

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

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PROJECT: KERSOLIFE 100

Funded by:



Goal:

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

Project coordination

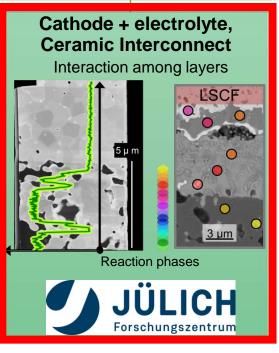


Long-term tests

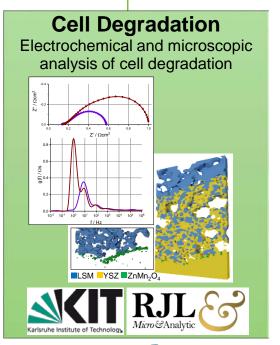
Models for degradation analysis

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



Anode Modeling of microstructural changes for lifetime prediction Combination of experimental and simulation methods Surface officials of the production of the production

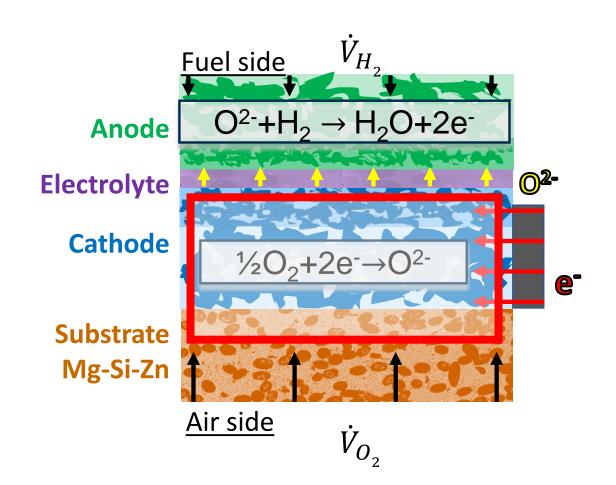






INERT SUPPORTED SOLID OXIDE FUEL CELL (SOFC)

- 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





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CONTENT OF PRESENTATION

Evaluation of cathodes within design:

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

Index of tested cathodes

LSM	La _x Sr _y MnO _{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 JÜLICH
Mitglied der Helmholtz-Gemeinschaft			Forschungszentrum

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CHEMICAL INTERACTIONS

Introduction Chemical interactions

Electrochemical performance

Microstructure

Co-sintering

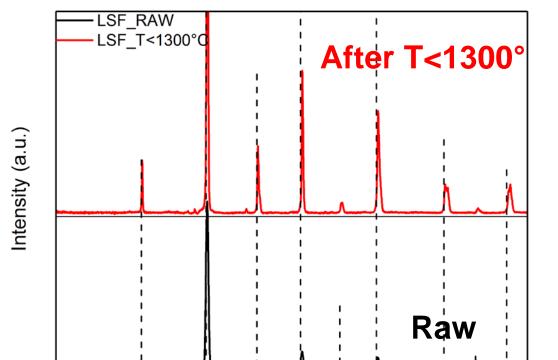
Summary





STABILITY OF PEROVSKITES AFTER THERMAL TREATMENT LSF

- 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



50

2-Theta

60

20





REACTIVITY SUPPORT SUBSTRATE AND CATHODES

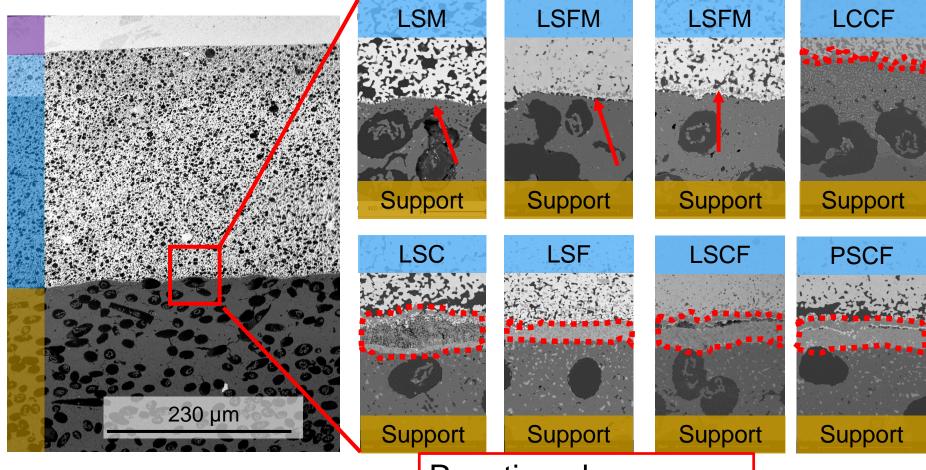
Co-sintered at <1300°C 5h, SEM image

Electrolyte 8YSZ dense

Cathode
La_{1-x}Sr_xMnO₃
+8YSZ
porous

Current collector La_{1-x}Sr_xMnO₃ 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]

