INTERACTIONS BETWEEN MAGNESIUM SILICATE SUPPORT SUBSTRATE AND STATE-OF-THE-ART CATHODES DURING CO-SINTERING OF AN ALL-CERAMIC SOFC

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Hilton Daytona Beach Resort and Ocean Center

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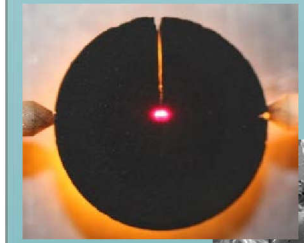
PROJECT: KERSOLIFE 100

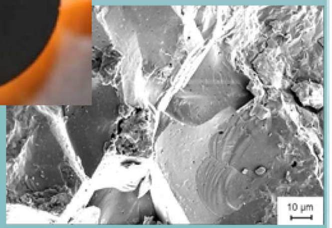
Funded by: Federal Ministry for Economic Affairs and Energy

Goal:
Understanding and modelling of material interactions and degradation mechanisms in all-ceramic SOFCs

Project coordination BOSCH
Long-term tests
Models for degradation analysis
Implementation of findings into industrial field

Ceramic support
Thermo-mechanical stability and reliability of ceramic support

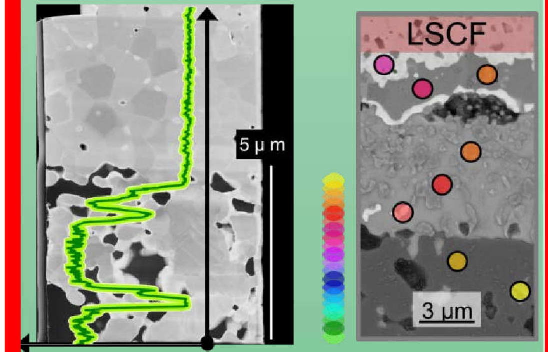

Measuring of temperature-dependent K_{IC}



Fractographical analysis

Hochschule Aalen, BOSCH

Cathode + electrolyte, Ceramic Interconnect
Interaction among layers

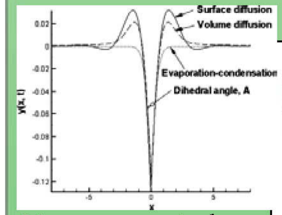


Reaction phases

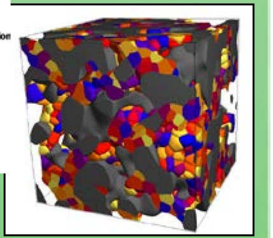
JÜLICH Forschungszentrum

Anode
Modeling of microstructural changes for lifetime prediction

Combination of experimental and simulation methods

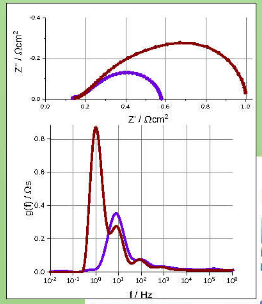
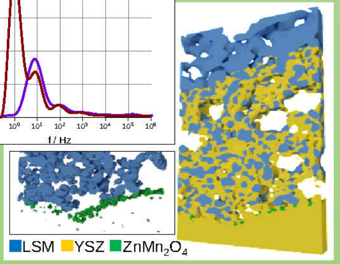


Measurement of GB*- profiles


Phase field Simulations

BOSCH, Hochschule Karlsruhe Technik und Wirtschaft, UNIVERSITY OF APPLIED SCIENCES

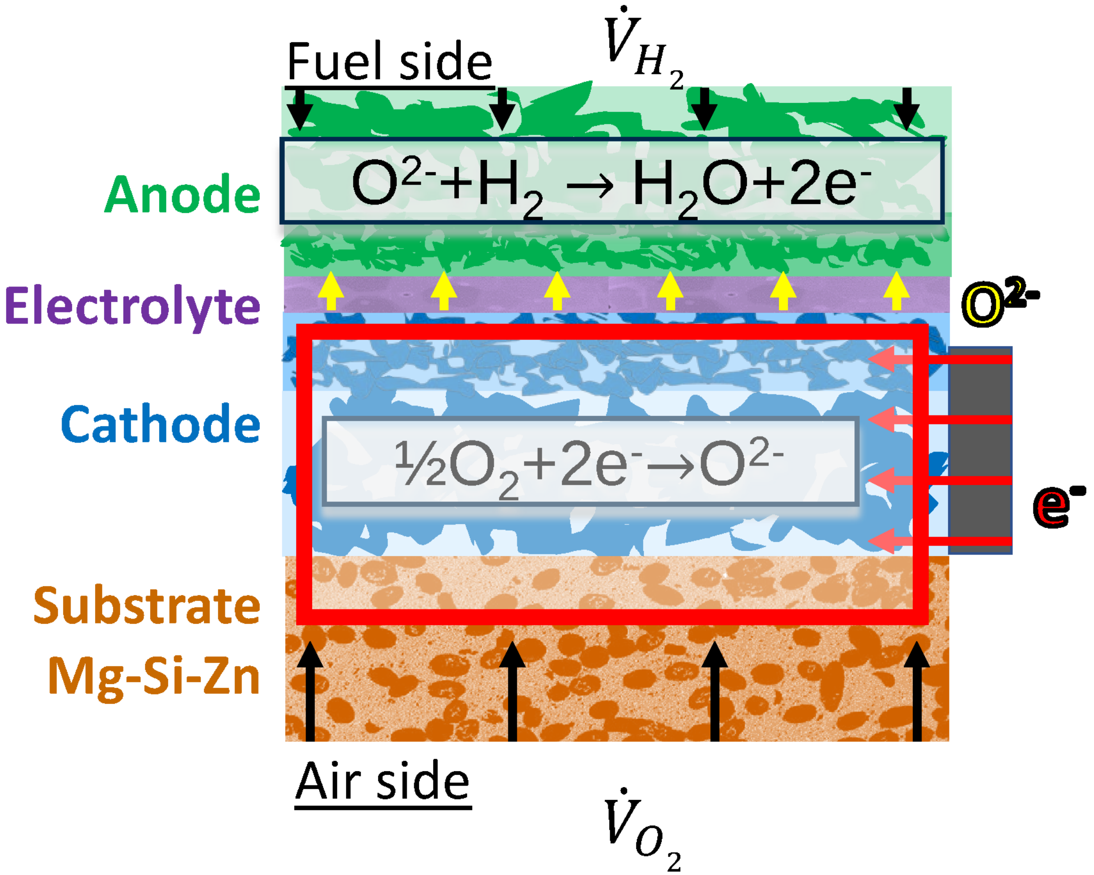
Cell Degradation
Electrochemical and microscopic analysis of cell degradation

KIT Karlsruhe Institute of Technology, RJL Micro&Analytic

INERT SUPPORTED SOLID OXIDE FUEL CELL (SOFC)

- All ceramic SOFC concept [1]
- Support material Zn-doped magnesium silicate (Mg-Si-Zn)
- Simplified manufacturing route: co-sintering
- Compromised sintering temperature <1300°C for all layers
- Materials of each layer adjusted to new processing route
- Here, focus on the cathode



[1] Patent DE102012221434A1, Robert Bosch GmbH, 2011

CONTENT OF PRESENTATION

Evaluation of cathodes within design:

1. Chemical interactions
2. Electrochemical performance
1. Microstructure
2. Co-sinterability
3. Summary

Index of tested cathodes

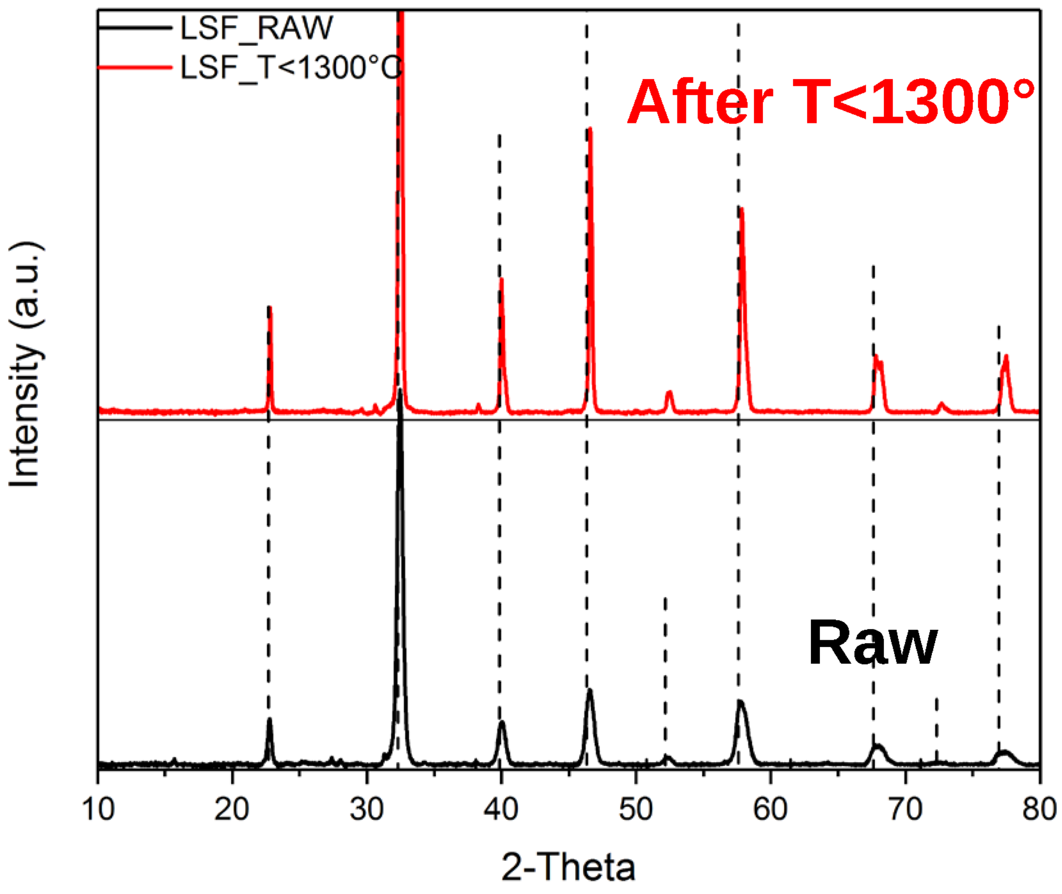
LSM	**$La_xSr_yMnO_{3-d}$ (baseline)**	LSF	$La_{0,58}Sr_{0,4}FeO_3$
PSCF	$Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_3$	LCCF	$La_{0.58}Ca_{0.4}Co_{0.2}Fe_{0.8}O_3$
LSCF	$La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_3$	LSFM_95S1M3	$(La_{0.9}Sr_{0.1})_{0.95}Fe_{0.7}Mn_{0.3}O_3$
LSC	$La_{0,58}Sr_{0,4}CoO_3$	LSFM_95S2M8	$(La_{0.8}Sr_{0.2})_{0.95}Fe_{0.2}Mn_{0.8}O_3$

CHEMICAL INTERACTIONS

STABILITY OF PEROVSKITES AFTER THERMAL TREATMENT

- XRD measurements
- Perovskite phase stability tested before and after sintering
- For all cathodes: LSC, LSCF, PSCF, LSM, LSFM, LSF:
  - perovskite appears stable after <1300°C, 5h
- Example given: LSF

LSF



REACTIVITY SUPPORT SUBSTRATE AND CATHODES

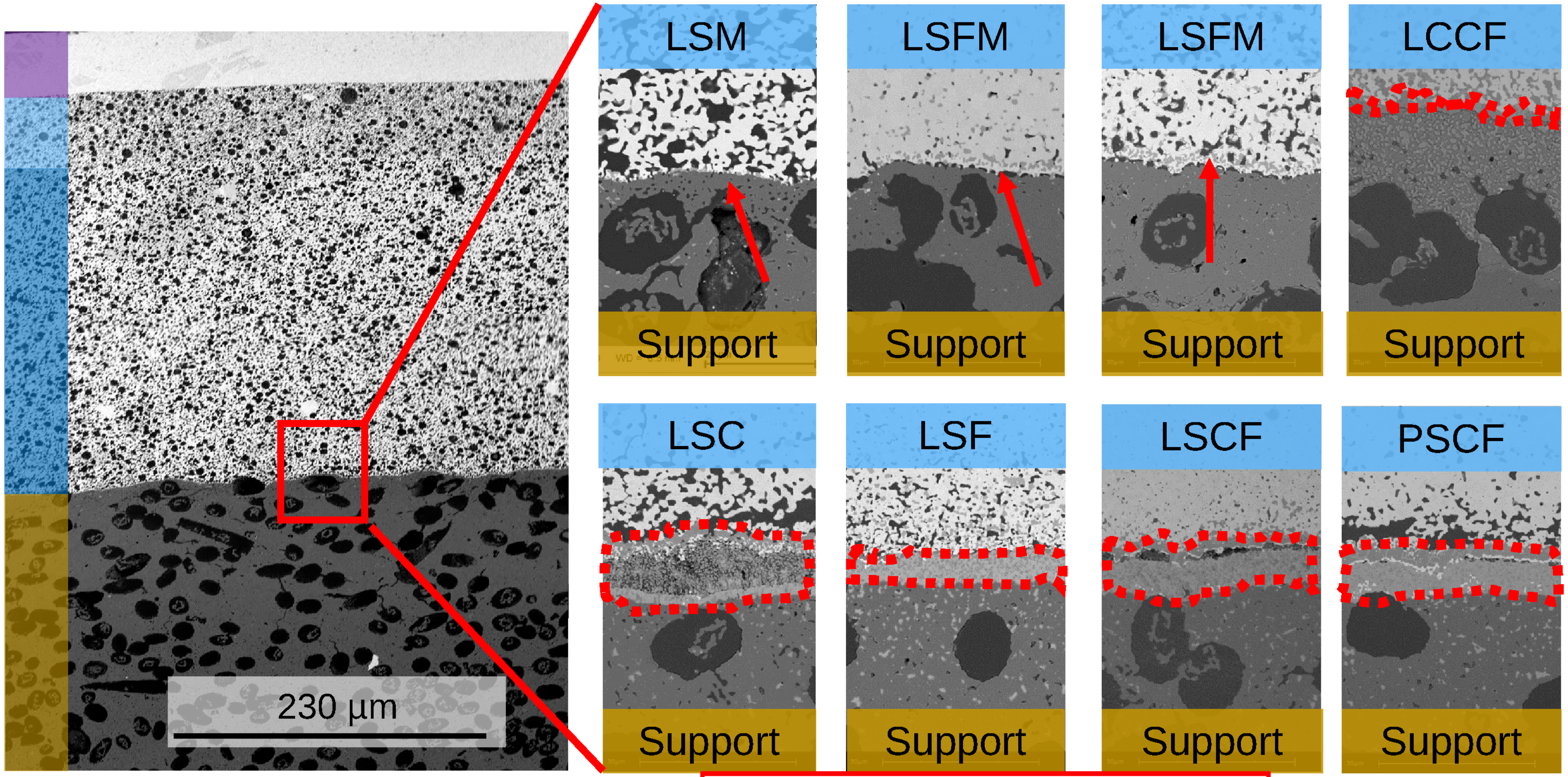
Co-sintered at <1300°C 5h, SEM image

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



Reaction phase segregations / layers

REACTIVITY SUPPORT SUBSTRATE AND CATHODES

Co-sintered at <1300°C 5h, SEM image

Zn diffuses „far“ into LSM cathode >200µm
Forms Mn-Zn spinel [1]

