SOFC DEGRADATION STUDIES THROUGH A MULTISCALE MODELLING

Process Engineering Research Team

Fiammetta Bianchi, Barbara Bosio

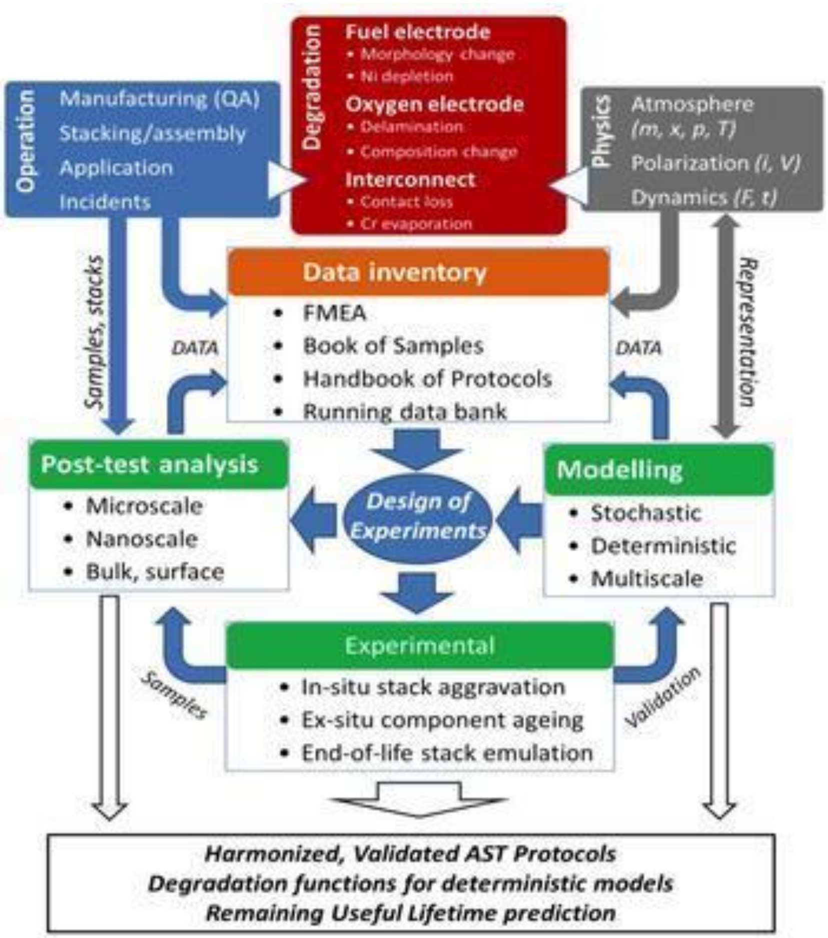
(5 July 2022 – Lucerne (CH))

CONTENTS

- AD ASTRA MODELLING ACTIVITY
- METHODOLOGY
- MACROSCALE ANALYSIS: GLOBAL CELL DEGRADATION DUE TO LONG LASTING OPERATION AND ACCELERATED STRESS TESTS
- MESOSCALE ANALYSIS: EFFECTS OF EX-SITU AGED COMPONENTS ON FULL CELL POLARIZATION LOSSES
- MICROSCALE ANALYSIS: MICROSTRUCTURAL CHANGE DEPENDENCES ON ELECTROCHEMICAL KINETICS
- CONCLUSIONS

AD ASTRA MODELLING ACTIVITY

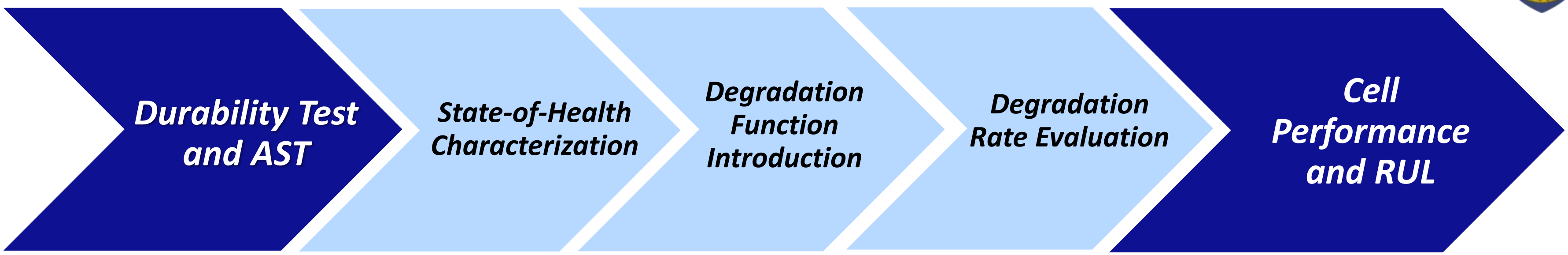
Multiscale Modelling Approach



- **Central role** of modelling activity within AD ASTRA research project for leading experimental tests, reaching better understanding of cell operation, building useful control systems, designing effective mitigation strategies
- Need of a **multiscale approach** in view of cell behaviour complexity by involving several degradation sources and multiple dependences among structural and working parameters

