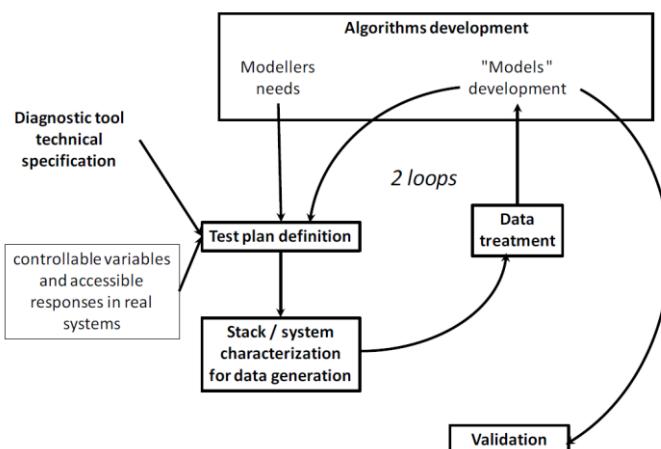


Fig. 7. GENIUS project structure.

Table 4 summarizes the different algorithms as well as the result from the different tests. In order to validate the most generic tool, three levels of validation were considered:

- "off-line" validation indicates that the validation is performed on data previously acquired that are split in two groups: one group for the model development and another for algorithm testing. The algorithm was not operated continuously with incoming data.
- "on-line ready" indicates that the algorithm is validated on previously acquired data which are fed continuously to it, simulating a continuous flow coming from a monitoring system. No interface with a monitoring system was done and tested on field.
- "on-line" indicates that the algorithm is tested during system operation with data coming from a monitoring system operating during the experiments.



Table 4. Synthesis of Algorithms and validation results.

		Data (Tester/manufacturer)						
Algorithms		Real SOFC	VTT / HTc	TopSoE	EIFER / Hexit	Wärtsilä	FC Lab in house	EBZ
FC Lab	K-means clustering	Off-line					Off-line	
	Bayesian networks		On-line ready				On-line ready	
	Wavelets		On-line ready				On-line ready	
UniGE	Data treatment tool	Off-line	Off-line		Off-line			Off-line
	Grey box model		Off-line	Off-line	On-line			On-line ready
UniSA	Data treatment tool	Off-line	Off-line	Off-line	Off-line	Off-line		Off-line
	Black box model		Off-line	Off-line	On-line	On-line		On-line ready

As it can be seen, the project resulted with a successful validation of several algorithms (Grey box model, Black box model) on at least two systems (Hexit, Wärtsilä) and of at least two algorithms on each SOFC-based system. Even if the implementation needs further customization by system manufacturers, the project validates the basis of the developed generic diagnostic approach on pre-commercial SOFC systems.

The results are published in [92, 99 - 104].

2.4.6. Green Industrial Hydrogen via Reversible High-Temperature Electrolysis GrInHY (GA 700300) (Info form EIFER)

GrInHy stands for green industrial hydrogen via reversible high-temperature electrolysis. The market area for such a system is in the industrial, mobility or energy sector where hydrogen applications can be combined with waste heat. Industrial hydrogen that is generated via high-temperature electrolysis replaces H₂ and partial carbon generated or extracted from fossil sources. Within this European project the aim is to integrate and validate, onsite of an iron and steel industry, one scalable module of 120 kW based on the Reversible Solid Oxide Cell technology, for the production of hydrogen via electrolysis and the production of electricity via the fuel cell technology.

GrinHy is mainly dedicated to take a large step towards improvement of maturity, scale and business cases related to the RSOC technology. Central element of GrInHy is the manufacturing, integration and operation of the worldwide most powerful reversible high temperature electrolyzer prototype at an integrated iron-and-steel works. Another focus is the technological improvement of robustness and durability on cell and stack level. During the operation of about 10 000 h in electrolysis, fuel cell or hot-standby mode, the prototype reached electrical efficiencies of 78 % LHV (without drying and compression) in electrolysis and 52 % LHV in fuel cell mode. In total, about 90 000 Nm³ of hydrogen were produced during electrolysis operation.

The GrInHy prototype demonstrates the technical feasibility of the integration of an RSOC system in an industrial environment as flexible load or power source. It is elaborated as an innovative technology that



contributes to the coupling of electrical sector using volatile Renewable Electricity Sources (RES) and chemical molecules (H_2 , natural gas), as chemical feedstock and for power generation.