Electrolyte 8YSZ
dense

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$La_{1-x}Sr_xMnO_3$
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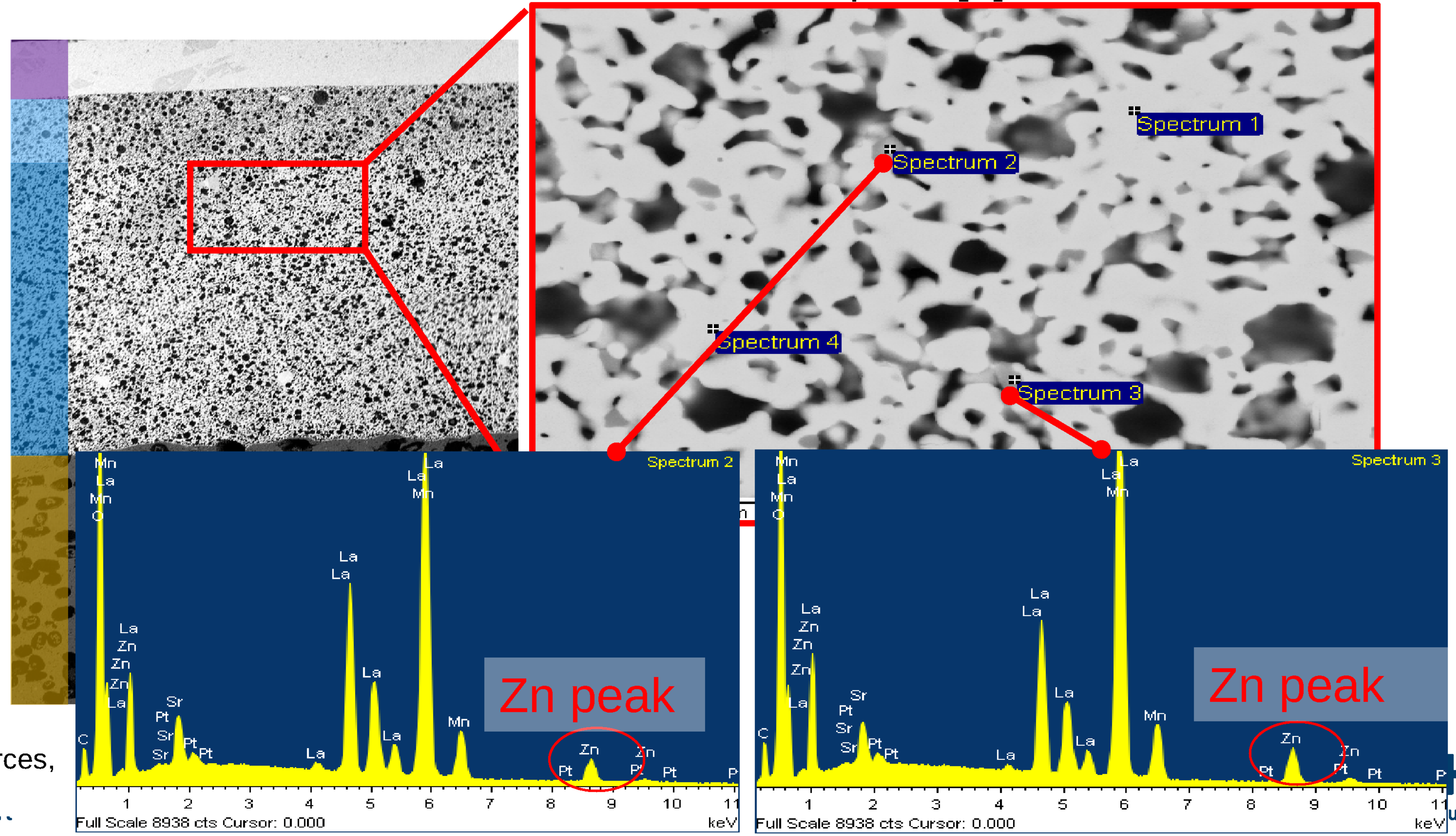
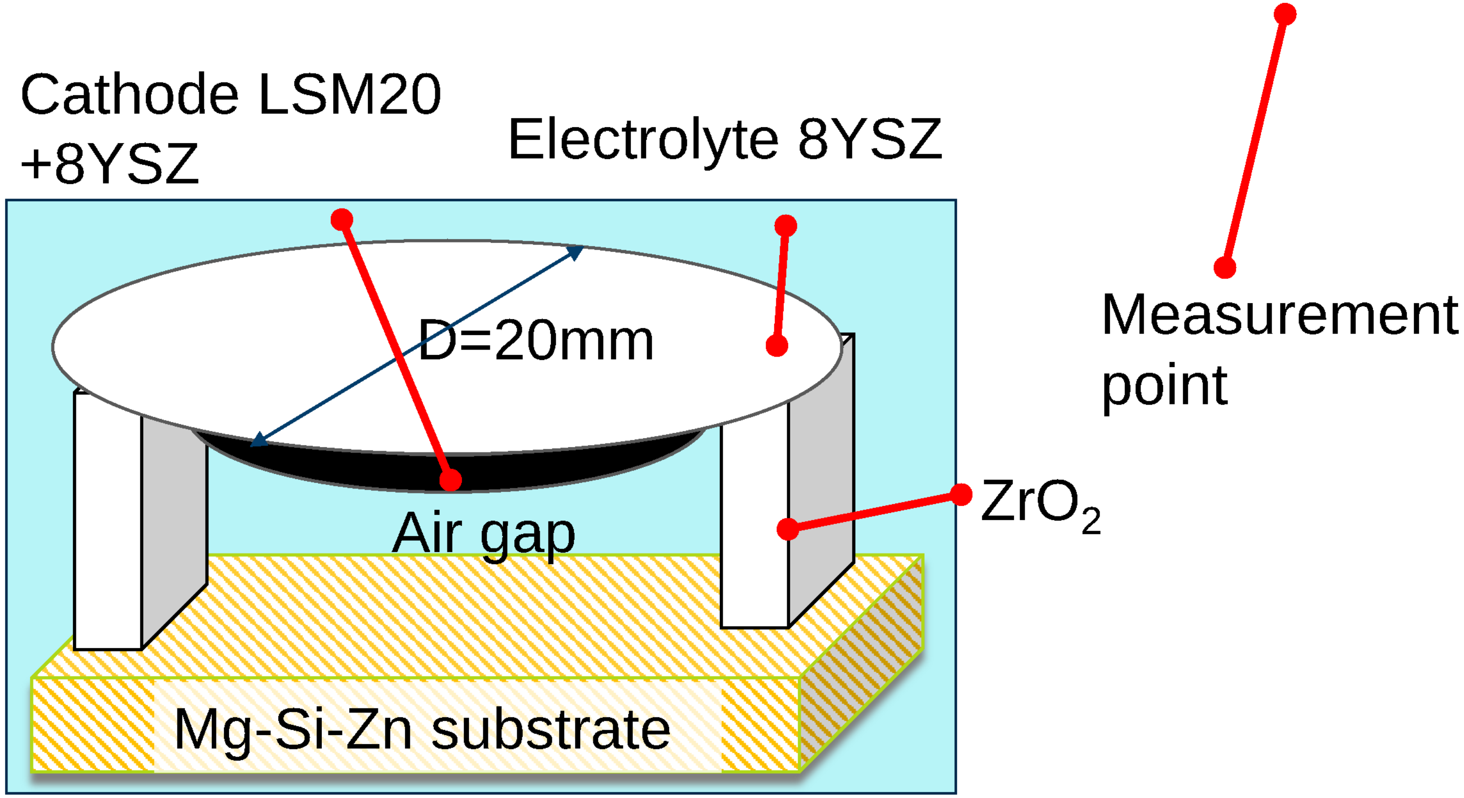


