Session: Applied holotomography

# SUCCESSES AND CHALLENGES OF SYNCHROTRON X-RAY NANO-TOMOGRAPHY FOR THE CHARACTERIZATION OF SOLID OXIDE CELLS MATERIALS

Workshop on Coherence at ESRF-EBS | 12-09-2019

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# ACKNOWLEDGMENTS

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# CONTEXT

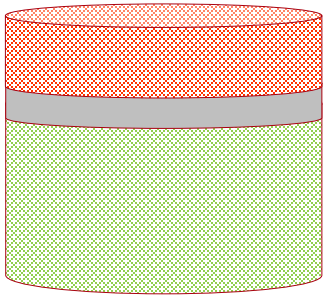
## High temperature Solid Oxide Cell (SOC)

| | |
|---|---|
| ☺ Efficient energy conversion system | ☹ Microstructural evolution |
| ☺ High flexibility: SOFC / SOEC modes | ☹ Electrode Poisoning |
| ☺ No expensive catalyst | ☹ Delamination |

**Insufficient lifetime for practical applicability of the technology**

## Materials and operation of a typical SOC

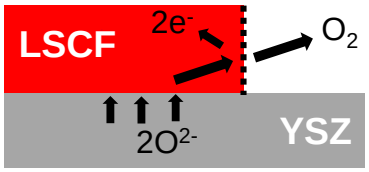
$O_2$ electrode
Electrolyte
$H_2$ electrode

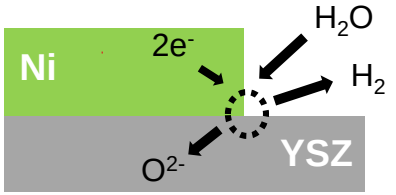


- LSCF: Lanthanum Strontium Cobalt Ferrite
- YSZ: Yttria stabilized Zirconia
- Ni-YSZ: ceramic-metallic composite

Reactive mechanisms illustrated in SOEC mode at both electrodes:

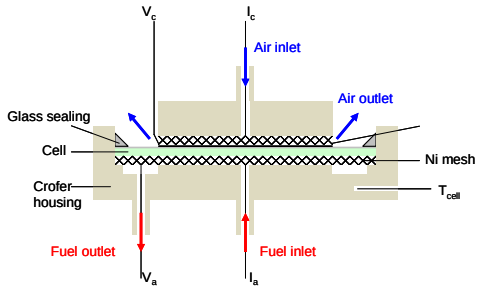
**Microstructure evolution detrimental on cell performances**



