17th Symposium on Modeling and Experimental Validation of Fuel Cells, Electrolysers and Batteries

3-D morphology-based modelling of Ni-YSZ electrodes microstructural evolution in solid oxide cells.

Session: C3 Solid Oxide cells microstructures

April 20th 2021

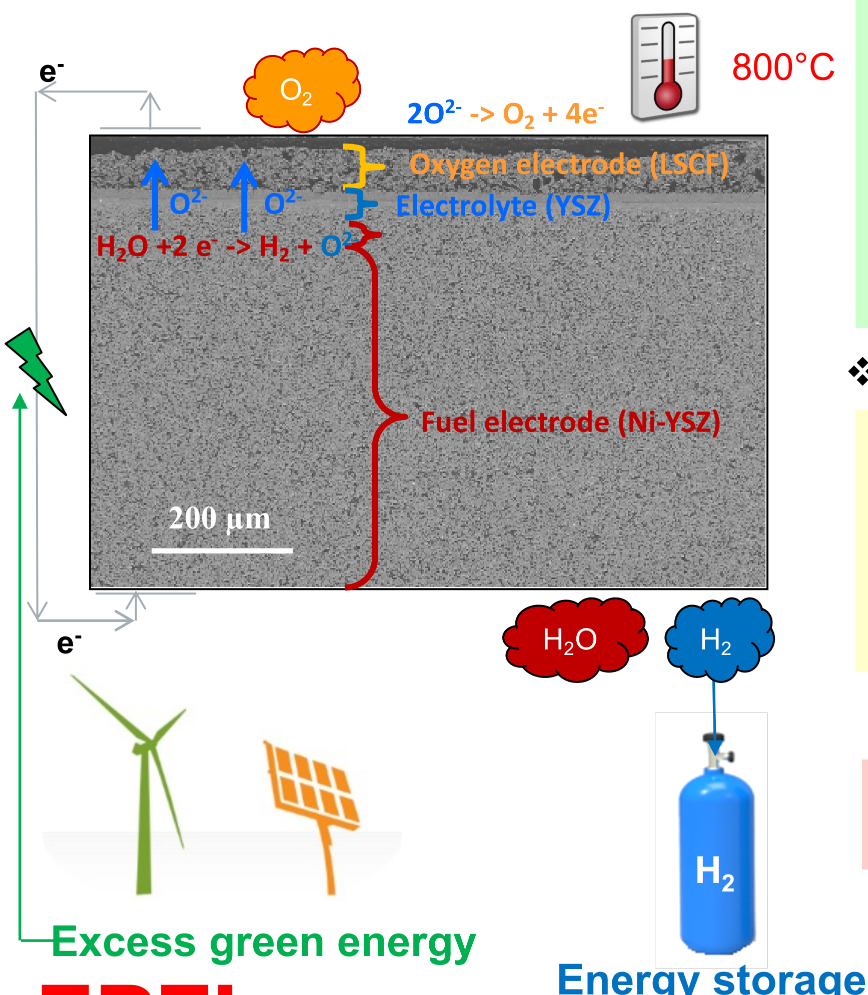
Hamza Moussaoui[1], Arata Nakajo[1], Giorgio Rinaldi[1], Maxime Hubert[2], Jérôme Laurencin[2], Jan Van herle[1]

(1) Group of Energy Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
(2) Univ. Grenoble Alpes, CEA/LITEN, 17 rue des Martyrs, 38054, Grenoble, France

EPFL

Context of study & Problematic

➢ **Solid Oxide Cell (SOC)**
(illustration in Electrolysis operation)



❖ **Advantages**

- ☺ **Flexibility** SOFC/SOEC mode (electrical power generation and H_2 production).
- ☺ **High efficiency** for both modes, without expensive catalyst (Pt).
- ☺ Large **fuel flexibility** in SOFC mode: CO oxidation, Direct feeding of SOFC under CH_4
- ☺ **Co-electrolysis possibility** of steam and CO_2 in SOEC mode

❖ **Drawbacks**

- ☹ **Degradation rate** is still relatively high to be industrialized on a large scale.
- ☹ The fuel electrode, and the **nickel** specifically is the weak link as it may undergo **morphological evolutions** and poisoning.