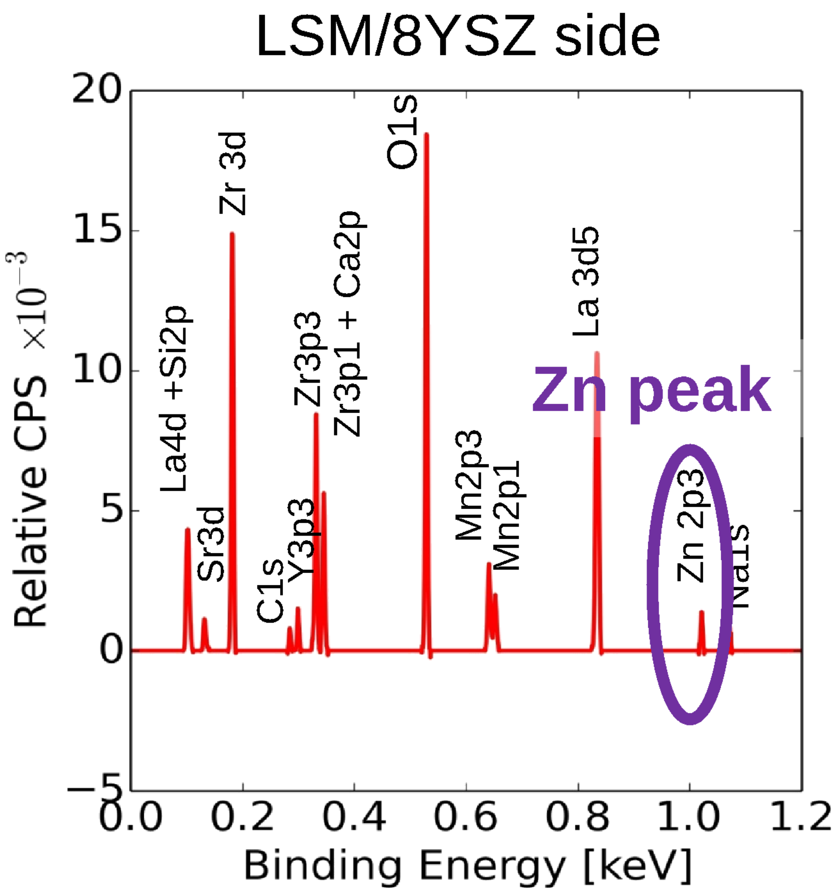
[1] Matté et al. J. Power Sources, 2018

GAS DIFFUSION TEST: X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS

- Detected Zn on LSM/8YSZ:
  - Gas diffusion of Zn



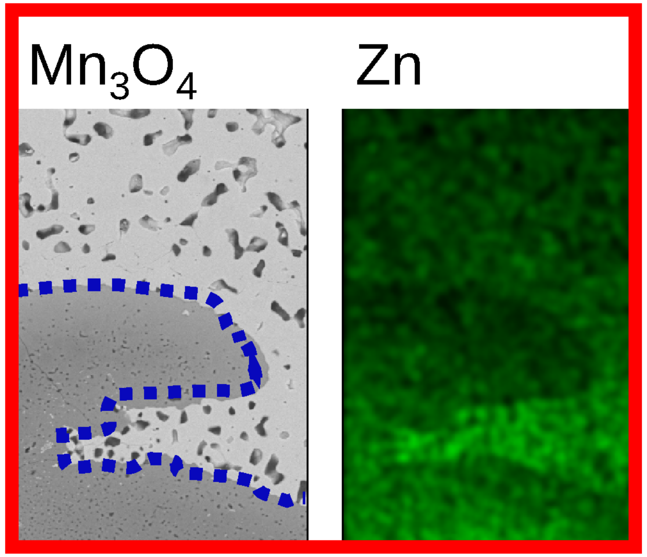
Annealing <1300°C, 5h

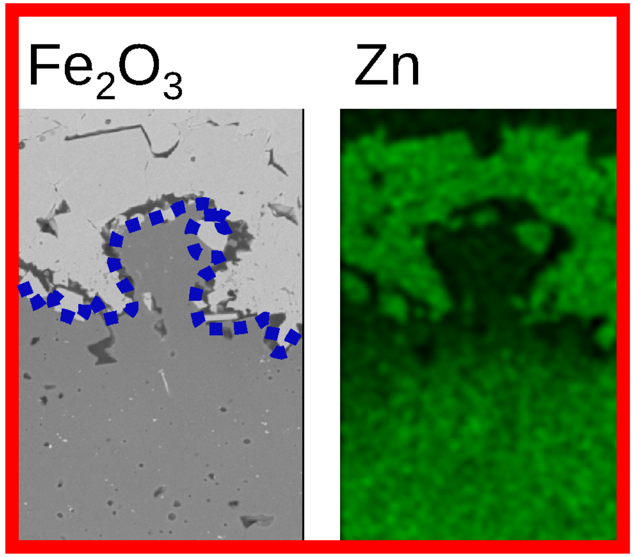


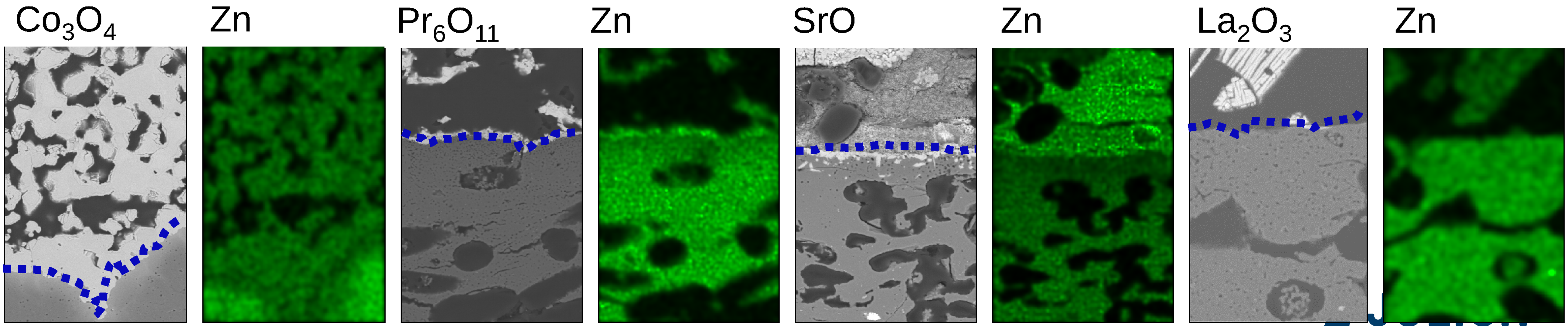
Post annealing <1300°C, 5h

REACTIVITY OF SINGLE OXIDES WITH Zn IN Mg-Si-Zn

- Possible getters for Zn identified
- Apparent high reactivity / solubility with Zn of single oxides
- Zn and Mn forms spinel phase [1]
    - ➢ Mn_3O_4 and Fe_2O_3 chosen for tests in LSM







[1] Matté et al. J. Power Sources, 2018

EDX mapping with Hitachi, post annealing

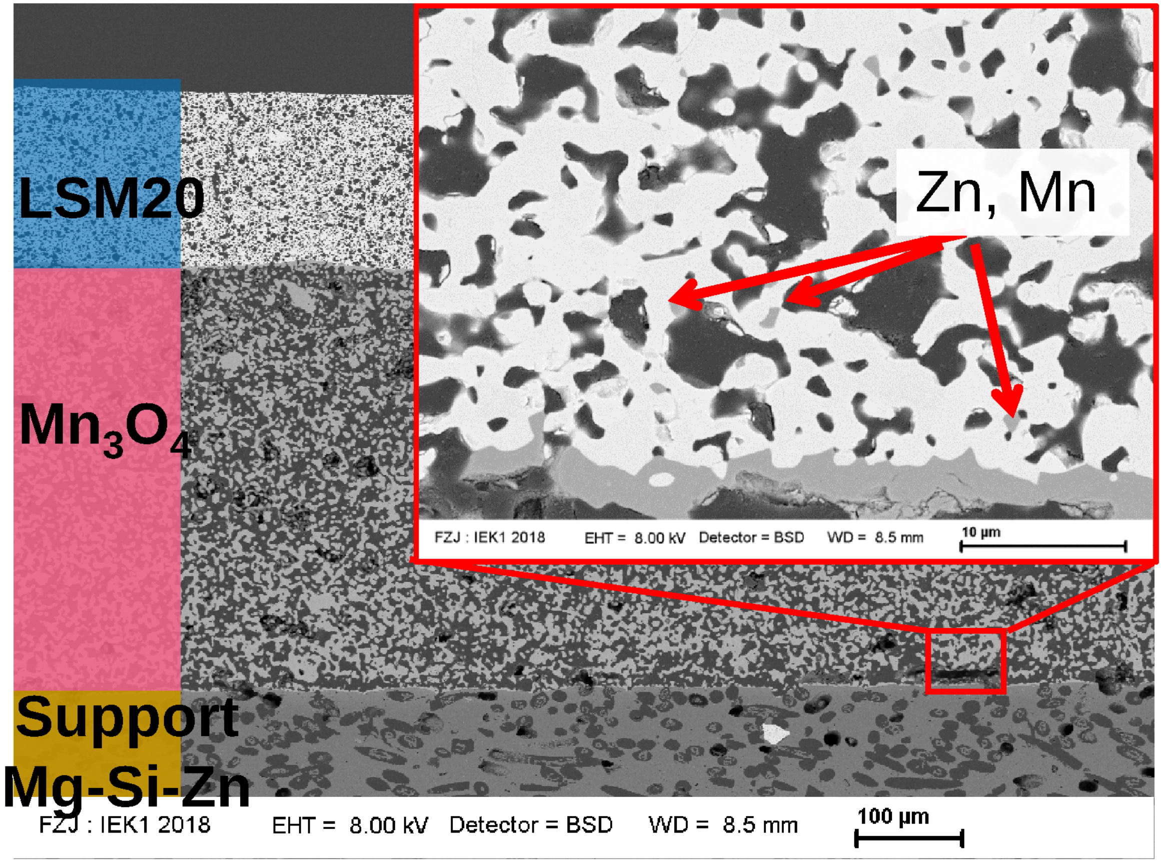
LSM: TEST WITH GETTER LAYERS

Zn diffusion depths:

- In Mn_3O_4 ~100µm,
  - no Zn found in LSM >400µm
- In Fe_2O_3 ~40µm,
  - Zn found in LSM >400µm

→ Mn_3O_4 is suitable Zn getter in LSM

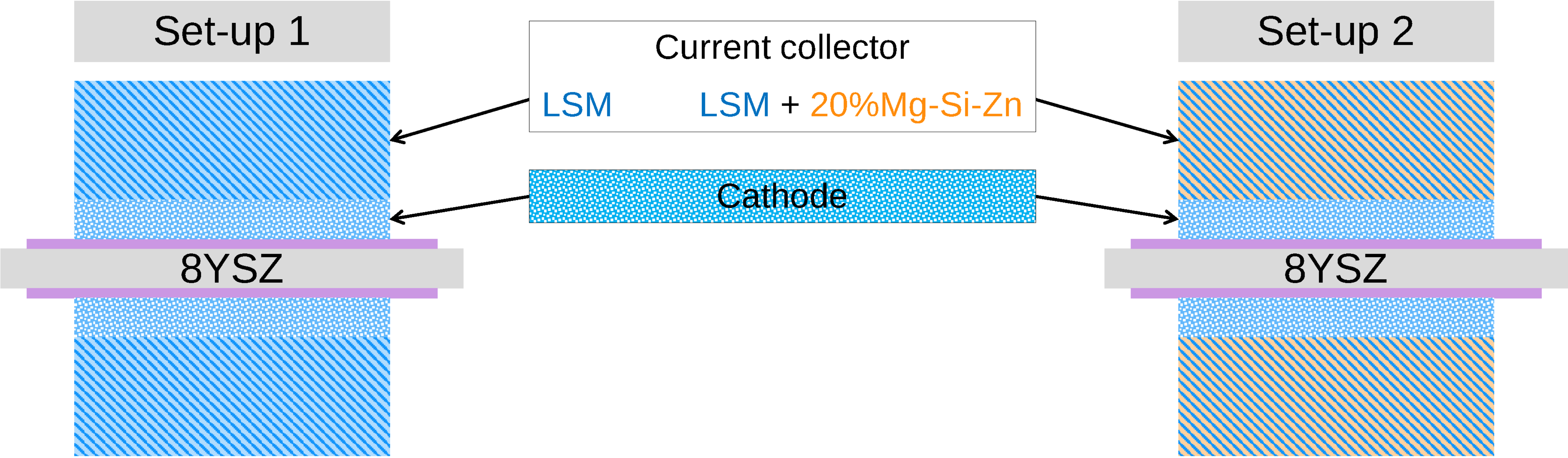
SEM images post annealing 1200°C, 5h



ELECTROCHEMICAL PERFORMANCE

Introduction | Chemical interactions | **Electrochemical performance** | Microstructure | Co-sintering | Summary

ELECTROCHEMICAL PERFORMANCE & EFFECT OF CHEMICAL INTERACTIONS WITH Mg-Si-Zn

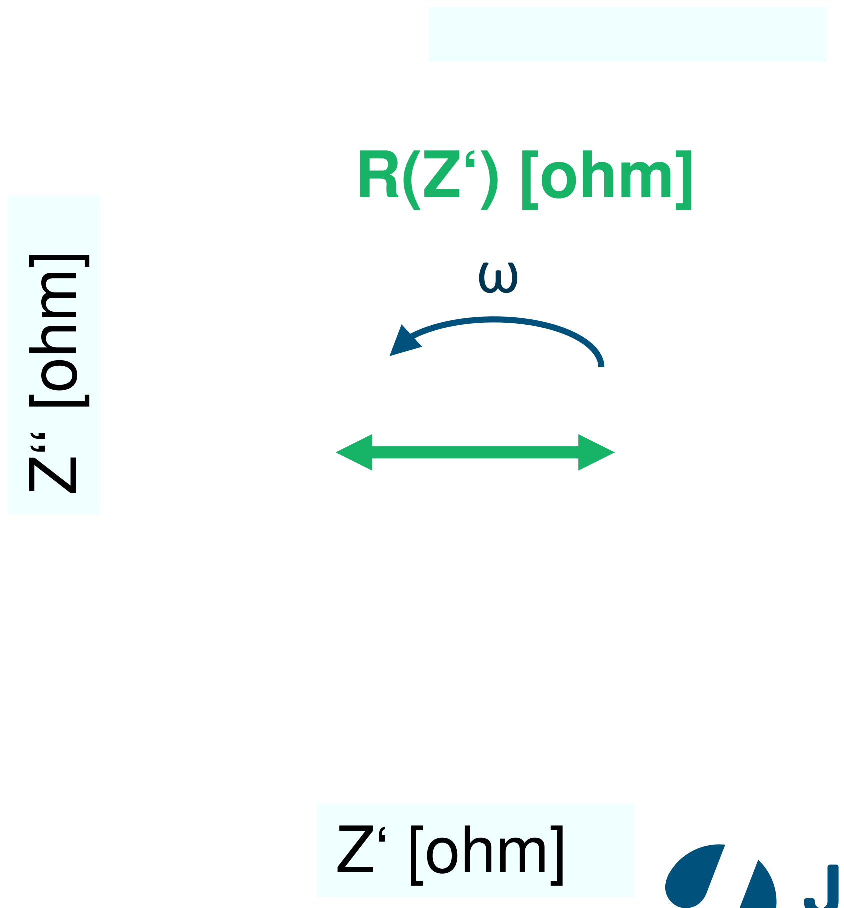


- Symmetric cells co-sintered at <1300°C
- Maximized Mg-Si-Zn content → maximized impact
- Baseline particle size of all cathode powders d_{50} ~0.8µm

ELECTROCHEMICAL PERFORMANCE & EFFECT OF CHEMICAL INTERACTIONS WITH Mg-Si-Zn

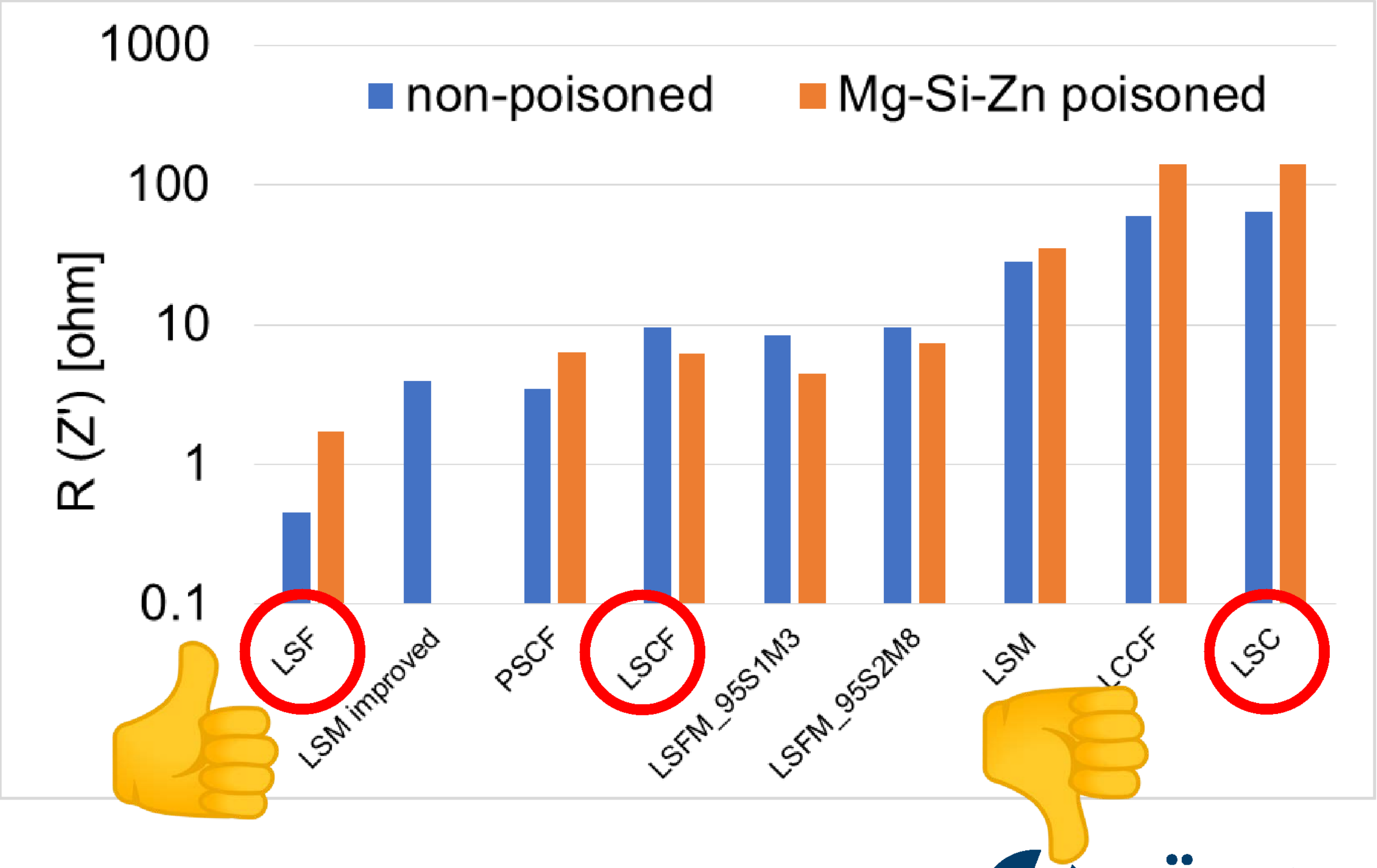
- Electrochemical impedance spectroscopy (EIS)
- Measured 700-800℃, $\omega=10^{6}-10^{-1}$Hz
- „Simple benchmarking“ value used:
    - Radius of Z‘ in the Nyquist plot @750℃

