Modelling and Characterization of Solid Oxide Cells: Impact of Microstructure and Reaction Mechanisms on Cell Performances and Degradation

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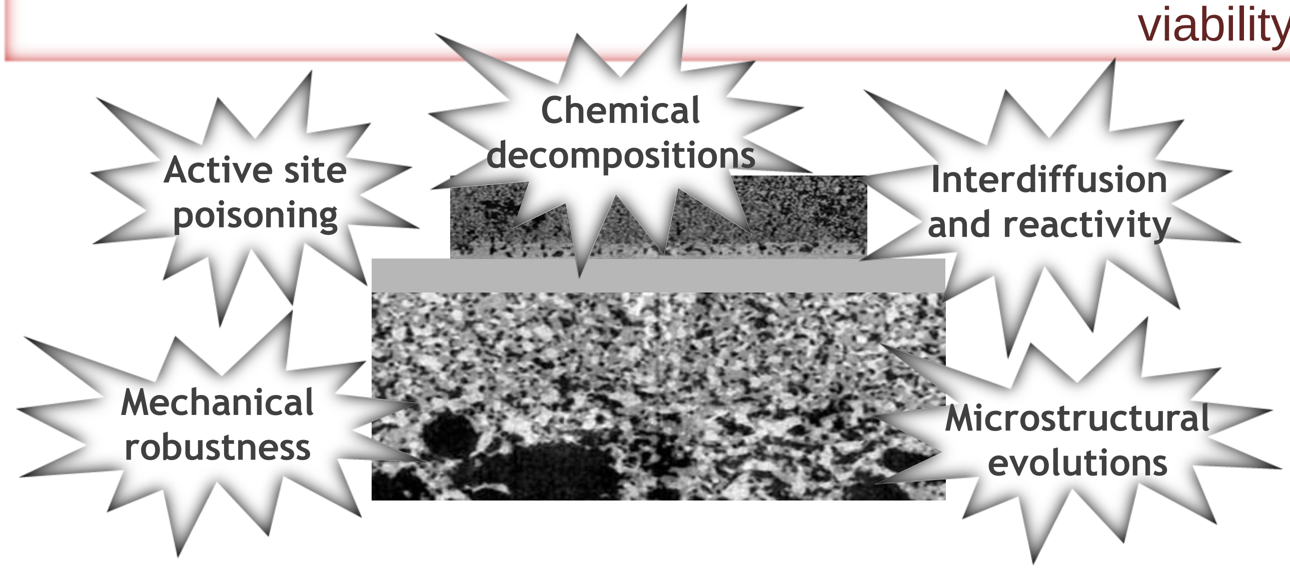
Context and Issues - Main advantages and limitations of high temperature electrochemical system

Many Advantages of Solid Oxide Cells (SOCs):

➲ High electrical efficiency, reversibility in electrolysis (SOEC) and fuel cell (SOFC) modes, fuel flexibility, etc.

Main drawback:

➲ The performances and durability (especially under electrolysis current) are still insufficient for economic viability



Instabilities activated at high temperature under polarizations

Main contributions:

- ➲ Ni depletion in the H_2 electrode
- ➲ LSCF destabilization and reactivity
- ➲ Micro-cracks in the YSZ backbone of the supported electrode during Ni redox cycles

It is still needed to improve the **performances and stability for both electrodes**

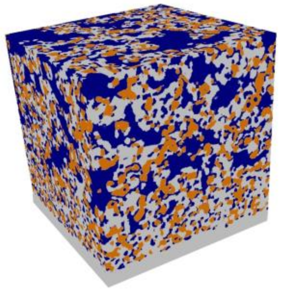
→ microstructural optimization, new materials, etc.

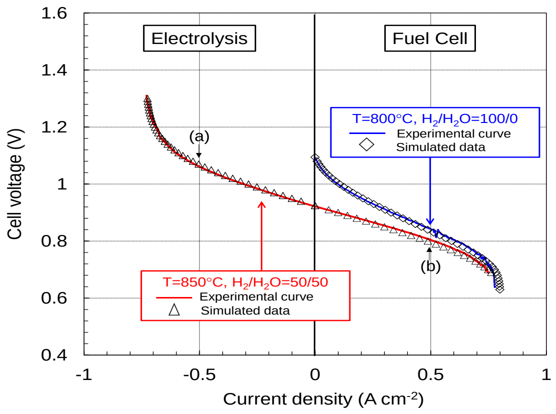
➲ However, **'basic' studies are still required as:**

① The role of microstructure,
② The driving force for the degradations,
③ The reaction pathway for the electrochemistry…

} **…Not fully understood yet.**

Methodology - A coupled experimental and modeling approach



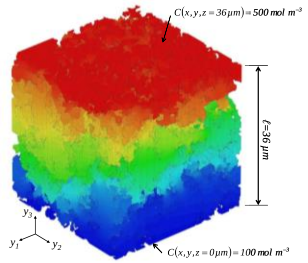


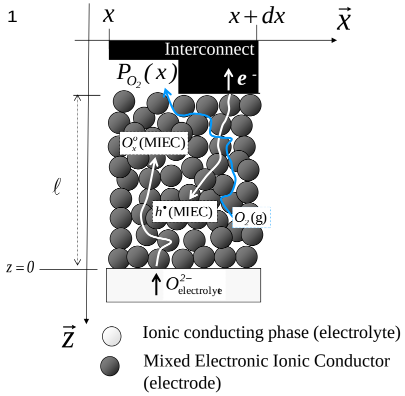
Electrochemical testing at the electrode and cell levels

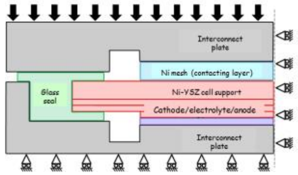
VALIDATED MODELS

Microstructural characterization and post-test analyses

Multi-scale modeling from microstructure to SRU







☑ "Microstructural and material properties ⬄ Reaction mechanisms ⬄ performances and degradation" depending on the operating parameters (SOFC vs SOEC polarizations, temperatures, etc.)

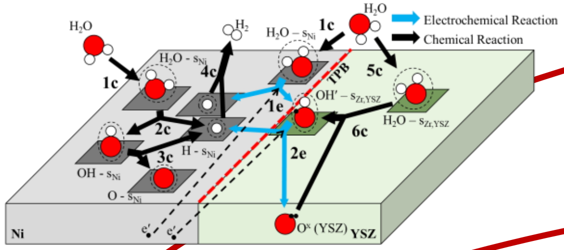
Methodology – multi-scale and multi-physic model from atomistic to macroscopic cell behavior

From atomic scale to cell level

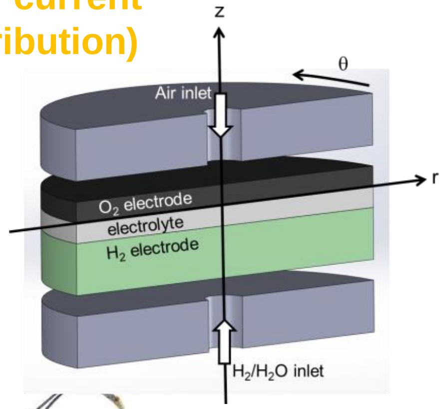
10^{-6} 10^{-3} 10^{-2}

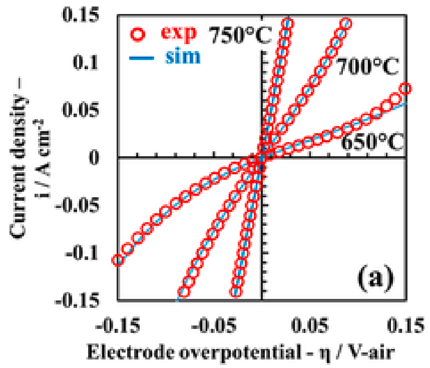
scale (m)

Microscale Electrode Models



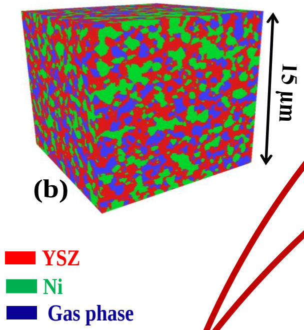
Single Repeat Unit
(cell + interconnects for current collection and gas distribution)



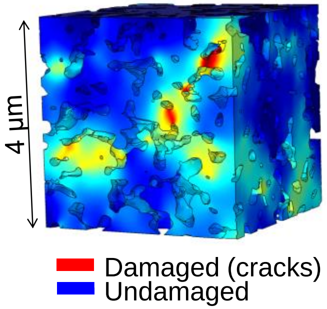


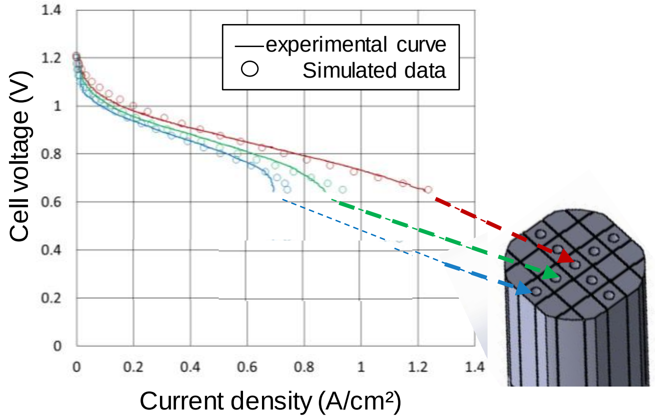
Global measurements

Microstructure (digital twin)



