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Towards a complete macroscopic modelling of the thermo-chemo-mechanical behaviour of MIECs

Olivier Valentin^{1,2}, Eric Blond¹ and Nicolas Richet³

¹Laboratory PRISME - University of Orléans
8 rue L. de Vinci, 45 072 Orléans, France
firstname.name@univ-orleans.fr

³Air Liquide CRCD, 1 chemin Porte des Loges BP126,
78354 Jouy en Josas, France

²now at Aurock, 54 Rue Gustave Eiffel, 81000 Albi,
France

Abstract

This paper proposes a macroscopic model of the thermo-chemo-mechanical behaviour of MIECs dedicated to mechanical engineering. Developed within the framework of phenomenological approach, the state variables of the model are the oxygen partial pressure, the temperature and the total strain. Oxygen bulk diffusion is describes by the local Onsager approach and surface exchange are modelled by the use of a mass Biot number. Not only focus on the semi-permeation induced strain, the proposed model also included the effect of the temperature. Strain predicted by a model based on defect equilibrium and strain predicted by the macroscopic approach are in good agreement as it is illustrates on the particular case of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$. The implementation of the model in the F.E.A code Abaqus allows the exploration of the evolution of the stress state during the membrane life, from sealing stage to reactor exploitation.

Keywords: MIECs, Chemical expansion, Thermo-chemo-mechanical behaviour

Introduction

Since more than twenty years, MIECs are promising sources of hot pure oxygen which have potential industrial applications like methane reforming or oxycombustion. Two fundamental keys points for the development of these technologies are the lifespan and the reliability of the membrane. The first point is mainly driven by the stability of the material under operating condition whereas the second point is directly linked to the mechanical stress induces in service¹. A lot of works focus on the material properties which ensure a high permeation rate and a good stability but few study deals with the mechanical reliability under operating conditions. The development of a model dedicated to the field of mechanical engineering for MIECs materials is necessary to investigate the reliability in service.

The work presented hereafter focus on the development of a macroscopic model of the thermo-chemo-mechanical behaviour of MIECs

accounting for oxygen permeation, thermal expansion and strain induced by the stoichiometry fluctuation. While the previous works have been firstly focus on the semi-permeation induced strain^{2,3}, the model in its current form take into account the effect of the temperature on the chemical expansion due to the defect equilibrium dependence to temperature. To test the ability of this model to predict the chemical strain, its results are compared to those of a more classical model based on the defect equilibrium considering the particular case of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$ (LSFG) for which the chemical strain under atmosphere have been extensively studied^{4,5,6,7}.

Finally, the current numerical implementation of the model in the F.E.A code Abaqus allows to investigate the stress state of a tubular membrane for syngas production taking into account the residual stress induced by each stages, from sintering to in-service sollicitations *via* sealing.

Thermomechanical behaviour

The chemical expansion is related to cations size variations or/and to the modification of the Coulomb repulsion between the defects induced by oxidation and reduction of the material. Various approaches to describe this phenomenon exist in the literature⁸⁻¹⁴. The model proposed hereafter is an extension of that presented in ref^{2,3,15}.

Chemical induced strain does not modify the elastic mechanical behaviour. Assuming the partition of small strains leads to write:

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_T + \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_c \quad (1)$$

Where $\boldsymbol{\varepsilon}$ is the strain second rank tensor divided in three parts: $\boldsymbol{\varepsilon}_T$ the thermal strain, $\boldsymbol{\varepsilon}_e$ the elastic strain and $\boldsymbol{\varepsilon}_c$ the chemical strain. In the rest of this paper, bold type refers to tensor, while normal type refers to scalar. Then, the stress – strain relationship is:

$$\boldsymbol{\sigma} = \mathbf{K} : \boldsymbol{\varepsilon}_e \quad (2)$$

Where \mathbf{K} is the four rank Hooke tensor and $\boldsymbol{\sigma}$ the second rank stress tensor. The thermal strain tensor depends on temperature variation in a reversible way:

$$\boldsymbol{\varepsilon}_T = \alpha(T - T_0)\mathbf{I} \quad (3)$$

Where α is the coefficient of thermal expansion, T_0 a reference temperature and \mathbf{I} the second rank identity tensor. The thermal deformation corresponds here exclusively to the deformation caused by temperature variation at constant composition and without any phase change.

