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

SOF-CH

Final Report EPFL-LENI 2007: **WP 5.1**: THERMO-MECHANICS

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Summary

The solid oxide fuel cell (SOFC) is a direct conversion process, which allows the production of electricity with high efficiency while maintaining pollutant emissions at low level. This technology is now far beyond the theoretical status, but extensive commercialization is not yet attractive. The main challenges to face are cost reduction, lifetime, reliability and volumetric power densities. Typical issues are the degradation rate of the performance during steady operation and the risk of failure during controlled or emergency shut-ups/start-ups. Post mortem analysis shows that the mechanical integrity of the cells is often not ensured.

Modelling of the thermo-electro-chemical behaviour of an intact or partially damaged SOFC stack is required to predict and reduce the degradation. The influence of small-scale defects and microstructural changes increases with respect to time and the number of thermal and loading cycles. A multiscale approach is suited to understand and characterize the phenomena at the membrane electrode assembly (MEA) level and study their impact and propagation at the repeat element (RE) level. Once critical conditions are identified, a control strategy is required to ensure the safe operation of an aging stack during both steady and transient operation.

1. State of the research

The above mentioned topics cover overlapping research areas: identification of the electrochemical phenomena which starts at the smallest up to the repeat element level, control strategy which dominates the research at the system scale and the few structural analyses which are conducted at the repeat element level [1]-[3]. Precise experiments are mainly carried out on electrochemical tests and repeat elements, whereas data from well-instrumented stacks are difficult to find.

From thermo-electro-chemical models of electrodes to system modeling

The mechanisms and kinetics of SOFC electrodes on YSZ electrolytes have been extensively studied. Electrochemical impedance spectroscopy (EIS), combined with observations with advanced microscropy, e.g. SEM, TEM, XPS, are used.

Experiments on composite cathodes or samples of dedicated geometry, such as point electrodes, are carried out to gain knowledge about the oxygen reduction mechanisms [5]-[7]. The emphasis is on the LSM-YSZ system. An equivalent circuit approach is often used: the curves obtained from EIS experiments are reported in the Nyquist diagram and fitted to serve as a basis for the understanding. SEM observations allow identifying parasitic phases and assessing the triple phase boundary (TPB) length. Researchers propose several models, considering different sequences and rate-limiting steps [8]-[10]. A consensus on the rate-limiting processes has not yet clearly appeared. On the cathode side, explanations involve the following mechanisms, with variation of the concerned species, depending on authors:

- Oxygen adsorption
- Oxygen dissociation
- Surface diffusion
- Bulk diffusion
- Charge transfer

On the anode side a study of different reaction pathways was performed: oxygen spillover from YSZ to Ni, hydrogen spillover from Ni to YSZ, interstitial hydrogen transfer via surface adsorption [11]. Efforts are mainly turned towards the case of hydrogen as fuel.

Refined modeling – so called μ-modeling- is also carried out, mostly focused on the cathode [8][9][13][14]. The field equations are solved to compute the distribution of potential and current in the electrode. One-dimensional approaches are common and analytical solutions were proposed in some cases. Percolation theory provides the morphological properties of the composite electrode. The purpose is to identify the dominating phenomena with respect to material, composition and grain size and the extension of the reaction zone. The second is to optimize the composition [13].

The interface between the electrodes and the electrolyte is not continuous. Therefore, finite element analysis (FEA) is used to study the effects of constriction on the current paths [15]. Even though this contribution comes from the electrolyte, not only the dc resistance is influenced and the effect on the ac impedance is not negligible, since contributions in the medium- and low- frequency domains are reported.

The above-mentioned studies focus on the phenomena occurring in the electrodes and at the electrolyte/electrode interface. The purpose is to model the behavior observed during EIS experiments. Therefore, isothermal and fixed gas concentrations in the channel are recurrent assumptions. Modeling work is therefore performed at the MEA level as well, to reproduce the current-potential characteristics (IV) obtained during electrochemical tests [16]-[20].

In the case of anode supported cells, significant efforts were performed on the modeling of the transport of species on the anode side. Several models of various complexities were tested. The Stefan-Maxwell approach, with an additional term for the Knudsen diffusion –so-called dusty gas model- showed the best performance, especially in critical conditions encountered in a repeat element, i.e. near the fuel outlet, were the fuel is already depleted. On the other hand, the terms for the additional contributions, extensively studied in the previously mentioned work on electrodes are simplified. In the most refined cases the empirical dependence on oxygen partial pressure – considered as not justified by [9]- is considered; sometimes neglected. The computed responses are successfully fitted to the experimental data, but the variation of operating conditions remains narrow. Calibration with simple empirical expressions was performed [16]. Such a description was intended for use in fast repeat elements models.