→ **Ni morphological evolution** still needs to be clearly understood to design more durable electrodes

Ni coarsening modelling

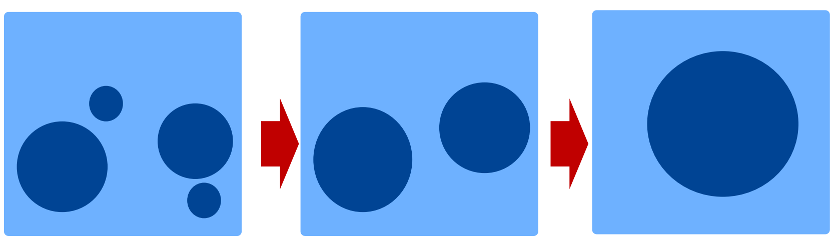
❖ Coarsening is a process by which a material's morphology evolves towards a state of minimal Gibbs free energy.

$$dG = \gamma dA \searrow$$

- G: Gibbs free energy
- γ: interfacial free energy
- A: Surface curvature

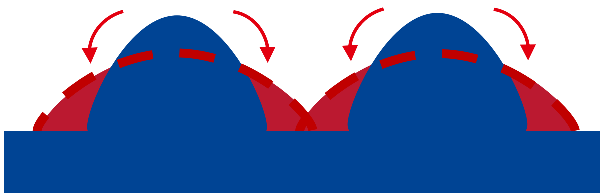
Mean field theories:

- Discreet set of spherical particles undergoing a competitive growth process



Topological theories:

1. Surface rounding
2. Network connectivity breakdown (Rayleigh instability)
3. Disconnected particles final stage



Model hypotheses

- Geometrical model based on Ni surface curvature minimization.

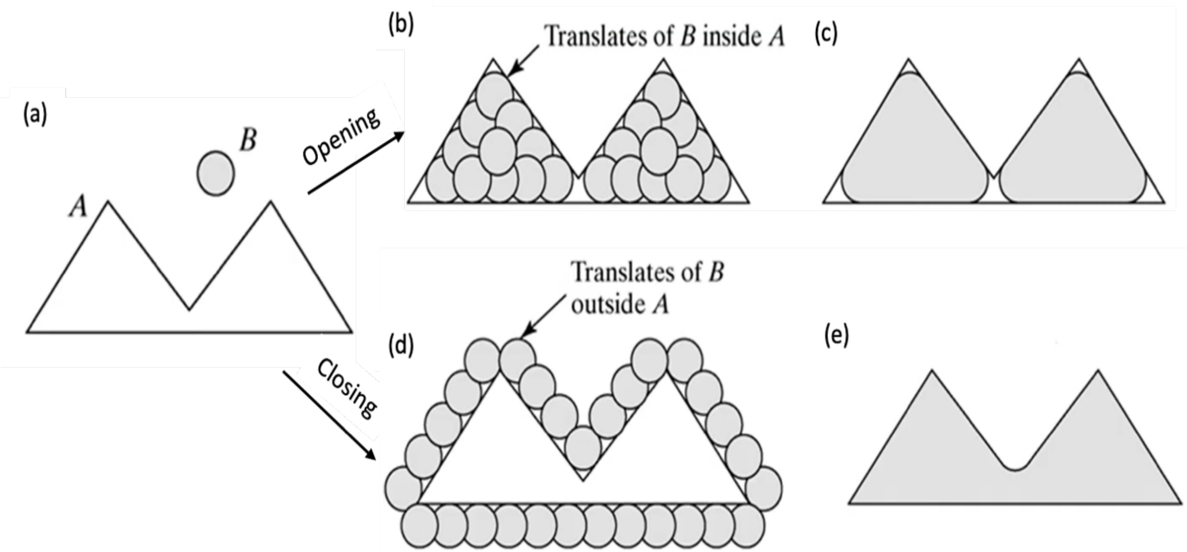
$$dG = \gamma dA \searrow$$

- G: Gibbs free energy
- γ: interfacial free energy
- A: Surface curvature

- Ni is relocated by using morphological operations (based on opening/closing by using a spherical structuring element).
- YSZ backbone is supposed to be unchanged
- Mass conservation is fulfilled
- Homogeneous agglomeration

