Modeling of Local Cell Degradation in Solid Oxide Fuel Cells: Cumulative Effect of Critical Operating Points

Zacharie Wuillemin, Antonin Faes, Stefan Diethelm, Arata Nakajo,
Nordahl Autissier, Jan Van herle, Daniel Favrat
Ecole Polytechnique Fédérale de Lausanne
Laboratoire d'Energétique Industrielle (LENI)
Station 9
CH-1015 Lausanne
Tel: +41-21-693 35 49
zacharie.wuillemin@epfl.ch

Abstract

A CFD model was developed to predict with accuracy the local electrochemical performance in an operating solid oxide fuel cell. A particular focus was given on the study of performance limitations and degradation sources caused by the design of the fuel cell, by the choice of materials and components, or by improper operating points.

The model is used to understand typical degradation effects observed on stacks tested in collaboration with HTCeramix - SOFCpower.

The model is able to predict several degradation effects caused by the use of compressive seal materials with remaining open porosity. Diffusion across seals is modeled, as well as the resulting parasitic combustion of air and fuel. The risk of local redox-cycling for the anode supported cell is evaluated locally, as well as an eventual local reduction of the cathode layers. The cracking of electrolyte caused by redox cycles is modeled locally, with increasing gas leakage at each cycle, allowing to model the cumulative effect of successive critical operating points.

The results are compared with experiments, showing an overall good agreement.

Introduction

The understanding of degradation sources and mechanisms is of key importance for the development of reliable solid oxide fuel cells. Experiments show the sensitivity of the degradation of solid oxide fuel cells on operating conditions, presence of pollutants, polarization, thermomechanical stress, etc. The design of the repeat-element or stack, the choice of materials, the gas supply, and the operating conditions are of key importance to allow optimal operation of the fuel cell, as well as to ensure an acceptable lifetime and reliability.

CFD models are commonly used in the design phase of a fuel cell to dimension and design the gas manifolds, in order to ensure an homogeneous gas feed and an optimal electrochemical reaction. But they can be extended to predict local degradation processes in the design phase, an also give an assessment of possible degradation mechanisms when comparing results to experimental data. The goal of the presented developments is to get a better understanding of degradation sources, in terms of stack design, choice of materials, and operating points.

Recent results [1] have shown that this CFD model is able to predict several degradation effects caused by the use of compressive seal materials with remaining open porosity and the resulting diffusive mass transport across seals. In particular, the model is able to predict the location of a nickel reoxidation frontier on the cell in the vicinity of the seals, frontier which moves depending on the gas mixture used or on the operating point. The displacement of this reoxidation frontier produces local redox cycling, which is critical in particular for anode supported cells [2].

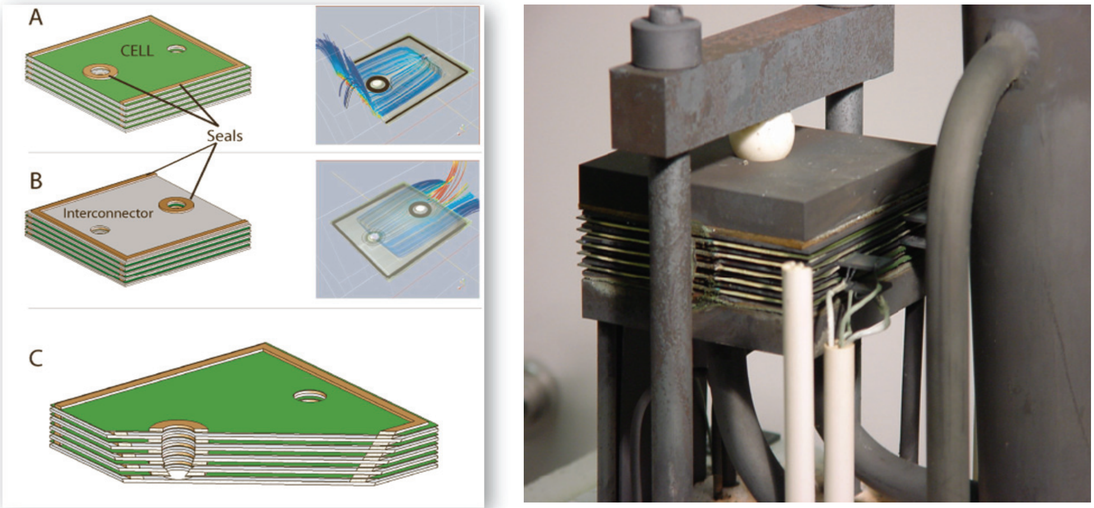
The effect of local redox-cycling on anode-supported cells was therefore investigated by scanning-electron microscopy (SEM). Samples were exposed to successive redox-cycles and observed. Micro-cracks were detected on the surface of the electrolyte, even after partial oxidation, their size and density increasing with the number of redox-cycles.
As the emergence of micro-cracks is not always accompanied by a complete failure of the anode support, the effect of such micro-cracks on cell performance and durability was studied.

A micro-model of the anode was developed to predict the effect on local electrochemical performance. The CFD model was consequently adapted to predict the effect of increasing crack density on the repeat-element. With a recording of the local redox-events on the cell, it is able to show the increasing damage on the cell resulting from the history of an experiment, not only on anode side, but also on cathode side where the electrode is damaged.