At the repeat-element/stack level, finite-element, finite-volume or finite differences codes are used to couple mass, momentum and energy balances [21][22]. Some groups used coupled approaches [23]. Most models can handle the internal reforming case, which is of main interest. A simple kinetics approach for the steam reforming reaction is used, whereas the water-gas shift is assumed at equilibrium. The overpotential terms are usually simplified, depending on the desired information. Uniform potential distribution is a usual assumption except in some cases [24]. The degree of refinement goes from tri-dimensional to faster one-dimensional models with simplified momentum equations. The distributions of the main variables such as temperature, gas concentrations and losses are studied, when varying the flow configuration and the inlet and surroundings conditions. It is well established that the counter-flow configuration leads to the highest performance at the cost of higher local current densities and thermal gradients. The main differences between the models lie in the handling of the electrochemistry. The handling of internal heat transfer by radiation is usually neglected. The few studies on this topic provided contradictory results [25][26].

Identified causes of degradation in the MEA

The anode support suffers from its weakness towards reduction-oxidation of the nickel, which can occur in critical parts. Possible causes are failure or poor performance of sealant, exposure occurrence of the thermodynamic condition at the electrolyte/anode interface during operation at high fuel utilization and failure of the fuel supply system. Such cycles modify the microstructure leading to a larger volume than in the initial oxidized state. The stress state in the electrolyte may therefore turn from compressive to tensile and might induce cracking of the electrolyte after a number of cycles. Studies were carried out to describe both the microstructural changes during cycles and the kinetics of the oxidation [29]. An increase of porosity within the NiO itself was observed, leading to cracks in the electrolyte [28]. The different behavior observed for fine or coarse structures was studied [29]. Controlled cycles on a SOFC stack were performed with large drops in performance [30].

Degradation under constant operation is a main concern in SOFC development. Several causes are now identified. On the anode side, undesirable formation of electrical insulating phases, such as silicate glass is reported at Ni-YSZ/YSZ interface. Nickel coarsening reduces the TPB length, hence the performance. Several groups clearly observed this mechanism [32]. On the cathode side, delamination induced by buckling or poor adhesion of the electrode on the electrolyte, as well as parasitic phases at the interface were observed [33]. The resistance of interconnects increases with time due to corrosion.

Few modeling work on the degradation phenomena has been published. A model considering the degradation of the interconnects was developed and the evolution of its effect on the field variables were simulated for several operating cases [34]. A diagnostic method was proposed to identify degradation due to the delamination of the cathode [35]. FE modeling was used to simulate the modification in the EIS spectra of a MEA due to a partial delamination of the cathode.

2. Overview of the research plan

The work will focus on planar, intermediate temperature SOFC cells. The aim is to gain knowledge on the contributions of identified mechanisms causing degradation during steady operation and the damages that SOFC stacks undergo during transient operations and cycles. The developed tools can be used as well for technical oriented work, such as assisting design and procedures for the last steps of the manufacturing process of a stack.

The first issue is degradation during steady operation. It requires a precise characterization of the behavior of the cells, with time dependent parameters, to model the stack and repeat element with accuracy. Suppliers of cells constantly improve their products. In particular, different types of cathodes can be sintered on the anode support. Therefore the intrinsic limitations of the cell and its time evolution have to be determined before any endurance test in stack conditions, where the influence of imperfect other components, e.g. sealants, interconnects and possible issues due to a deficient design appear. In addition, a properly calibrated law is a starting point for a comprehensive simulation of the previously mentioned imperfections.

The experimental data provided by DLR showed that a law of satisfactory accuracy yet reasonable in computing time could be derived when combining suitable experiments to parameter estimation tools. It was observed that the choice of a proper sequence of operating conditions is of main importance. On the other hand the degree of accuracy obtained let foresee the possibility to deduce a time dependent law. Up to now, the following main concerns appear:

- A large amount of data is needed and thus automatic procedures are required.
- The model has to be based on physical processes and to avoid as much as possible empirical relations. It is a necessary feature to integrate the degradation mechanisms studied in detail by many groups. Such a modeling approach can give access to non-measurable values. In particular, the condition at the TPB is of main interest but almost impossible to measure by direct means. The intrinsic limitation of the cells will induce reoxidation of nickel at this interface first, even in the absence of any fuel feeding error or seal leak.
- The list of parameters may then become large but some can be derived from dedicated experiments. EIS can provide among others the ohmic contribution to the total resistance, whereas microscopy and suited image processing can provide accurate measurements of the porosity or quantify the nickel coarsening. It can be argued that precise information provided by EIS can be directly used. However, the amount of required experiments due to the necessity to vary the conditions combined to the time dependence is likely to become unfeasible. A mixed approach is much more time effective and offers thus the possibility to set it as a standard.
- The existing electrochemical law is now well suited for operation with hydrogen as fuel, but the need to fully extend its capabilities to other fuels is obvious.