AD ASTRA MODELLING ACTIVITY

Aim of Work

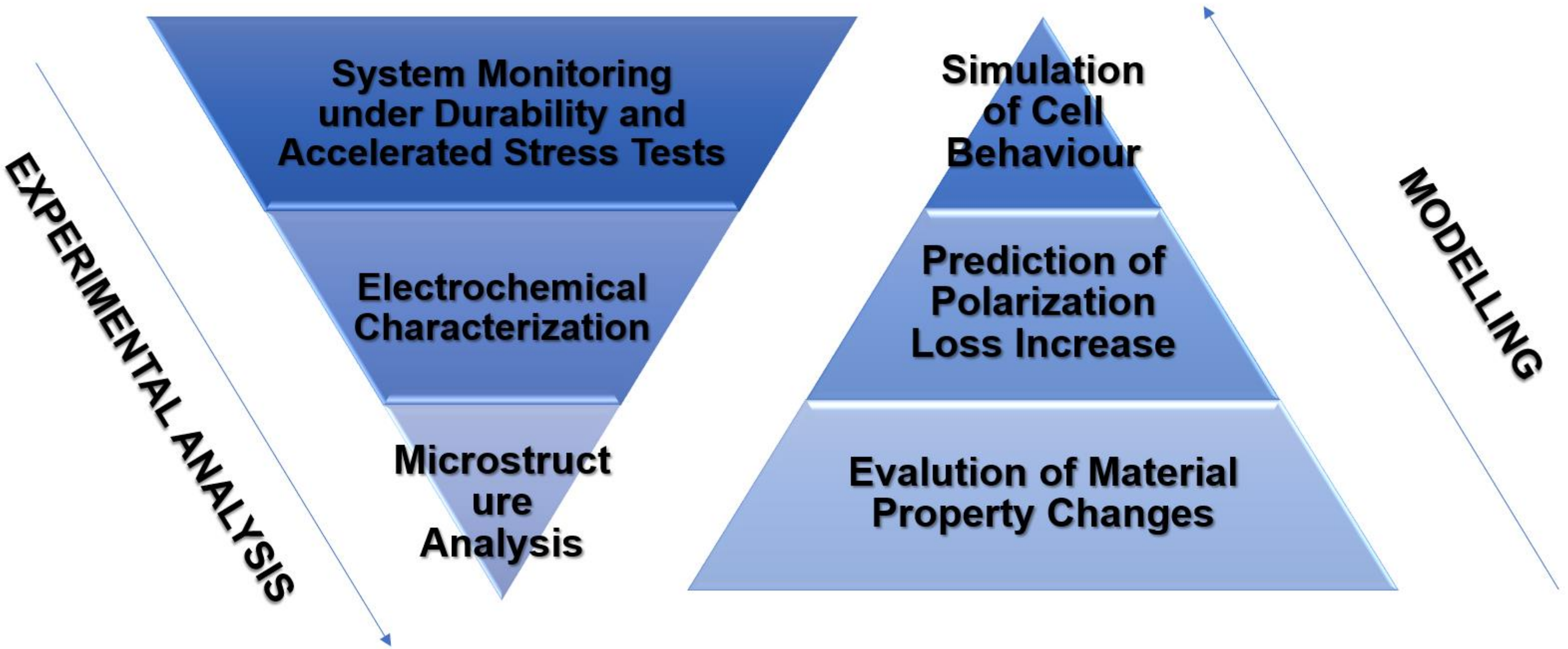


TASK TARGET: Multiscale model predicting solid oxide fuel cell performance and durability as a function of working and microstructure parameters

- Degradation study looking at durability test and Accelerated Stress Test (AST) on full cells or single components
- Preliminary model validation on cell operation at nominal state (i.e., time equal to zero) and reference performance characterization
- Introduction of specific degradation functions at different scales according to experimental observations and desired level of detail
- Multiscale approach to evaluate degradation influence on electrochemical performance and kinetics aiding at Remaining Useful Life (RUL) estimation

METHODOLOGY

Multiscale Studies through Experiments and Simulation



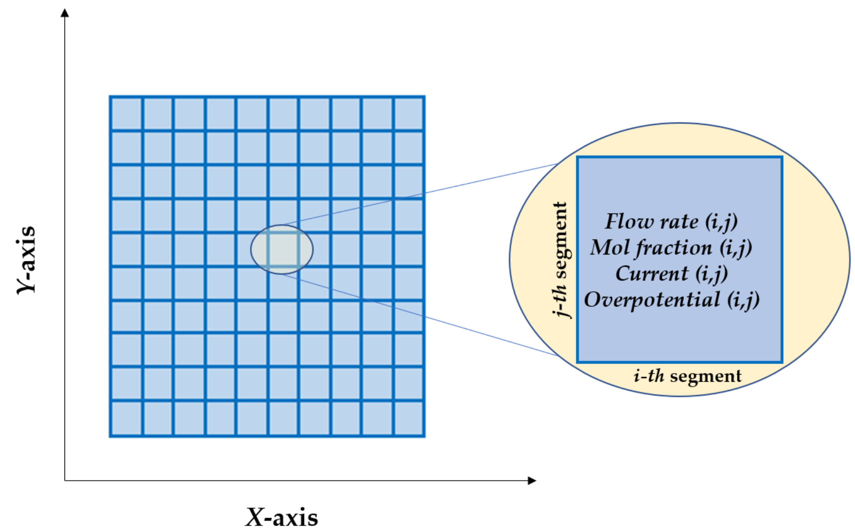
- **MACROSCALE LEVEL:** Global performance evaluation in terms of available voltage/power as a function of working point and operation time
- **MESOSCALE LEVEL:** Degradation effects on polarization losses looking at cell electrochemical kinetics in details
- **MICROSCALE LEVEL:** Material property dependences on microstructural features and their time variations under specific working conditions

METHODOLOGY

SIMFC: SIMulation of Fuel Cells

Kinetics Formulation → *Conservation Equations* → *0D Model* → *Discretization on Cell Plane* → *2D Model*

- **Physical based model** for high temperature cell simulation
- **Conservation equation** resolution in term of material, energy, momentum and charge balances
- **Lumped-parameter model** for global cell performance evaluation, easy integrated in commercial process simulation software Aspen Plus to study system balance of plant
- **Higher level model** for detailed analysis by discretizing the cell plane to compute global behaviour as a function of physicochemical feature local maps