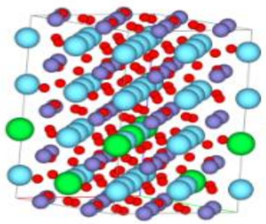
Fracture mechanic



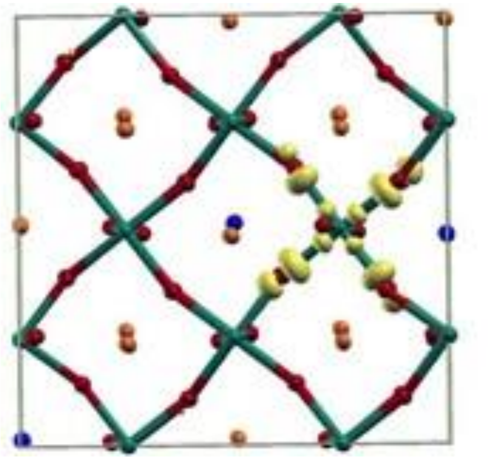


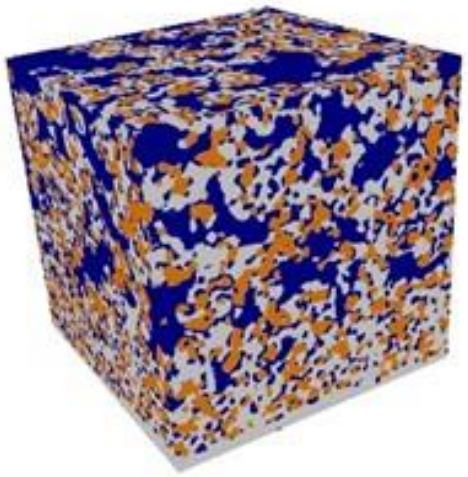
Local measurements

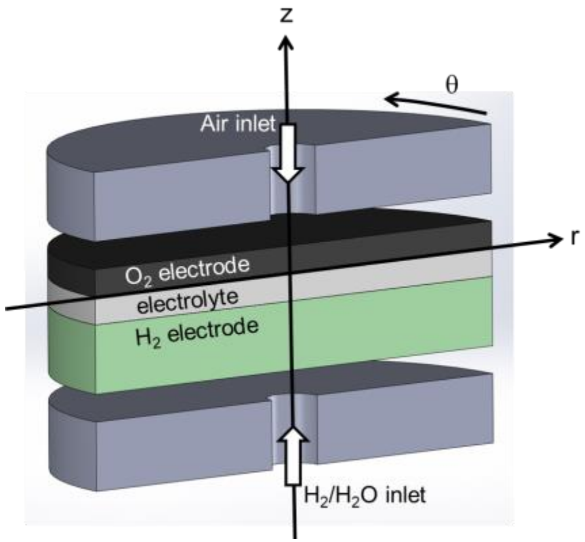
DFT simulations



Part I:
PRESENTATION OF THE MULTISCALE AND MULTI-PHYSIC APPROACH







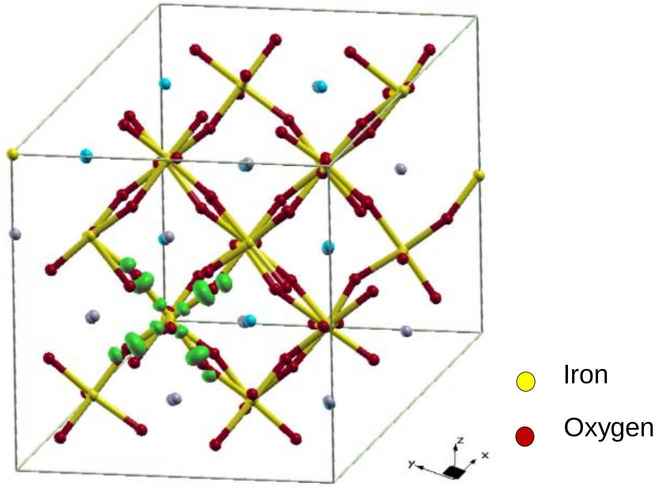
DFT modelling – Hole localization in $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$

Ab-initio simulations applied to the oxygen electrode materials

➲ Bulk properties of the oxygen deficient perovskites (LSF and LSCF).

C. Hartmann et al., ECS Transactions (2021)

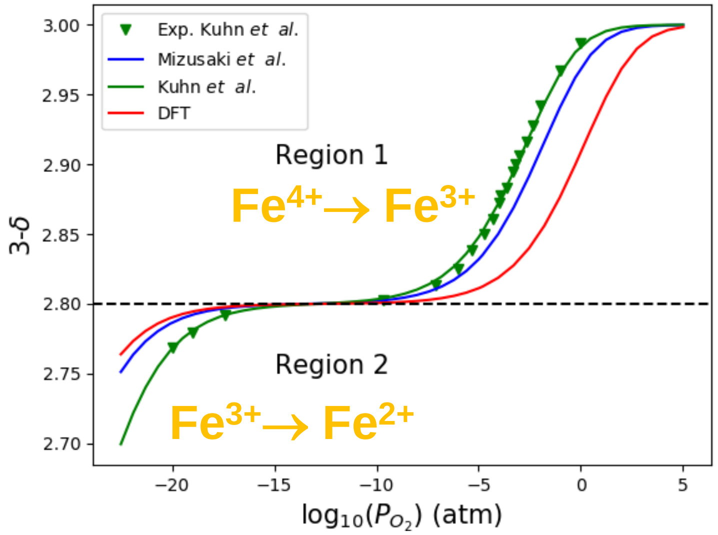
Visualisation of holes in $La_{0.4}Sr_{0.6}FeO_{3-\delta}$



- ☑ Holes are located around iron which becomes 'Fe^{4+}'
- ☑ Extension to surrounding oxygens

Calculation of oxygen vacancies concentration as a function of oxygen partial pressure by coupling DFT simulations and a thermodynamic model

J. Mizusaki et al., J. Solide State Chem. (1985)



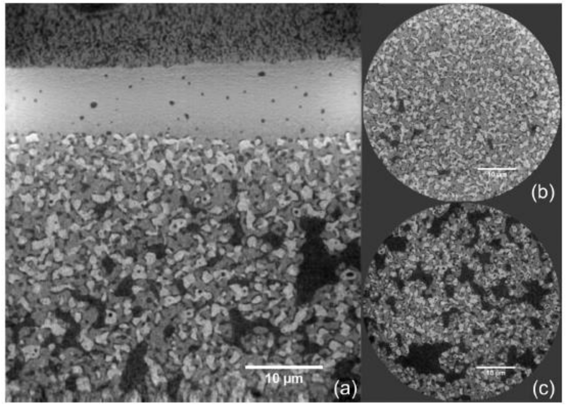
- ☑ Prediction coupling the defect model with the DFT is in quite good agreement with the results using the experimental enthalpy changes

➲ DFT Simulations provide input data for kinetic models.

✓ Presentation B1605 of Cintia Hartmann at EFCF (08/07 – 13h30)

Microstructure – 3D characterization and generation of numerical microstructures by geo-statistical modelling

⚐ Phase contrast imaging method based on synchrotron radiation at high energy

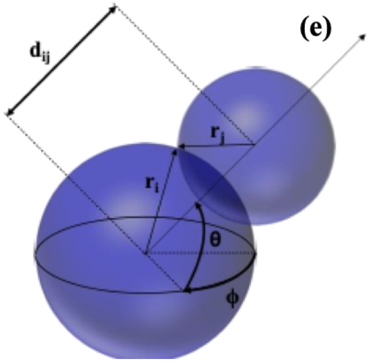


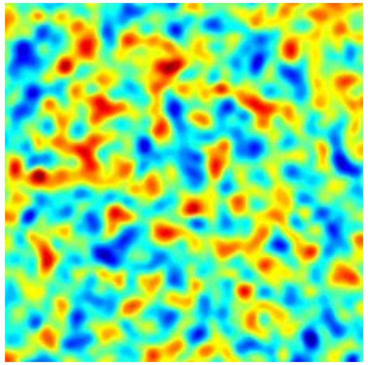
ESRF

⚐ Two methods for two approximations of the reality

① Original sphere packing algorithm
➲ The solid phase is filled by overlapping spheres in an specific iterative process.

② Non-iterative mathematical methods:
➲ The truncated Gaussian random field model.