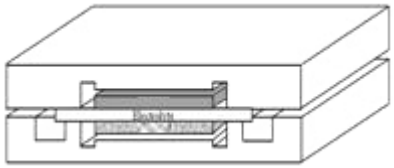



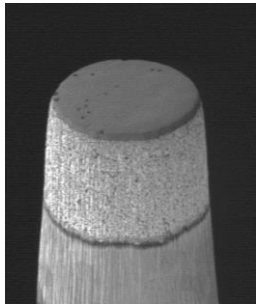
# METHODOLOGY

## A coupled experimental and modelling approach

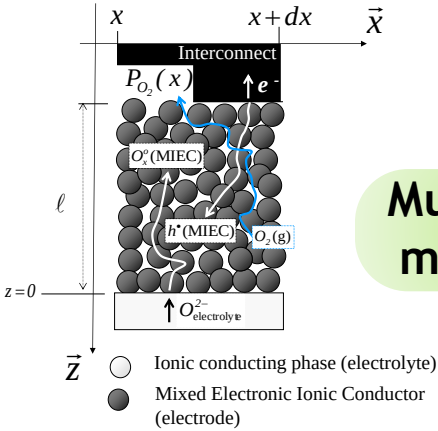



Electrochemical test



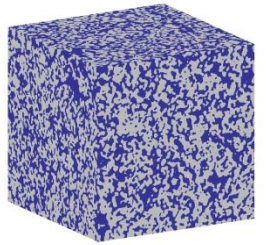


Forecast Modelling of SOC




Multi-scale modelling

Microstructural characterization

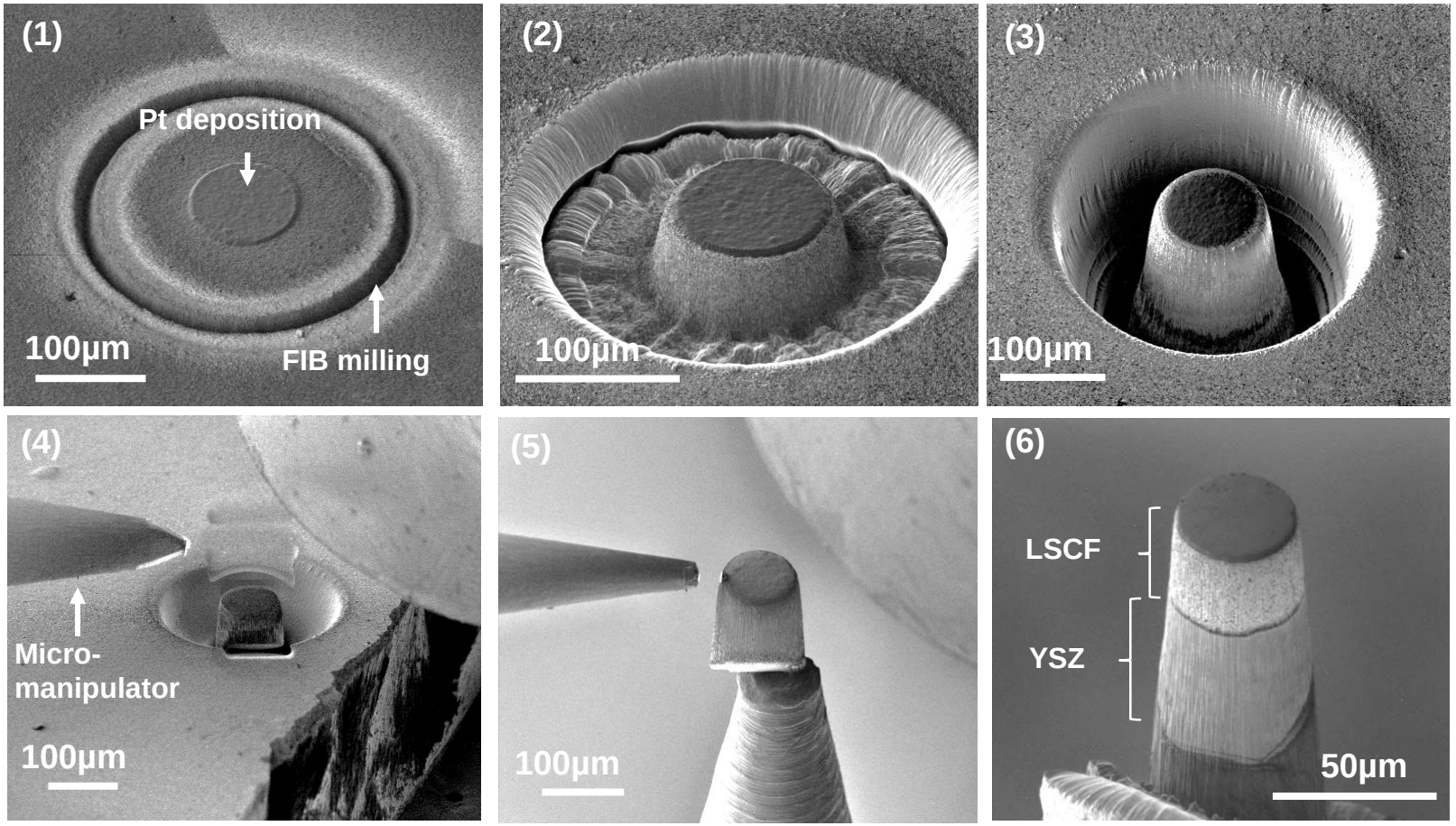


**Performance ↔ Microstructure ↔ Degradation**

# SAMPLE PREPARATION

## Specific process with Xe Plasma-FIB

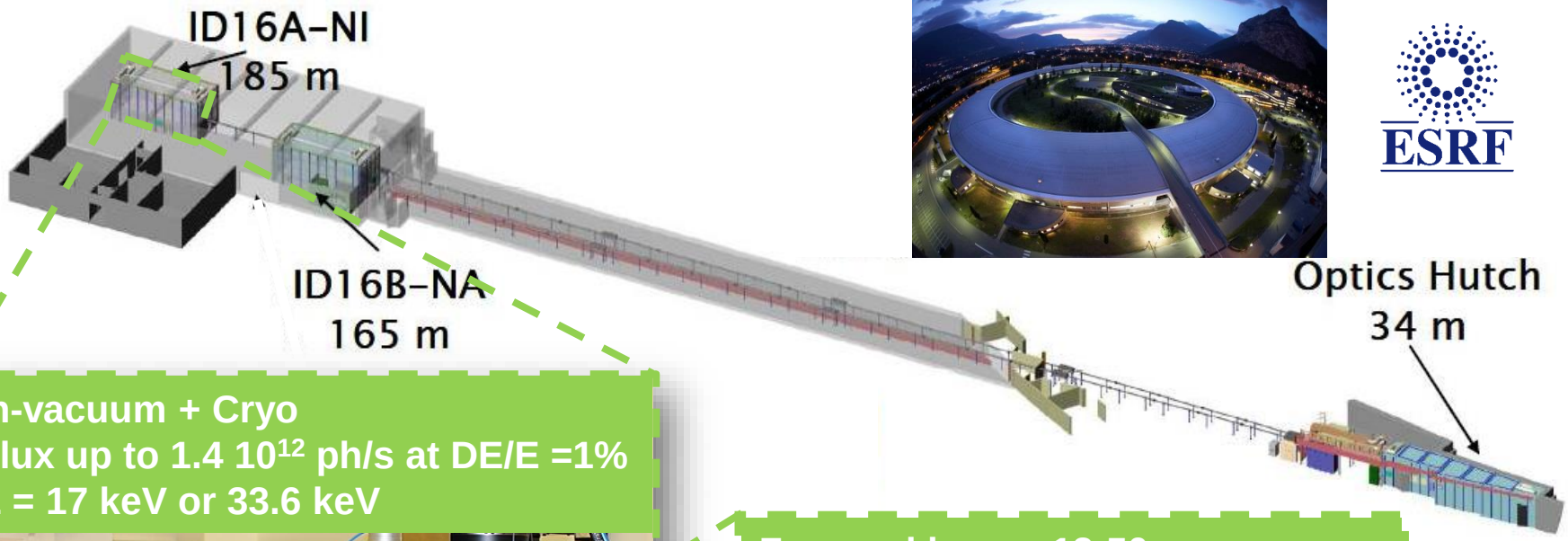
- Faster than conventional Ga FIB
- Sample size and localization easily chosen
- Axisymmetric geometry well adapted to tomography




M. Hubert et al. , Solid State Ionics (2016)

# MICROSTRUCTURAL CHARACTERIZATION

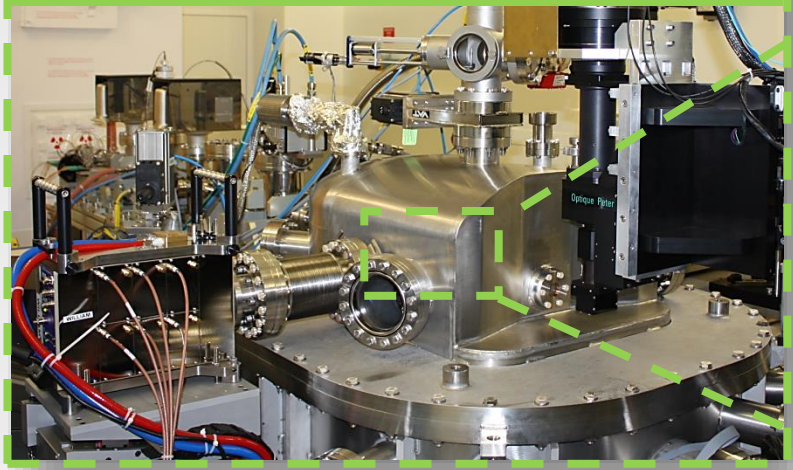
## The Nano-Imaging ID16A beamline before EBS