Model steps

❖ **Elementary morphological operations**

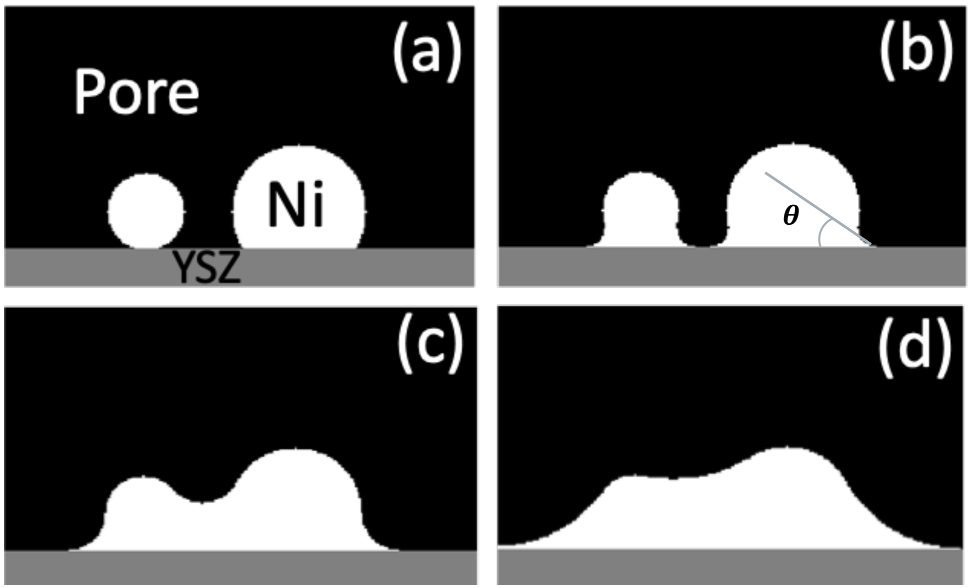


- **Opening**: The union of all the translations of B that fit entirely within A. In practice, it erases the Ni regions with a convex surface curvature higher than the one of the structuring element.
- **Closing**: The complementary of the volume we can reach when a sphere of radius r_{SE} is swept outside of the Ni phase without exceeding its borders. In practice, this will fill the neck regions with a concave surface curvature higher than the one of the structuring element.

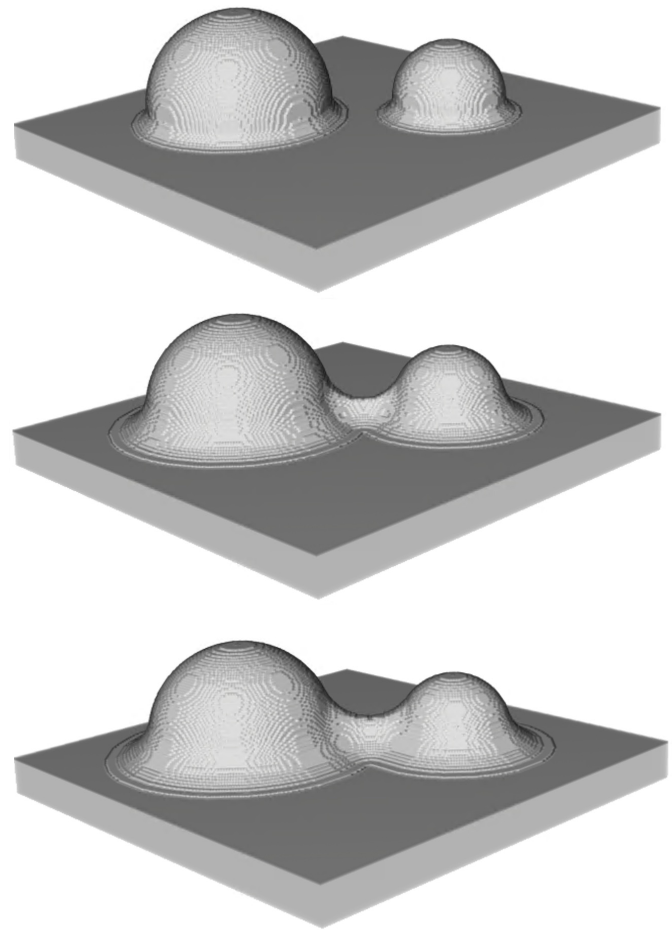
- **Step 1: Morphological opening:** It reduces surface rugosity by erasing the Ni regions with highly convex surface curvature ('humps'). This has the effect of smoothening the Ni particle boundaries.
- **Step 2: Morphological closing:** It creates necks between Ni particles and fills small holes. It acts on the highly concave Ni regions ('hollows').
- **Step 3: Dilation:** growing Ni boundaries uniformly without changing its surface curvature. In order to satisfy Ni mass conservation.