Chemical expansion model

The chemical strain is due to the oxydation state of the material. For a constant temperature, the oxydation state is drive by the oxygen partial pressure of the atmosphere, whereas at constant oxygen partial pressure the oxydation state is drive by the temperature. Indeed, the Gibbs law, and so the temperature, drive the stoichiometry of the defect equilibrium. But, the equilibrium with the surrounding atmosphere impose the oxygen activity in the material, and so the defect stoichiometry too. Then, a macroscopic model of the chemical expansion behaviour should take into account the effect of temperature and oxygen partial pressure. Moreover, assuming an isotropic chemical strain, only the scalar expression which multiplies the second rank identity tensor needs to be defined.

The first assumption of the proposed approach is the reversible dependence of the chemical strain with oxygen partial pressure variation. This assumption has been previously validated by isothermal expansion and XRD measurement under different atmosphere on different MIECs¹⁶. The second assumption is that, thanks to the admissible stoichiometry fluctuation in accordance to Gibbs rule, the temperature drives the range of the chemical expansion induced by the atmosphere change. Then, it leads to:

$$\varepsilon_c = \beta \ln\left(\frac{P_{O_2}}{P_{ref}}\right) + \varepsilon_c^T \leq \varepsilon_c^{max} \quad (4)$$

The first term of (4) corresponds to the part of the chemical expansion induced by the atmosphere change, in agreement with the previously proposed expression¹⁵. In this term, β is the chemical expansion coefficient, P_{O_2} the current oxygen partial pressure and P_{ref} the oxygen partial pressure corresponding to chemical strain equal to zero (i.e. often equal to oxygen partial pressure of the sintering atmosphere). The second part, ε_c^T , represent the chemical strain induce by the temperature change. The latest term, ε_c^{max} , is the maximum chemical strain amplitude which corresponds to the larger acceptable stoichiometry fluctuation for the considered material.

In this step towards a complete macroscopic model, let us proposed a linear expression for the thermal effect on chemical expansion:

$$\varepsilon_c^T = \alpha_c(T - T^\times) \quad (5)$$

Where α_c is the thermal chemical expansion coefficient, T^\times is the temperature of activation of this effect and $\langle x \rangle$ is the positive part of x .

The identification of $\alpha_c, \beta, T^\times, \varepsilon_c^{max}$ requires cyclic thermal expansion test with atmosphere change between each cycles¹⁶. For LSFG, the obtained values are $\alpha_c = 2.5 \cdot 10^{-6} K^{-1}$, $\beta = -2 \cdot 10^{-4}$, $T^\times = 500^\circ C$, $\varepsilon_c^{max} = 0.25\%$. Then, it is possible to plot the evolution of chemical strain versus oxygen partial pressure and temperature, like proposed on figure 1.

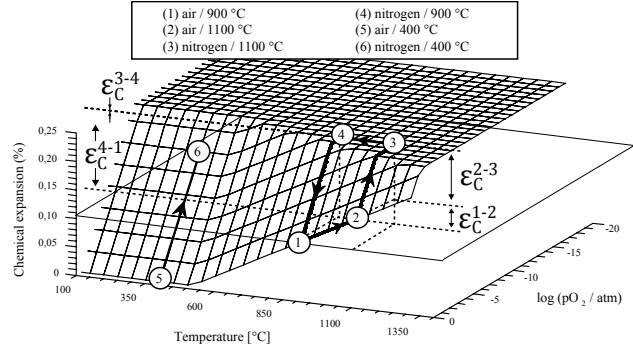


Figure 1: Macroscopic model of the chemical strain

Results predicted by this macroscopic model can be compared to those of a model based on the defect equilibrium and identified for LSFG⁷. Figure 7 presents prediction of this second model, assuming that the equilibrium defect is never reach under 700°C, then, the strain is "frozen" for lower temperature. It is worth nothing to underline that, without this assumption, a model based on the defect equilibrium will always predict no strain at room temperature because it corresponds to the thermodynamic equilibrium, that will be never reach.