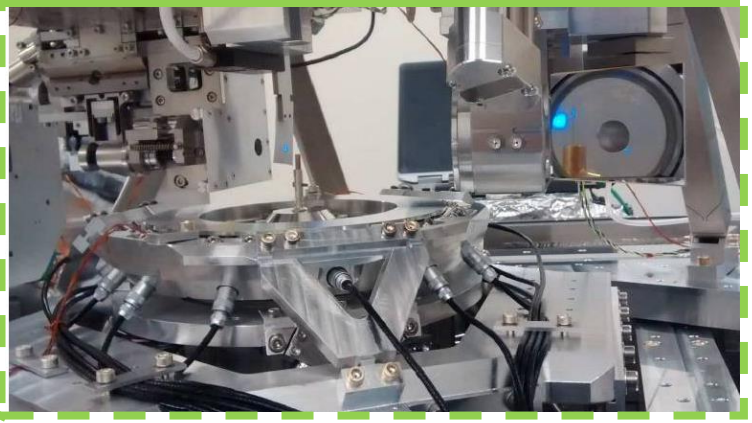



ESRF

**In-vacuum + Cryo**
**Flux up to 1.4 $10^{12}$ ph/s at DE/E =1%**
**E = 17 keV or 33.6 keV**



**Focused beam: 12-50 nm**

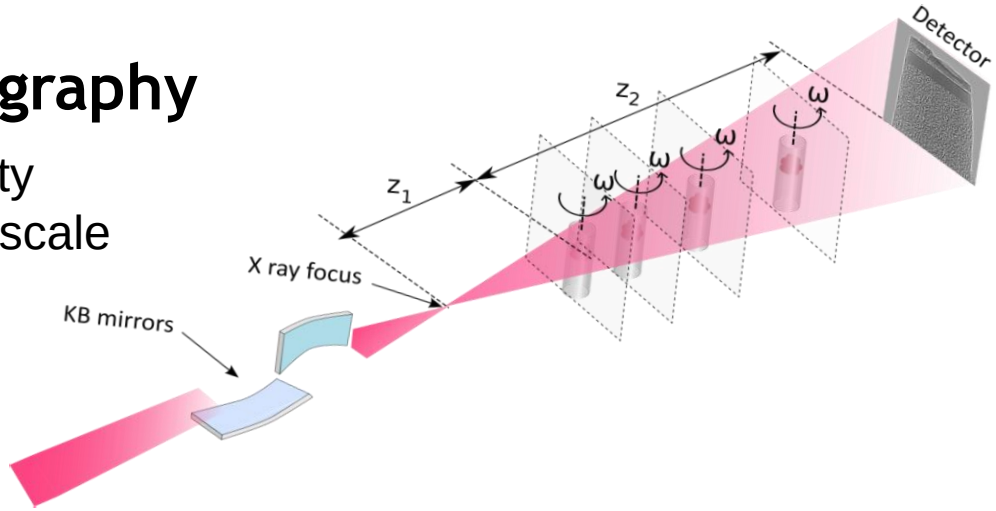


J. C. da Silva et al. , Optica (2017)

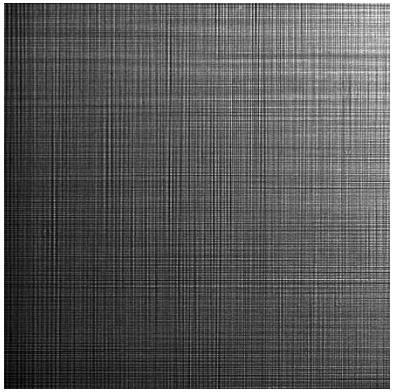
# MICROSTRUCTURAL CHARACTERIZATION

## Magnified holotomography

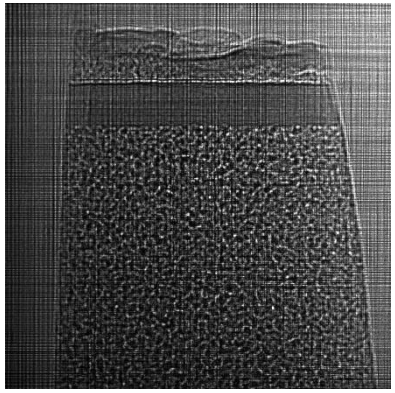
- High electron density sensitivity
- Zoom-in effect, ideal for multi-scale approaches
- Large field of view



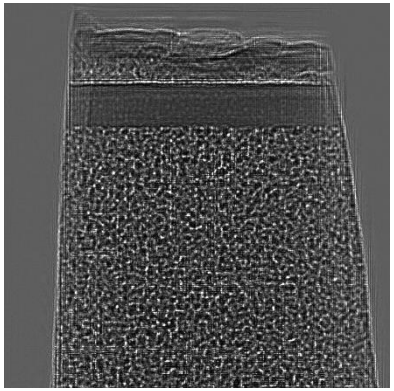

## The empty beam correction



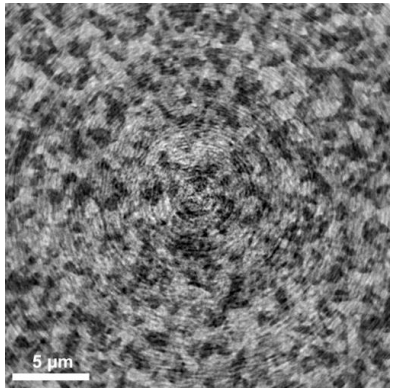
$I_{empty}$



$I_{mixed}$



$$\frac{I_{mixed}}{I_{empty}} \approx I_{object}$$




Reconstructed slice
Hydrogen electrode
25nm voxel size

**Empty beam correction is non-valid**

# MICROSTRUCTURAL CHARACTERIZATION

## A new acquisition process

Simple model assuming a weak defocusing distance:

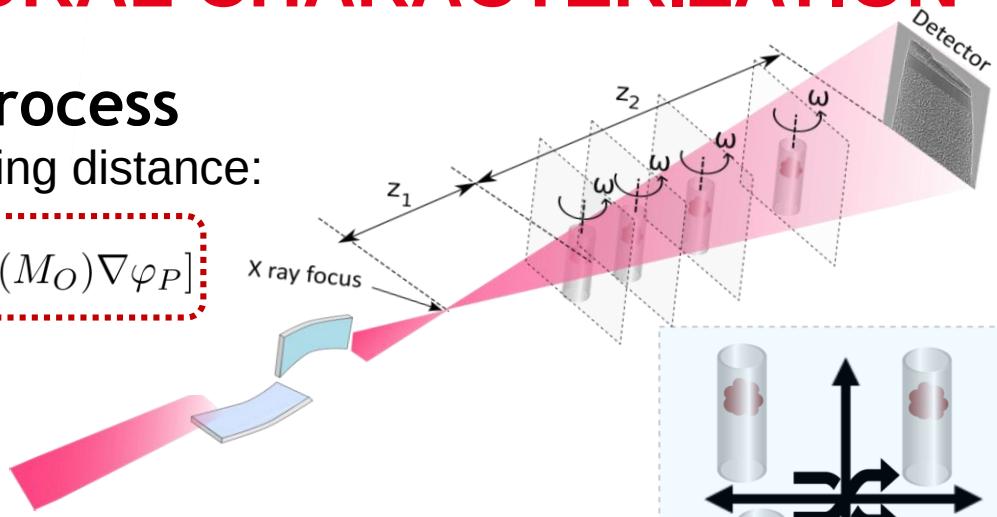
$$\frac{I_{\text{mixed}}}{I_{\text{empty}}} \simeq I_{\text{obj}} - \frac{\lambda z}{\pi} M_O^2 \left[\nabla \ln(M_P)\nabla\varphi_O + \nabla \ln(M_O)\nabla\varphi_P\right]$$

"good" term

"parasitic" term

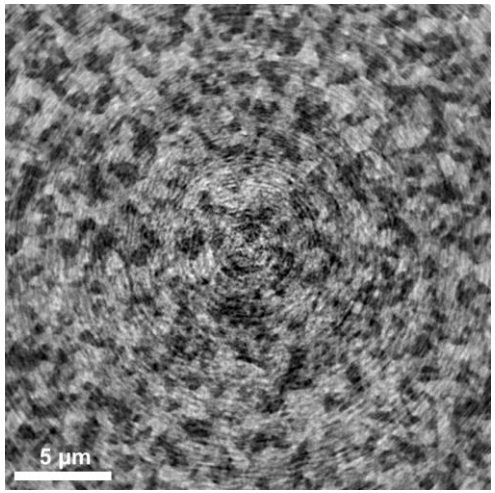
Object: $O = M_O \times e^{i\varphi_O}$

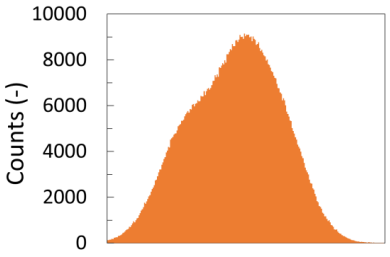
Probe: $P = M_P \times e^{i\varphi_P}$

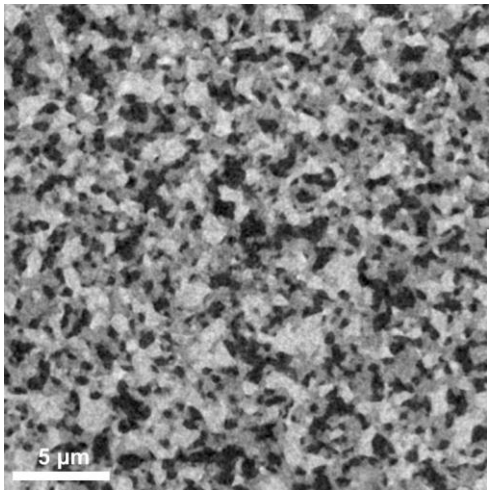


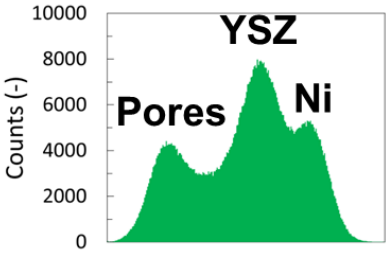



**Random sample displacement smears out the artefacts**




**Without random**

**With random**

M. Hubert et al. , Appl. Phys. Lett (2018)

# MICROSTRUCTURAL CHARACTERIZATION

## A new acquisition process

Simple model assuming a weak defocusing distance:

$$\frac{I_{\text{mixed}}}{I_{\text{empty}}} \simeq I_{\text{obj}} - \frac{\lambda z}{\pi} M_O^2 \left[\nabla \ln(M_P)\nabla\varphi_O + \nabla \ln(M_O)\nabla\varphi_P\right]$$