Once critical conditions have been identified, modeling at the repeat element level will reveal the redistribution of the temperature, gas concentrations and current density inside an ageing or partially damaged cell. In particular, transient operation is required to identify whether safe transient operation with a new stack might not turn into critical with an aged cell. Experiment test rigs at LENI-EPFL were recently upgraded for extended capabilities of control during transient operations or characterization. Thus, more refined experiments can be carried out and used for the validation of the model.

3. Work performed from the beginning of the SOF-CH

Improved electrochemical model

The starting point is the electrochemical model, which was developed at LENI-EPFL, within the frame of collaboration with the German Aerospace Center (DLR). The calibration of the parameters was performed on experimental data from DLR segmented test rig.

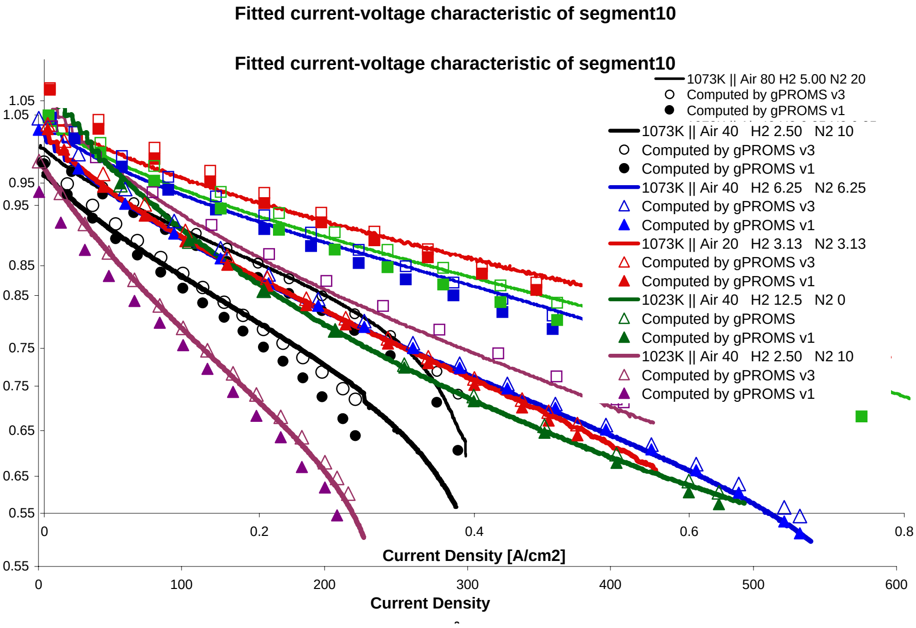


Figure 1: **Simulations with v3 and v1 model against experimental data on two different cells**

This model had several limitations, even though the accuracy of the model was satisfactory. A first revision was performed within the SOF-CH project:

- v3: Reference version. It is calibrated on experimental data (Figure 1).
- v4: the ionic conductivity of the electrolyte were slightly changed and the temperature dependence of the electronic conductivity of the electrolyte was introduced.
- v5: the computation of the diffusion losses can handle multi-component mixtures. Its behaviour is quite close to v3.
- v6: the equilibrium of the water-gas shift reaction within the anode is considered. The onset of limitation appears at higher fuel utilization, for the same set of physical parameters. At this stage, the implementation of reformate fuel is consistent within the considered assumption.

The latest evolutions could not be calibrated yet due to the lack of experimental data. However, their respective behavior was tested on a 2D thermo-electrochemical model of repeat element. Figure 2 depicts simulations of the IV curves with different versions of the model under reformate fuel. The onset of limitation, which occurred at too low fuel utilizations with the v3 model, could be shifted to more reasonable fuel utilizations. Such a detailed model allows accessing to more information, such as the gas composition at the anode-electrolyte interface. Figure 3 shows the computed values of the molar fraction within the anode.

Such information is paramount for a proper implementation at the repeat element scale of the knowledge acquired in WP1 and WP2.