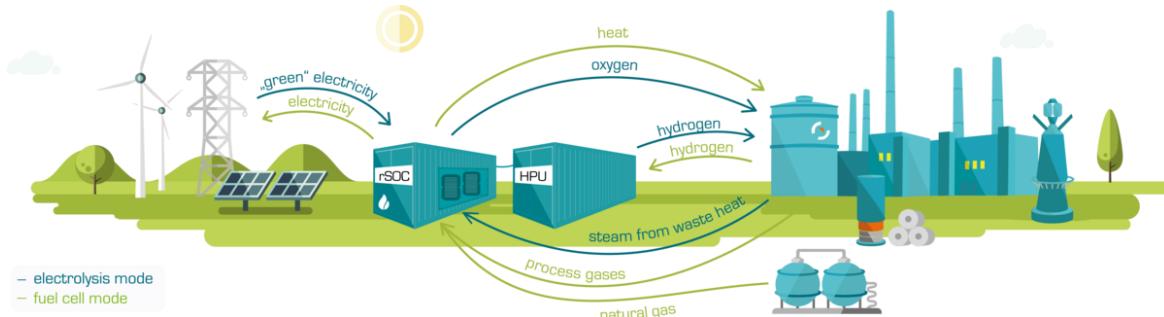


Fig. 7. The GrInHy concept.

The results are published in [105 - 110].

To summarize: The analysis of the FCH JU projects related to degradation monitoring and performance improvement frames the achievements, good practices, identified problems and ideas for improvement which is a good basis for the next steps – this which is expected from the implementation of AD ASTRA. A good synergy is observed between the projects. It is interesting to mark an increased attention on interconnects (NELLHY, ENDURANCE, SOFC SCORED2:0), on the interfaces where the electrochemical reactions take place, as well as on the operation in electrolysis mode (BALANCE, ENDURANCE, GrInHY). An efficient approach to start with already tested (several thousand hours) stacks subjected to post mortem analysis is introduced (ENDURANCE). Although a good combination between experimental and modelling is demonstrated (ENDURANCE, GENIUS), the summarized results illustrate the need for a step forward towards sophisticated stress test approaches and protocols and predictive modelling for state of health evaluation and life time prediction.



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4. ABBREVIATIONS

ALS	Adler Lane Steel
APS	Atmospheric Plasma Spray
ASR	Area Specific Resistance
AST	Accelerated Stress Tests
BALANCE	“Increasing penetration of renewable power, alternative fuels and grid flexibility by cross-vector electrochemical processes” Project
CGO	Gadolinium Doped Cerium Oxide
CFD	Computational fluid dynamics
DoE	Design of Experiments
DR	Degradation Rate
EIFER	European Institute for Energy Research
EIS	Electrochemical Impedance Spectroscopy
ENEA	Italian national agency for new technologies, energy and sustainable economic development
ENDURANCE	“Enhanced Durability Materials for Advanced Stacks of New Solid Oxide Fuel Cells” Project
EPFL	École Polytechnique Federale de Lausanne
FC	Fuel Cell
FCH JU	Fuel Cells and Hydrogen Joint Undertaking
FIB-SEM/EDX	Focused Ion Beam Scanning Electron Microscopy/Energy Dispersive X-ray
GDC	Gadolinium Doped Ceria
GENIUS	“Generic Diagnosis Instrument for SOFC Systems” Project
GrinHY	“Green Industrial Hydrogen via Reversible High-Temperature Electrolysis” Project
IEES	Institute of Electrochemistry and Energy Systems



LSM	(La,Sr)MnO ₃
LSCF	(La,Sr)(Co,Fe)O ₃
LHV	Low Heating Value
NELLHY	New all-European high-performance stack: design for mass production” Project
Ni-YSZ	Nickel-yttria stabilized zirconia
MIC	Metal Interconnect
MCFC	Molten Carbonate Fuel Cell
OCP	Open Circuit Potential
PEMFC	Proton-Exchange Membrane Fuel Cell
PLD	Pulsed Laser Deposition
PVD	Physical Vapor Deposition
RES	Renewable Electricity Sources
RSOC	Reversible Solid Oxide Cell
RUL	Remaining Useful Lifetime
SCORED 2:0	“Steel Coatings for Reducing Degradation in SOFC” Project
SEM	Scanning Electron Microscopy
SEM-WDX	Scanning Electron Microscopy - Wavelength Dispersive X-ray Spectroscopy
SOC	Solid Oxide Cells
SOE	Solid Oxide Electrolysis
SOEC	Solid Oxide Electrolyzer Cell
SOEL	Solid Oxide Electrolyzer
SOFC	Solid Oxide Fuel Cell
SoH	State of Health
SotA	State of the Art
SRU	Single Repeating Unit



STEM-EDX



Scanning Transmission Electron Microscopy-Energy Dispersive X-ray



TEM-EDX

Transmission Electron Microscopy-Energy Dispersive X-ray

TFBs

Triple Phase Boundaries

TPBIs

Triple Phase Boundaries Lines

TXM

Transmission X-ray Microscop

VTT

Technical Research Centre of Finland

XNT

X-ray Nanotomography

XRD

X-ray Powder Diffraction

YSZ

Yttria-Stabilized Zirconia