Results are presented thereafter on experimental observations and on their comparison to the modelling predictions.

Experimental Work

Experiments on stacks



HTceramix' R-Design stack
A: anode side. B. cathode side. C: stack assembly

Figure 1 : HTceramix's R-design. Detail of the gas manifold and seals.

In collaboration with HTceramix-SOFCpower, SOFC stacks and repeat-elements have been tested and analysed. Based on the experience gained on HTceramix's reference design (called 'R-design'), two new stack designs were developed with use of modelling tools to enhance reliability and performance.
While the R-design stack is limited to a 250W_{el} output (16 repeat-units), the new 'S-design' is able to reach a 1kW_{el} output with 72 repeat-units of the same active-area. The latest design, developed for the FP6 European Project 'FlameSOFC', aims to reach a power output of 2.5kW_{el}. It was conceived to avoid the problems described above, with use of the CFD model presented here.

The present work focuses on the 'R-design'. It is based on planar anode-supported cells of 50cm^2 pressed between metallic interconnects on which compressive seals are placed. The gas diffusion layers (GDL) are made of SOFConnex^{TM} material. The gas supply is made internally, through holes in the cells (Figure 1), in a counter-flow arrangement. The seal system is made of internal seals around the gas supplies, and of lateral seals on three of the repeat-element sides. With the design option of open post-combustion, the non-converted fuel is burned directly at the stack periphery.

The seals are made of compressive materials such as mica paper. On the sides, the cell is pressed between the anode and cathode seal, which means that the edges of the cell are exposed to the oxidizing atmosphere around the stack. Diffusion occurs through the seal, causing a local parasitic combustion. A redox-frontier exists therefore on the cell at this place. Moreover, the models have shown that this frontier moves depending on the adjacent fuel composition [1], and hence on the fuel utilization (FU). It results in cracks at the edges of the cells, and finally often to failure.

In numerous experiments, a permanent decay in OCV and in performance was observed after polarization cycles (iV-characterizations), as shown in Figure 2. It was therefore of interest to clarify their cause, to investigate the limitations of this particular stack design, and also to define safe operating points for the stack.

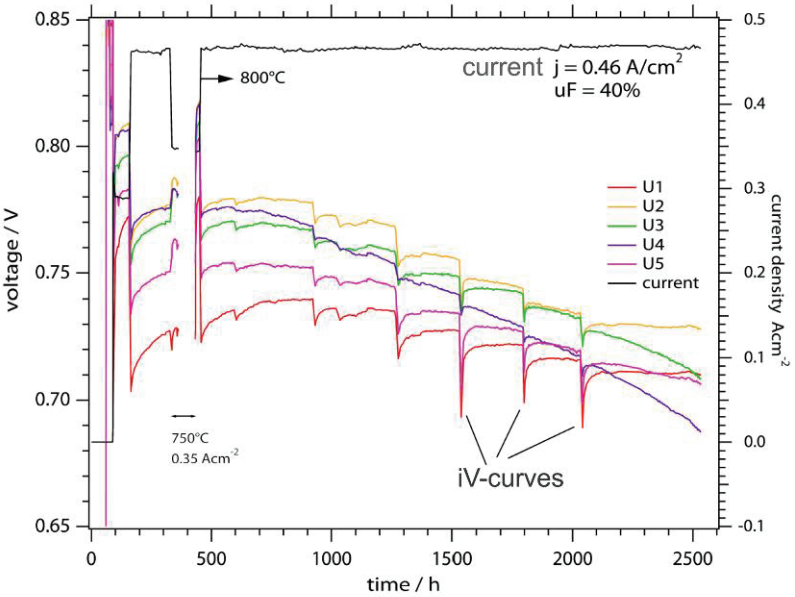


Figure 2: Drop in performance after iV-characterizations

Investigations on redox-cycling by SEM

To investigate the effects of local redox-cycling on cells, samples were reduced and oxidized several times and at various temperatures. In addition, post-experiment analyses were performed on cell edges that had been damaged during stack operation.
The microstructure of a damaged cell edge is shown in Figure 3.

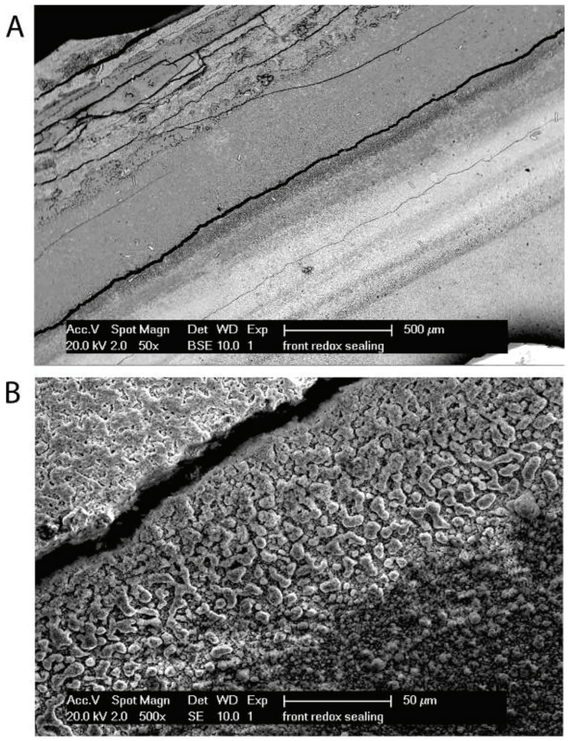


Figure 3: damaged cell edge after operation. A) Parallel cracks of the anode support B) detail of sintered microstructure

The anode support is cracked in a direction parallel to the cell edge. Details of the microstructure on the surface show sintered nickel particles due to the local post-combustion.