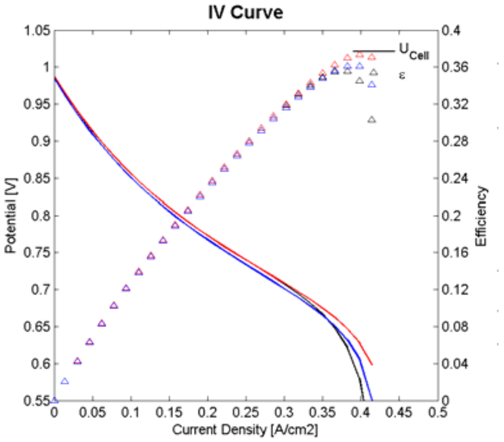
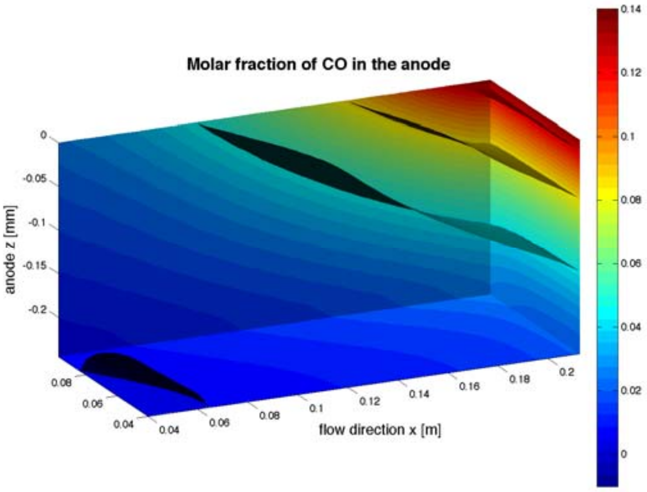
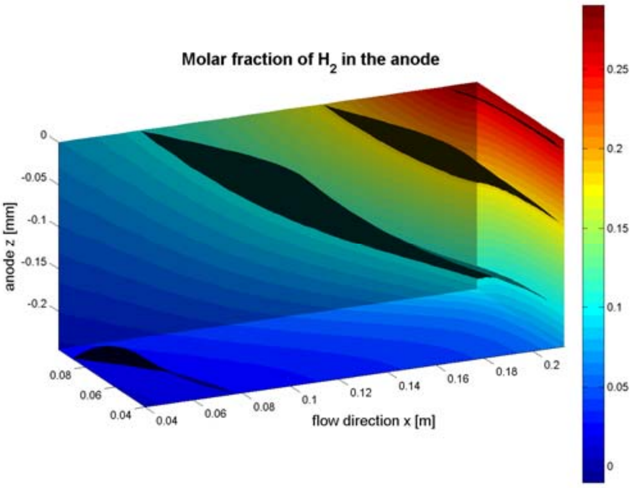


Figure 2: IV curves at full load for different versions of the model and flow configurations: co-flow with the water-gas shift in both fuel channels and anode (v6) (black), counter-flow (v6) (red) and counter-flow with the water-gas shift only in the fuel channels (v5) (blue). 8.665 nmlpm/cm^2 on fuel side.





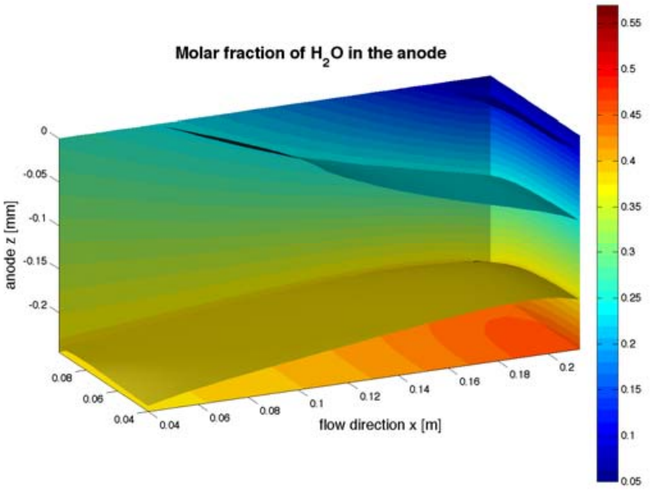


Figure 3: **Molar fraction in the anode, counter-flow configuration, full load. 8.666 nmlpm/cm^2**

Development of a versatile one-dimensional model

A parameter estimation run with the previously mentioned electrochemical model is currently very fast since it is uncoupled from the model which computes the conservation of the species and energy. The latter step is performed by MATLAB routines. The level of refinement is coarse. Therefore CFD simulations were used to estimate the error. They showed a difference of approximately 1% on the computed Nernst potential for the considered set of experimental data.

The time scale of the SOF-CH project allows overcoming this simplification:

- The validity of this assumption relies on the set of experimental data. Thus, the versatility and abilities of the model is limited.

- The model considers a non-infinite electronic resistance of the electrolyte. The conservation of the species is therefore affected by the parameters that control this phenomenon.

- Previous attempts showed that distributed models are still compatible with parameter estimations.

Therefore, a new one-dimensional model was developed. The electrochemical model was implemented. Its main features are:

- The required conservation equations are solved for each layer, i.e. upper and lower MICs, PEN, gases and. This is not relevant for the simulation of large stacks, but the accuracy of single repeat element simulations such as segmented ones can be affected by this assumption.