MINES Saint-Étienne
Une école de l'IMT

Correlated Gaussian random field

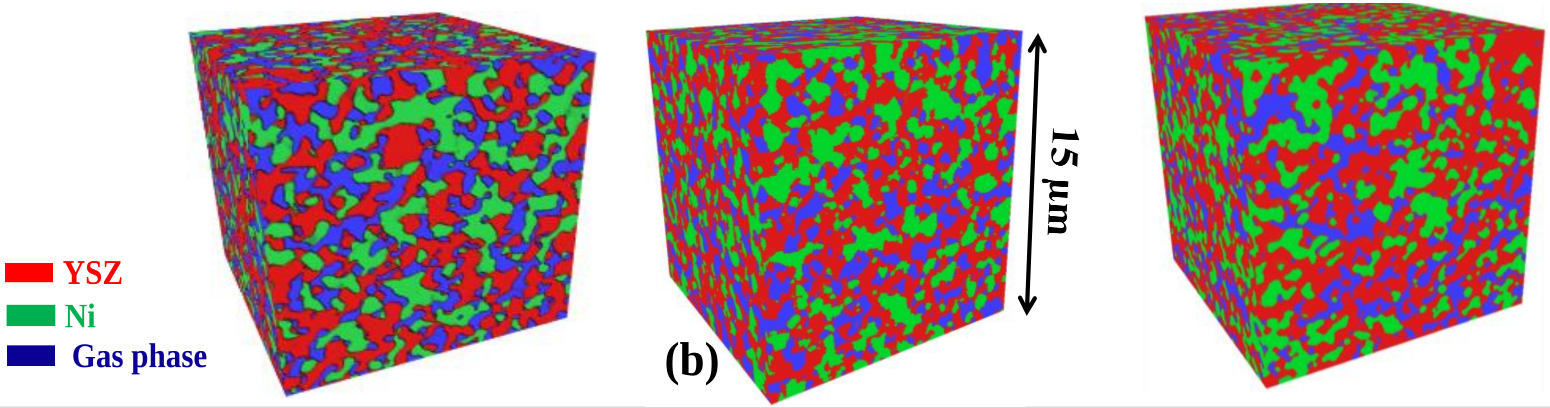
H. Moussaoui et al., Powder Tech. (2020)

H. Moussaoui et al., Comput. Mater. Sci. (2018)

☑ **Model adapted for the three-phase electrode (e.g. porous Ni-YSZ)**

☑ **Validation using real 3D reconstructions of different electrodes**

Random field | **Real electrode** | **Sphere packing**

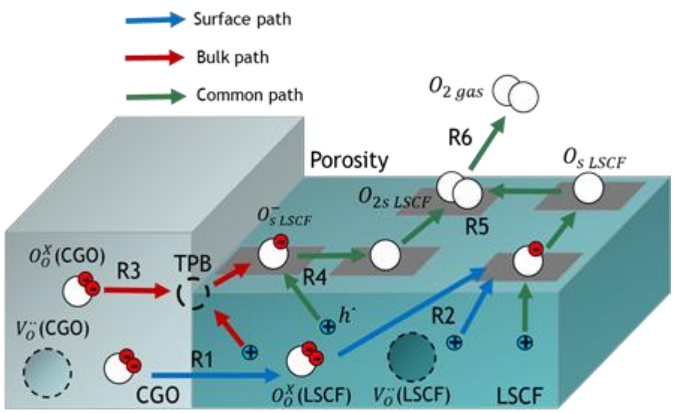


➲ **The two methods are complementary (sphere packing is flexible while the random field is fast) and have been combined to establish new microstructural correlations**

Micro-scale electrode modelling – Electrode model calibration with 3D reconstruction and electrochemical characterizations

1D Micro-kinetic model

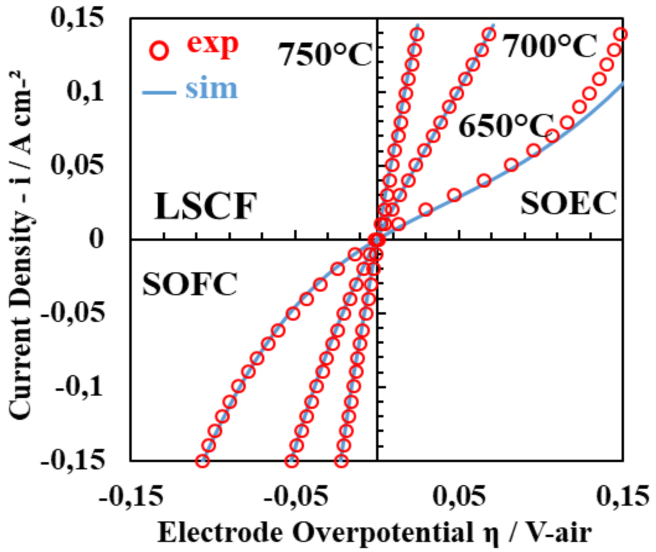
Reaction mechanism is divided in a sequence of elementary steps



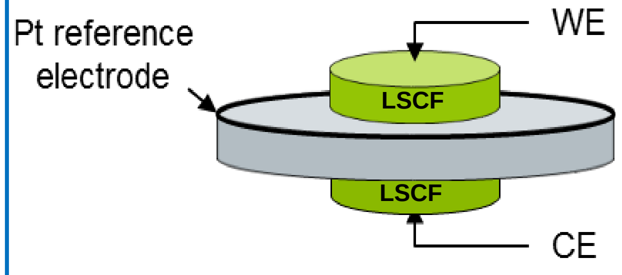
- ☑ Mass and charge fluxes are dependent on the microstructure
- ☑ Kinetics rates are expressed as a function of morphological properties

➲ The kinetic constants are the unknown parameters of the model.

E. Effori et al., Solid State Ionics (2021)
E. Effori et al., J. Electrochem. Soc. (2021)

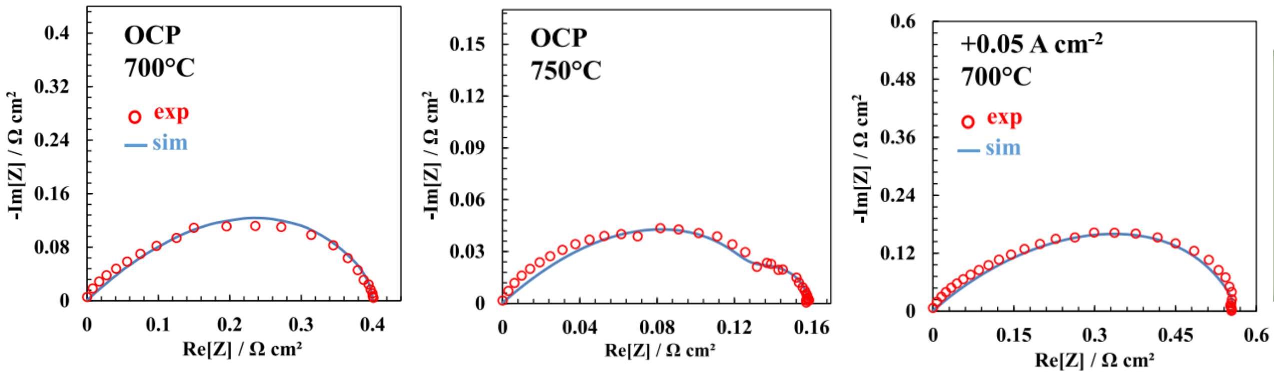


EXPERIMENT



Three-electrode setup with symmetrical cells

➲ Model calibration using one experimental polarization curve in a given operating condition.



✓ Presentation B1601 of Lydia Yefsah at EFCF (08/07 – 13h30)

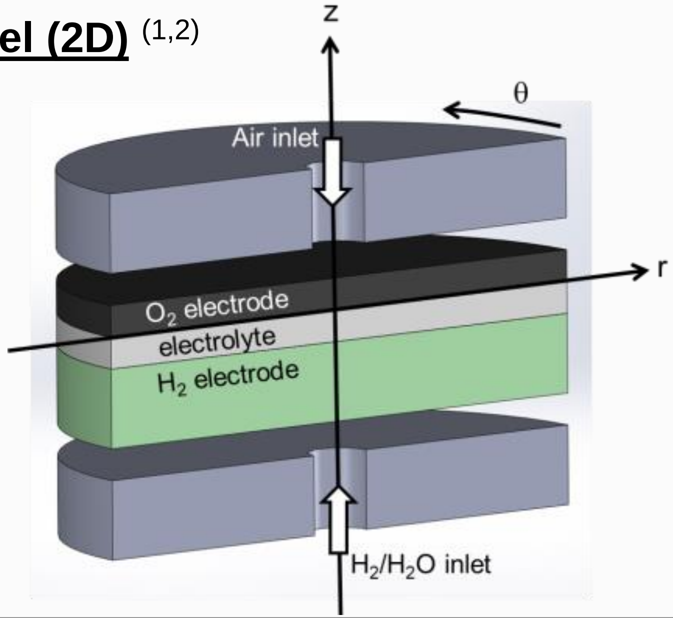
➲ Model validation using polarization curves, electrochemical impedance spectra and cyclic voltammetry under different operating conditions.