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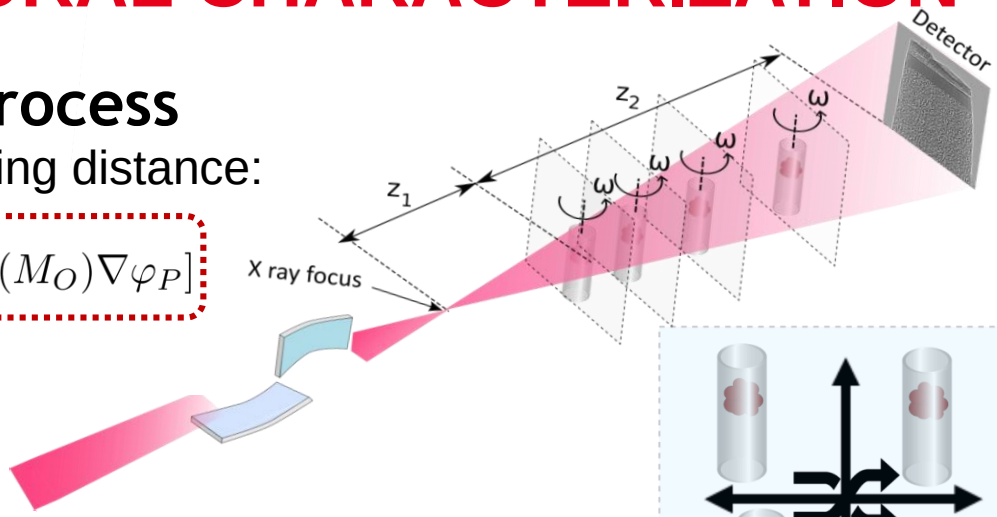


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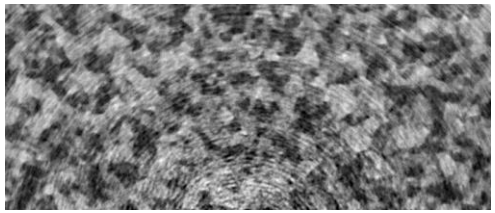
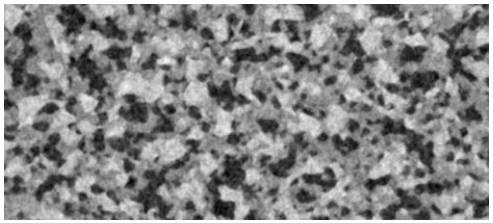




| Properties | Pores | YSZ | Ni |
|---|---|---|---|
| Percolated volume fraction (-) | 0.280 ±0.014 | 0.436 ±0.003 | 0.262 ±0.013 |
| Mean particle diameter ($\mu$m) | 0.96 ±0.06 | 0.60 ±0.00 | 1.01 ±0.03 |
| Specific surface area ($\mu m^{-1}$)* | 2.48 ±0.07 | 3.62 ±0.03 | 2.09 ±0.09 |
| Tortuosity factor (-) | 8.46 | 2.27 | 7.45 |
| Active Triple phase boundary length density ($\mu m^{-2}$) | | 4.75 ±0.08 | |

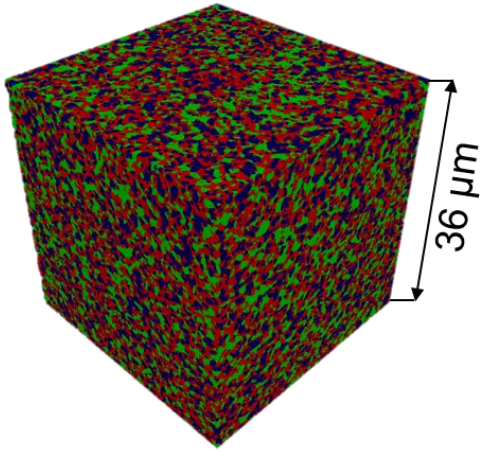
**Microstructural properties of the Ni-YSZ electrode**

M. Hubert et al. , Appl. Phys. Lett (2018)

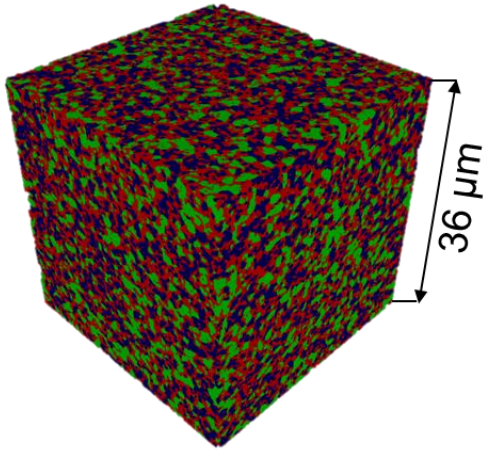
# MICROSTRUCTURE ANALYSES

## Nickel agglomeration in $H_2$ electrode

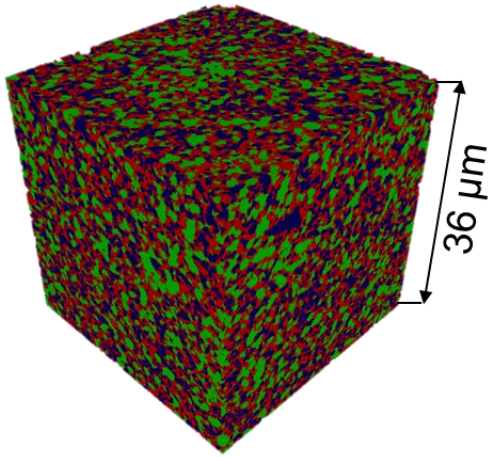
**Reference**




**Aged 1000h**




**Aged 9000h**




**Ni** **YSZ** **Pores**

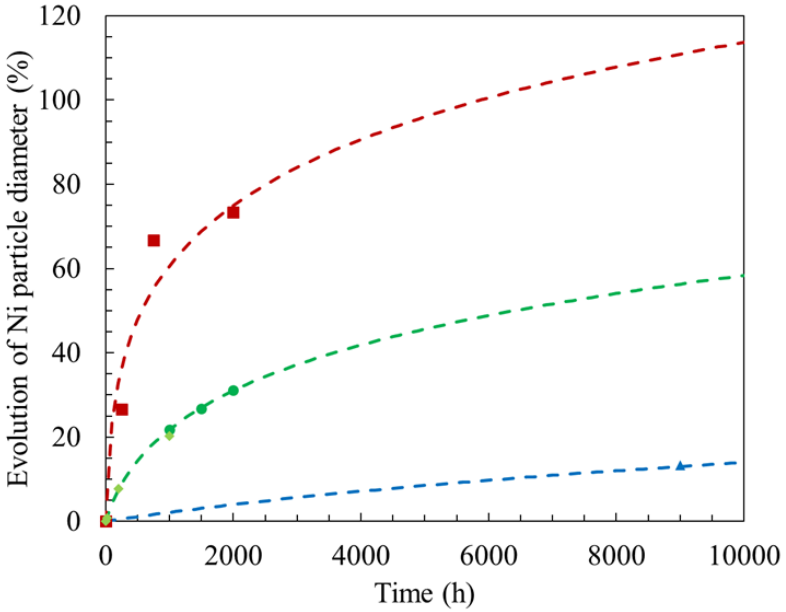
M. Hubert et al. , J. Power Sources (2018)