- The model is fast and was designed to be modular. It is made of several units, mainly reformer, inlet and outlet area, active area and flanges, which can be combined to simulate large stack, or segmented experiments. As a test, simulations of stack with up to 50 repeat elements were carried out.

- This model has both steady state and dynamic capabilities. The sensitivity of the results on the test procedures can thus be investigated.

- Operation with reformate fuel can be simulated. In particular, the way the equations were implemented was chosen to allow a straightforward and consistent handling of methane internal reforming.

Figure 4 to Figure 6 shows an overview of the features of the one-dimensional model.

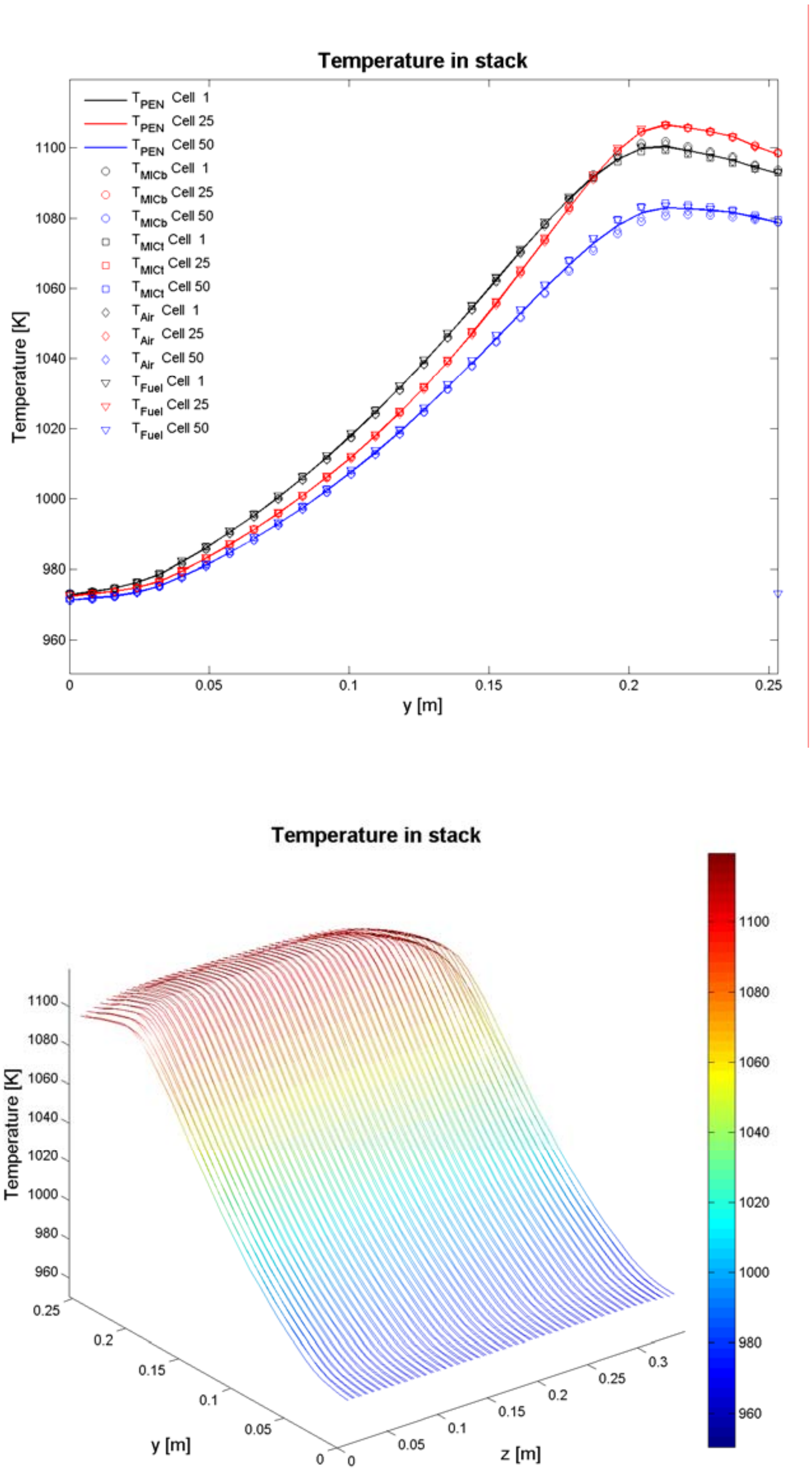


Figure 4: Temperature distribution within a 50RE stack fed with CPOx reformate at full load. Counter-flow configuration