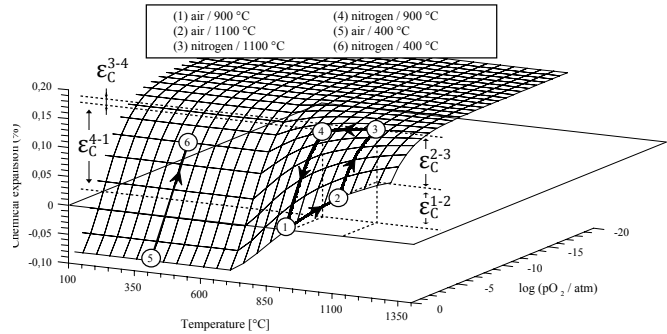


Figure 2: Microscopic model of the chemical strain

Noting that the origin of strain is different on figure 1 and 2, it can be observed that the two predictions are in agreement. The average gap between the models is around 6% and locally it never exceeds 14 %. The defect based model better fit with strain estimate by XRD measurement of lattice parameter whereas the macroscopic model better fit with thermal expansion measurement. For

the two models, the gap between associated experimental values does not exceed 5 %.

The main differences are: the activation temperature; the total amplitude; the shape of the strain step. While the defect model considers solely the stoichiometry change in respect to defect equilibrium, the macroscopic approach encompasses all phenomena that can induce a stoichiometry change (e.g. diffusion). Indeed, for its identification, the macroscopic approach does not need to assume the equilibrium of defect but only the equilibrium of the oxygen activity and temperature between the material and the surrounding atmosphere. It may explain the difference in activation temperature. The maximal chemical strain is higher from the macroscopic measurement (i.e. thermal expansion) than that extrapolate from XRD measurement of the lattice parameter change. Some little scattering are observed for the thermal expansion, and it may be justified by the scale effect. The shape of the strain step predicted by the defect model is smoother than that of the macroscopic model because of the assumption of a linear thermal dependence. Obviously, this thermal dependence should be linked to the evolution of the equilibrium constant, and it is not truly linear. This point will be better treated in a close future.

Semi-permeation model

The oxygen bulk diffusion can be model using the Onsager principle, which leads to the local expression of the bulk density J_b of oxygen flux:

$$J_b = S_0 e^{-Q/RT} \text{grad}(\ln a) \quad (6)$$

Where a is the oxygen activity, S_0 the “intrinsic” oxygen diffusivity, Q the activation energy and R the ideal gas constant. For LSFG, value of $S_0 = 100 \text{ m}^2 \cdot \text{s}^{-1}$ and $Q = 138 \text{ kJ}$ have been estimated by inverse identification¹⁷.

The surface exchange steps correspond to the adsorption and dissociation of the reacting gas molecule and the incorporation of the dissociated species. Considering equilibrium at surface between the oxidation and reduction rate, the oxygen surface flux J_s is described by the equation¹⁸:

$$J_s = k \ln \left(\frac{a_s}{p_{O_2}} \right) \quad (7)$$

Where k is the surface exchange coefficient. While in steady state the knowledge of the limited step is enough to determine the oxygen activity gradient in the membrane, in transient stage this gradient change with time and space depending on the ratio between surface and bulk kinetics. The dimensionless Biot number B_i can be used to characterized the bulk to surface exchange ratio:

$$B_i = \frac{ke}{S} \quad (8)$$

Where e is the thickness of the membrane and D the oxygen diffusivity at the considered temperature. A high Biot correspond to a bulk limited permeation while a low Biot correspond to a surface limited permeation. A Biot in the range around 0.6 to 10 corresponds to mixed regime¹⁵.

Numerical simulations

The mechanical behaviour accounting for the chemical strain (4) has been implemented in the finite element code Abaqus thanks to the user subroutine UMAT. The bulk diffusion behaviour (7) has been also implemented in Abaqus using the appropriate user subroutine UMATHT. The surface exchange flux (7) has been implemented thanks to the user subroutine DFLUX.

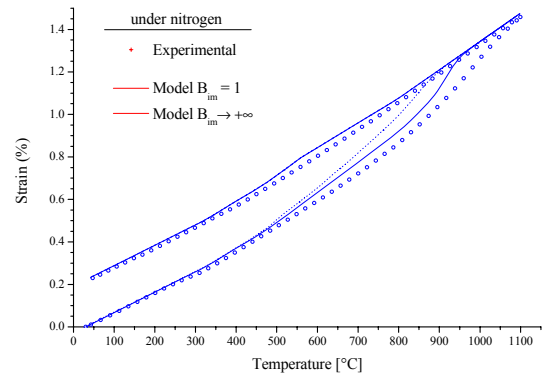


Figure 3: Thermal expansion under nitrogen for LSFG sintering under air.