Nyquist plot



ELECTROCHEMICAL PERFORMANCE & EFFECT OF CHEMICAL INTERACTIONS WITH Mg-Si-Zn

- LSF lowest polarization resistance, LSC the highest
- Unexpected poisoning effects
- Usually LSC and LSCF are high performance cathodes [1]
- Effect of microstructure?



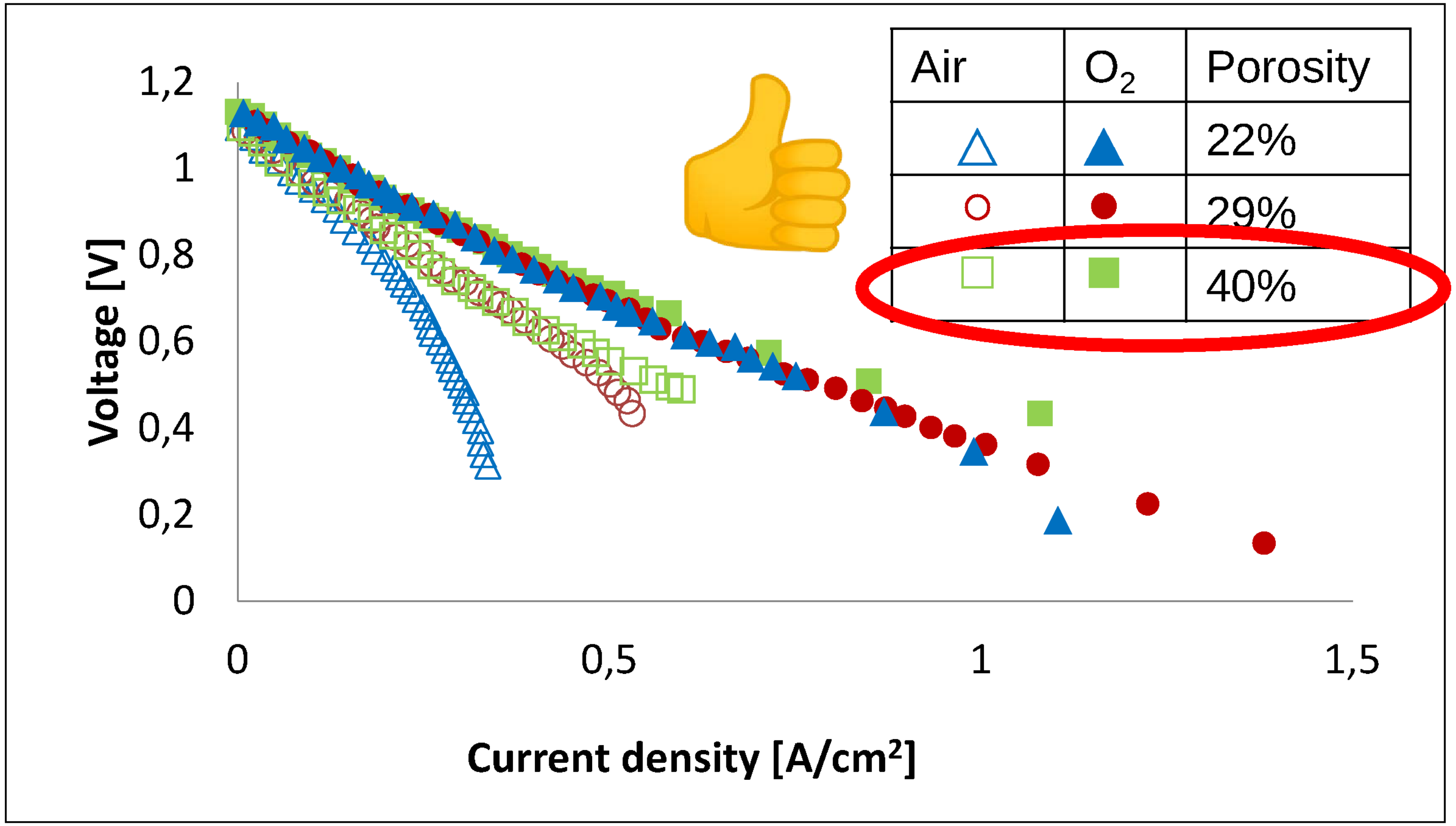
Han *et al.*, J Power Sources, 2012

MICROSTRUCTURE

Introduction | Chemical interactions | Electrochemical performance | **Microstructure** | Co-sintering | Summary

REQUESTED MICROSTRUCTURAL POROSITY

For $La_{0.8}Sr_{0.2}MnO_3$+8YSZ cathode



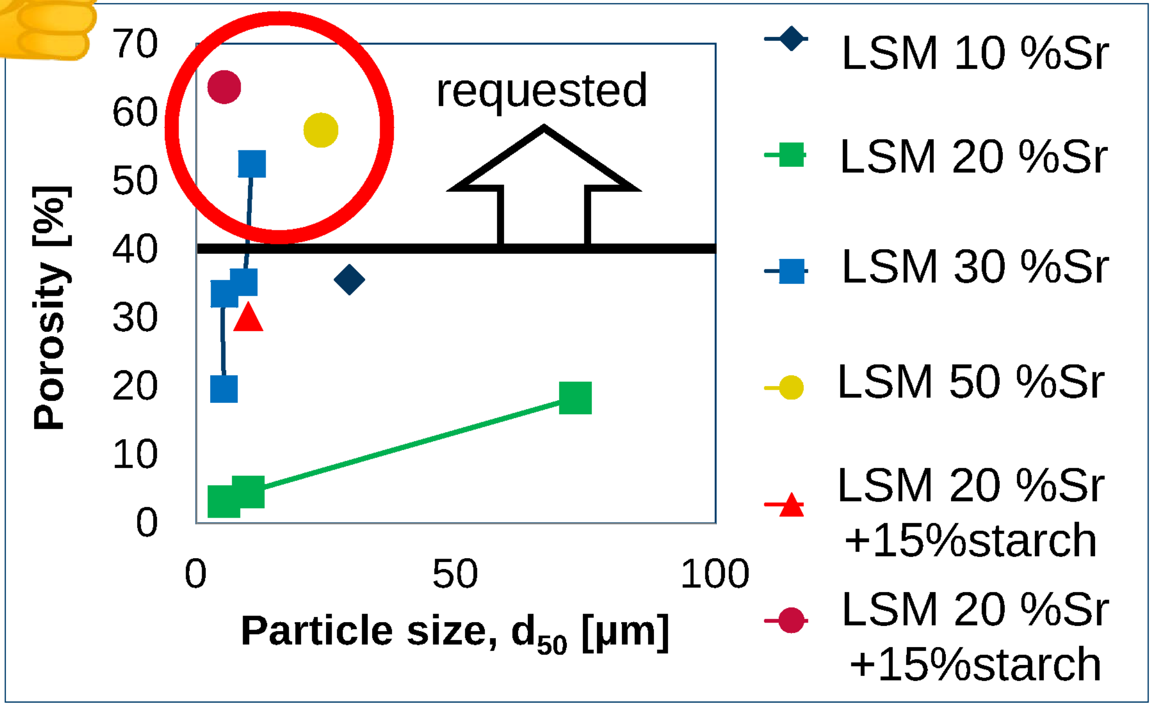
Best cathode performance found at 40% porosity [1]