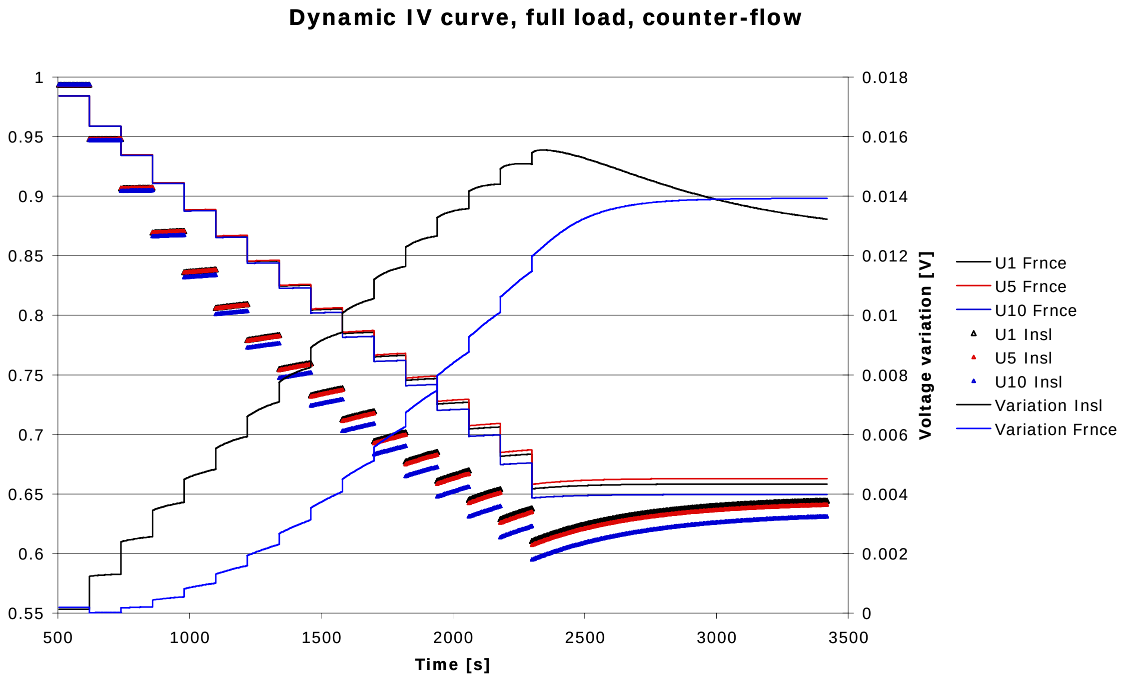
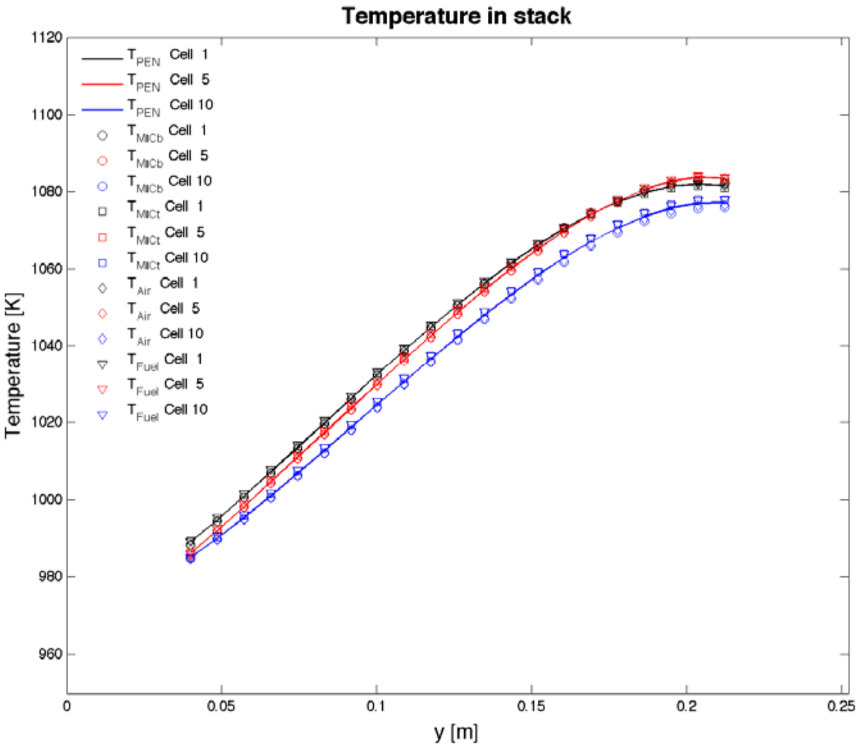


Figure 5: Comparison of different boundary conditions. Dynamic simulation.