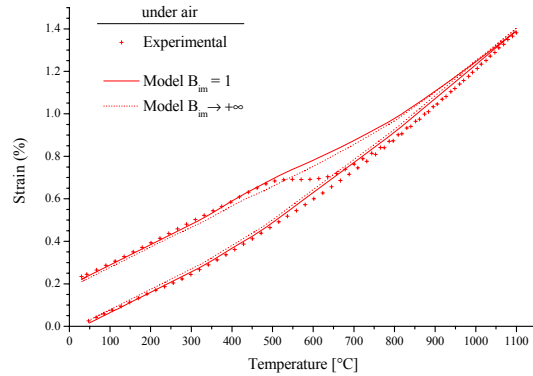


Figure 4: Thermal expansion under air for LSFG initially stabilized under nitrogen (starting point at 0.2% of strain at RT).

Figure 3 and 4 show the comparison between experimental results of thermal expansion test under atmosphere and numerical prevision. The strain amplitude is quite good whereas the kinetic does not fit the curves. Kinetics seems too fast under air and too slow under nitrogen. It underlines that the simplified semi-permeation model used here need to be refined. However, considering only the case of stationary states, the chemical strain is quantitatively good. Then, it allows to use the model to estimate the mechanical stress induce by stoichiometry change in stationary state.

To illustrate the possibility offer by such macroscopic model, the case of a tubular membrane of LSFG, close at one end, has been study. After sintering, the membrane is sealed at its based. This process generates mechanical stress that can damage the tube. Then, the membrane is set in the methane reforming reactor to produce syngas. Feed air arrives inside, while methane flow is at the outside face. Before reach the steady production parameters in term of atmosphere and temperature, different intermediate state need to be passed. Then, after a reasonable production time, the reactor may need to be stopped. Each one of this stage may impact the stress field reach in the next stage and could damage the membrane. Then, all the solicitations have to be computed accounting for the cycle process.

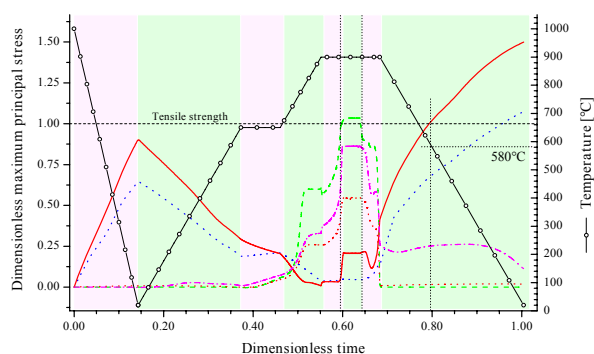


Figure 5: Evolution of dimensionless maximum principal stress at different localization along the membrane life.

Figure 5 shows the evolution of the maximal principal stress at different localization in the membrane. The red line describes stress evolution near the sealment, the green one near the closure on the top and other colors correspond to intermediate level. Firstly, it is assumed that the membrane is stress free at the beginning of the cooling of the sealment under air. So, after cooling, the thermal expansion coefficient mismatch between LSFG, sealment material and steel, combine to the geometry of the sealment, produce a high stress close to the tensile strength. After being installed in the reactor, the start up process can begin. The heating up under neutral gas permit to relax stresses while switching to air on inner face and methane on outer face induce an increase of the mechanical solicitations, but stresses still being lower than after the sealing. Finally, for the example, the particular case of an inappropriate gas atmosphere management during the stop of the reactor is simulated and it is observed that it can produce the fracture of the membrane.

Conclusions

The macroscopic model briefly presented in this paper has been developed to study the effect of reactor design or management on mechanical

reliability of the membrane. The temperature and the partial pressure have been deliberately choose as state variables because they can be “easily” measure and manage in service. The results show that, whereas the chemical expansion is well reproducing, the surface exchange needs to be refined. However, the model permit to quantify the mechanical stress in the membrane in steady-state service condition, accounting for geometry and mechanical design of each part of the reactor. Such macroscopic model dedicated to mechanical engineering of MIECs should give a help to the development of industrial application of these promising materials.

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