INTERACTIONS BETWEEN FORSTERITE SUPPORT MATERIAL AND LSM CATHODE DURING CO-SINTERING OF AN ALL-CERAMIC SOFC

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KERSOLIFE 100 PROJECT

Publicly funded project (BMWi): Cooperation with industry and academic partners within Germany

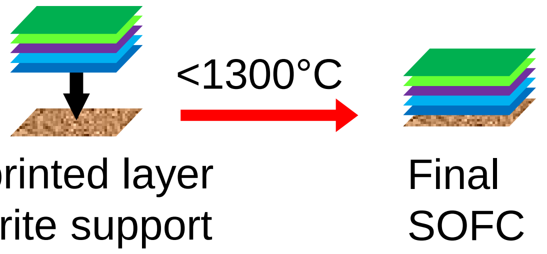
Goal:

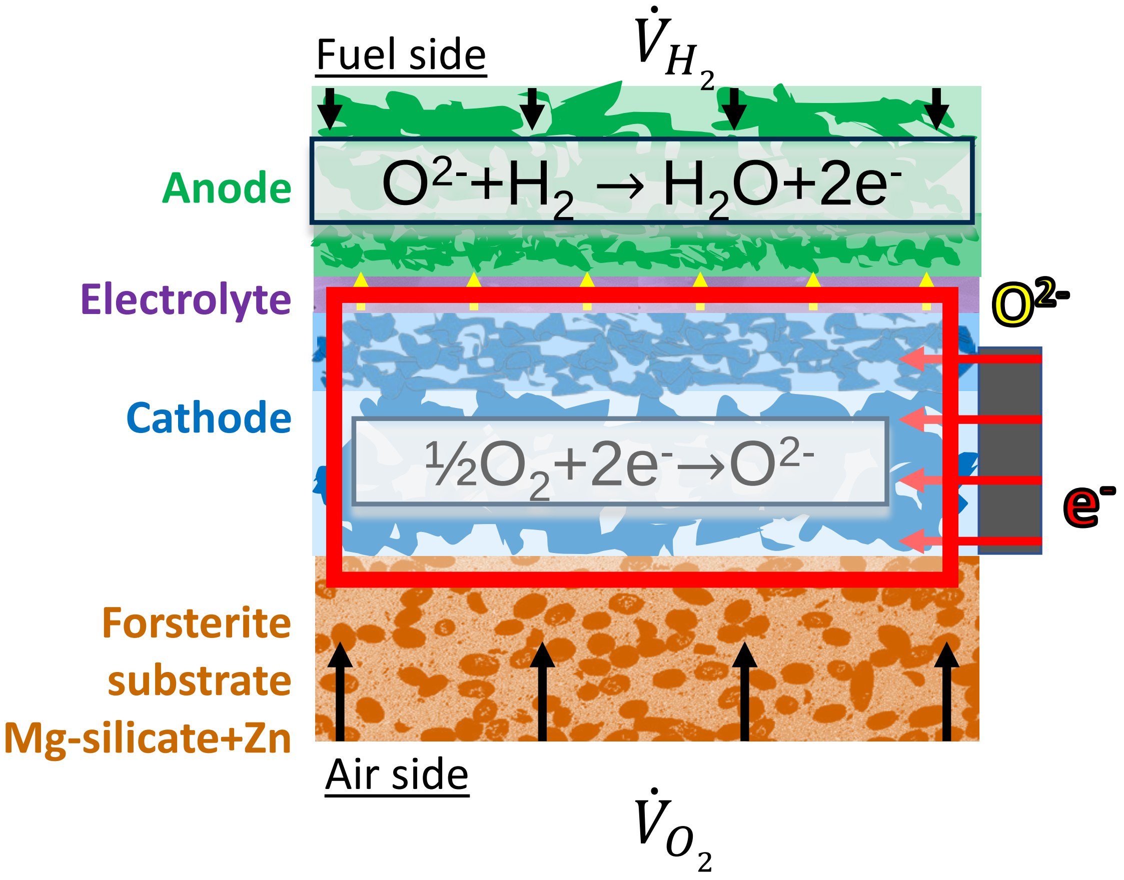
Understanding and modelling of materials interactions and degradation mechanisms in fully ceramic SOFCs

LOW-COST INERT SUPPORTED SOLID OXIDE FUEL CELL (SOFC) MANUFACTURING ROUTE

Simplified manufacturing route: co-sintering:

- Compromised sintering temperature <1300°C for all layers
- Materials of each layer adjusted to new processing route
  - **Interactions during sintering cathode–adjacent layers**
  - **Cathode microstructure/co-sintering properties**





CATHODE MATERIAL: LSM/8YSZ COMPOSITE

Case study pre-evaluation

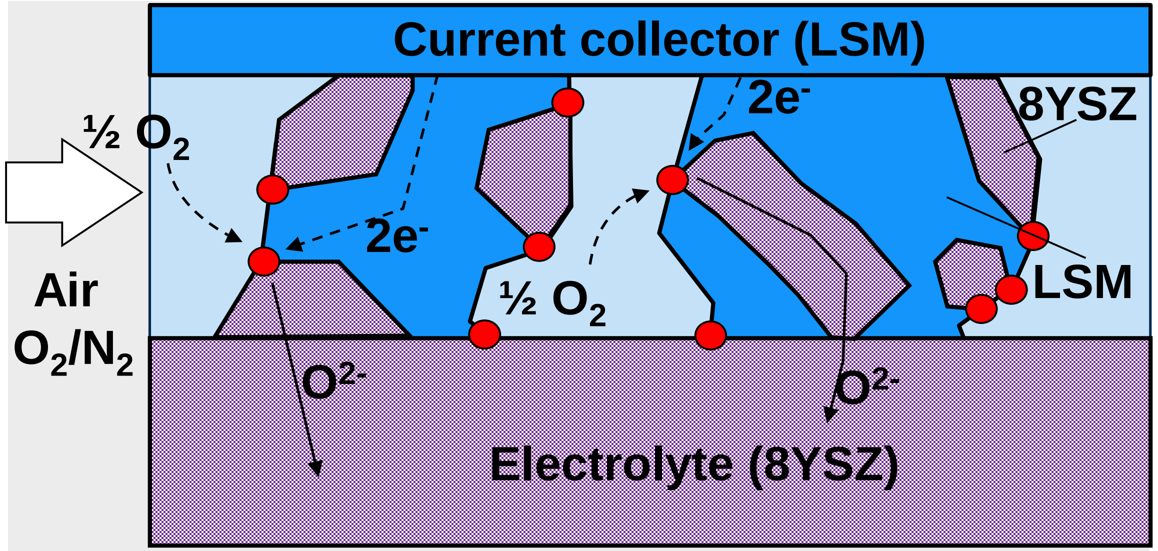
Advantages of LSM/YSZ composite:

- Good performance at $T_{operation}$ (~800°C)
- Low reactivity to electrolyte [1]
- Nearly matching σ_T with electrolyte and support
- Co-sintering adhesion

Challenges/drawbacks:

- Microstructure crucial to functionality:
  - T_{sinter}(1080°C [2]→<1300°C) → increased coarsening → fewer triple phase boundaries
- Lower electrochemical performance than mixed conductors/other composites

LSM/8YSZ-oxide composite: separated conduction pathways



Electrochemically active zone limited to triple phase boundaries

LSM = $(La_xSr_{1-x})_yMnO_{3-d}$

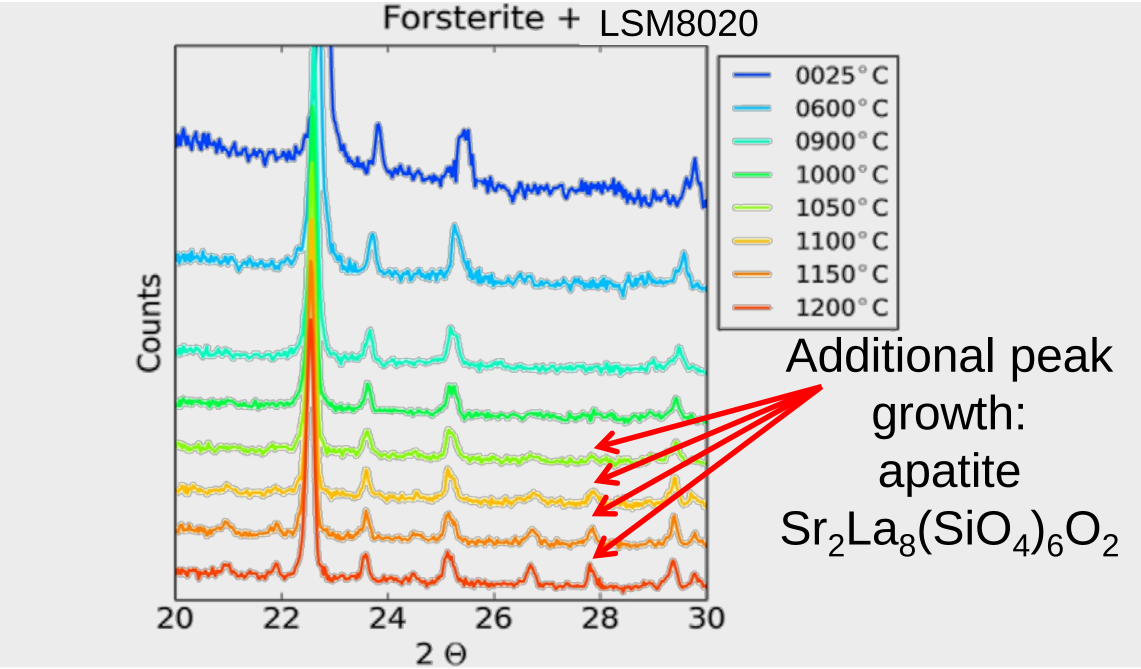
8YSZ = $Zr_{0.85}Y_{0.15}O_{1.925}$

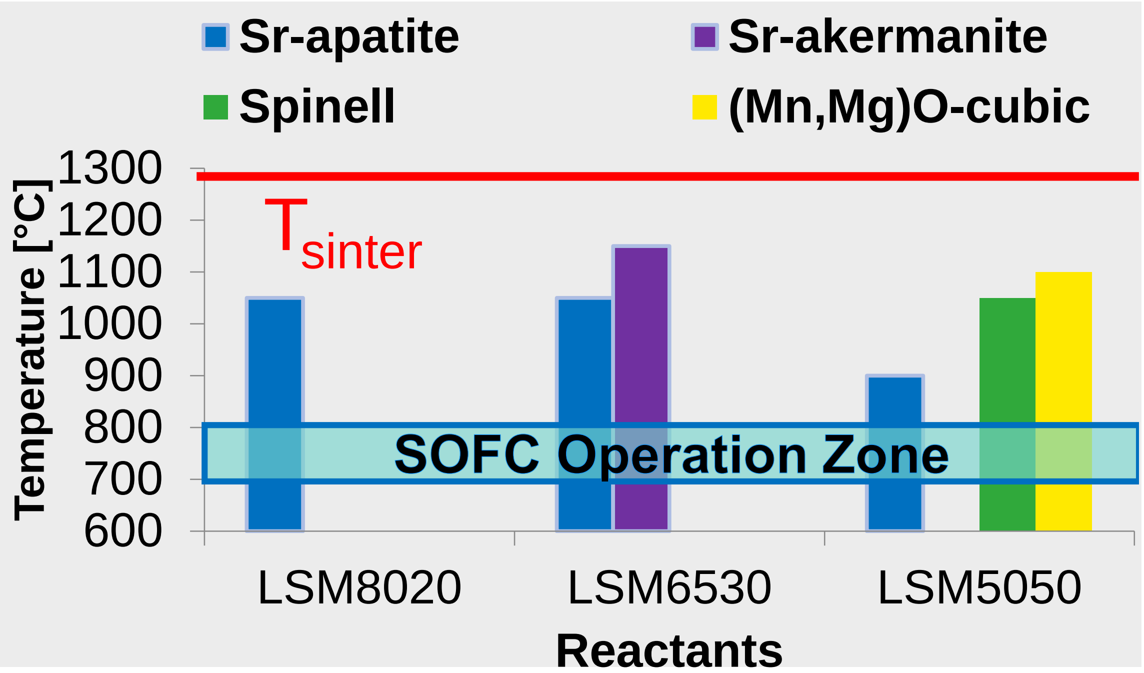
Stochniol *et al.*, J. of Am Cer. Soc., 1995. [2] Hanappel *et al.*, Journal of power sources, 2005.