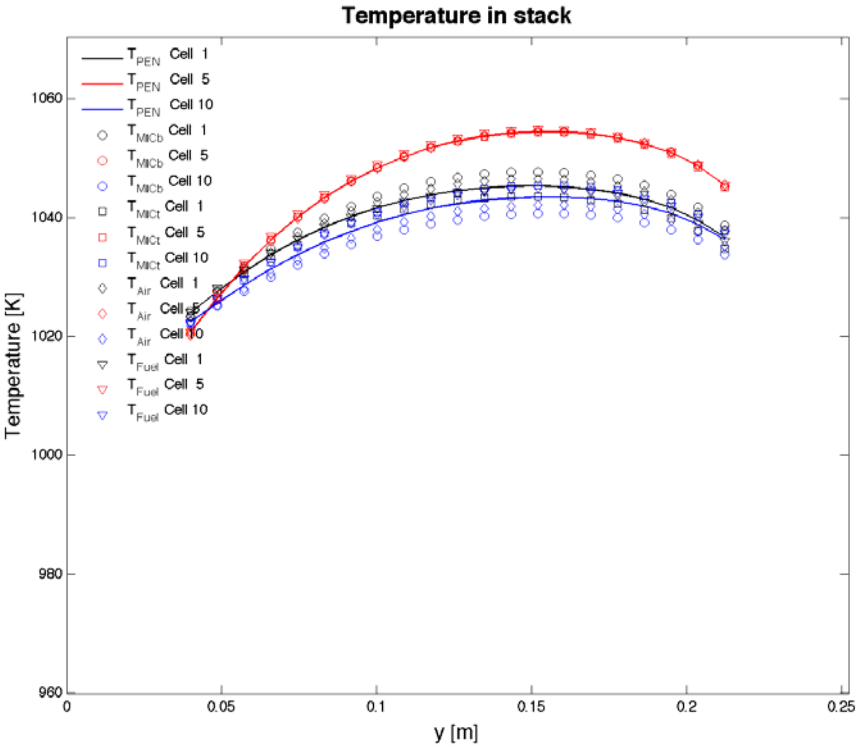


Figure 6: **Temperature distribution over the active area during operation in an insulation (top) and a furnace (bottom). Co-flow case.**

Références

[1] Y.L. Liu, C Jiao, Microstructure degradation of an anode/electrolyte interface in SOFC studied by transmission electron microscopy, Solid State Ionics, 176, 435-442, 2005

[2] J. Van Herle, Y. Membrez, O. Bucheli, Biogas as a fuel source for SOFC co-generators, Journal of Power Sources, 127, 300-312, 2004

[3] C.Stiller, B. Thorud, S.Seljebø, Ø.Mathisen, H.Karoliussen, O.Bolland, Finite-volume modeling and hybrid-cycle performance of planar and tubular solid oxide fuel cells, Journal of Power Sources (2004), Article in Press.

[4] Y.L. Liu, C Jiao, Microstructure degradation of an anode/electrolyte interface in SOFC studied by transmission electron microscopy, Solid State Ionics, 176, 435-442, 2005

[5] H. Kamata, A. Hosaka, J. Mizusaki, H. Tagawa, High temperature electrocatalytic properties of the SOFC air electrode La0.8Sr0.2MnO3/YSZ, Solid State Ionics, 106, 237-245,1998.

[6] M.J. Jørgensen, M. Mogensen, Impedance of Solid Oxide Fuel Cell LSM/YSZ Composite Cathode, J. Electrochem. Soc., Vol.148, A433-A442, 2001

[7] A. Mitterdorfer, L.J. Gauckler, La0.85Sr0.15MnyO3, O2(g)|YSZ system, Solid State Ionics, 111, 185-218, 1998

[8] S.H. Chan, X.J. Chen, K.A. Khor, Cathode Micromodel of Solid Oxide Fuel Cell, J. Electrochem. Soc., Vol.151, A164-A172, 2004

[9] A.M. Svensson, S. Sunde, K. Nisancioglu, Mathematical Modeling of Oxygen Exchange and Transport in Air-Perovskite-YSZ Interface Regions, J. Electrochem. Soc., Vol.151, A164-A172, 2004

[10] F.H. van Heuveln, H.J.M. Bouwmeester, Electrode Properties of Sr-Doped LaMnO3 on Yttria-Stabilized Zirconia II. Electrode Kinetics, J. Electrochem. Soc., Vol.144, 1997

[11] W.G. Bessler, J. Warnatz, D.G. Goodwin, The influence of equilibrium potential on the hydrogen oxidation kinetics of SOFC anodes, Solid State Ionics, 177, 3371-3383, 2007

[12] M. Mogensen, K.V. Jensen, M.J. Jørgensen, S. Primdahl, Progress in understanding SOFC electrodes, Solid State Ionics, 150, 123-129, 2002