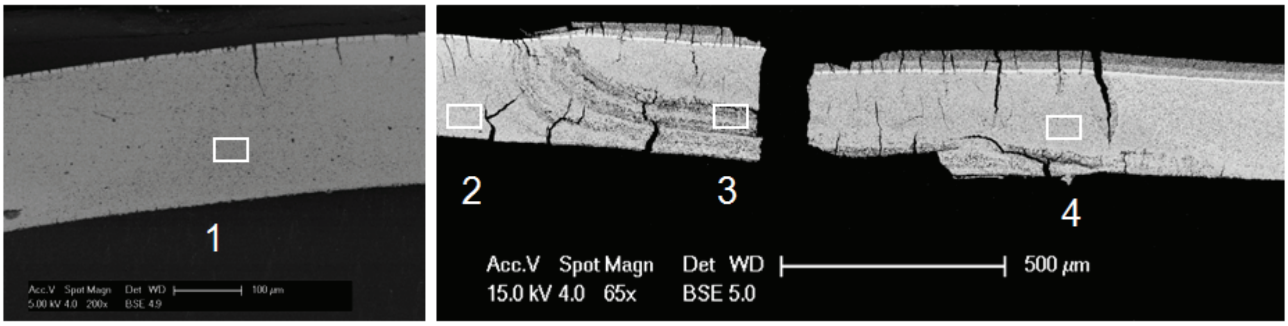
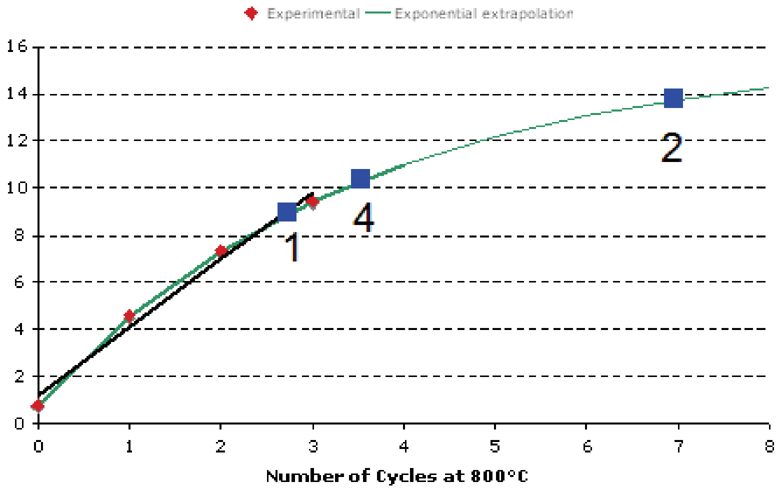


Figure 4: Cross section of a damaged cell edge located under a seal

Figure 4 shows a cross-section of a damaged anode-support situated under a seal. Large cracks are present in the anode support. A porous microstructure is visible in a layered arrangement, probably resulting from parasitic combustion in the anode support itself. The picture also shows the cracking of the electrolyte, propagating across the cathode and current collection layers.

In a previous study, Faes et al. estimated the local porosity at the points marked in Figure 4 by image processing. A relation was established between the porosity of the damaged anode support and the number of local redox-cycles (Figure 5).



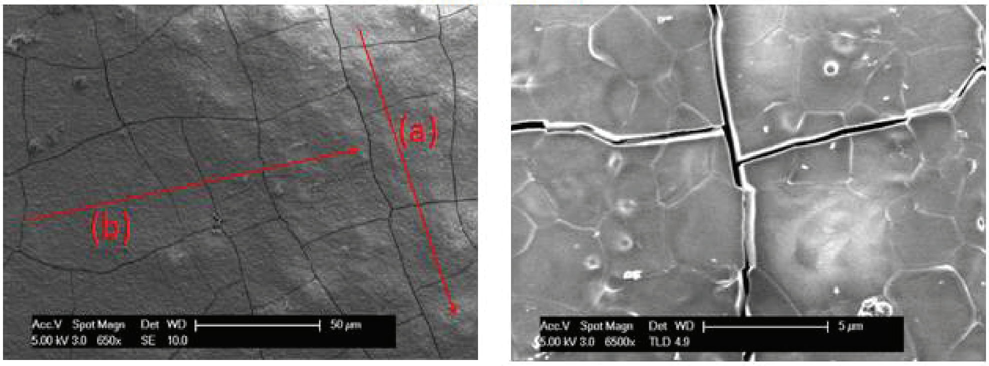
$$p(N) = p_{\max}\left(1 - Exp\left(-\frac{N}{\tau}\right)\right) + p_0$$

p_{max}: porosity maximum
p_0: initial porosity
N: number of RedOx cycles
τ: exponential constant

Figure 5: Relation between number of redox-cycles and porosity(%)

The surface of the electrolyte was observed after reoxidation at various temperatures (Figure 6), allowing to measure the fractured surface, as well as the width of the cracks.