REACTION PHASES TEMPERATURE DEPENDENCY

- **Powder mixtures, insitu-XRD**

$T_{reaction}$ > $T_{operation}$ | $T_{reaction}$ < $T_{sintering}$





LSM8020=$(La_{0.8}Sr_{0.2})_{0.98}MnO_3$
LSM6530=$La_{0.65}Sr_{0.3}MnO_3$
LSM5050=$La_{0.5}Sr_{0.5}MnO_3$

T below $T_{reaction}$

EDX INVESTIGATIONS OF LAYER INTERACTIONS

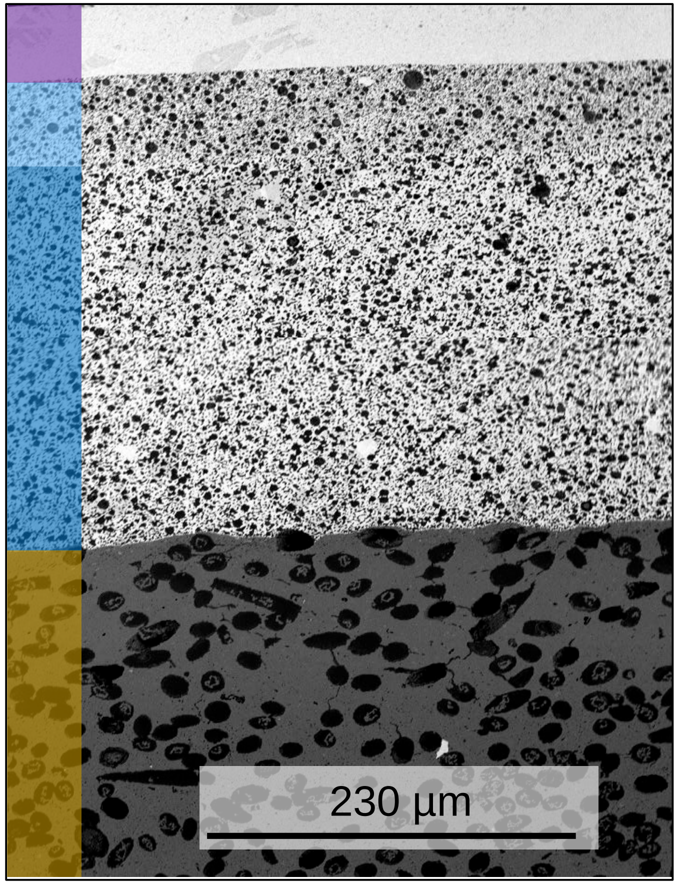
Co-sintered at <1300°C 5h, SEM image

Electrolyte 8YSZ
dense

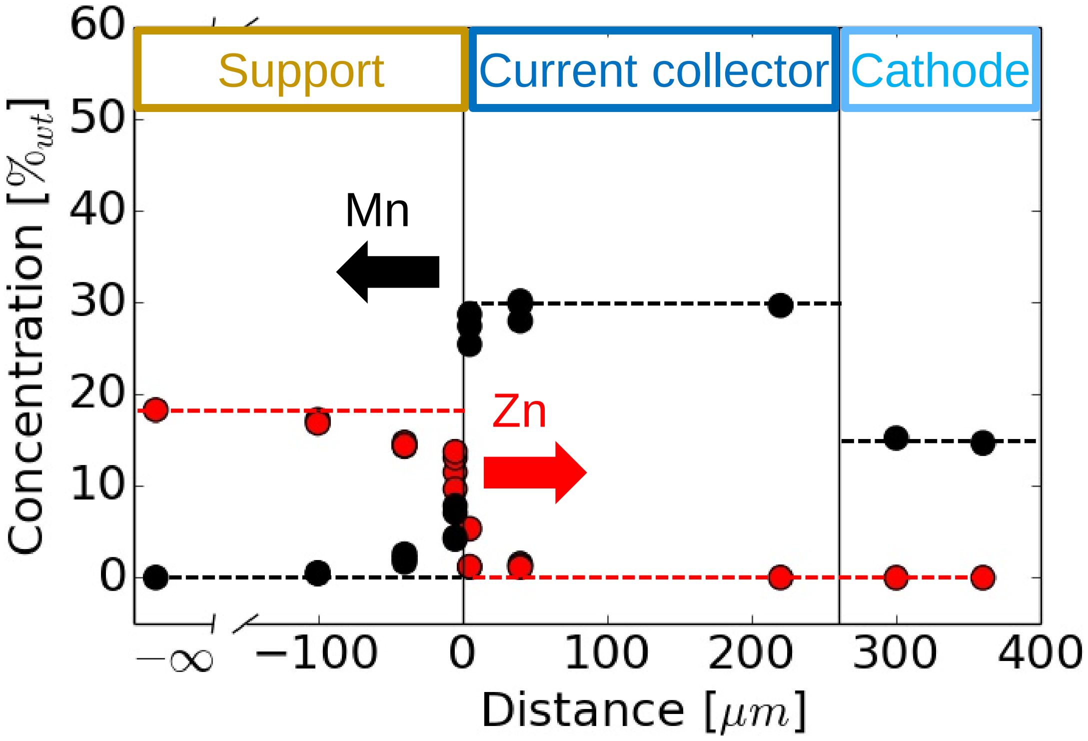
Cathode
$La_{1-x}Sr_xMnO_3$
+8YSZ
porous

Current collector
$La_{1-x}Sr_xMnO_3$
porous

Support
Mg, Si, Zn
Porous



Semi-quantitative concentrations [1]



No other observed diffusion,
or effect of LSM stoichiometry

[1] Bruker's QUANTAX energy dispersive X-ray spectrometry

TEM INVESTIGATIONS OF LAYER INTERACTIONS

Co-sintered at <1300°C 5h, SEM image

Cut-out lamellas for TEM (Dark Field Images)