Macro-scale electrochemical model – Taking into consideration gas channels and cell design

SRU model (2D) [1,2]

(1) J. Laurencin et al. J. Power Sources (2011)

(2) L. Bernadet et al. Electrochimica Acta (2017)

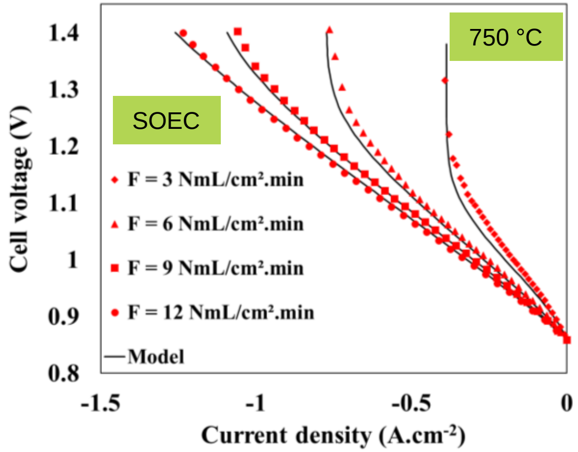


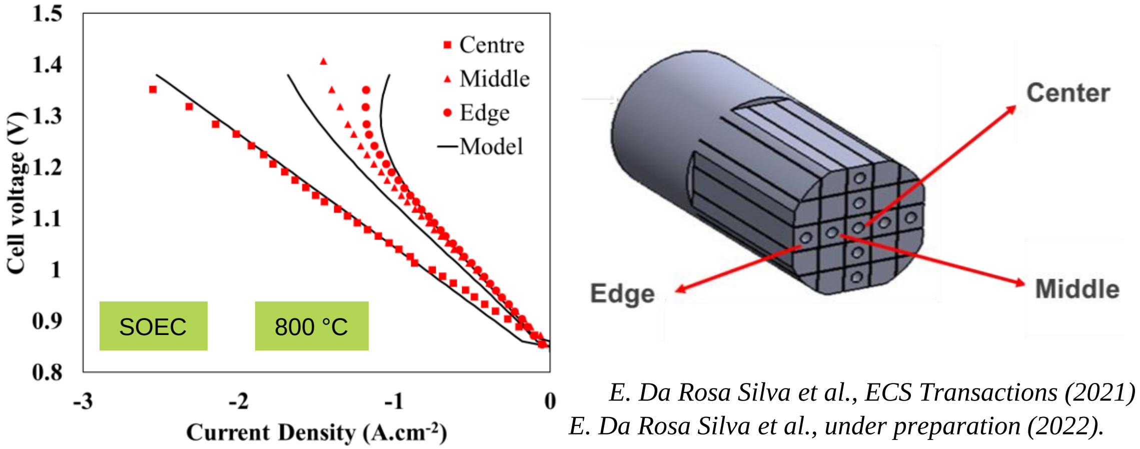
- ➲ 2D model taking into account the geometry of the cell and design of gas channels.
- ➲ Distribution of partial pressures, overpotentials and current density along the cell radius.
- ➲ Apparent kinetics on interfaces are calibrated using the micro-scale electrode models
- ➲ Global and local response in SOFC and SOEC mode

☑ Macro-scale SRU model validated on 'classical' cell i-V curves…

☑ …but also on local current measurements…

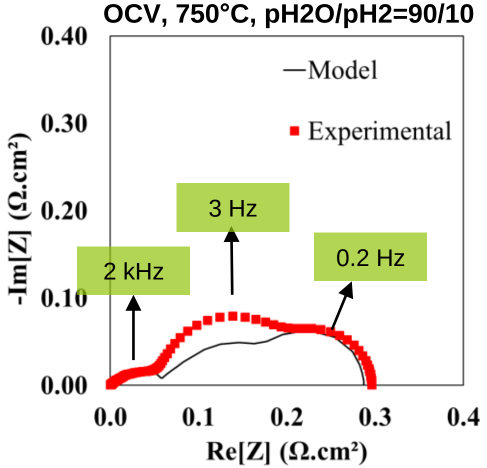
☑ …and impedance spectra.





E. Da Rosa Silva et al., ECS Transactions (2021)

E. Da Rosa Silva et al., under preparation (2022).

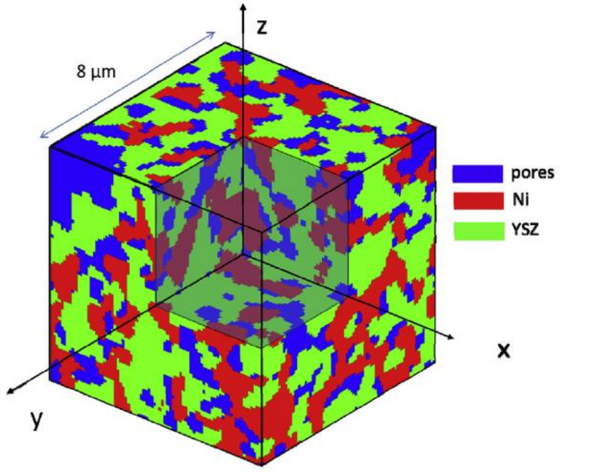


Micro-scale mechanical model – Mechanical properties and fracture mechanic in a porous electrode

Thermo-mechanical properties of SOC electrodes.

➲ Homogenization for the elastic properties on 3D volumes.

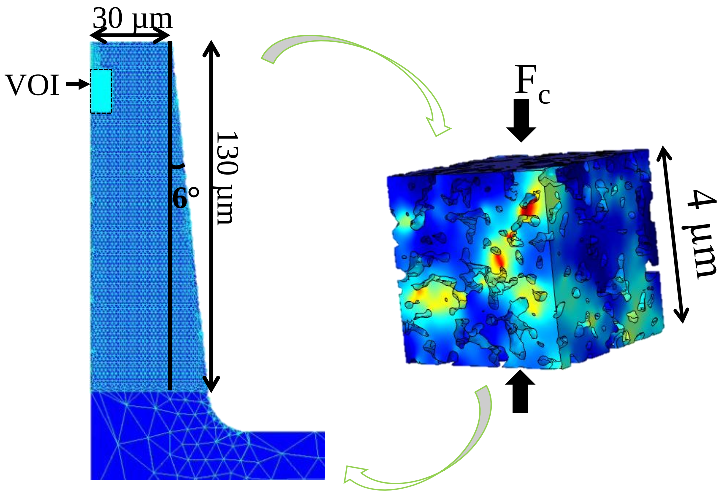
G. Delette et al., Int. J. Hydrogen Energy (2013)

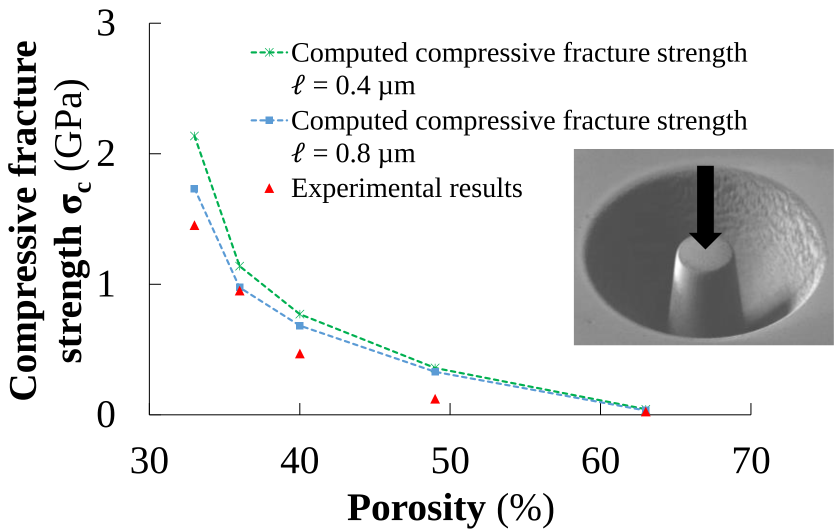


Predictive numerical tool for the fracture of porous ceramics.

➲ Phase Field Model (PFM) applied to fracture mechanic.

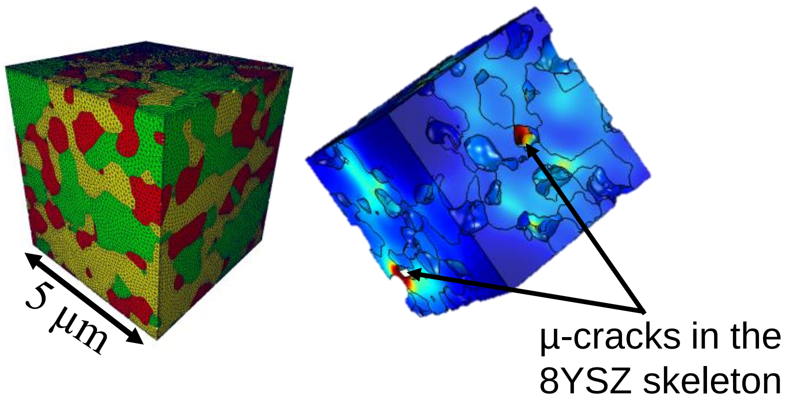
A. Abaza et al., ECS Trans. (2021) ; A. Abaza et al., J. Eur. Ceram. Soc .(2022) ; A. Abaza et al., Theor. Appl. Fract. Mech.(2022)





☑ PFM is able to predict correctly the experimental dependence of the compressive fracture strength with the porosity.