METHODOLOGY

SIMFC Electrochemical Kinetics

Term	Formulation
Cell voltage	$V_{SOFC} = E_{eq} - V_{ohm} - V_{act} - V_{diff}$
Equilibrium voltage	$E_{eq} = E^0(T) + \frac{RT}{zF}\ln\left(\frac{p_{H_2}p_{O_2}^{0.5}}{p_{H_2O}}\right)$
Ohmic overpotential	$V_{ohm} = \sum \frac{\delta}{\sigma}J = P_1 T \exp^{\left(\frac{P_2}{T}\right)} J$
Activation overpotential	$V_{act} = \frac{2RT}{zF}\sinh^{-1}\left\lvert\frac{J}{2J_0}\right\rvert$ where $J_{0,fuel} = \gamma_{fuel}(y_{H_2})^A(y_{H_2O})^B \exp^{-\left(\frac{E_{act,fuel}}{RT}\right)}$ $J_{0,air} = \gamma_{air}(y_{O_2})^C \exp^{-\left(\frac{E_{act,air}}{RT}\right)}$
Diffusion overpotential	$V_{diff,fuel} = \frac{RT}{zF}\ln\left\{\frac{\left[1+\frac{RTJ}{zFp_{H_2O}}\left(\frac{\delta_{sup}}{D_{H_2O\_sup}}+\frac{\delta_{act}}{3D_{H_2O\_act}}\right)\right]^{2B}}{\left[1-\frac{RTJ}{zFp_{H_2}}\left(\frac{\delta_{sup}}{D_{H_2\_sup}}+\frac{\delta_{act}}{3D_{H_2\_act}}\right)\right]^{2A}}\right\}$ $V_{diff,air} = \frac{2RTC}{zF}\ln\left[\frac{p_{O_2}\theta_{O_2}}{p-(p-p_{O_2}\theta_{O_2})\exp\left(\frac{\theta_{O_2}RT\delta_{air}J}{zFpD_{O_2}}\right)}\right]$

Semi-empirical electrochemical kinetics derived from Nernst, Ohm and Butler-Volmer equations

List of symbols

A, B, C = Kinetics orders, D = Diffusion coefficient, E_0 = Reversibile voltage, E_{eq} = OCV voltage, E_{act} = Activation energy (*fuel*= anode, *air*=cathode), F = Faraday constant, J = Current density, J_0 = Exchange current density, P = Electrochemical parameter, p = Pressure, R = Ideal gas constant, T = Temperature, V = Cell voltage-overpotential, y = Molar fraction, z = Number of transferred electrons, γ = Pre-exponential coefficient depending on TPB, δ = Electrode thickness (*act*= active layer, *sup*= support), θ = Diffusivity ratio coefficient.

Padinjarethil, A.K.; Bianchi, F.R.; Bosio, B.; Hagen, A. Electrochemical Characterization and Modelling of Anode and Electrolyte Supported Solid Oxide Fuel Cells. Front. Energy Res. 2021, 9, 668964

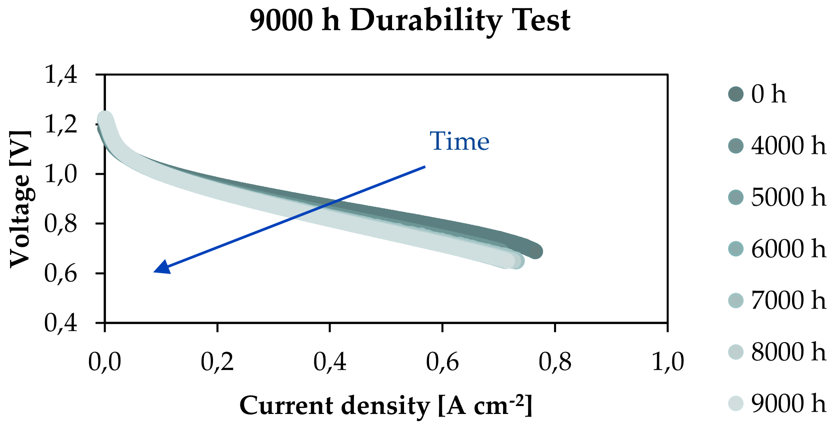
MACROSCALE DEGRADATION ANALYSIS

Global Cell Degradation due to Long Lasting Operation and Accelerated Stress Tests

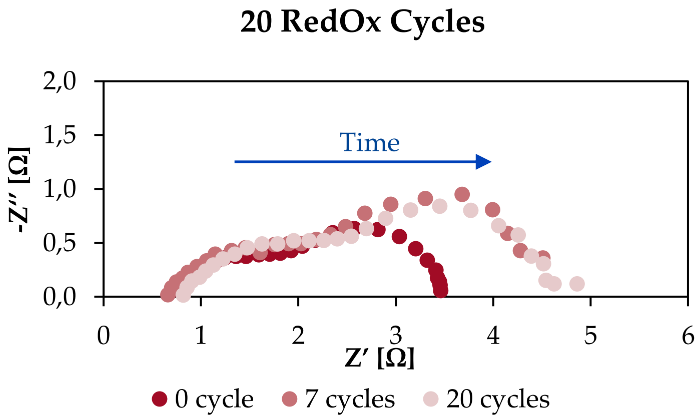
Experimental activity: Anode support small scale cells composed by Ni-YSZ/YSZ/LSCF-CGO

Tests	Testing Conditions	Electrochemical Characterization	Reference Working Conditions
Durability Test	9000 h working under 0.5 A cm^{-2}	Voltage monitoring, EIS and IV curve measurements every 1000 h working (A)	Pure H_2 as fuel and dry air as oxidant at 1023 K
Accelerated Stress Test	20 RedOx Cycles by alternating oxidised and reduced environment at anode	Intermediate EIS and IV curve measurements between cycles (B)	

(A)