Electrolyte 8YSZ
dense

Cathode
$La_{1-x}Sr_xMnO_3$
+8YSZ
porous

Current collector
$La_{1-x}Sr_xMnO_3$
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Support
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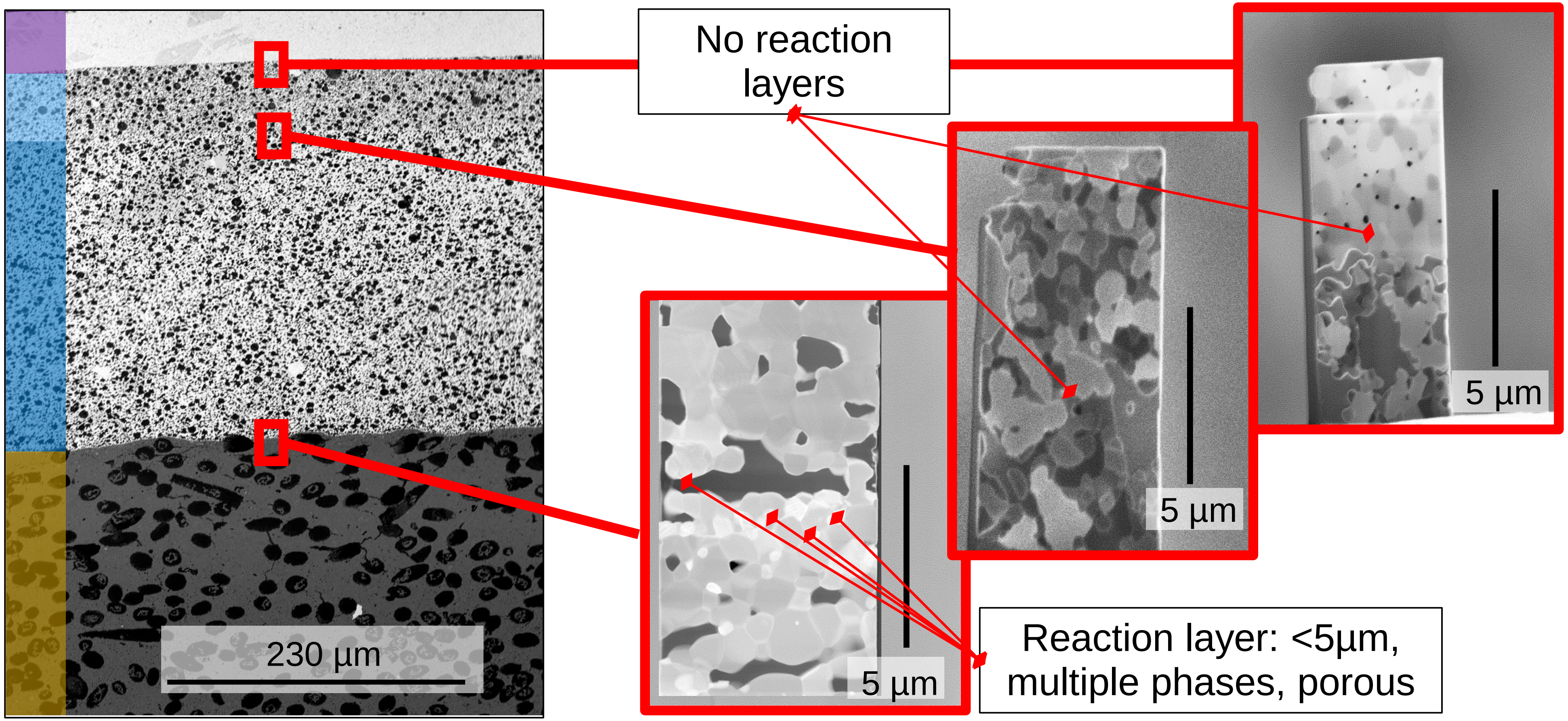
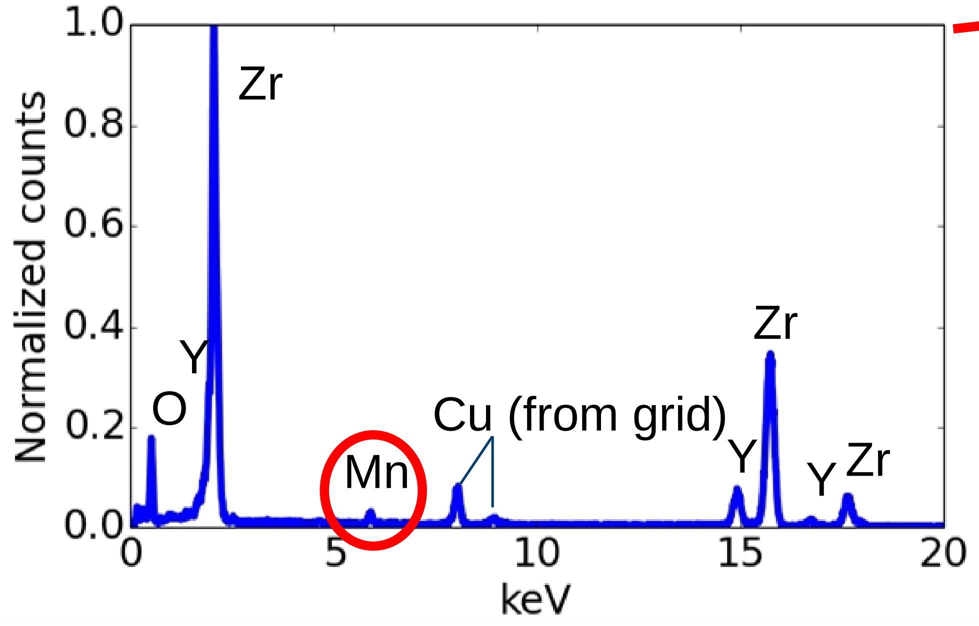