Preliminary study



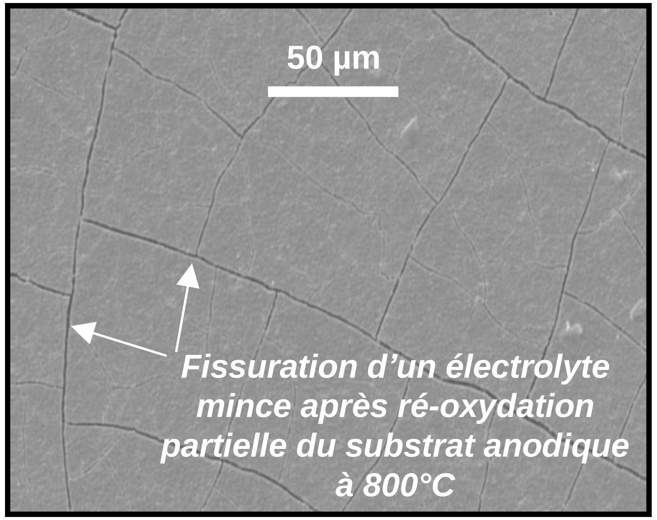
☑ PFM is able to simulate the µ-cracks during redox cycle.

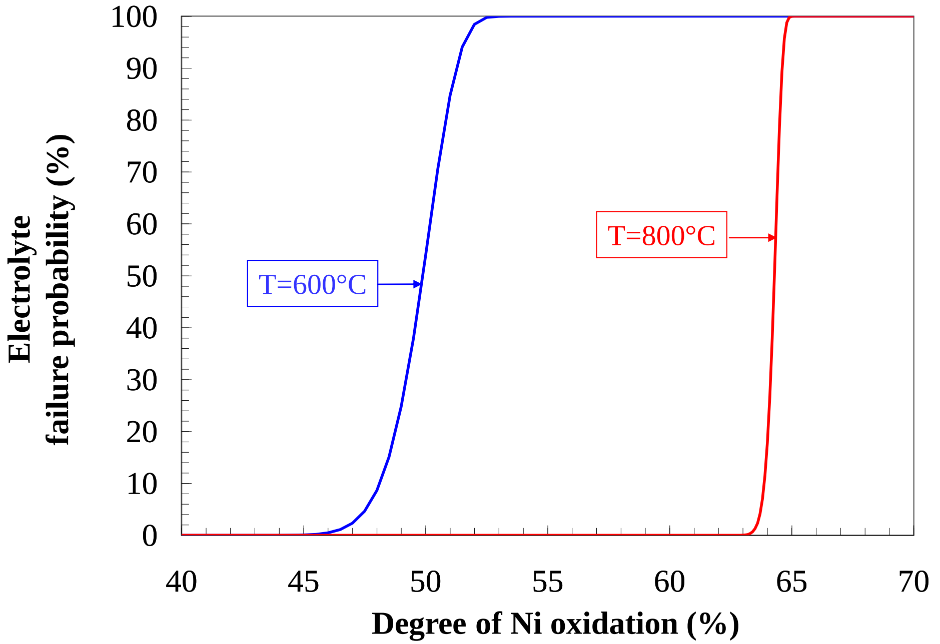
➲ Additional investigations are on-going.

Macro-scale mechanical model – Mechanical degradation with different cell configurations

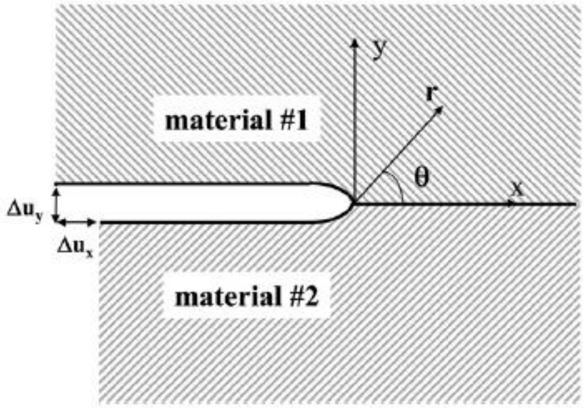
Cell models for mechanical degradation.

➲ Analytical and numerical models to compute the internal stress states after manufacturing, in operation after redox/thermal cycling.





- ☑ Probability of failure of the electrolyte during Ni re-oxidation (Weibull and Batdorf).
- ☑ Crack extension at the interface under a mixed mode of loading.
- ☑ Stresses induced by a thermal gradient.

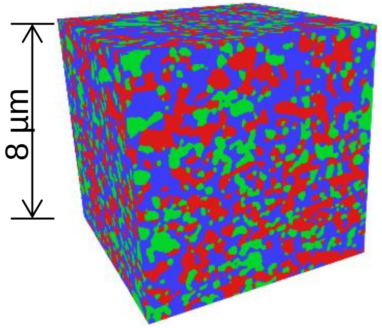


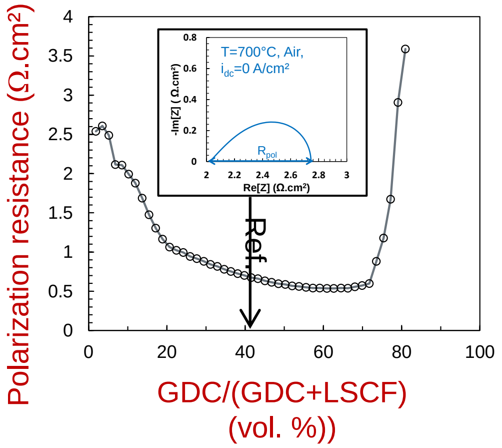
J. Laurencin et al., J. Eur. Cer. Soc. (2008) ; J. Laurencin et al., J. Power Sources (2009) ; G. Delette et al., Eur. J. Mechanics A (2012) ; J. Laurencin et al., Int. J. Hydrogen Ener. (2012)

Part II:

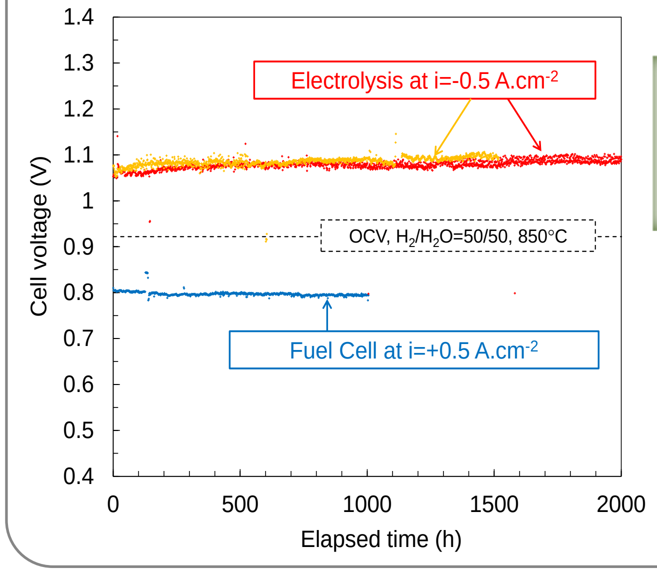
CELL PERFORMANCES AND DURABILITY: SOME ILLUSTRATIONS FOR SPECIFIC STUDIES

Part II.1 Performances





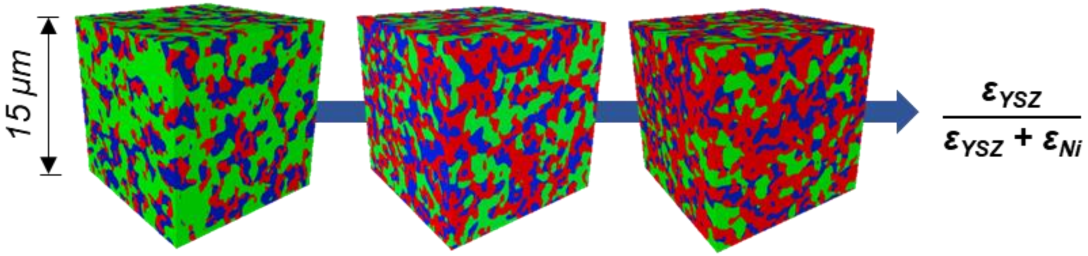
Part II.2 Degradations



➲ Degradation rates are higher under electrolysis current.