Validation on reference cases

➢ *2 Ni spherical particles on a YSZ substrate:*



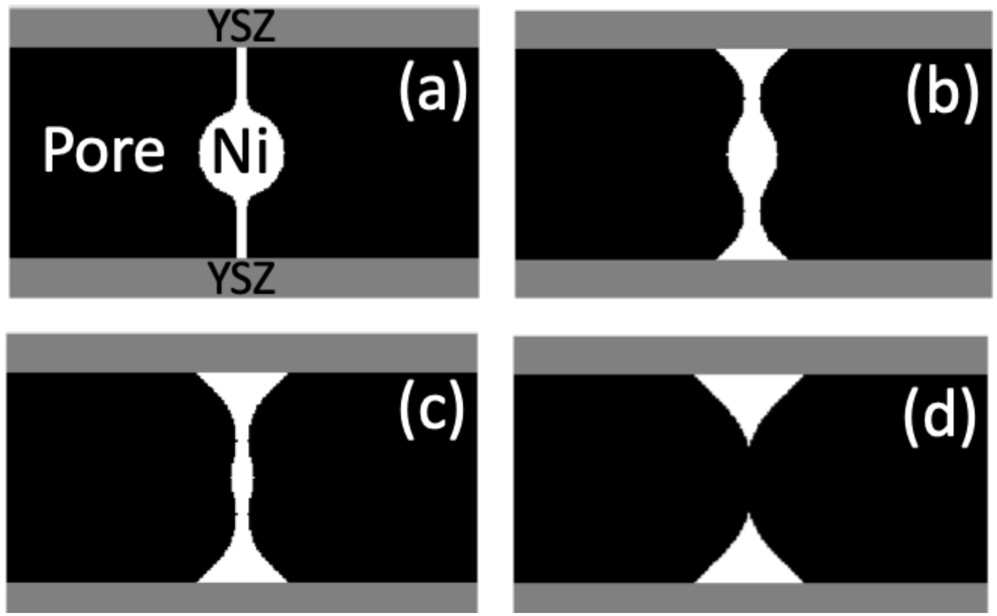
(a) Initial state of two spherical particles of Ni on a flat substrate of YSZ
(b-c) intermediate levels of coarsening
(d) final long-term evolution



✓ Competitive growth of the larger particles over the smaller ones is well modeled

Validation on reference cases

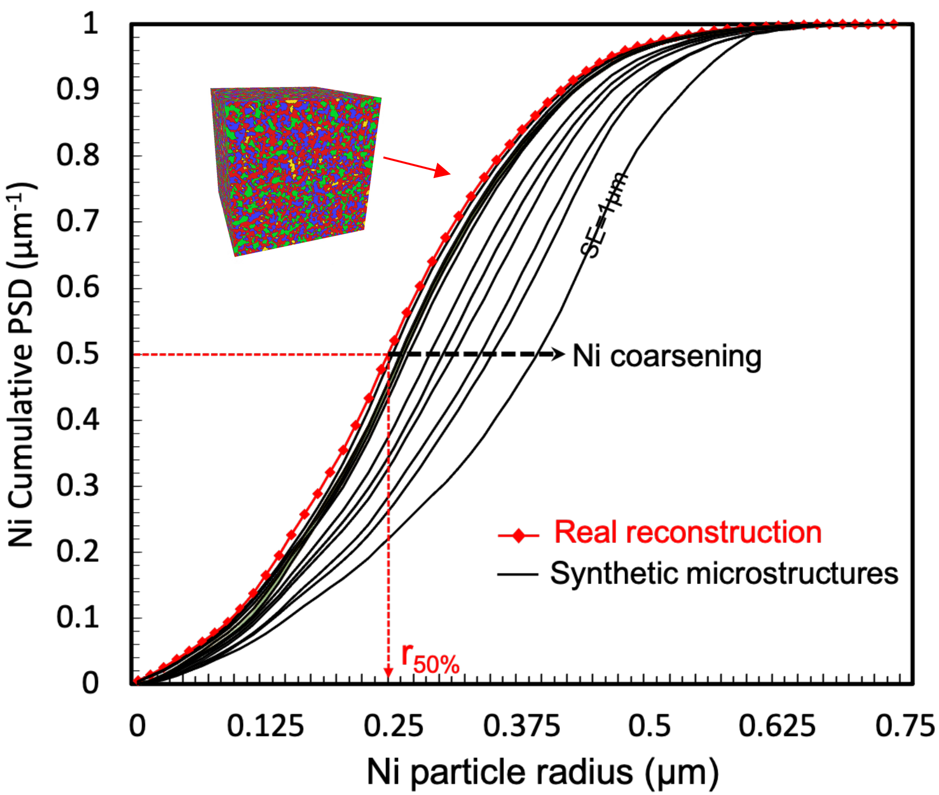
➢ *Ni 'neck' particle in contact with two YSZ substrates (Rayleigh instability):*