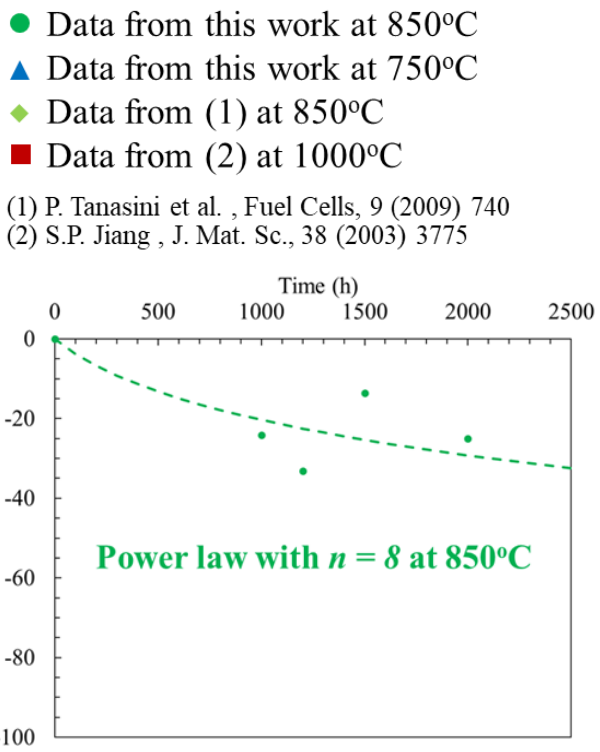
F. Monaco et al. , ECS (2019),to be submitted

# MICROSTRUCTURE ANALYSES

## Nickel agglomeration in $H_2$ electrode

**Microstructure analysis**




- Significant Ni agglomeration
- Significant decrease of the electrochemically active sites
- Inhibiting effect of the YSZ backbone on Ni agglomeration

**Contribution of Ni agglomeration on performance losses can be extracted from these analyses (about 25-30%)**

M. Hubert et al. , J. Power Sources (2018)
F. Monaco et al. , ECS (2019),to be submitted

# MICROSTRUCTURE ANALYSES

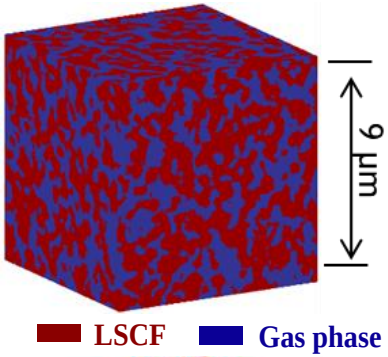
## Synthetic microstructure modelling

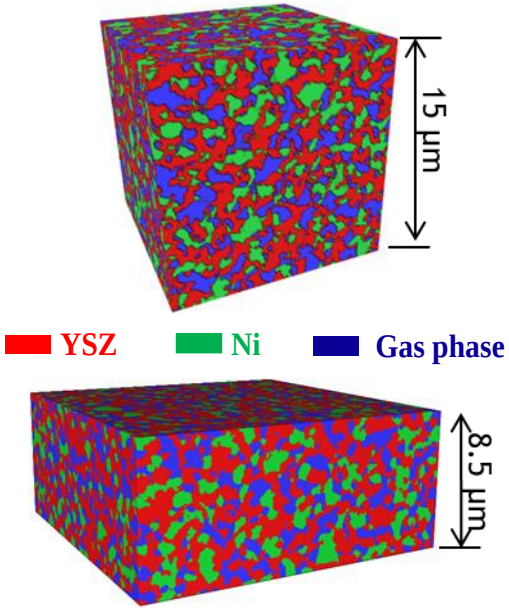
- Experimental approach based on the manufacturing and characterization of many samples is time consuming

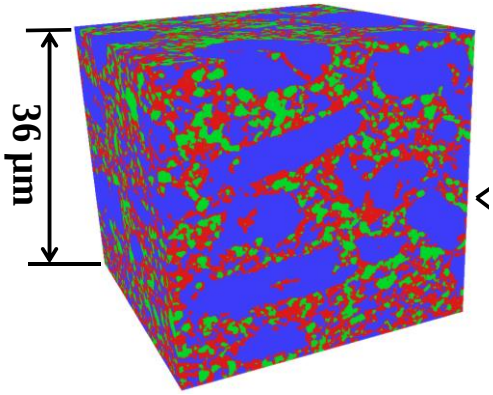
  → The modeling of synthetic microstructure can be an alternative method