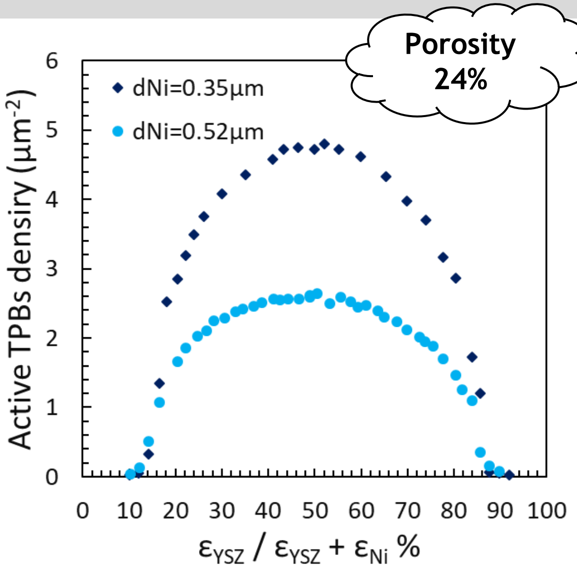
Microstructural optimization – case of the Ni-YSZ composite (H_2 electrode)

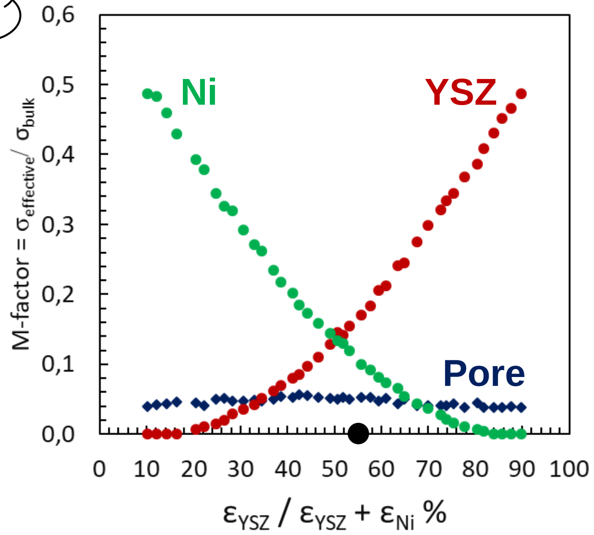
Microstructural computations



30% *55% (reference)* *70%*

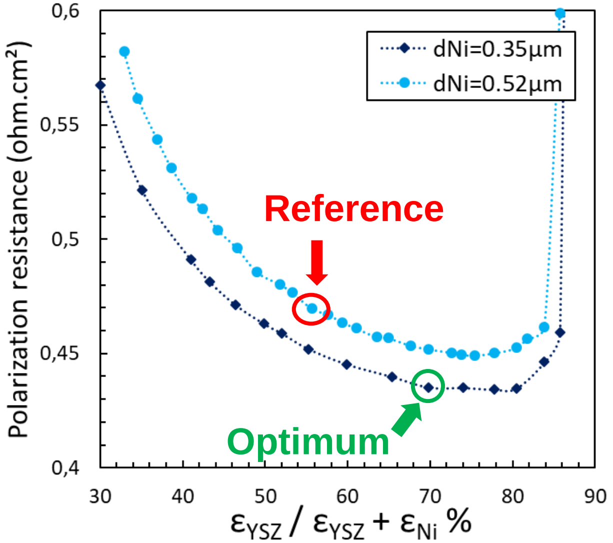
(YSZ proportion in the solid phase)



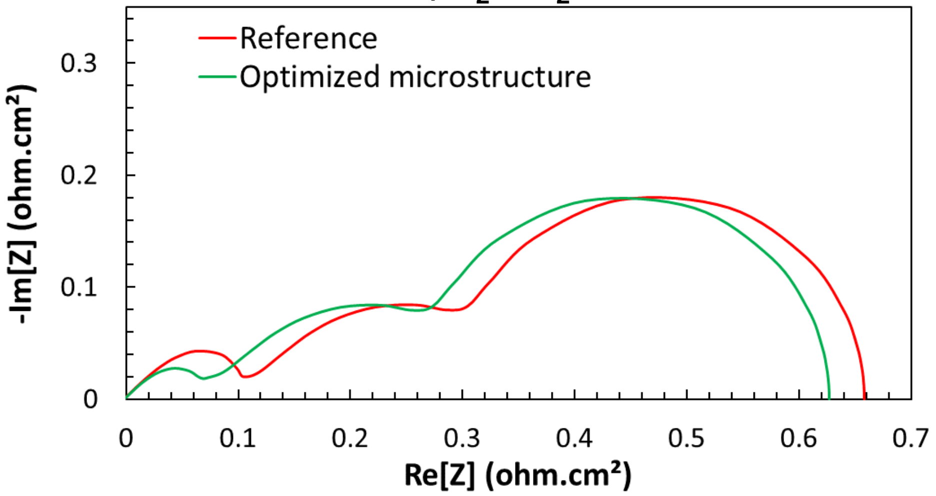


➲ The multi-scale approach developed at the laboratory is used to evaluate the effect of microstructure on electrode and cell response

750°C, H_2O/H_2=90/10 at OCP



Simulated EIS of the complete cell at OCV
750°C, H_2O/H_2=90/10



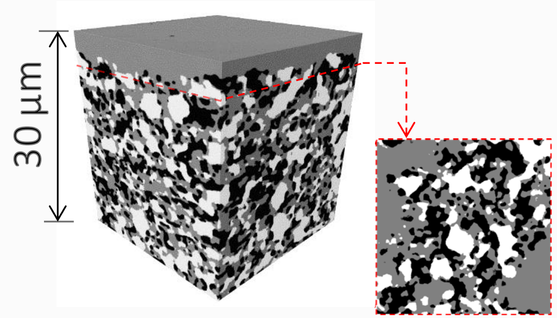
- ➲ The global shape is inverse to the one of TPB since they are the electrochemical active sites.
- ➲ As expected, a smaller Ni particle size allows improving the performances of this electrode.

✓ Presentation B1602 of Manon Prioux at EFCF (08/07 – 13h30)

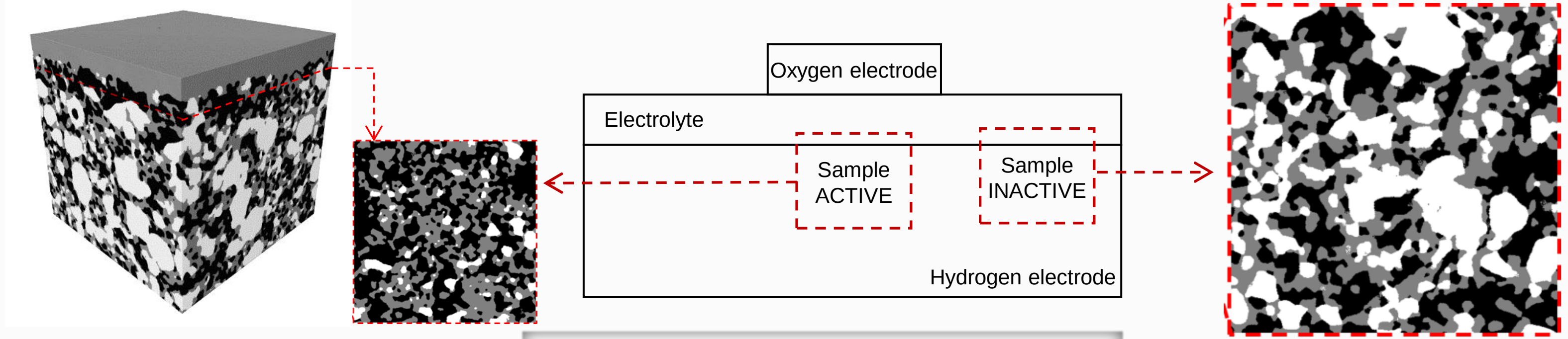
M. Prioux et al., under preparation (2022).

H_2 electrode durability – Ni migration away from the electrolyte interface

3D reconstructions at the electrode/electrolyte interface



Pristine cermet



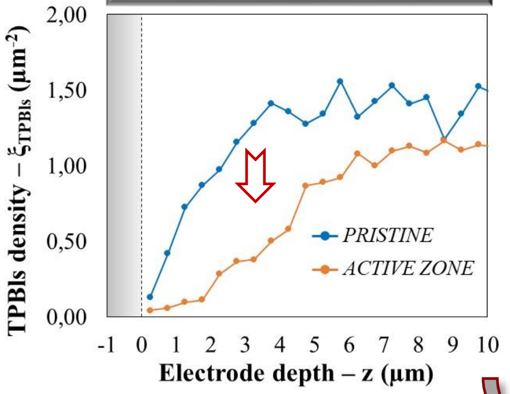
F. Monaco et al. J. Electrochem. Soc. (2019)

Operated in electrolysis at 800°C

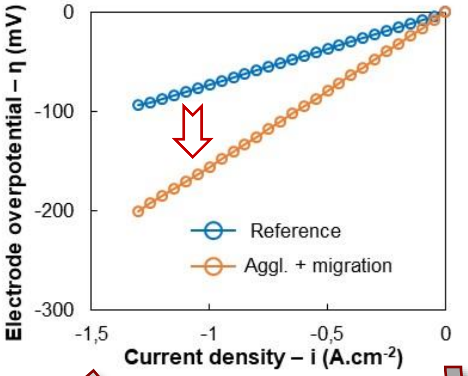
Ni pores YSZ

➲In SOFC mode, no significant Ni redistribution.
➲In SOEC mode, a severe depletion detected… but, only in the active part of the cell.