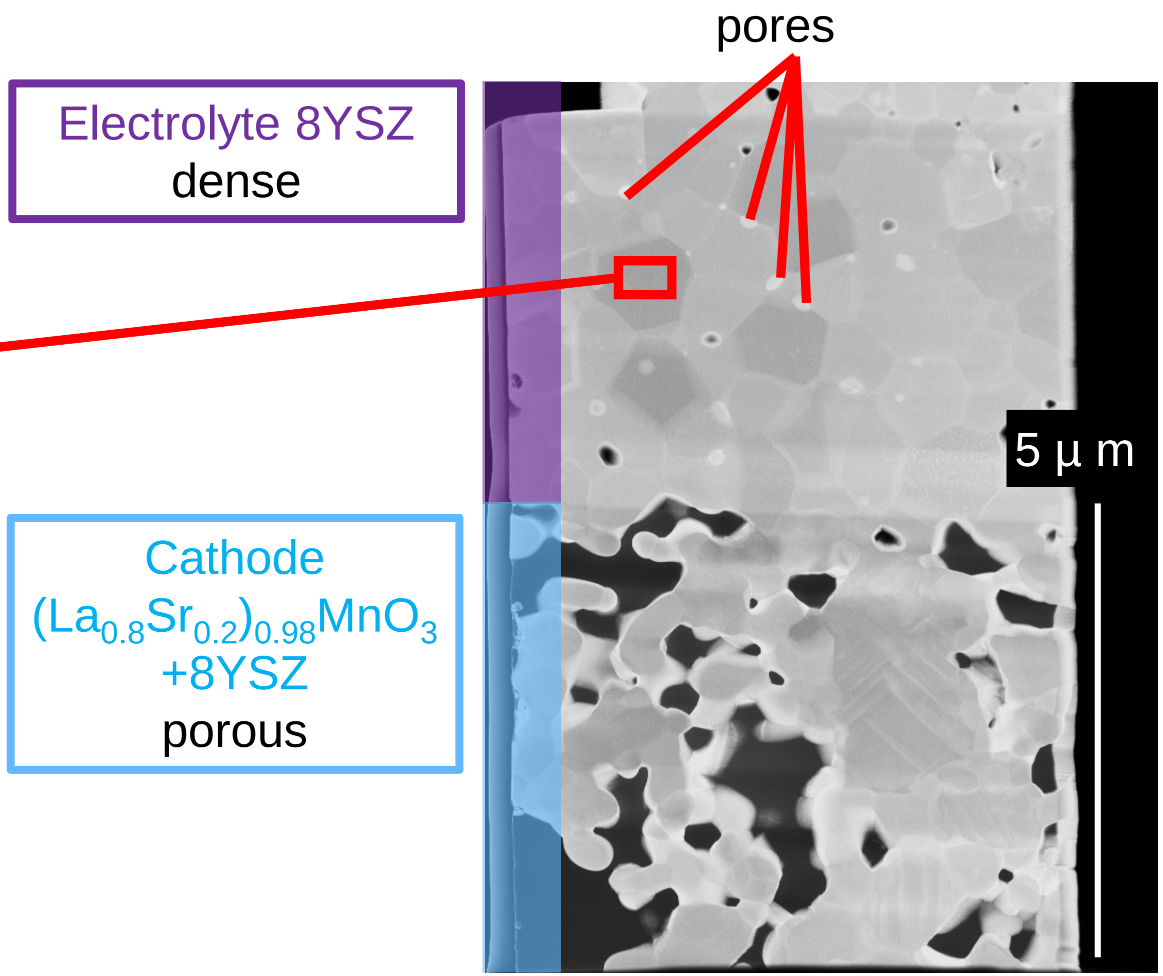
GFE, RWTH Aachen

INTERACTION CATHODE – ELECTROLYTE (STEM)

Detected:

- **Mn** diffuses to 8YSZ electrolyte bulk
- Possible: MnO_X formation → cracking, delamination [1]

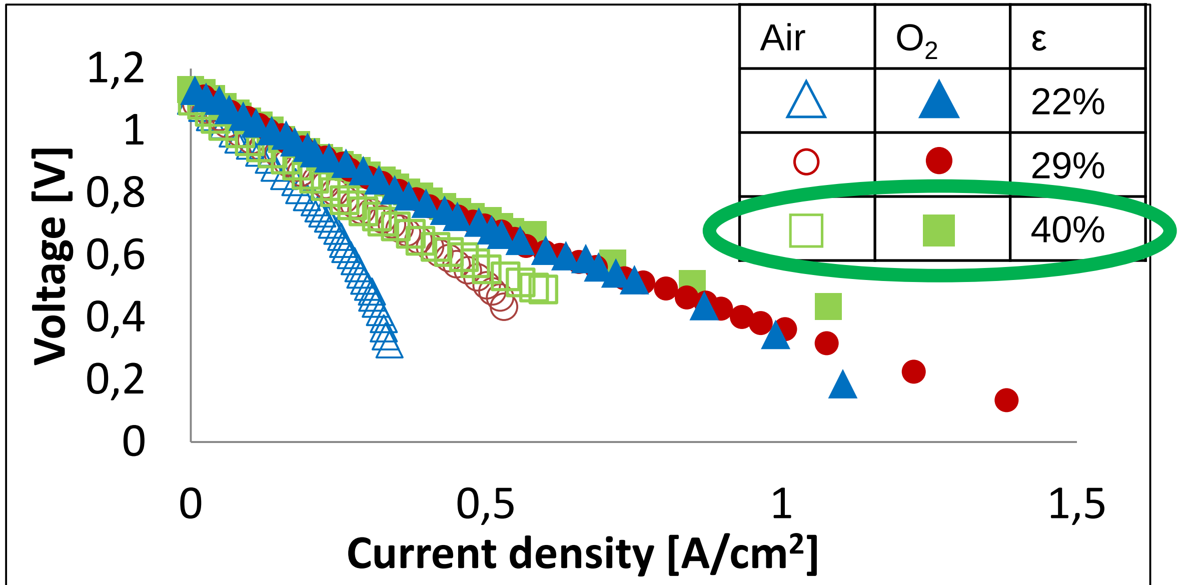




[1] Menzler *et al.*, Journal of Power Sources, 2018.