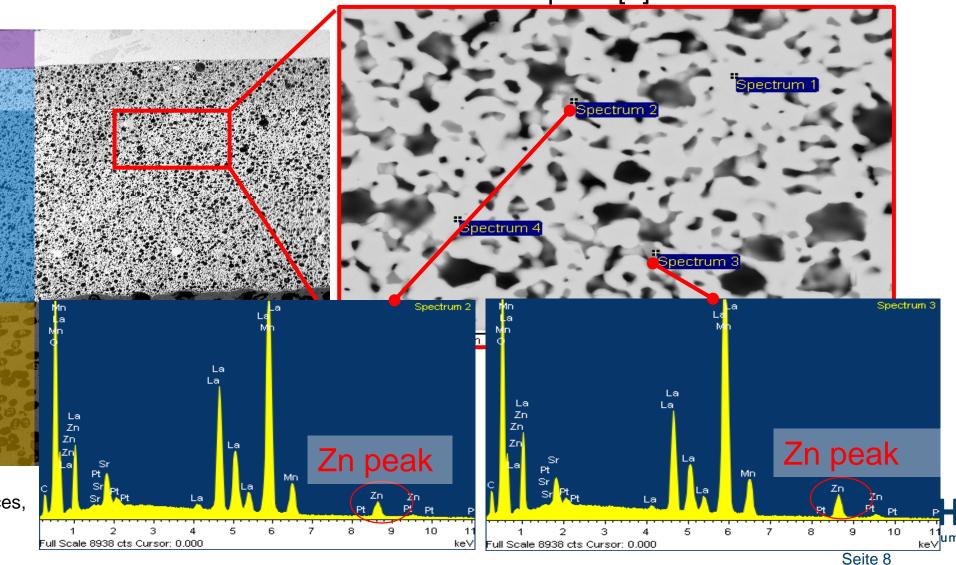
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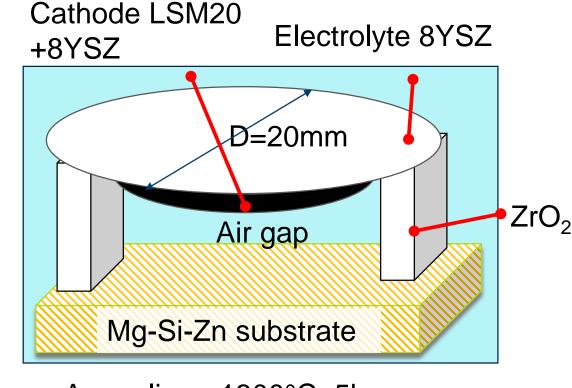
[1] Matté et al. J. Power Sources, 2018