Oxidation at 800°C



Oxidation at 1000°C

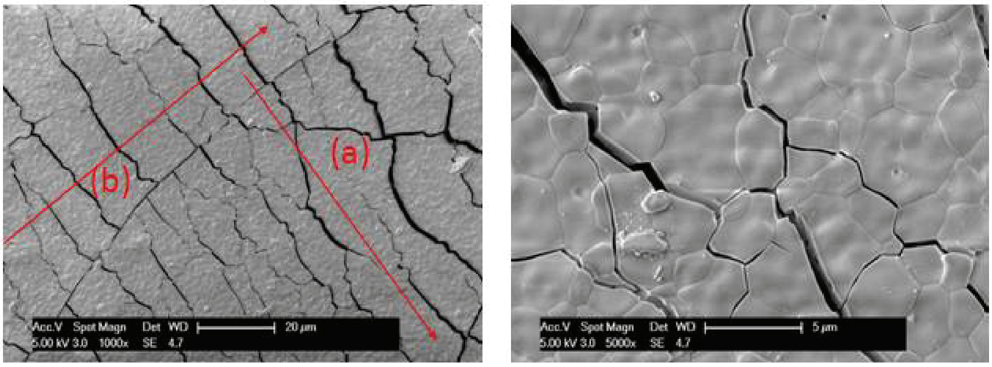


Figure 6: Microcracks in the electroylte surface after redox-cycles

Modelling of cracked electrolyte

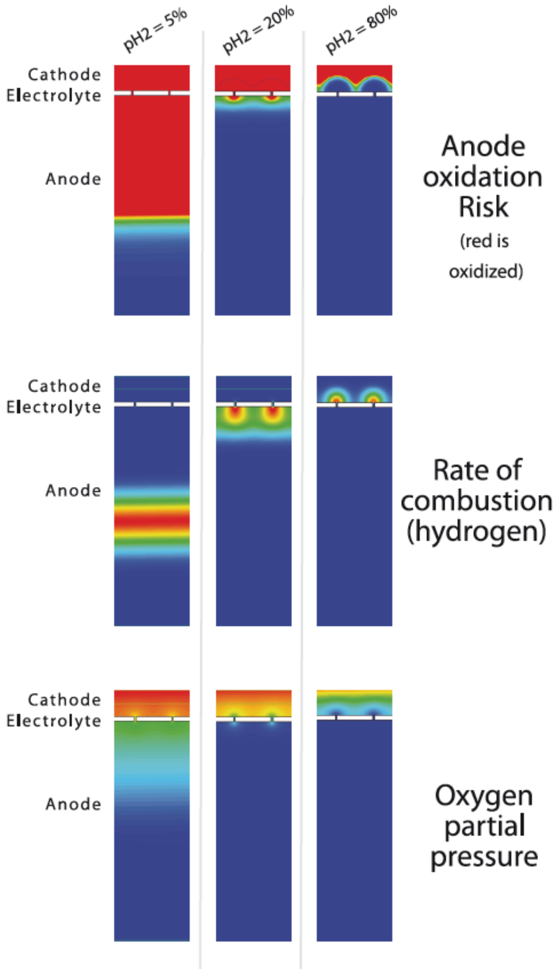


Figure 7: Micromodel of a cell with cracked electrolyte under varying fuel composition. (Top) Risk of oxidation of anode support. (Middle) Rate of combustion. (Bottom) Oxygen partial pressure

In order to understand the effect of micro-cracks in the electrolyte on the local electrochemical behaviour, a model was developed that allows to study the diffusion of oxidant and fuel through the electrodes resulting in parasitic combustion. The model was established in 2-dimensions, but respecting the ratio of crack area over total area of the electrolyte observed experimentally.

As the anode support is exposed to varying fuel compositions, which is particularly true near the seals and under varying fuel utilizations, the effect of fuel composition was studied. An example is given for a hydrogen-steam mixture on fuel side (Figure 7), with cracks of 2 microns width in the electrolyte.

The model shows the zone where the anode support should be exposed to oxidizing atmosphere at various hydrogen partial pressures (Figure 7, top).

Below 20% H_2 , the anode support is oxidized under the electrolyte, which should disable the electrochemical reaction. Combustion of hydrogen and oxygen occurs in the anode support, which corresponds to the porous layers observed in Figure 4.

Above 20% H_2, the model predicts that the combustion front reaches the electrolyte, passing on cathode side and starting to reduce the cathode layers. At 80% H_2, the cathode layer is completely exposed to reducing atmosphere, with additional degradation due to parasitic combustion.

Even if the values may vary depending on the properties of the porous electrodes and on the density of cracks, the model allows to illustrate the process occurring in such areas. From the model, it can be concluded that, once the electrolyte is cracked and for most of the fuel compositions, either the anode is being re-oxidized under the electrolyte, or the cathode is exposed to a reducing atmosphere. In both cases, the electrochemical reaction should be highly affected.

As it is not possible to solve this micro-model over the whole cell area in a repeat-unit model, a simplified model is established. As it is known from experiments that cracking of the electrolyte occurs at the first redox-cycle, the electrochemical reaction is therefore simply disabled after the first local redox-cycle. In addition, a leakage flux is computed, which depends on the above mentioned function that links the porosity of the anode to the number of local redox-cycles registered by the model.