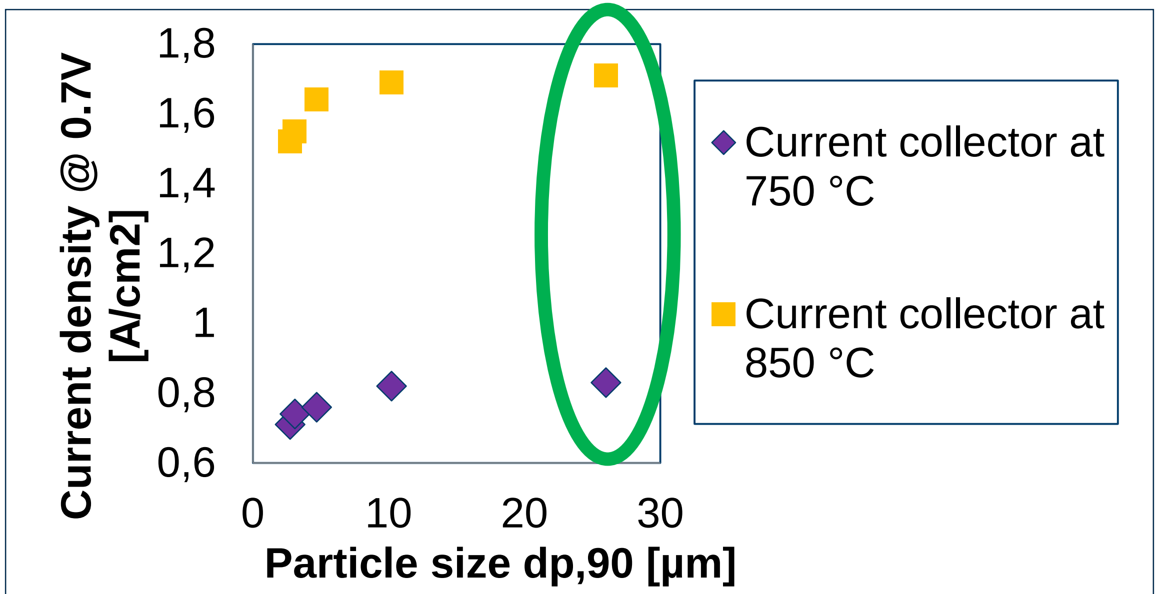
REQUESTED MICROSTRUCTURAL PARAMETERS

For $(La_{1-x}Sr_x)_yMnO_3$ + 8YSZ cathodes



$La_{0.8}Sr_{0.2}MnO_3$+8YSZ cathodes, data extracted from [1]

Best performance found at 40% porosity [1]

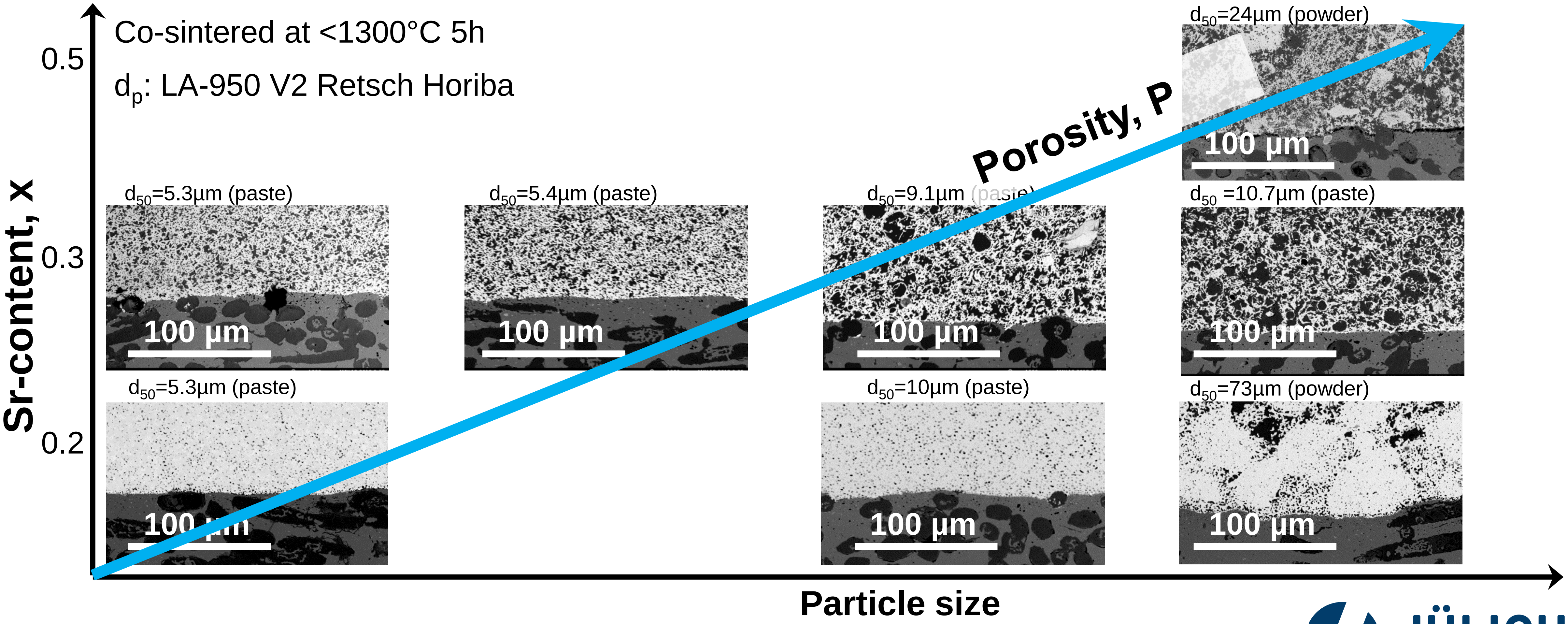


$La_{0.65}Sr_{0.3}MnO_3$ + 8YSZ cathodes, data extracted from [2]

Current collector: larger particle size → better performance [2]

[1] Tsai *et al.*, Solid state Ionics, 1997. [2] Hanappel *et al.*, Journal of power sources, 2005.