[13] J. Deseure, Y, Bultel, L. Dessemond, E. Siebert, Theoretical optimization of a SOFC composite cathode, Electrochemica Acta, 20, 2037-2046, 2005

[14] P. Costamagna, P. Costa, V. Antonucci, Micro-Modelling of solid oxide fuel cell electrodes, Electrochimica Acta, 43, 375-394, 1998

[15] J. Fleig, J. Maier, The influence of Current Constrictions on the Impedance of Polarizable Electrodes, J. Electrochem. Soc., Vol.144, No.11, 1997

[16] D. Larrain, J. Van Herle, F. Maréchal, D. Favrat, Thermal modeling of a small anode supported solid oxide fuel cell, Journal of Power Sources, 118, 367-374, 2003

[17] H. Zhu, R.J. Kee, A general mathematical model for analyzing the performance of fuel-cell membrane-electrode assemblies, Journal of Power Sources, 117, 61-74, 2003

[18] S.H. Chan, K.A. Khor, Z.T. Xia, A complete polarizazion model of a solid oxide fuel cell and its sensitivity to the change of cell components thickness, Journal of Power Sources, 93, 130-140,2001

[19] R.E. Williford, L.A. Chick, G,D. Maupin, S.P. Simner, J.W. Stevenson, Diffusion Limitation in the Porous Anodes of SOFCs, J. Electrochem. Soc., Vol.150, A1067-A1072, 2003

[20] R. Suwanwarangkul, E. Croiset, M. W. Fowler, P. L. Douglas, E. Entchev and M. A. Douglas , Performance comparison of Fick’s, dusty-gas and Stefan–Maxwell models to predict the concentration overpotential of a SOFC anode, Journal of Power Sources, 122, 1 (2003), 9-18

[21] E. Aschenbach, Three-dimensional and time-dependent simulation of a planar solid oxide fuel cell stack, Journal of Power Sources, 49, 333-348, 1994.

[22] D.Larrain, J. Van Herle, F.Maréchal, D.Favrat, Generalized model of planar SOFC repeat element for design optimization, Journal of Power Sources 131 (2004) 313-319.

[23] Y-P. Chyou, T-D Chung, J-S Chen, R-F Shie, Integrated thermal engineering analyses with heat transfer at periphery of planar solid oxide fuel cell, Journal of Power Sources, 139, 126-140, 2005

[24] H. Yakabe, T. Sakurai, 3D simulation on the current path in planar SOFCs, Solid State Ionics, 174, 295-302, 2004

[25] K.J. Daun, S.B. Beale, F. Liu, G.J. Smallwood, Radiation heat transfer in SOFC electrolytes, Journal of Power Sources

[26] David L. Damm, Andrei G. Fedorov, Radiation heat transfer in SOFC materials and components, Journal of Power Sources

[27] A. Müller, S.Goswami, W. Becker, D. Stolten, L.G.J. de Haart, R.W. Steinbrech, Assessement of the Sealing Joints within SOFC Stacks by numerical Simulation, Fuell Cells 06, 2006, No.2, 107-112.

[28] J. Malzbender, E. Wessel, R. W. Steinbrech, Reduction and re-oxidation of anodes for solid oxide fuel cells, Solid State Ionics, 176 (2005), 2201-2203.

[29] D. Waldbillig, A. Wood, D.G. Ivey, Thermal analysis of the cyclic reduction and oxidation behaviour of SOFC anodes, Solid State Ionics, 176 (2005), 847-859

[30] D. Waldbillig, A. Wood, D.G. Ivey, Electrochemical and microstructural characterization of the redox tolerance of solid oxide fuel cell anodes, Journal of Power Sources, 145 (2005), 206-215

[31] Y.L. Liu, C.Jiao, Microstructure degradation of an anode/elctrolyte interface in SOFC studied by transmission electron microscopy, Solid State Ionics, 176 (2005), 435-442

[32] D. Simwonis, F. Tietz, D. Stöver, Nickel coarsening in annealed Ni/8YSZ anode substrates for solid oxide fuel cells, Solid State Ionics, 132 (2000), 241-251

[33] Mai, M. Becker, W. Assenmacher, F. Tietz, D. Hathiramani, E. Ivers-Tifée, D. Stöver, W. Mader, Time-dependent performance of mixed-conducting SOFC cathodes, Solid State Ionics, 177 (2006), 1965-1968

[34] D, Larrain, J. Van Herle, D. Favrat, Simulation of SOFC stack and repeat elements including interconnect degradation and anode reoxidation risk, Journal of Power Sources, 161 (2006), 392-403.

[35] J.I. Gazzarri, O. Kesler, Non-destructive delamination detection in solid oxide fuel cells, Journal of Power Sources, 167 (2007), 430-441