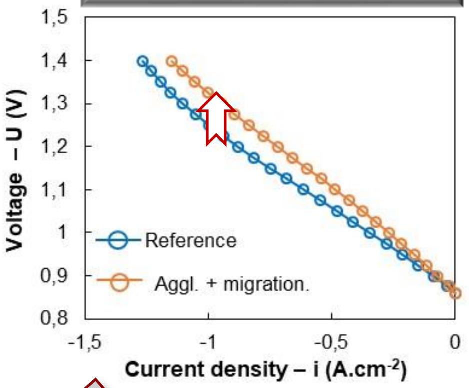
Gradients in µstructural properties



Simulated electrode response



Simulated cell response



➲ Substantial degradation of electrode and cell performances

➲ A part of the higher degradation rates in SOEC must be explained by Ni depletion.

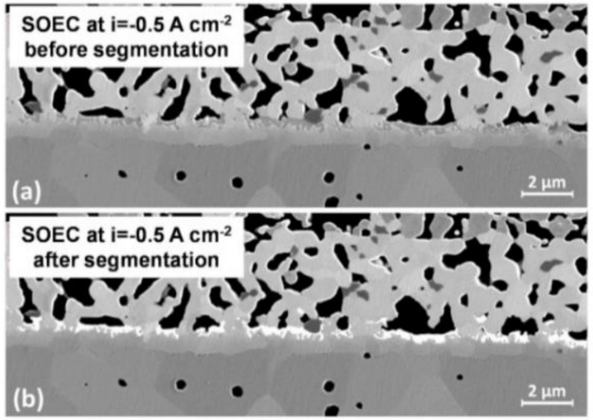
➲ A mechanism of the Ni migration is under development by the group.

✓ Presentation B0605 of Léa Rorato at EFCF (06/07 – 16h30)

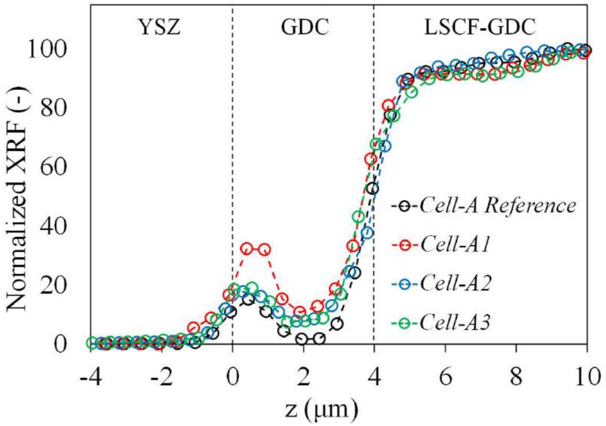
O_2 electrode durability – LSCF destabilization and reactivity with the electrolyte

Advanced characterizations for distribution of chemical elements and crystalline phases identification.

SEM cross section



µ-XRF profile

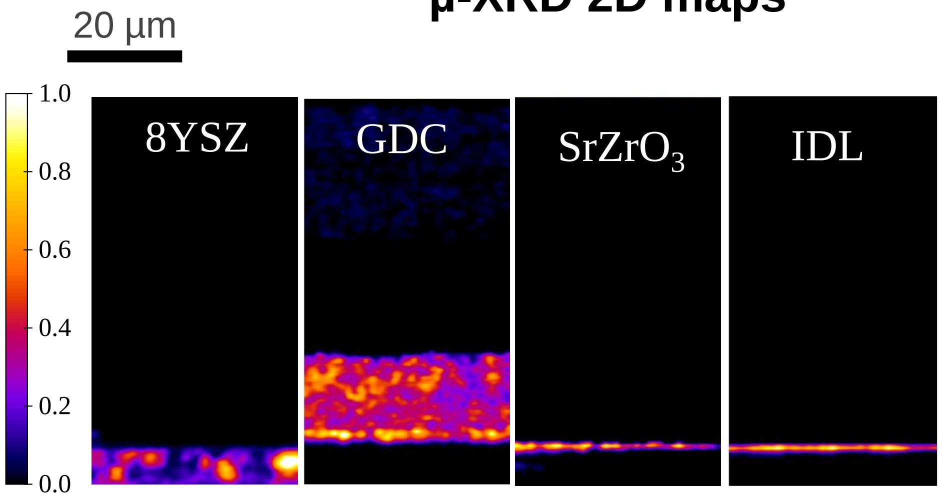


- Accumulation of Sr-rich phase observed at the interface with the electrolyte.
- Amount of Sr-rich phase is much larger in electrolysis mode than the quantity measured on the SOFC aged sample.

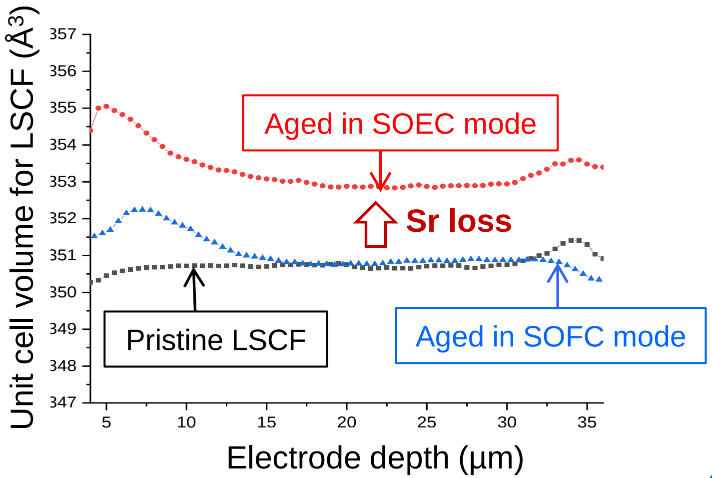
J. Laurencin et al., Electrochimica Acta. (2017)

F. Monaco et al., Int. J. Hydrog. Energy. (2021)

µ-XRD 2D maps



Rietveld refinement



- The Sr-rich phase is identified as $SrZrO_3$ zirconates.
- Sr release from the electrode material after ageing in electrolysis mode.
- Formation of an Inter-Diffusion Layer (IDL) at the interface with the electrolyte

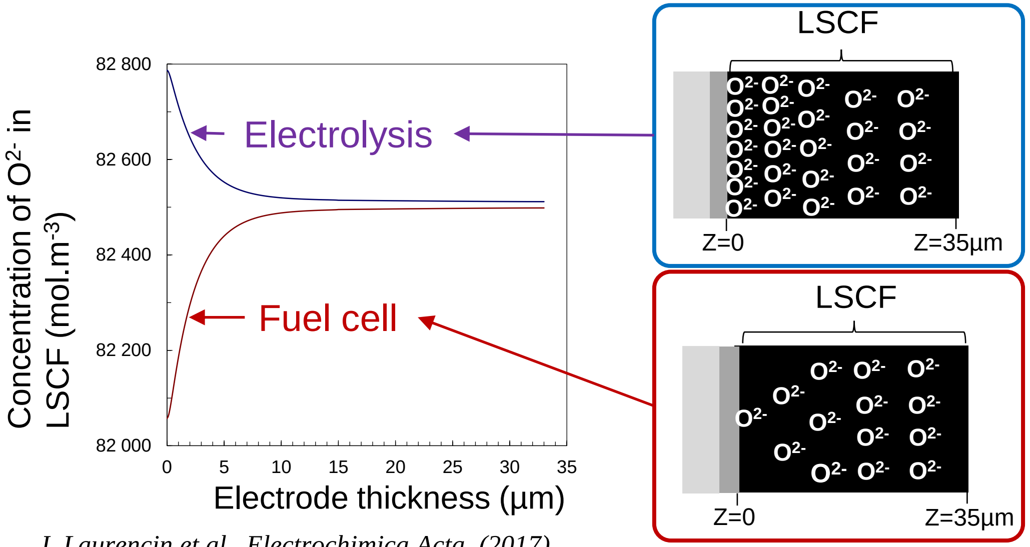
How to explain these observations ?

O_2 electrode durability – Mechanism for LSCF destabilization and reactivity with the electrolyte

Proposed mechanism to explain LSCF destabilization and formation of $SrZrO_3$ triggered under SOEC mode.

- Computation of the local quantities with the micro-model in the O_2 electrode in the conditions of cell ageing (SOEC, 850ºC).

  - ☑ Strong accumulation of O^{2-} in LSCF upon electrolysis operation.