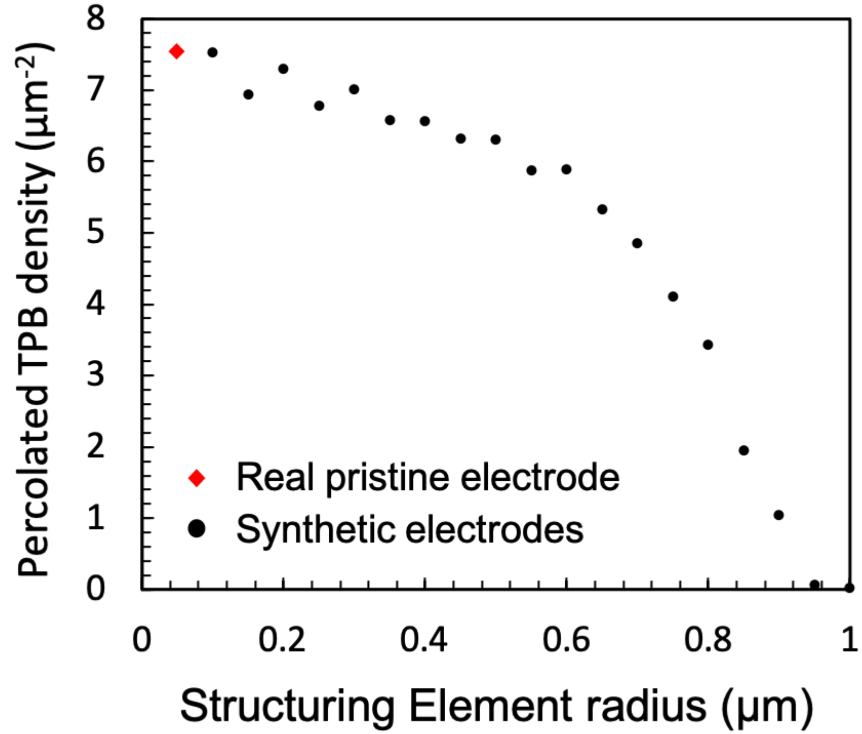


(a) Initial state of a Ni particle in contact with two YSZ substrates
(b-c) intermediate levels of coarsening
(d) final long-term evolution

✓ 'Pinch-off' is well simulated by the model

Microstructures generation

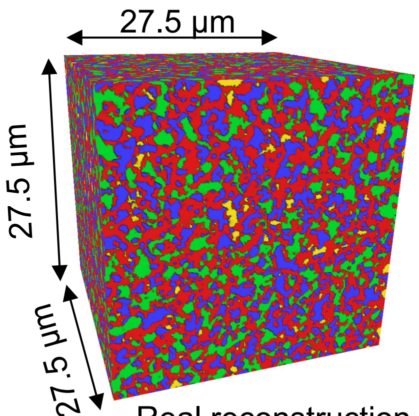




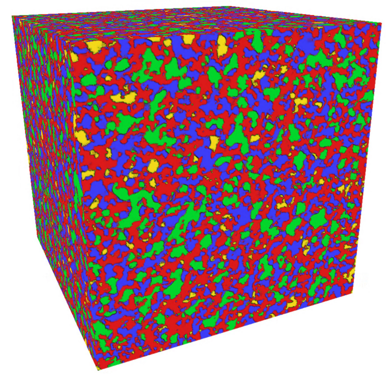
→ Different degrees of agglomeration can be modeled by controlling the structuring element size