[1] Tsai *et al.*, Solid state Ionics, 1997

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]



Co-sintered at <1300°C 5h

Porosity: image analysis

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

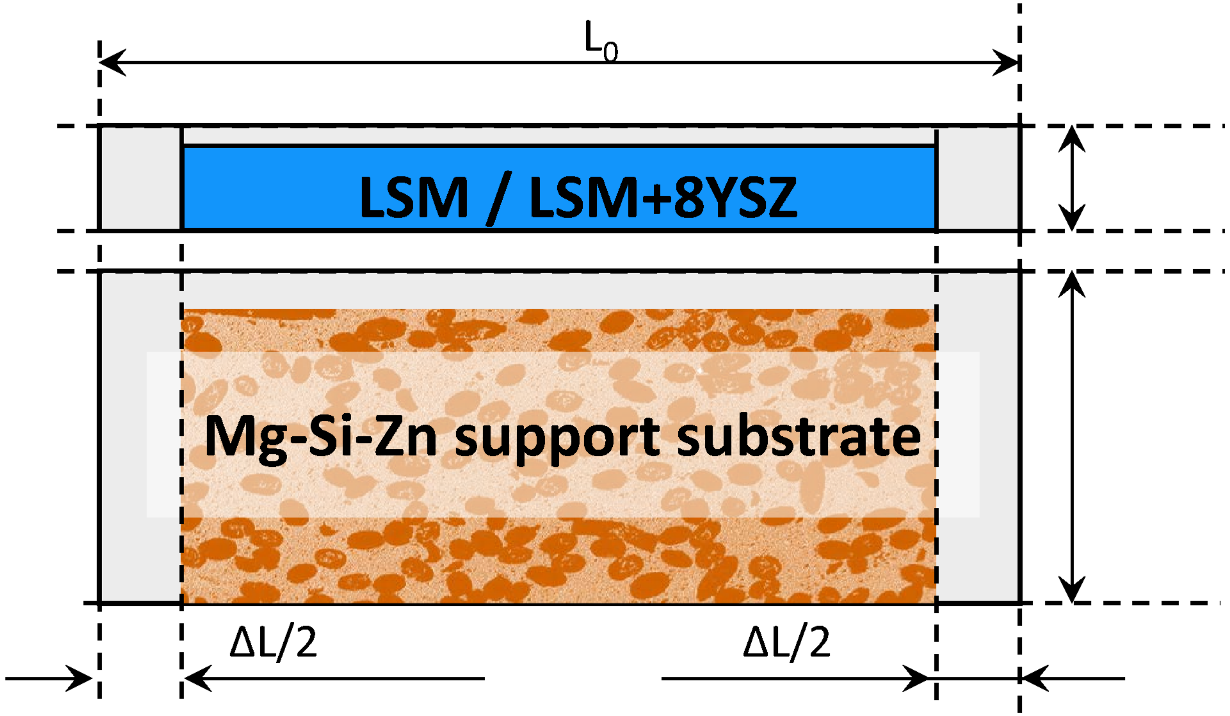
[1] Roosmalen *et al*., Solid State Ionics, 1993. [2] Wolfenstine *et al*., Solid State Ionics, 1996.
[3] Wolfenstine *et a*l., Journal of Materials Research, 1996. [4] Palcut, Journal of Physical Chemistry C, 2007.
[5] Takeda *et al*., Material Research Bulletin, 1991.

CO-SINTERING

FREE SINTERING: LSM+8YSZ CATHODE, SUPPORT SUBSTRATE

Free sintering strain behavior depends on:
- Powder (paste) properties
- Temperature

Material optimization:
- Matching of time and temperature dependant strain rate $\dot{\epsilon}_T$ or
- Adaptation of rheological properties



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

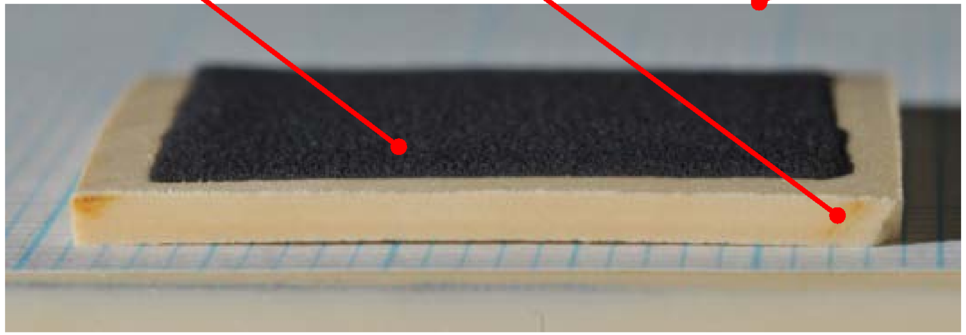
CO-SINTERABILITY PREREQUISITE

LSM/8YSZ cathodes and current collectors, sintering behavior adjusted:

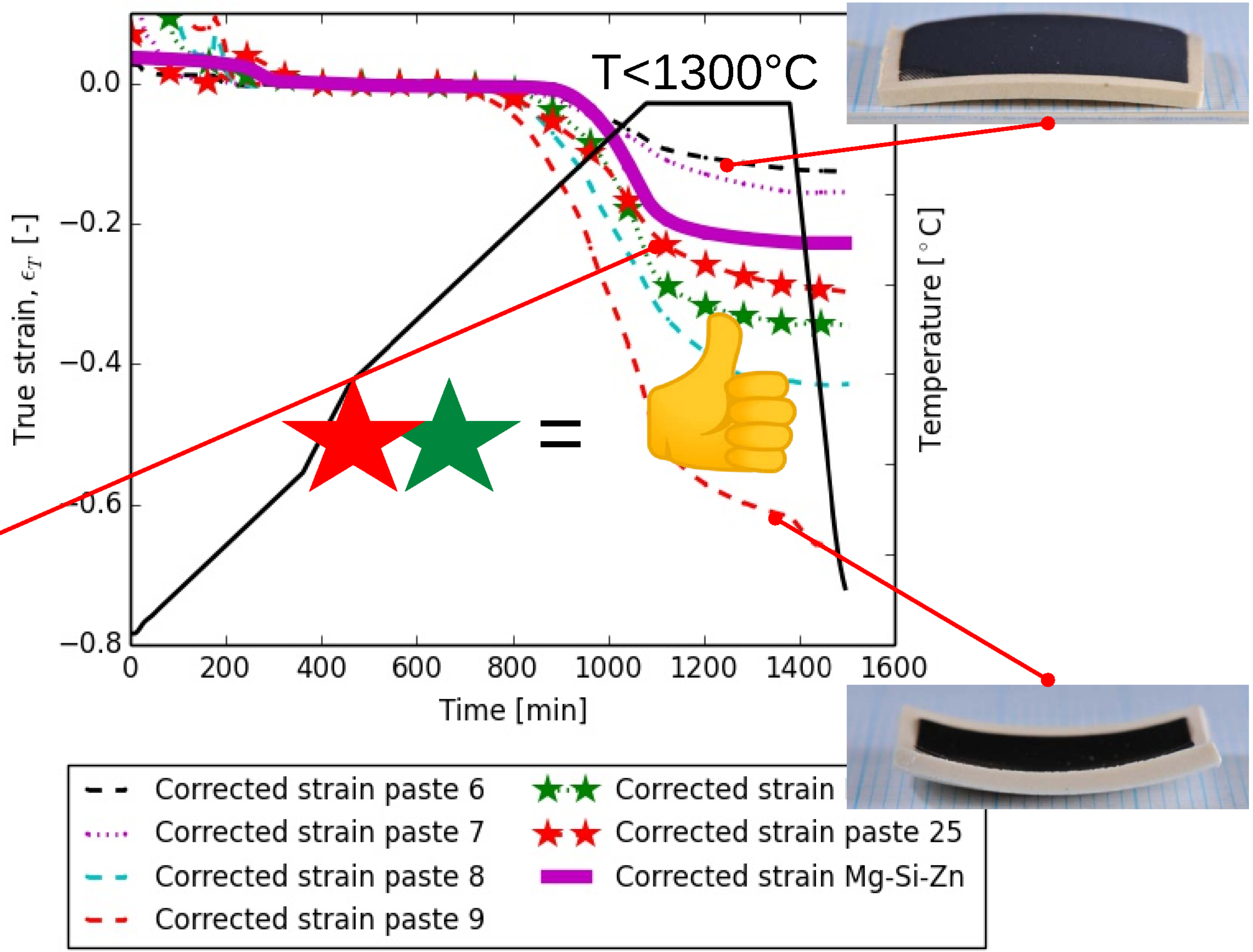
- Particle size, Sr-content
- Pore formers added