(B)



MACROSCALE DEGRADATION ANALYSIS

Global Cell Degradation due to Long Lasting Operation and Accelerated Stress Tests

Modelling activity: 0D model implemented in Aspen Plus

- Degradation functions derived only from electrochemical characterization
- Introduction of **further overpotential terms** to consider voltage reduction during time

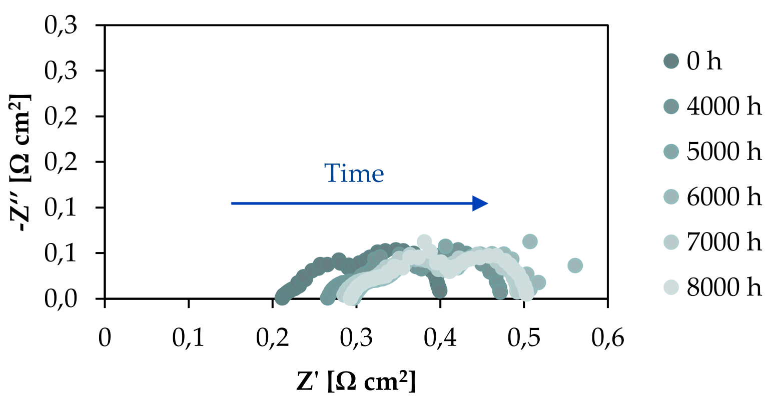
$$V_{SOFC} = E_{eq} - V_{ohm} - V_{act} - V_{diff} - \sum V_{deg}(t,J)$$

Where *t* refers to working hours in durability test, while to number of RedOx cycles in AST

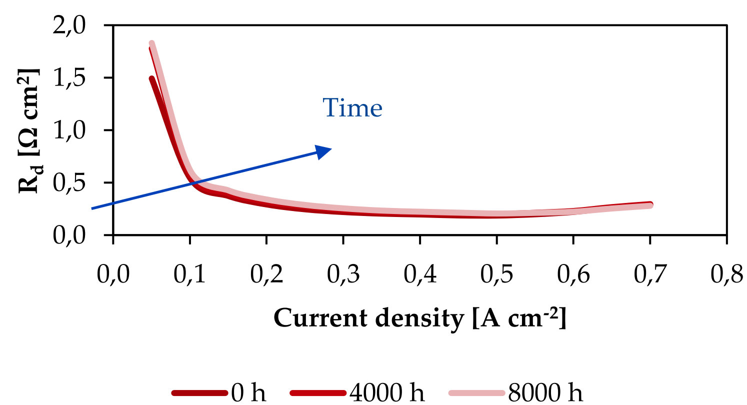
$\boldsymbol{V_{ohm\_deg}(t,J)}$ → internal resistance time evolution from EIS (A)

$\boldsymbol{V_{pol\_deg}(t,J)}$ → IV slope time changes from differential resistance (B)

(A) **9000 h Durability Test**



(B) **9000 h Durabilitity Tests**

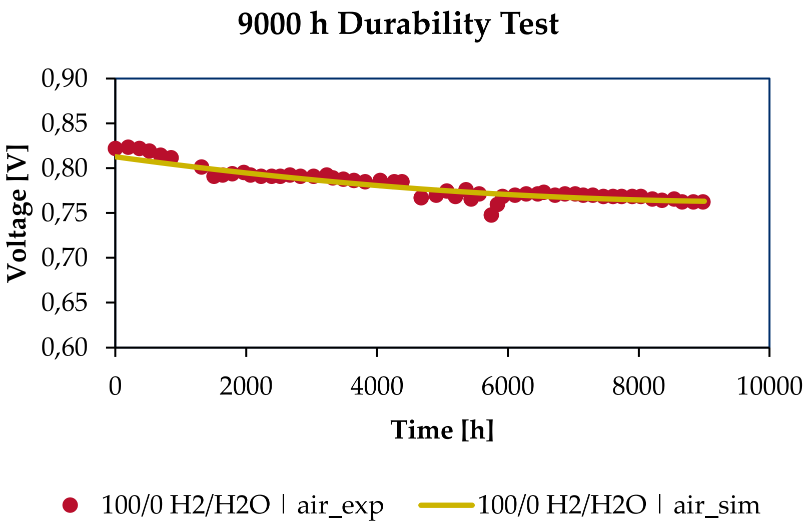


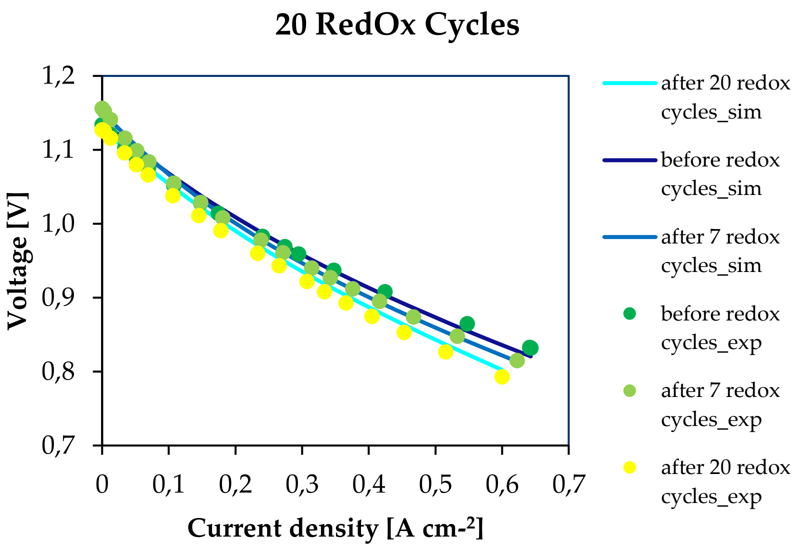
MACROSCALE DEGRADATION ANALYSIS

Global Cell Degradation due to Long Lasting Operation and Accelerated Stress Tests