Representativeness validation on an aged electrode in SOEC mode

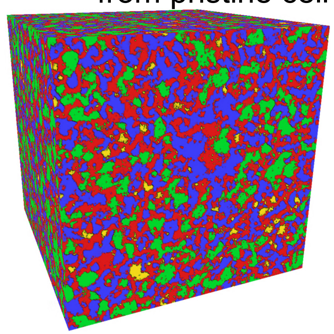
-0.5 A/cm² @850 degC during 1500 h



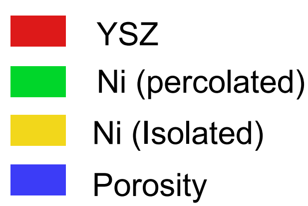
Real reconstruction from pristine cell

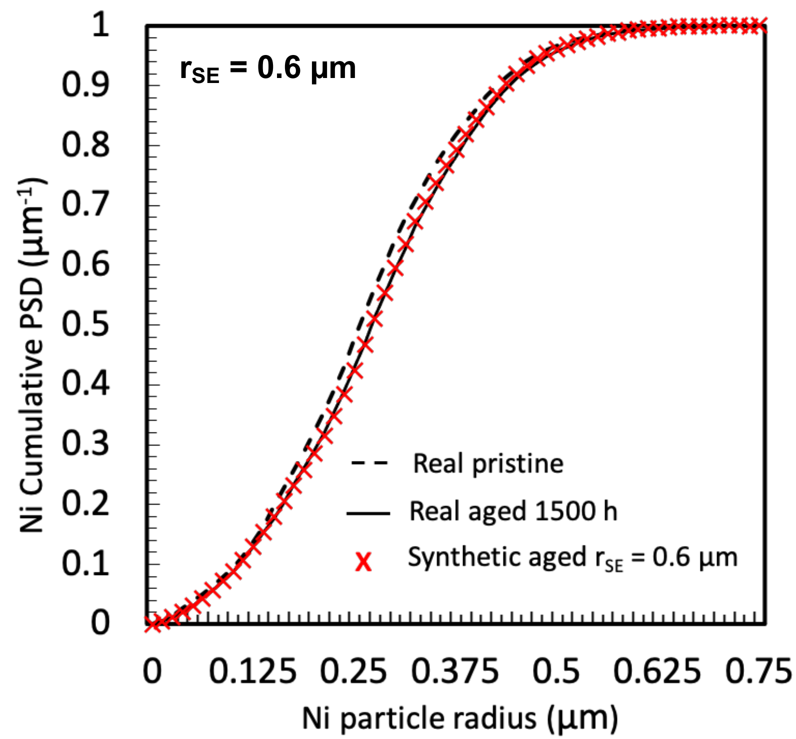


Synthetic microstructure after Ni evolution modelling using r_{SE} = 0.6 µm



Real reconstruction from aged cell after 1500 h





	Connected Ni volume fraction	Ni Phase diameter	Pore phase diameter	Ni Surface Area	Pore Surface Area	Ni M-factor	Pore M-factor	Connected TPB density
Real pristine reconstruction	26.16 %	0.47 µm	0.39µm	2.07 µm^{-1}	2.53 µm^{-1}	7.74	8.81	7.56 µm^{-2}
Real reconstruction from 1500h aged	25.78 %	0.55 µm	0.42 µm	1.84 µm^{-1}	2.42 µm^{-1}	9.38	4.25	6.13 µm^{-2}
Simulated microstructure	25.90 %	0.55 µm	0.42µm	1.91 µm^{-1}	2.45 µm^{-1}	9.12	4.66	5.98 µm^{-2}