The CFD model

The base of the CFD model has been described in earlier studies [1, 3]. It is written for the FLUENT^{TM} solver, with an electrochemical model developed in house. The electrochemical model was fitted by Nakajo et al. on experimental data [4] for a wide range of operating conditions. The current density is computed as a function of the local Nernst potential, cell potential, temperature, oxidant and fuel composition.

Modelling of the seal materials

The seals are modelled as a porous medium in which multi-component diffusion occurs. The Darcy coefficient of the seal material, which determines the pressure-driven mass transport in the seals, is determined experimentally. The porosity and tortuosity of the seals, which are difficult to determine for compressive seals,are adapted to match the open circuit voltage obtained experimentally, as this value is particularly sensitive to the steam partial pressure and hence to leaks. This method has shown correct predictions in previous studies [1].

Parasitic combustion

A single repeat-unit of HTceramix' R-design stack is modelled, including its surroundings where open post-combustion is also modelled (Figure 8). Combustion is modelled with simple Arrhenius kinetics.

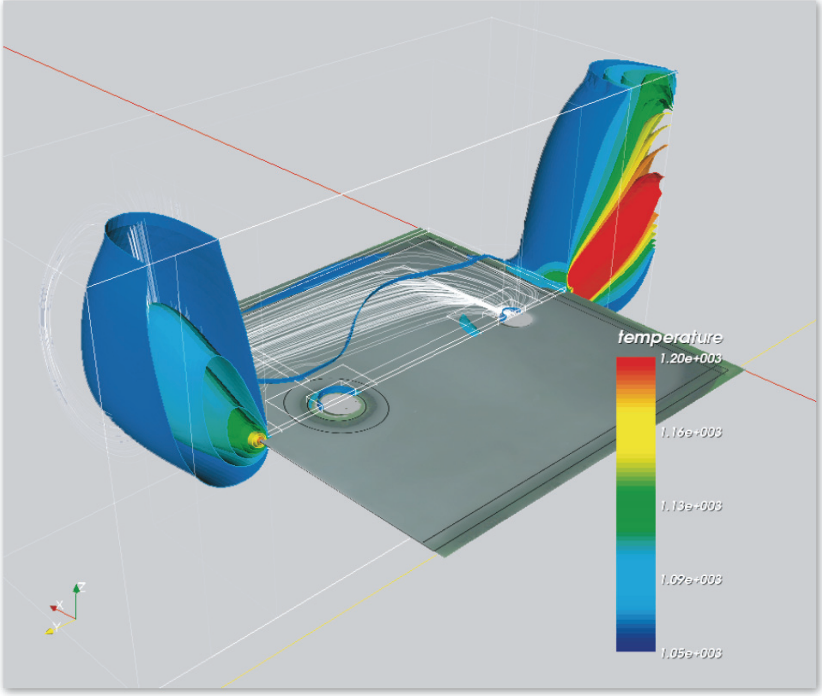


Figure 8: Picture of the modelled repeat-unit. Picture of a cell with combustion around the stack. Left: postcombustion at the fuel outlet. Right: parasitic combustion through a seal near the fuel inelt.

Modelling of anode re-oxidation

The model computes the local gas composition and current density over the anode, as a function of the desired operating point. Figure 9 shows the typical distribution of hydrogen under polarization. In the corners near the fuel inlet, depleted areas are apparent, as well as low partial pressures along the lateral seals.