J. Laurencin et al., Electrochimica Acta. (2017)

F. Monaco et al., Int. J. Hydrog. Energy. (2021)

- Proposed scenario for the degradation in electrolysis mode

① Sr release

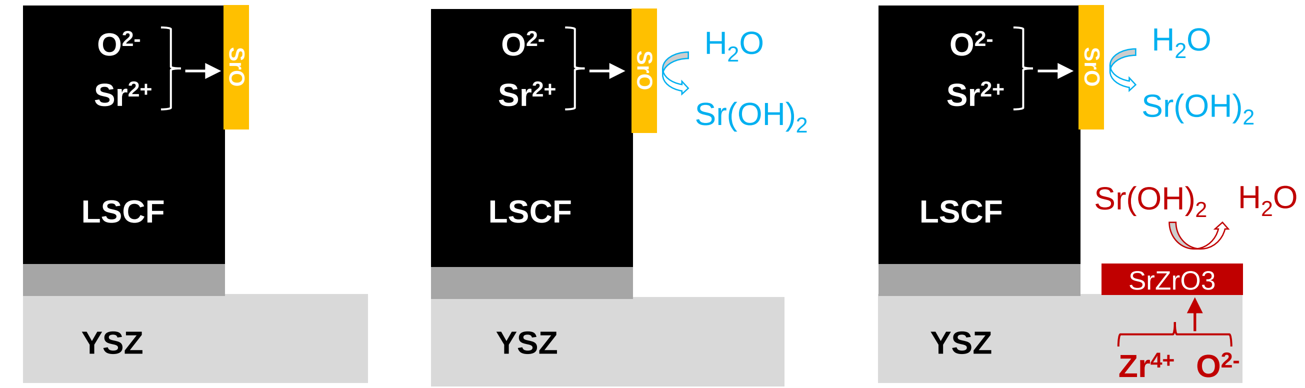
$Sr^{+2}+O^{2-}\rightarrow SrO$

② Evaporation

$SrO+H_2O\rightarrow Sr(OH)_2$

③ Reactivity

$Sr(OH)_2+Zr^{4+}+2O^{-2}\rightarrow SrZrO_3+H_2O$



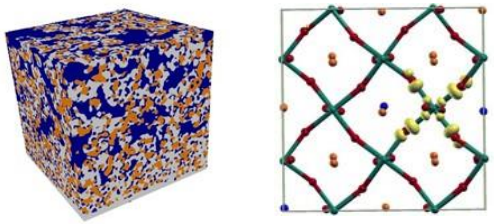
- The SrO passivation film hinders the surface reactions.
- Sr loss induces a decrease in oxygen chemical diffusivity for LSCF

- LSCF destabilization could explain, in part, the higher degradation rates in electrolysis mode.

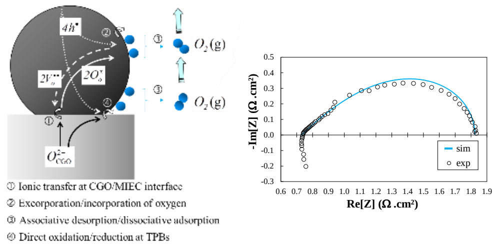
- Role of the IDL must be clarified.

Concluding remarks - Electrochemical, Thermal and Mechanical response of the SOFC/SOEC

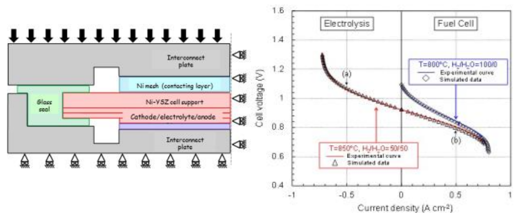
μ-structure (nm)

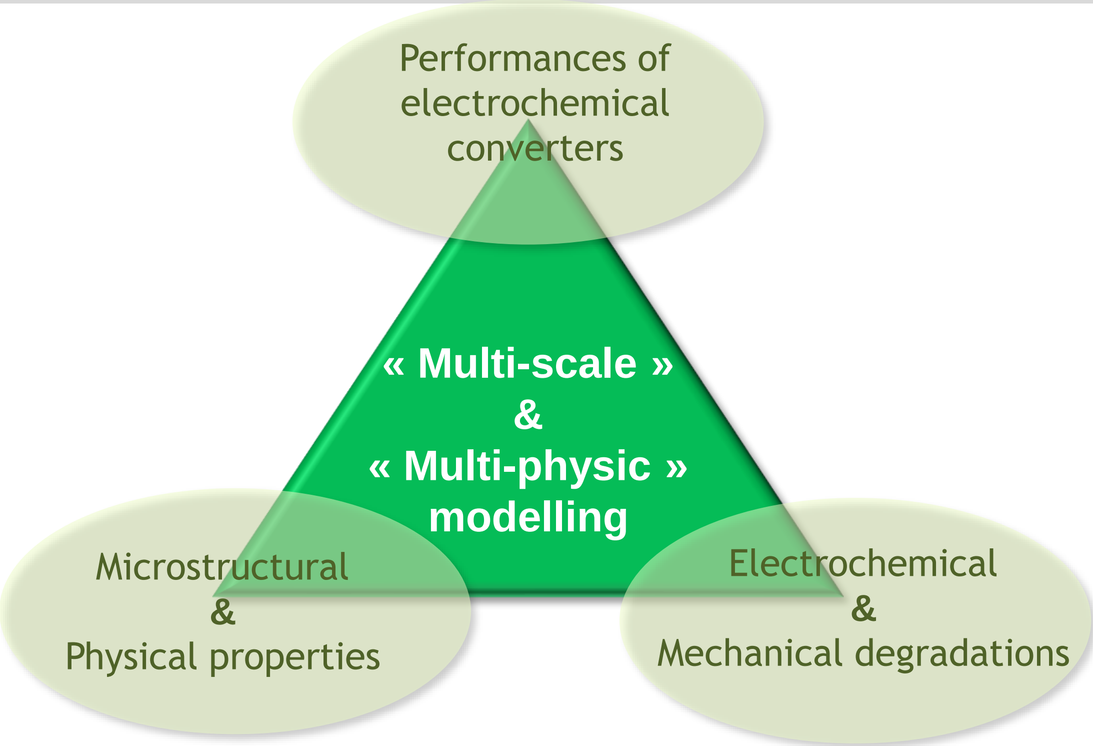


Electrode (μm)



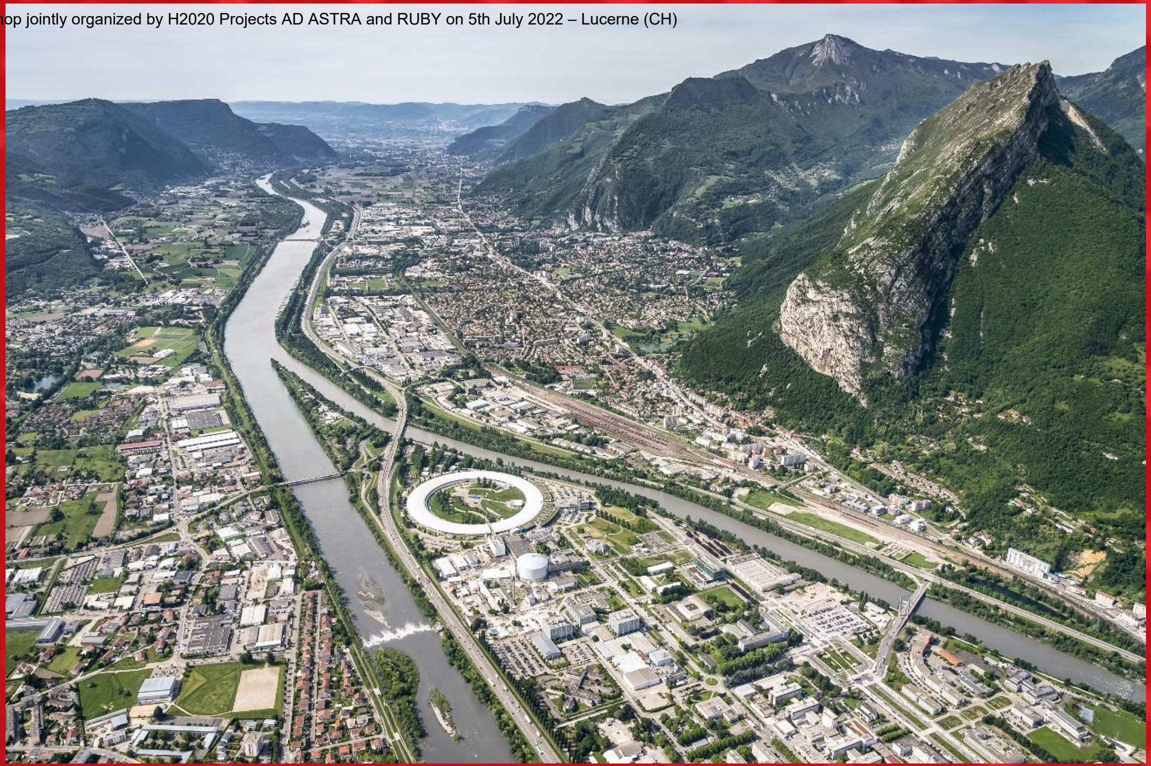
Cell + Interconnect (mm)





- Development of a methodology based on modeling and advanced post-test characterizations
- Analysis of the main issues of SOCs: performances and durability
- Application to new electrode materials (LNO,Pr_6O_{11})
- First principle studies for a better understanding of SOCs

Thank you for your attention



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