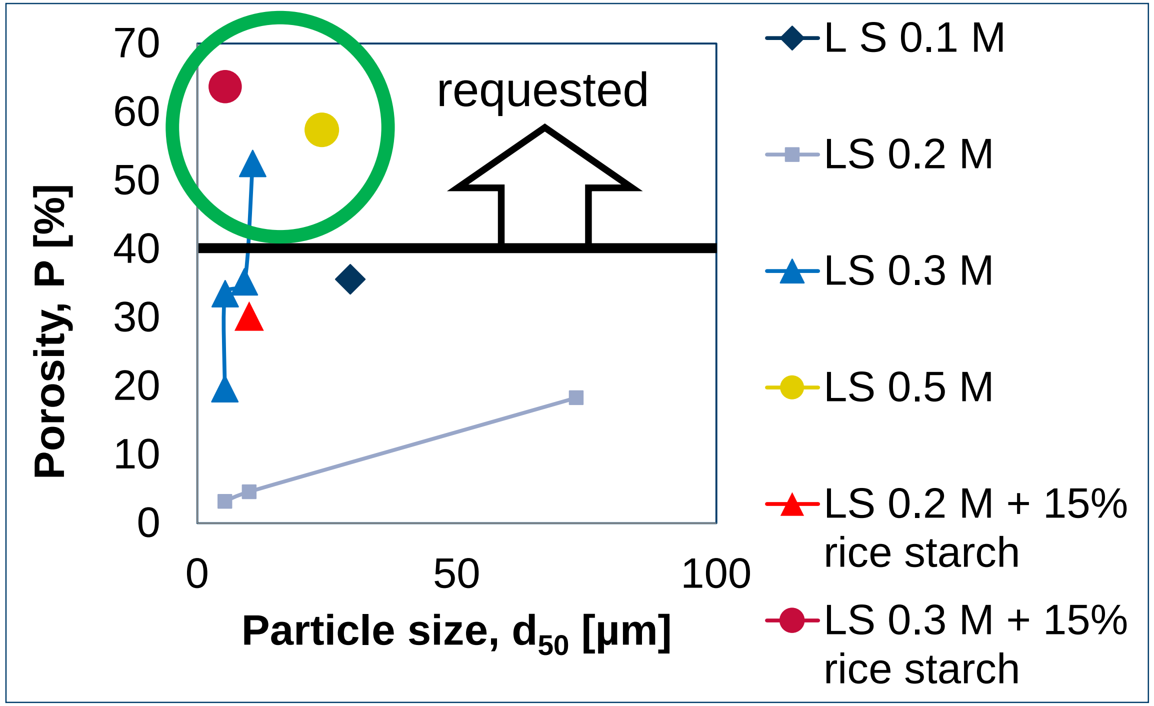
IMPACT OF PARTICLE SIZE AND Sr-CONTENT ON SINTERED MICROSTRUCTURE $(La_{1-x}Sr_x)_yMnO_3$



EVALUATION OF MICROSTRUCTURAL PARAMETERS

For $(La_{1-x}Sr_x)_yMnO_3$

- Porosity of ≥40% at co-sintering <1300°C with:
  - various combinations of:
    - Sr-content
    - particle size
    - pore formers
- Sintered porosity increases with Sr-content (x≤0.5) [1, 2]
  - Sintering mass transport: La/Sr- lattice vacancy diffusion controlled [3, 4]
  - La/Sr- lattice vacancies decrease with increasing Sr-content [2, 5]
  - Results here mostly follow trend



Co-sintered at <1300°C 5h

Porosity: image analysis

Particle size d_{50}: LA-950 V2 Retsch Horiba

[1] Roosmalen *et al*., Solid State Ionics, 1993. [2] Wolfenstine *et al*., Solid State Ionics, 1996.
[3] Wolfenstine *et a*l., Journal of Materials Research, 1996. [4] Palcut, Journal of Physical Chemistry C, 2007.
[5] Takeda *et al*., Material Research Bulletin, 1991.

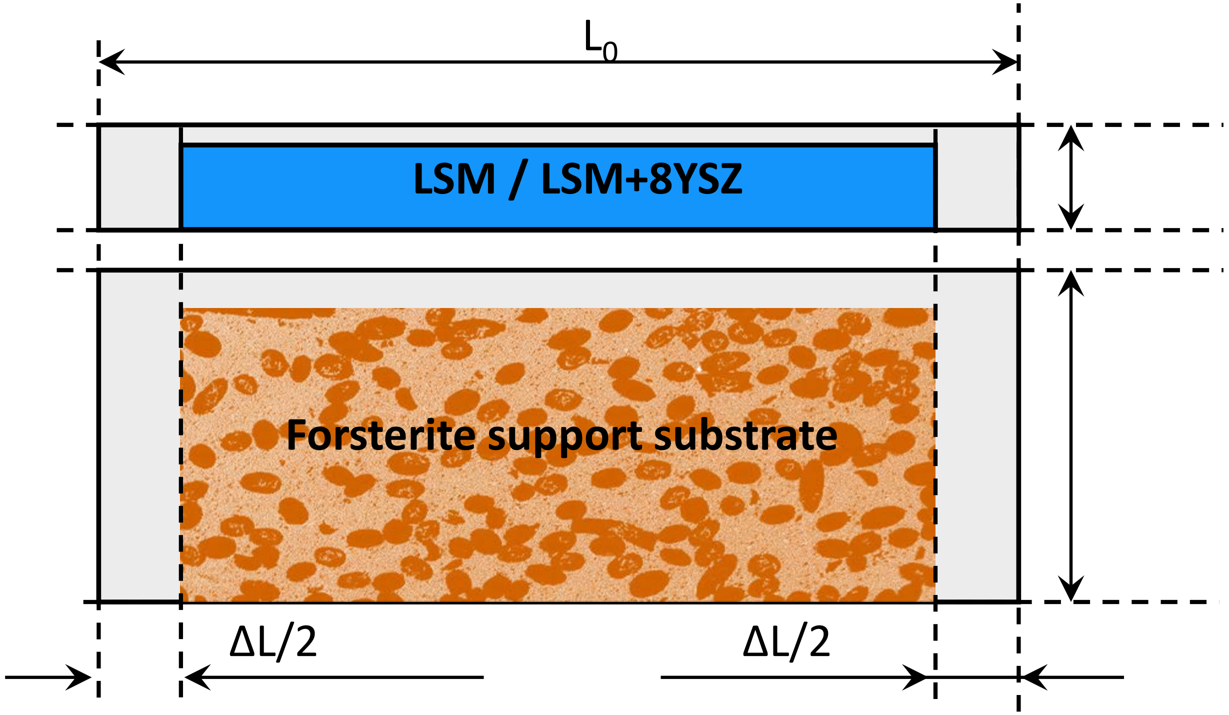
FREE SINTERING: LSM+8YSZ CATHODE, SUPPORT SUBSTRATE

Free sintering strain behaviour depends on:

- Powder (paste) properties
- Temperature

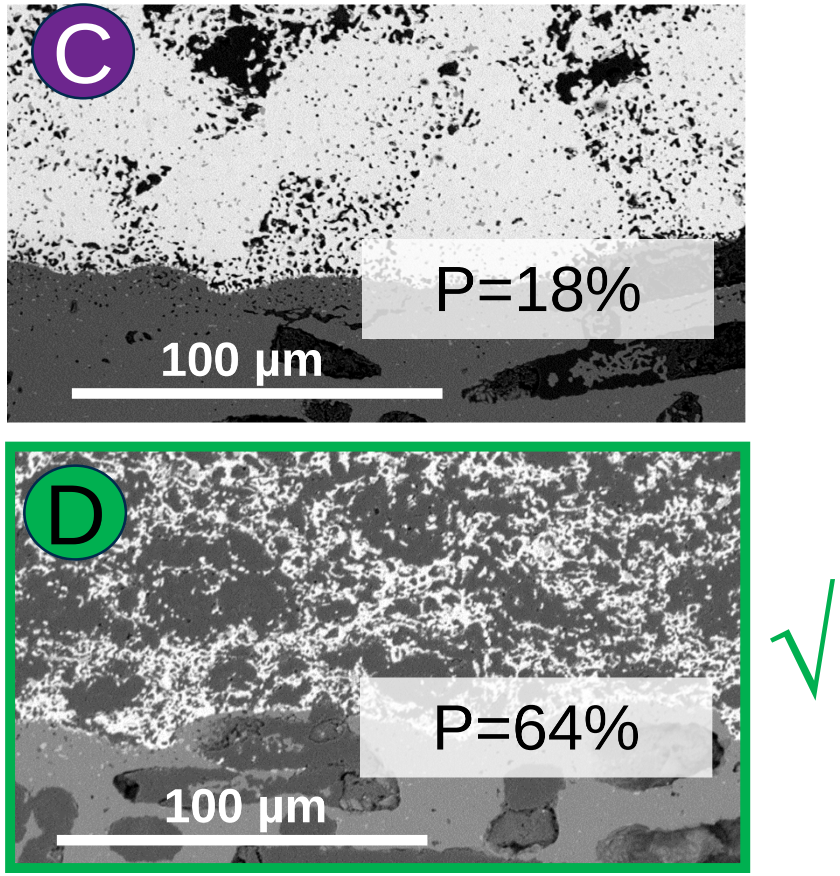
Material optimization:

- Matching of time and temperature dependant strain rate $\dot{\epsilon}_T$ or
- In some cases tailoring of $\dot{\epsilon}_T$:
  - Forging
  - Retiring of adjacent layer
- Adaptation of rheological properties

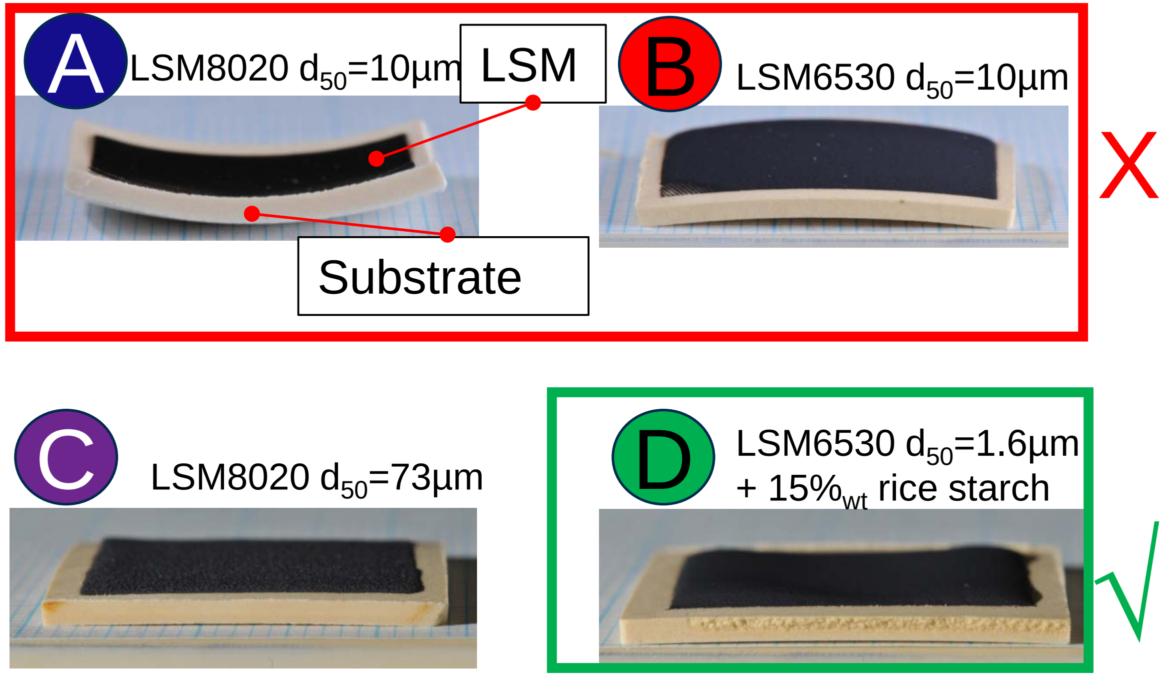


True strain rate: $\dot{\epsilon}_T = \frac{\partial}{\partial t} \log(1 + \Delta L / L_0)$

EFFECT OF STRAIN RATE ON MACROSCOPIC DIMENSION



Co-sintered substrate and LSM



Adapting the sintering behavior
→ dimensional control
+ Ensure suitable microstructure

SUMMARY AND OUTLOOK

- LSM/8YSZ cathodes remain promising for low-cost SOFC design:
- **Interactions** substrate-cathode during co-sintering:
  - Only thin, porous reaction layers: $<T_{sintering}$ | $>T_{operation}$ √
  - Zn diffuses to cathode (all stoichiometries), but not to electrochemically active zone √ ?
  - Mn diffuses to support and electrolyte, problematic for long-term operation? ?
- **Microstructure:** Requested current collector porosity reached at $T_{sintering}$ by:
  - Increasing Sr-content in LSM
  - Increasing particle size √
  - Adding pore formers
- **Macroscopic:** Defect-free co-sintering obtained by adapting sintering behavior √
- **Outlook:** Influence of findings on cell performance? Long term behaviour?
- Further investigate Mn-diffusion to electrolyte ?

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BOSCH

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RJL Micro&Analytic

Colleagues at Forschungszentrum Jülich for support in investigations

EFFECT OF PASTE PROPERTIES ON SINTERED CATHODE MICROSTRUCTURE $(La_{1-x}Sr_x)_yMnO_3$+8YSZ

- Goal: maximize triple phase boundaries (fine particle size), 40% porosity, P
- Fine porosity improved with pore formers/particle size