Results:

- Model validation in term of cell voltage → relative error < 2 % for both durability test (A) and AST (B)





- 9000 h durability tests → ohmic overpotential increase as the main variation (from 57 % to 66 % of global losses)
- 20 RedOx cycles → changes on ohmic and above all activation overpotential correlated to anode aging
- **RedOx Cycles → effective accelerating source** permitting a voltage reduction due to just anode degradation comparable to 3330 h cell operation in durability test

MESOSCALE DEGRADATION ANALYSIS

Effects of Ex-situ Aged Components on Full Cell Polarization Losses

Experimental activity: Ex-situ tests on CuMnO/AISI441 interconnects

Test	Testing Condition	Electrochemical Characterization
Durability Test	400 h working under atmospheric air at 1023 K	Area Specific Resistance (ASR) measurements during operation and cooling ramps at different times

Modelling activity: 2D model for industrial scale cells

- Introduction of **specific degradation function only for cathodic coated interconnects** to evaluate their specific weight
- Arrhenius type formulation for interconnect ohmic resistance time evolution

$$R_{ohm}(t) = \gamma_{ohm}(t)\exp^{\left[\frac{E_{act,ohm}(t)}{RT}\right]}$$

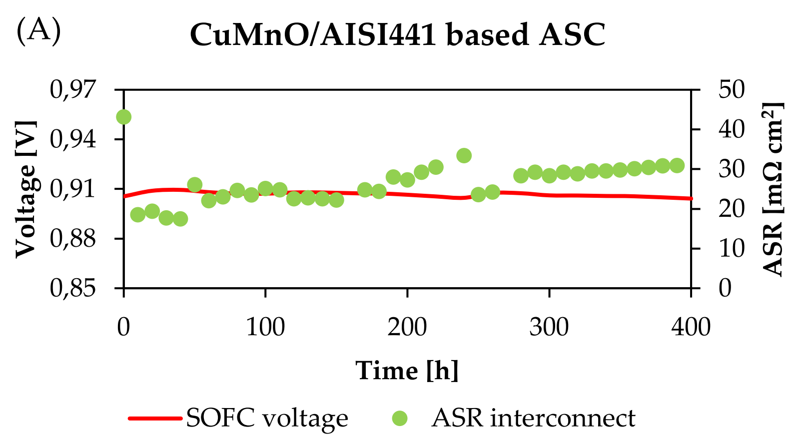
- Local simulation of anode supported cell performance assuming an adiabatic galvanostatic operation feeding direct hydrogen or a biogas

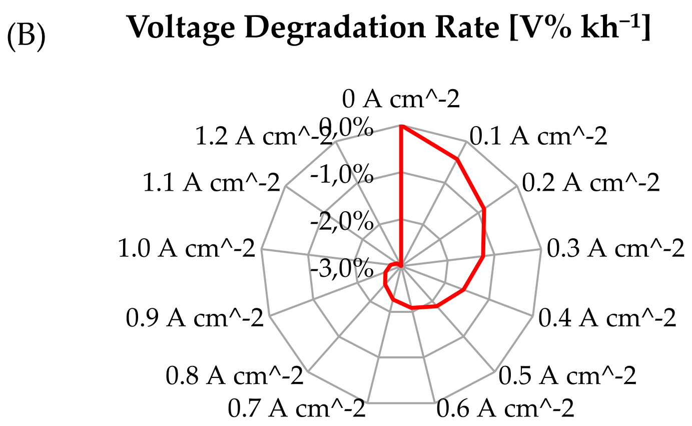
Spotorno, R.; Bianchi, F. R.; Paravidino, D.; Bosio, B.; Piccardo, P. Test and Modelling of Solid Oxide Fuel Cell Durability: A Focus on Interconnect Role on Global Degradation. Energies 2022, 15 (8), 2762.

MESOSCALE DEGRADATION ANALYSIS

Effects of Ex-situ Aged Components on Full Cell Polarization Losses

Results: Ni-YSZ/YSZ/LSCF-CGO anode supported cell fed by wet hydrogen





H_2 Direct Oxidation Conditions	
Active Area	80 cm^2 in co-flow
Inlet Gas Temperature	1023 K
Gas Composition	96/4 %mol H_2/H_2O mixture and air
Load	0.4 A cm^{-2} (11% as fuel utilization)

- Performance index → Degradation Rate

$$DR = \left(\frac{V_t - V_0}{V_0}\right)\frac{1000}{time}\ \%$$

- ASR almost doubling after 400 h→ **-0.35 V% kh^{-1} at 0.4 A cm^{-2}** as *DR* (A)
- Higher weight by increasing current density → **-3 V% kh^{-1}** as *DR* **at 1.2 A cm^{-2}** (B)

Spotorno, R.; Bianchi, F. R.; Paravidino, D.; Bosio, B.; Piccardo, P. Test and Modelling of Solid Oxide Fuel Cell Durability: A Focus on Interconnect Role on Global Degradation. Energies 2022, 15 (8), 2762.