**Real electrode microstructures are required for model validation**

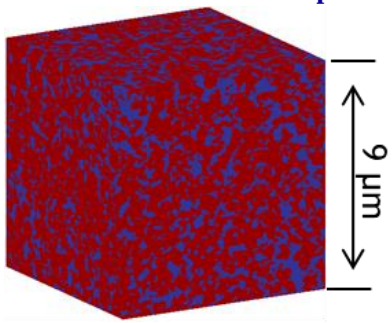
**Cell-1**



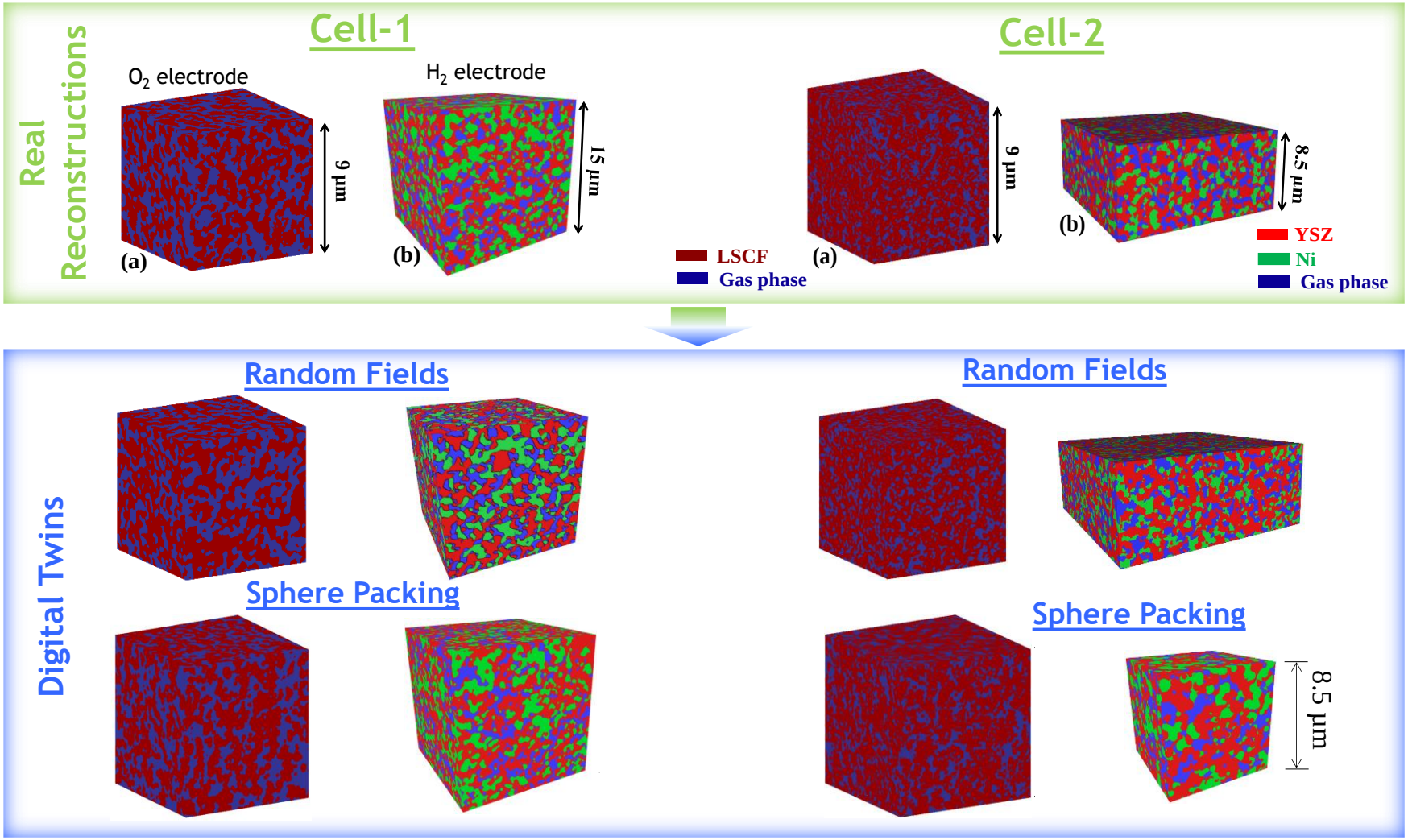

**Cell-2**




**Large range of real 3D electrode microstructure**

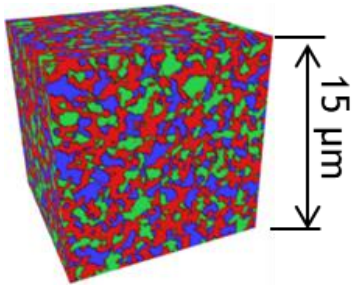
H. Moussaoui et al., Comput. Mater. Sci. (2018)

# MICROSTRUCTURE ANALYSES



# MICROSTRUCTURE ANALYSES

## Illustration on a Ni-YSZ electrode




| | YSZ Phase | | | | | | |
|---|---|---|---|---|---|---|---|
| | Volume fraction (%) | Phase diameter (µm) | Specific Surface Area(µm$^{-1}$) | Geometrical tortuosity factor (-) | Constri-ctivity (-) | M-factor (-) | Active TPBL density (µm$^{-2}$) |
| **Random field** | ~0% | +3% | -1% | ~0% | ~0% | ~0% | -1% |
| **Real reconstruction** | 44.08 | 0.28 | 3.68 | 1.43 | 0.13 | 0.189 | 4.78 |
| **Sphere packing** | ~0% | ~0% | -4% | -1% | -3% | +2% | +4% |

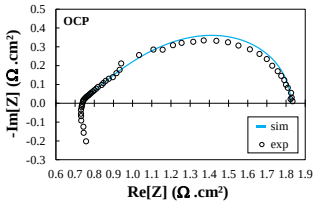
| | Gas phase | | | | | | Ni phase | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Volume fraction (%) | Phase diameter (µm) | Specific surface area (µm$^{-1}$) | Geometrical tortuosity factor (-) | Constri-ctivity (-) | M-factor (-) | Volume fraction (%) | Phase diameter (µm) | Specific surface area (µm$^{-1}$) | Geometrical tortuosity factor (-) | Constri-ctivity (-) | M-factor (-) |
| **Random field** | ~0% | ~0% | -1% | -3% | +22% | +21% | ~0% | +3% | +1% | -3% | +22% | +22% |
| **Real reconstruction** | 28.04 | 0.28 | 2.67 | 1.67 | 0.09 | 0.03 | 27.88 | 0.33 | 2.30 | 1.75 | 0.08 | 0.041 |
| **Sphere packing** | ~0% | ~0% | -2% | -3% | +16% | +17% | ~0% | ~0% | -2% | -6% | +18% | +21% |