Matching sintering curves→ Successful co-sintering

Cathode Mg-Si-Zn substrate



Measured with Netsch dilatometer



SUMMARY

Introduction | Chemical interactions | Electrochemical performance | Microstructure | Co-sintering | **Summary**

SUMMARY

- Novel all ceramic SOFC design; evaluation of cathodes within new design and processing conditions:
- *Chemical interactions:* All cathodes react with elements in support
  - But, reactions may be decreased / suppressed by getters
- *Electrochemical performance*: so far LSF shows the highest performance in EIS
- *Microstructure:* at new processing conditions needs optimization
- *Co-sinterability:* must be considered during material optimization

} Succesful with LSM

- **OUTLOOK:** Improve microstructure of LSF / LSCF
- Most promising cathodes → single cell measurements

ACKNOWLEDGMENT

A special thanks to MSc Fabian Grimm for conducting measurements

BMWi

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Project partners for their cooperation

BOSCH

JÜLICH Forschungszentrum

Hochschule Karlsruhe Technik und Wirtschaft UNIVERSITY OF APPLIED SCIENCES

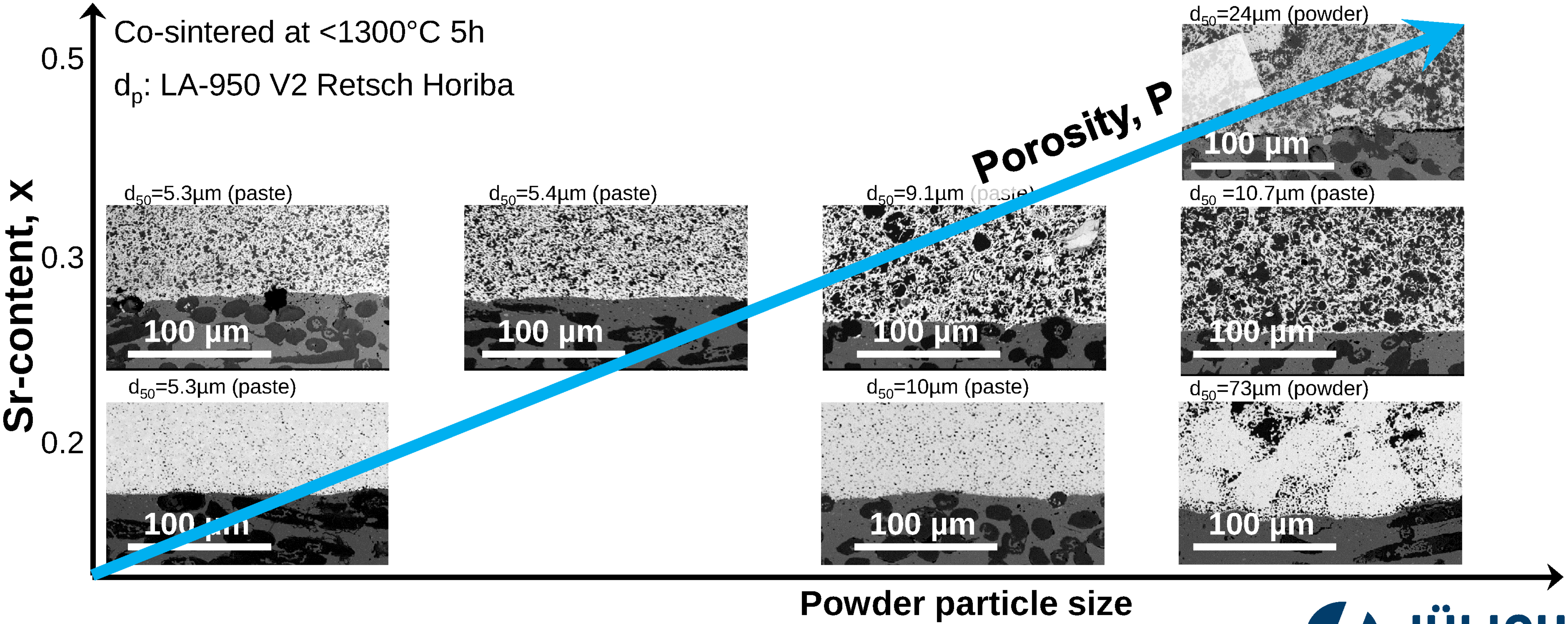
KIT Karlsruher Institut für Technologie

Hochschule Aalen

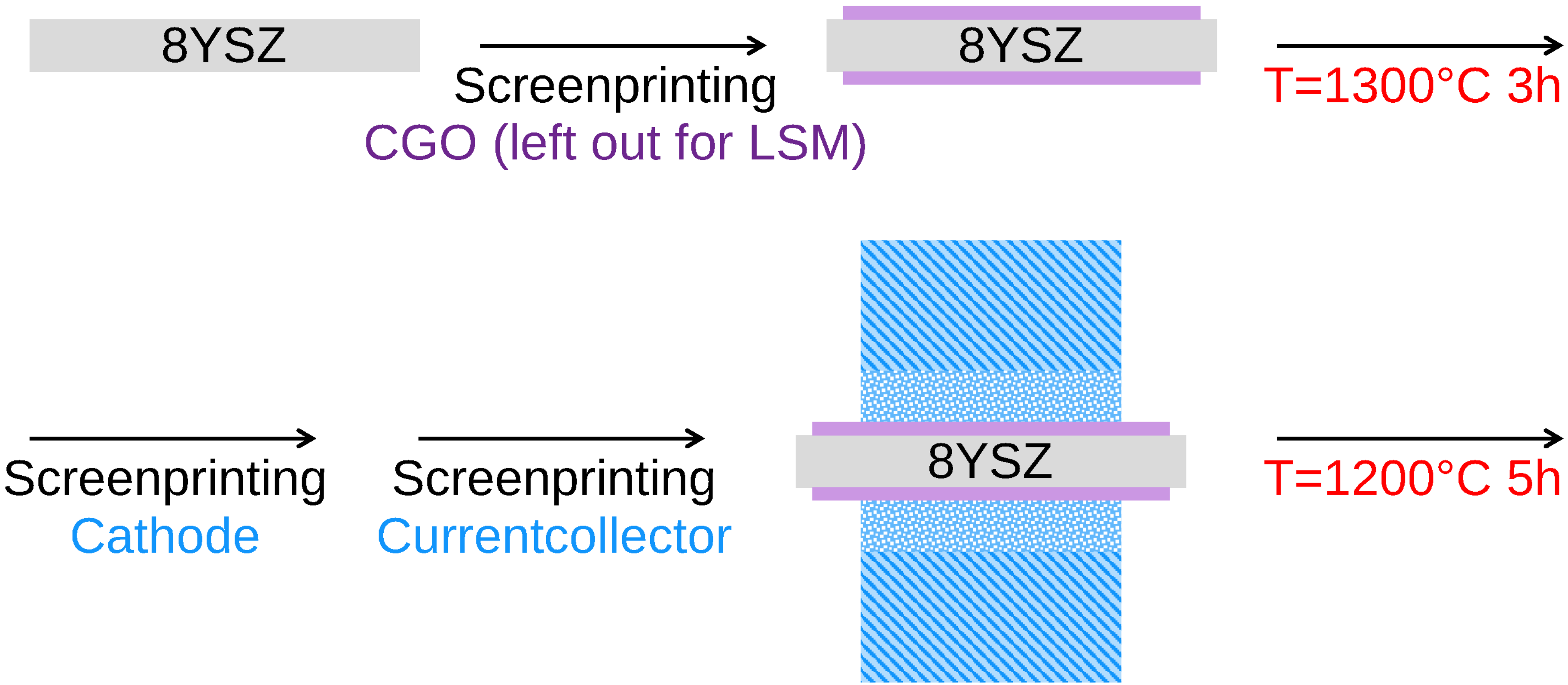
RJL Micro&Analytic

Colleagues at Forschungszentrum Jülich for support in investigations

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



ELECTROCHEMICAL PERFORMANCE & EFFECT OF CHEMICAL INTERACTIONS WITH Mg-Si-Zn



- Impedance-measurements samples: symmetric cells