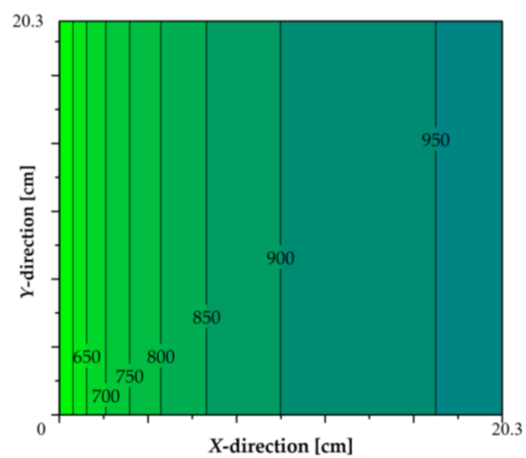
MESOSCALE DEGRADATION ANALYSIS

Effects of Ex-situ Aged Components on Full Cell Polarization Losses

Results: Ni-YSZ/YSZ/LSCF-CGO anode supported cell fed by biogas

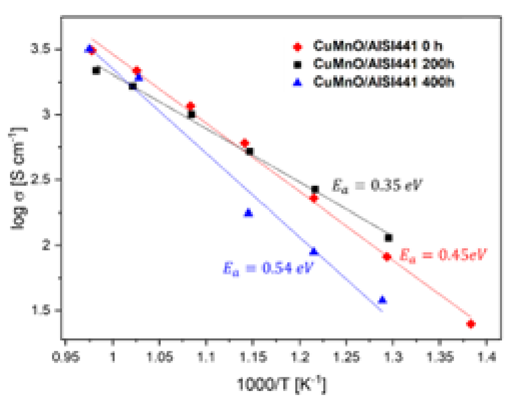
(A)

Fed Reactants →



(B)

CuMnO/AISI441 Resistance Dependence on Temperature and Time



Direct Internal Reforming Conditions	
Active Area	80 cm^2 in co-flow
Inlet Gas Temperature	1023 K
Gas Composition	Biogas (S/C >2) and air
Load	0.4 A cm^{-2}

- Performance index → Degradation Rate

$$DR = \left(\frac{V_t - V_0}{V_0}\right)\frac{1000}{time}\ \%$$

- Higher performance loss than previous case → **-3.1 V% kh^{-1}** as *DR* **at 0.4 A cm^{-2}** as *DR*
- Higher thermal gradient on cell plane (A) → Interconnect resistance increase (B)

Spotorno, R.; Bianchi, F. R.; Paravidino, D.; Bosio, B.; Piccardo, P. Test and Modelling of Solid Oxide Fuel Cell Durability: A Focus on Interconnect Role on Global Degradation. Energies 2022, 15 (8), 2762.

MICROSCALE DEGRADATION ANALYSIS

Microstructural Change Dependences on Electrochemical Kinetics

Experimental activity: Ni-YSZ/YSZ/LSCF-CGO anode supported cell (16 cm^2 area)

Test	Testing Condition	Electrochemical Characterization	Durability Test Working Conditions
Durability Test	1000 h working under 0.4 A cm^{-2} (11% as fuel utilization)	Voltage monitoring, EIS and IV curve measurements pre and post testing	96/4 %mol H_2/H_2O mixture as fuel and air as oxidant at 1023 K in co-flow

Modelling activity: 2D model for local performance control

- Detailed formulation through **percolation theory** for **H_2 electrode performance** resulting the most degraded layer
- Main kinetic parameters as a function of microstructure properties

Kinetics terms	Physicochemical features
Activation overpotential	$l_{TPB}^{eff} = f\,($particle radius, phase fraction, porosity$)$
Ohmic overpotential	$\sigma_i^{eff} = f\,($particle radius, phase fraction, porosity$)$
Diffusion overpotential	$D_i^{eff} = f\,($particle radius, phase fraction, porosity, tortuosity$)$

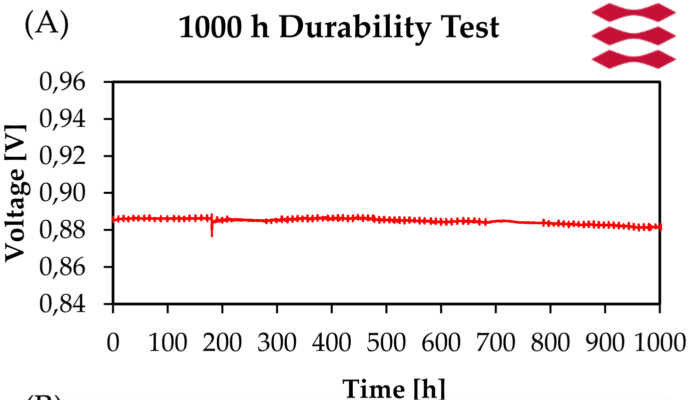
Bianchi, F. R.; Padinjarethil, A. K.; Hagen, A.; Bosio, B. Multiscale analysis of Ni-YSZ and Ni-CGO anode based SOFC degradation: From local microstructural variation to cell electrochemical performance. International Journal of Hydrogen Energy. (Under review)