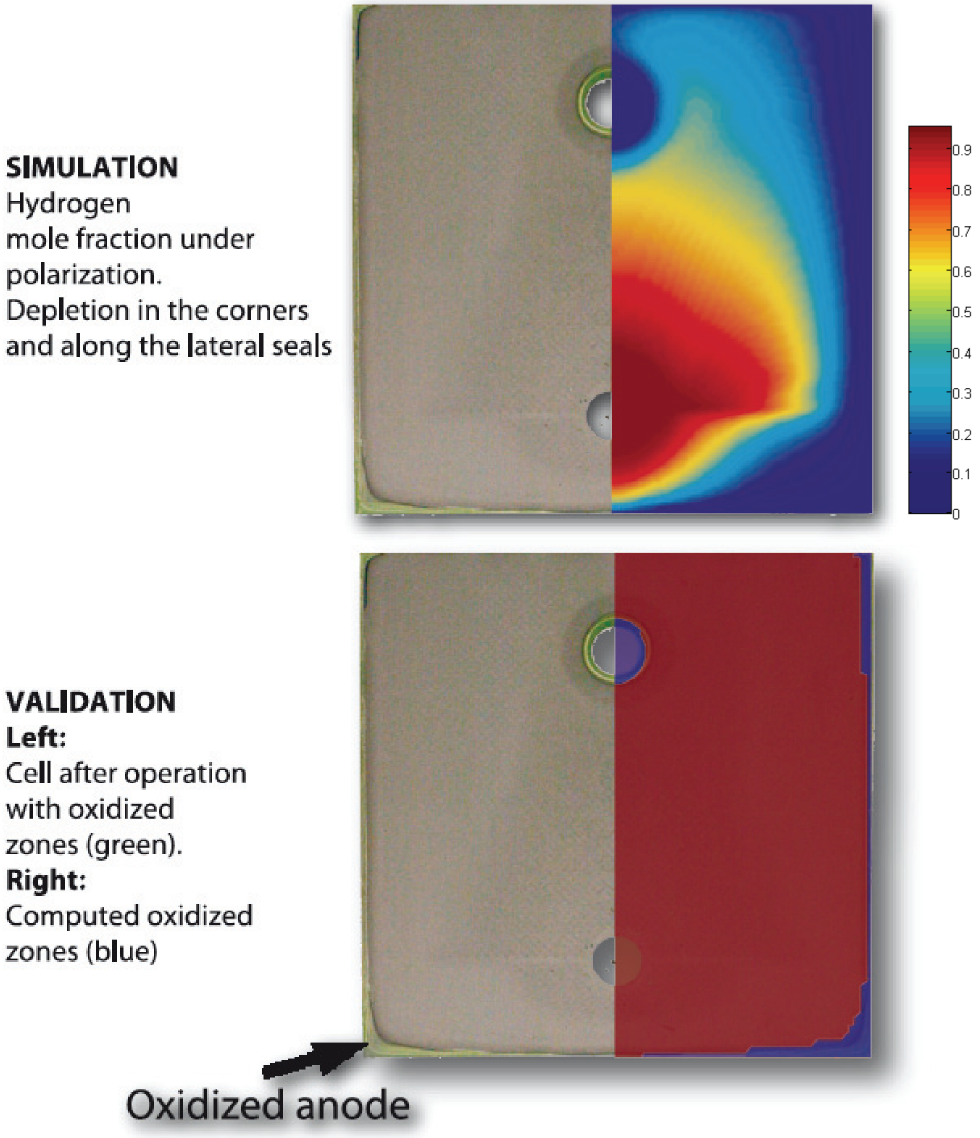
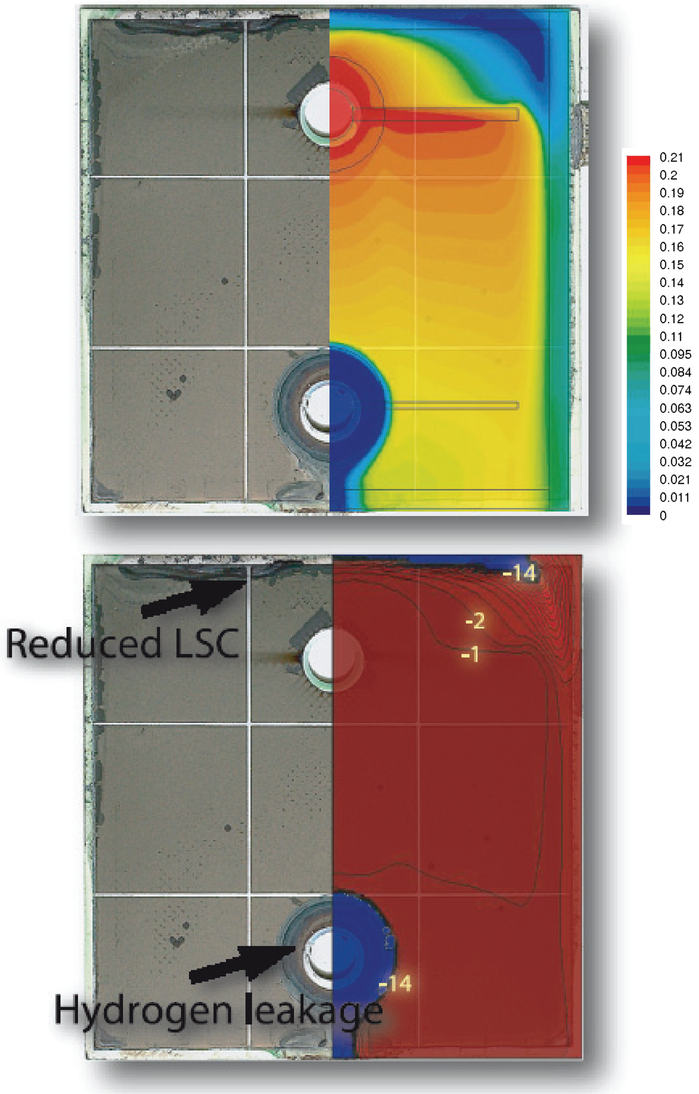


Figure 9: Top: Computed mole fraction of hydrogen at 40% fuel utilization.
Bottom: computed reduced (red) and oxidized area (blue) and picture of a cell after operation.

From the local gas composition, the equilibrium partial pressure of oxygen is computed, and compared to the equilibrium partial pressure for the re-oxidation of nickel. If the pO_2 in the gas mixture exceeds the equilibrium partial pressure over the nickel, oxidation of the latter will start. The concerned areas are plotted in Figure 9 (bottom), where the predicted oxidized area is indicated in blue. The comparison with a picture of a cell after operation, where the oxidized cell edges have a green colour, shows an excellent agreement between model and experiment.

Modelling of cathode reduction

From thermodynamic data, the equilibrium partial pressure for cathode reduction can be computed. In particular, HTceramix uses a LSC cathode current collection layers due to its high electronic conductivity, a material which is more easily reduced than other cathode materials. The affected areas are depicted below.