→ Good agreement between the experimentally aged electrode and the simulated one

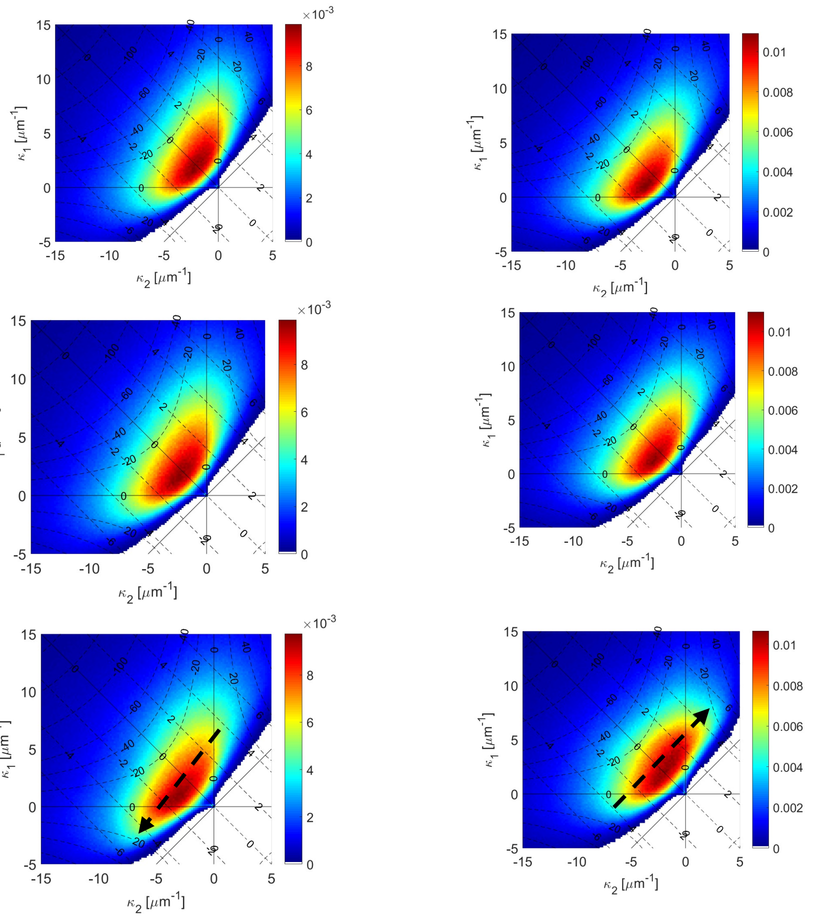
Interfacial Shape Distribution of the modelled electrodes

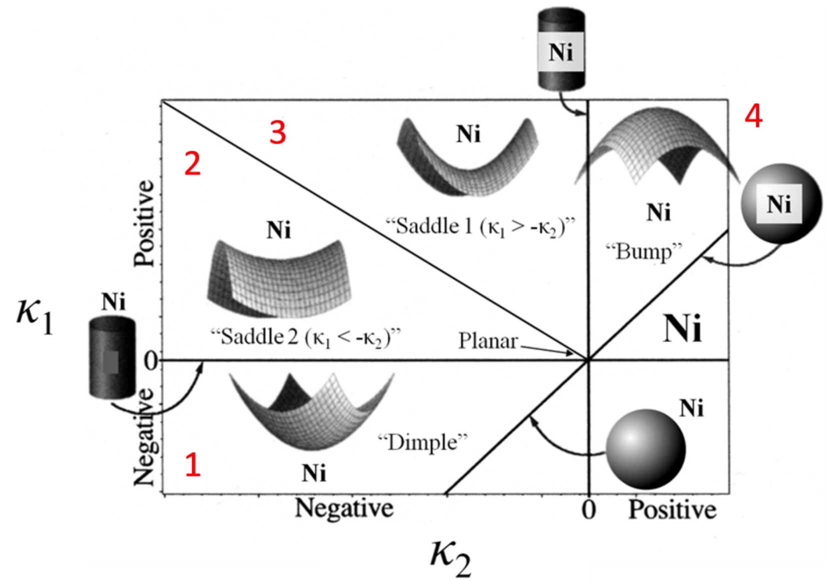
Porosity | Nickel

Initial microstructure

Intermediate level of Ni coarsening

Advanced level of Ni coarsening





- *Increase in Ni 'bumps' density, and decrease in Porosity 'dimples' density.*
- *Evolution in accordance with experimental results from real aged microstructures(*)*

→ Good agreement on the local morphology near TPBs.

(*) A. Nakajo et al., Evolution of the Morphology Near Triple-Phase Boundaries in Ni–Yttria Stabilized Zirconia Electrodes Upon Cathodic Polarization." ASME. J. Electrochem. En. Conv. Stor. (2020) 17(4): 041004

Conclusions & outlook

Conclusions

- *A morphological-based model is developed to simulate Ni agglomeration in Ni-YSZ fuel electrodes*
- *A large range of microstructures are generated by the model simulating different degrees of Ni evolution.*
- *The model showed a good agreement with the experimental data acquired from real reconstructions*

Ongoing and future work

- Use the model to investigate the effect of Ni agglomeration on the overall microstructural evolution
- Use the model to propose recommendations to mitigate Ni evolution, by microstructural optimization for example.
- Extend the model to simulate Ni migration

Thank you for your attention

This work has received funding from the Fuel Cells and Hydrogen Joint Undertaking under grant agreement N° 101007175 (REACTT), 875148 (SWITCH), and 825027 (AdAstra). This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation program, Hydrogen Europe and Hydrogen Europe research.