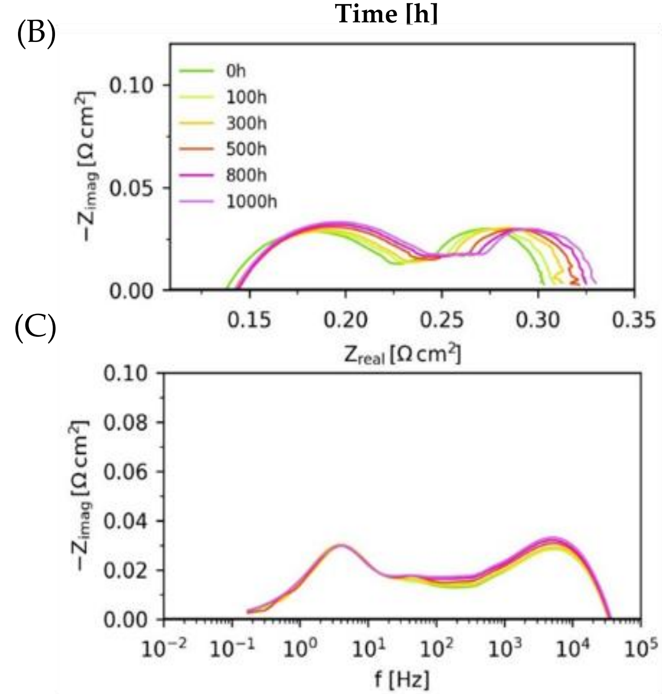
MICROSCALE DEGRADATION ANALYSIS

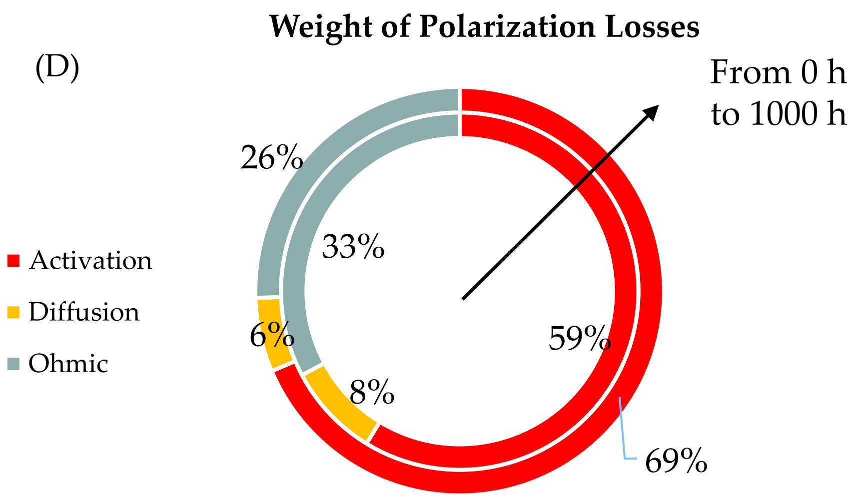
Microstructural Change Dependences on Electrochemical Kinetics

Results: Global performance

- Voltage degradation rate → **-0.6 V% kh^{-1}** (A)
- Polarization loss linear increase as 20 mΩ cm^2 kh^{-1} (B) → Changes interesting **high frequencies** above all (i.e., anodic losses) (C)
- **Activation overpotential** increase of ~46 % (D) → Kinetics main variation
- More than double anodic ohmic resistance → Still low values compared to electrolyte term







Bianchi, F. R.; Padinjarethil, A. K.; Hagen, A.; Bosio, B. Multiscale analysis of Ni-YSZ and Ni-CGO anode based SOFC degradation: From local microstructural variation to cell electrochemical performance. International Journal of Hydrogen Energy. (Under review)

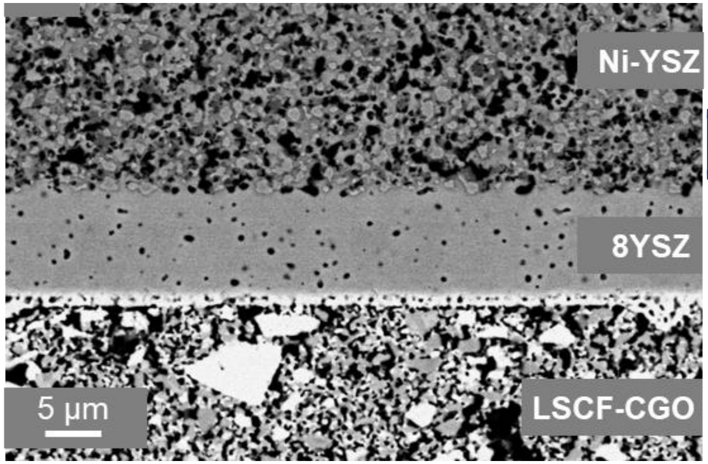
MICROSCALE DEGRADATION ANALYSIS

Microstructural Change Dependences on Electrochemical Kinetics

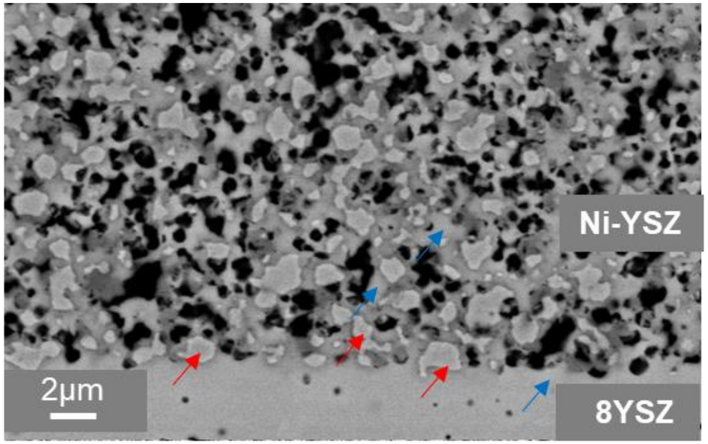
Results: H_2 electrode performance

- Main variations occurring within **active layer** (~10 μm) → Ni particle agglomeration and loss of a continuous percolating network (A)
- **Ni agglomeration** → Radius increase of 40 % (red arrows in B)
- **Ni instability** → Decrease of 50 % Perc Ni and increase of 3 times Non-perc Ni (C)

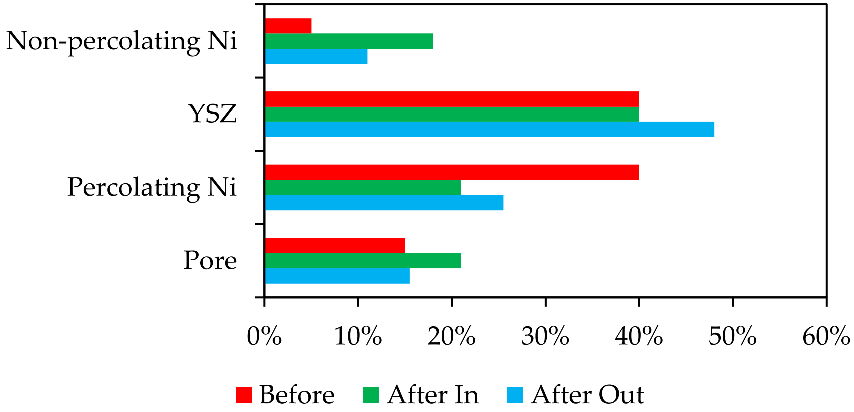
(A) Reference Cell Structure



(B) Ni Agglomeration in Active Layer



(C) Ni-YSZ phase fraction [-]