SIMULATION
Oxygen mole fraction
under polarization
on cathode side:
depleted areas
in the corners
and under the seals

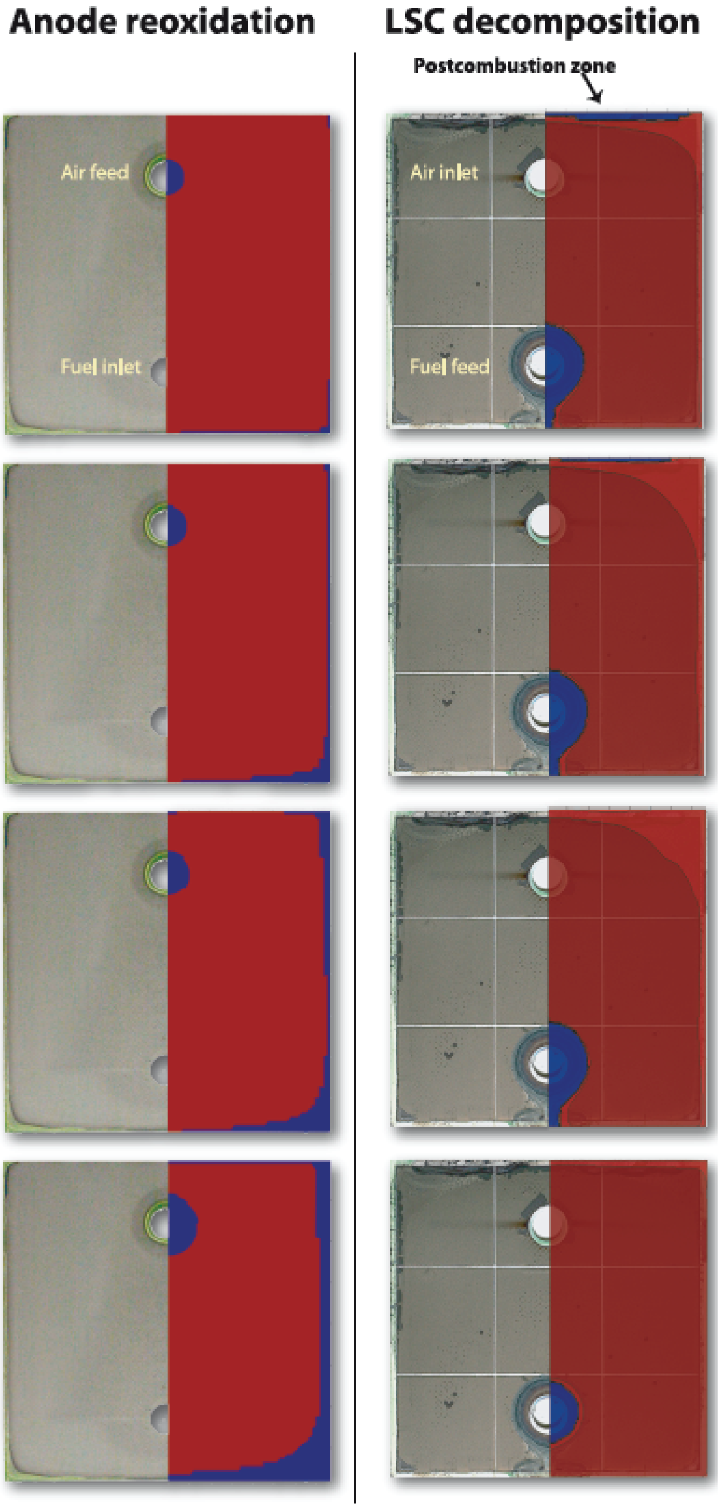
VALIDATION
Left:
Damaged cell after operation
Right:
Field of log (pO2).
Zones where
pO2 < 1E-14 (blue)
match degraded areas

Figure 10: Simulation of oxygen partial pressure on cathode side (top).
Bottom: comparison between predicted and observed reduction of the cathode material

The oxygen partial pressure is computed over the cathode. Depleted areas are observed in the corners near the air inlet. Across the lateral seal placed behind the air inlet, postcombustion of fuel occurs, exposing the cell to reducing conditions. As hydrogen diffuses easily, parasitic combustion occurs in the seals, leading to a degradation of the cathode in the vicinity. In Figure 10 (bottom), the predicted reduced areas are indicated in blue. The comparison with a cell after operation shows good agreement between model and experiment.

Critical operating phases

As the model is able to predict local anode and cathode reduction, it can be used to investigate which phases of the stack operation are critical for the reliability of the stack. Examples are given below.



OCV (6 SMLPM/cm^2, 800°C): At OCV, the corners of the anode support are already oxidized. The hole for air feed presents a ring of oxidation under the seal. On air side, large affected areas in the vicinity of the postcombustion zone and around the fuel supply

40% FU (6 SMLPM/cm^2, 800°C): Anode: Oxidized areas increase in the corners and near the air supply. Cathode side: lower effect of the postcombustion.

60% FU (6 SMLPM/cm^2, 800°C): Anode: Oxidized areas increase along the lateral seals. Corners are heavily affected. Cathode side: no more effect of the postcombustion.

Thermal cycle (4 SMLPM/cm^2, 600°C): During thermal cycles, the fuel flux is lowered and diluted. Anode: large oxidized areas in the corners and near the air supply.