**The mismatch does not exceed few percents (except for constrictivity)**

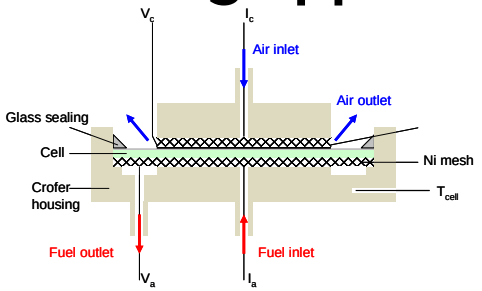
**Similar results with the other electrodes**

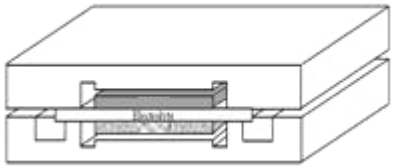
# OVERVIEW

## Integrated experimental and modelling approach

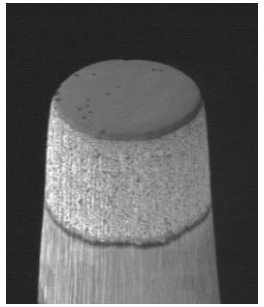



Electrochemical test

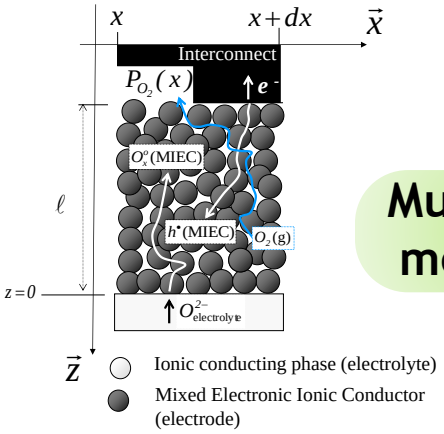


« Multi-scale »
&
« Multi-physic »
modelling

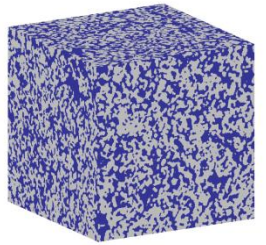


ESRF



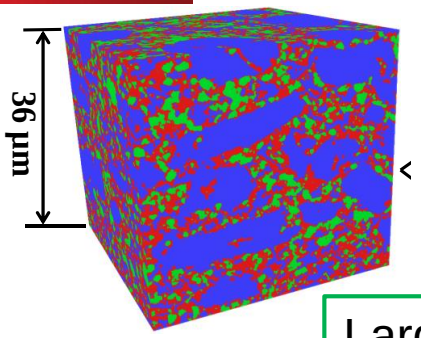

Multi-scale modelling

Microstructural characterization

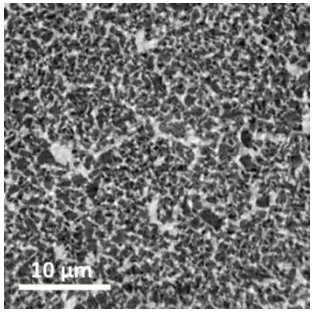


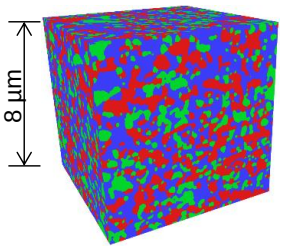
**Validated numerical tools to investigate SOC**

# NEW OPPORTUNITIES WITH EBS




Larger field of view



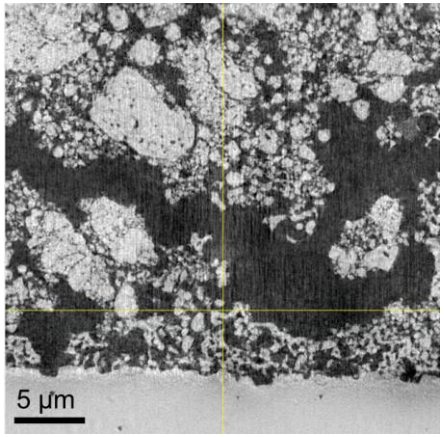

GDC LSCF pores

Higher contrast

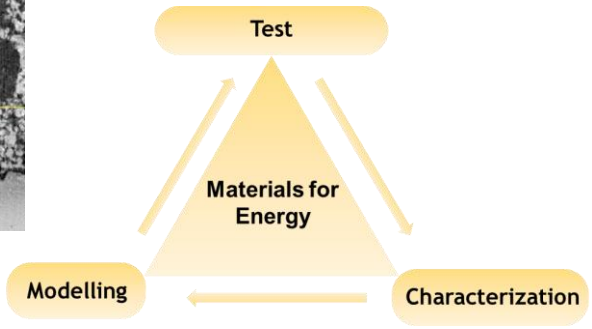
E. Effori et al., Fuel Cells (2019)

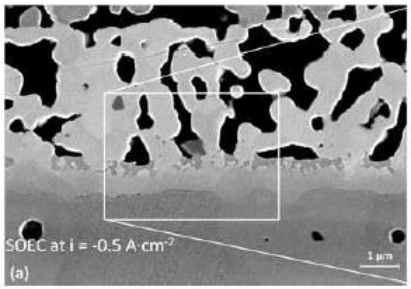

Higher spatial resolution

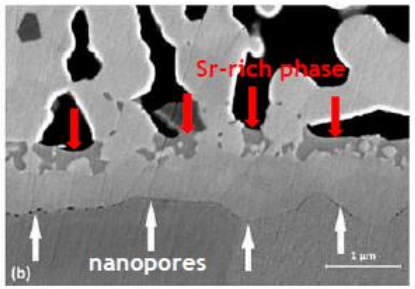
Coupled characterizations




Extend method to materials for energy




J. Laurencin et al., Electrochimica Acta (2017), 459-476


# Thank you for your attention

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