Bianchi, F. R.; Padinjarethil, A. K.; Hagen, A.; Bosio, B. Multiscale analysis of Ni-YSZ and Ni-CGO anode based SOFC degradation: From local microstructural variation to cell electrochemical performance. International Journal of Hydrogen Energy. (Under review)

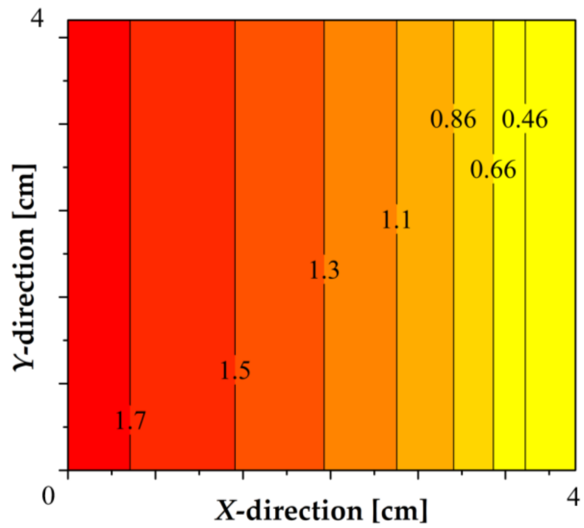
MICROSCALE DEGRADATION ANALYSIS

Microstructural Change Dependences on Electrochemical Kinetics

Results: H_2 electrode performance

- TPB length → 3.1 μm^{-2} @ 0 h vs. 1.25 μm^{-2} @ 1000 h (A)
- Cermet conductivity → 3 order of magnitude lower @ 1000 h
- Higher variation at cell outlet → **Water as accelerating degradation source**
- Anodic activation overpotential increase → Minimum local profile on aged cell plane (B-C)

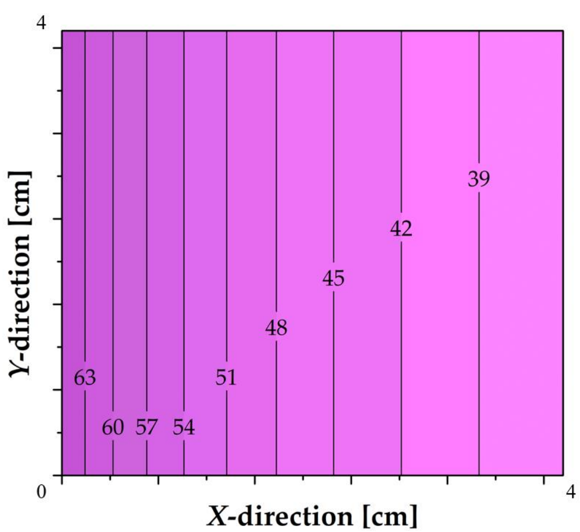
(A)



TPB length of aged cell [μm^{-2}]

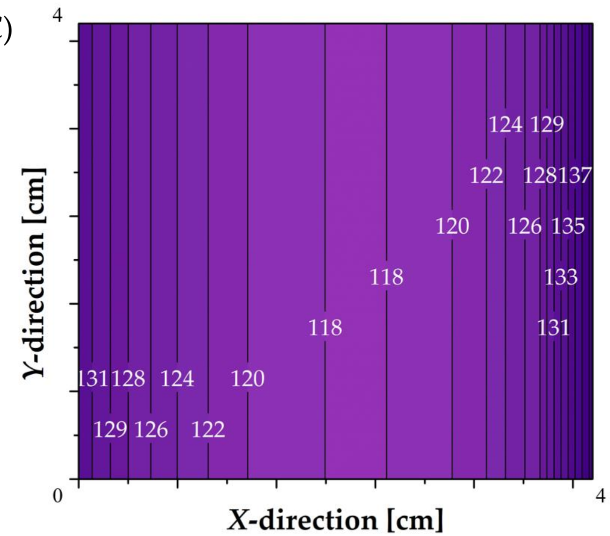
(B)

Fed Reactants →



Anodic activation overpotential at 0 h (B) and at 1000 h (C) [mV]

(C)



Bianchi, F. R.; Padinjarethil, A. K.; Hagen, A.; Bosio, B. Multiscale analysis of Ni-YSZ and Ni-CGO anode based SOFC degradation: From local microstructural variation to cell electrochemical performance. International Journal of Hydrogen Energy. (Under review)

CONCLUSIONS

AD ASTRA TASK: Modelling of solid oxide cell performance and durability

- SIMFC (SIMulation of Fuel Cells): physical based model for multiscale analysis

From lumped-parameter model to higher level one depending on system scale and analysis detail

From macro empirical to micro detailed degradation functions into electrochemical kinetics

- MACROSCALE LEVEL: Introduction of **empirical further overpotentials** to consider degradation derived from electrochemical characterization and validation for both durability and accelerated stress tests
- MESOSCALE LEVEL: Introduction of **time dependent parameters** into reference kinetics and application pairing ex-situ tests on single layer to full cell performance simulation
- MICROSCALE LEVEL: Formulation of **kinetics parameters as a function of microstructure time variations** and application evaluating specific degradation mechanisms with a focus on H_2 electrode aging

ACKNOWLEDGEMENTS

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under **Grant Agreement No 825027**. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe.

www.ad-astra.eu