Figure 11: affected areas under specific operating conditions

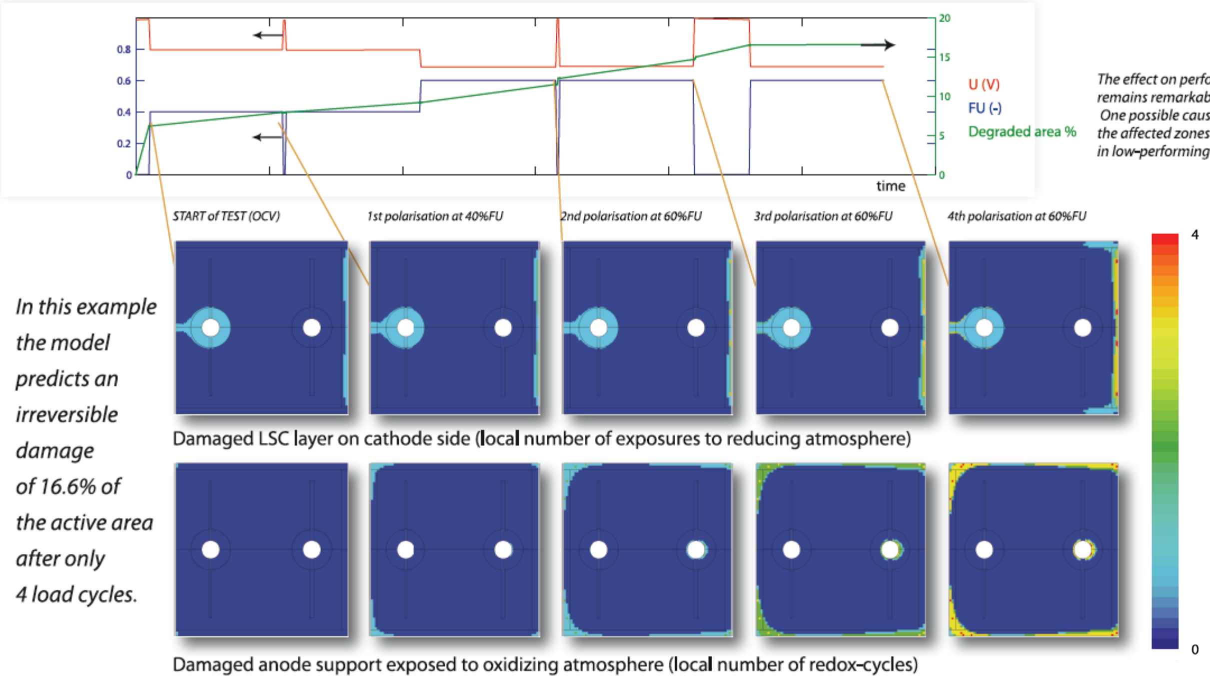
The here presented pictures show the instantaneous effect of degradation phenomena, not taking into account the cumulative effect of successive operating points.

Cumulative effect of critical operating phases

As developed above, the successive exposition of the anode support to oxidizing conditions causes a deactivation of the local electrochemical reaction, as well as an increase in leakage through the cracked electrolyte. With an increasing anode porosity and crack density with each local redox cycle, a cumulative effect appears, which has an incidence both on cathode and anode side.

As an example, a series of 4 successive load cycles is modelled, first up to 40% fuel utilization, and then three times to 60% fuel utilization. In Figure 12, the affected areas are indicated by color changes depending on the number of local reoxidations (anode) or reductions (cathode). Interestingly, it shows that the degraded area increases with the number of cycles, with areas cumulating the damaging cycles.

Simulated increase in degraded area during a complete test. Effect of test history on degradation.



The effect on performance remains remarkably low. One possible cause is that the affected zones are located in low-performing areas.

In this example the model predicts an irreversible damage of 16.6% of the active area after only 4 load cycles.

Damaged LSC layer on cathode side (local number of exposures to reducing atmosphere)

Damaged anode support exposed to oxidizing atmosphere (local number of redox-cycles)

Figure 12: Increasing damage on cathode and anode side by successive load cycles.

This increase in damaged areas can explain the successive drops in performance reported in Figure 2, as well as the presence of highly damaged cells at these locations after operation. In addition, it can partly explain the observed losses in performance accompanying thermal cycles with this design, due to the large oxidizing areas on anode side under diluted fuel mixtures.

This result shows the limits of this particular stack design, for which a polarisation to even 60% fuel utilization can be considered as critical. It is evident that a large number of local redox-cycles would finally lead to a failure of an anode-supported cell, at least with the present cell technology.

Conclusion

The combined experimental knowledge and CFD simulation has allowed to describe and understand with precision some of the damages observed on a specific stack design. Using detailed experimental observations, our CFD model was completed to predict local redox-cycling of the anode, as well as local reduction of the cathode in some areas. A cumulative effect of critical operating points was demonstrated, with increasing damage and risk of failure.

As a conclusion for experimental degradation studies, it shows the importance on the overall degradation of critical operating points, in particular during transients such as thermal cycles. It also helps to define constraints in the stack design to ensure a safer operation, and also to define operating constraints on system level, in order to ensure a proper lifetime of the stack.

Acknowledgements

The authors would like to thank all persons who actively participated to this prject, both at EPFL and at HTceramix - SOFCpower. Sincere thanks also to the FP6 European Project 'RealSOFC' (SUSDEV-CE6-502612) and to the Swiss National Science Foundation (SNF n°200020-109-643) for funding.

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