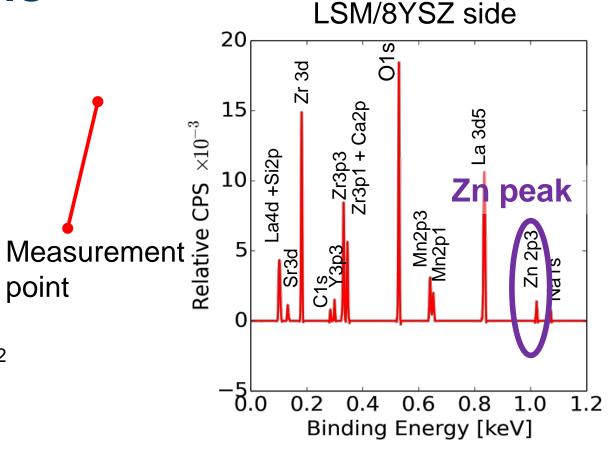




GAS DIFFUSION TEST: X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS

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



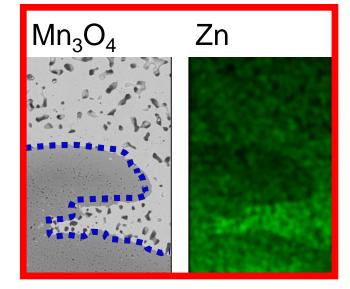


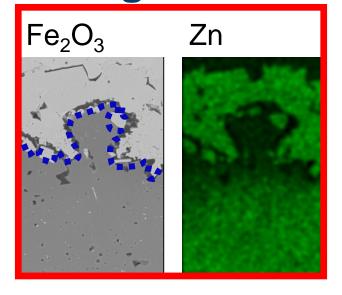
Post annealing <1300°C, 5h

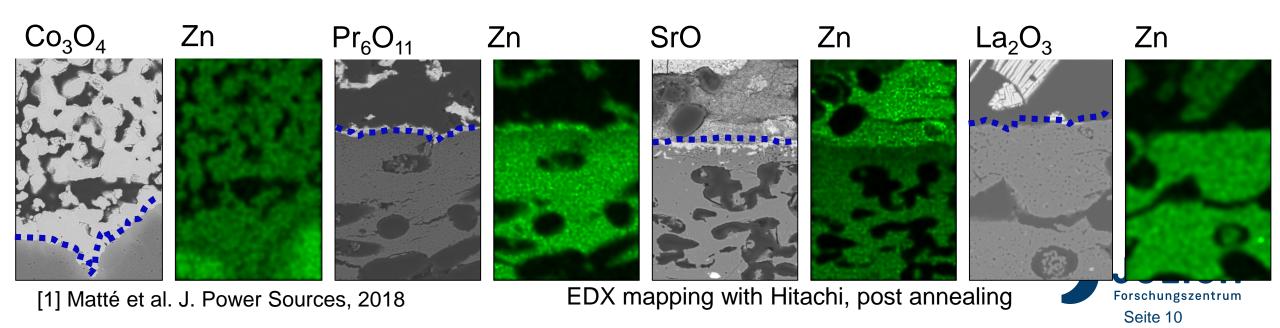


REACTIVITY OF SINGLE OXIDES WITH Zn IN Mg-Si-Zn

- Possible getters for Zn identified
- Apparent high reactivity / solubility with Zn of single oxides
- Zn and Mn forms spinel phase [1]
 - Mn₃O₄ and Fe₂O₃chosen for tests in LSM







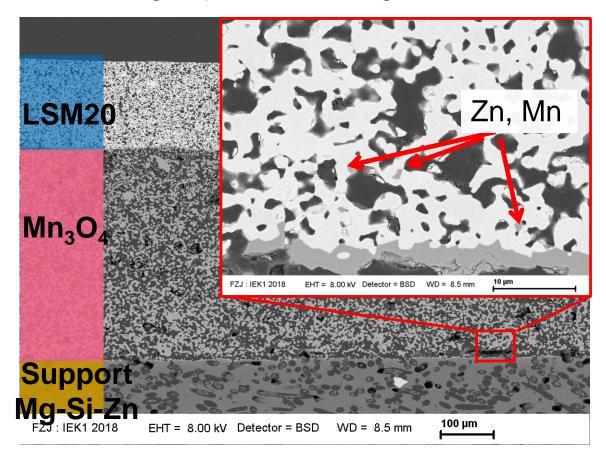


LSM: TEST WITH GETTER LAYERS

Zn diffusion depths:

- In $Mn_3O_4 \sim 100 \mu m$,
 - no Zn found in LSM >400μm
- In $Fe_2O_3 \sim 40 \mu m$,
 - Zn found in LSM >400µm
- → Mn₃O₄ is suitable Zn getter in LSM

SEM images post annealing 1200°C, 5h





ELECTROCHEMICAL PERFORMANCE

Introduction

Chemical interactions

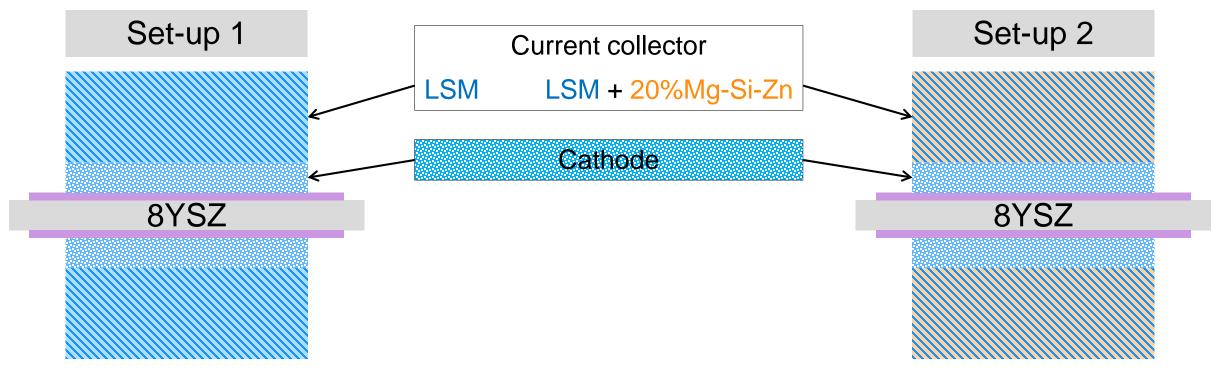
Electrochemical performance

Microstructure

Co-sintering

Summary





- Symmetric cells co-sintered at <1300°C
- Maximized Mg-Si-Zn content → maximized impact
- Baseline particle size of all cathode powders d₅₀ ~0.8μm



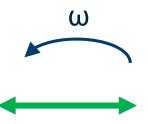


- Electrochemical impedance spectroscopy (EIS)
- Measured 700-800°C, $\omega = 10^6-10^{-1}$ Hz
- "Simple benchmarking" value used:
 - Radius of Z' in the Nyquist plot @750°C

Z" [ohm]

Nyquist plot

R(Z') [ohm]

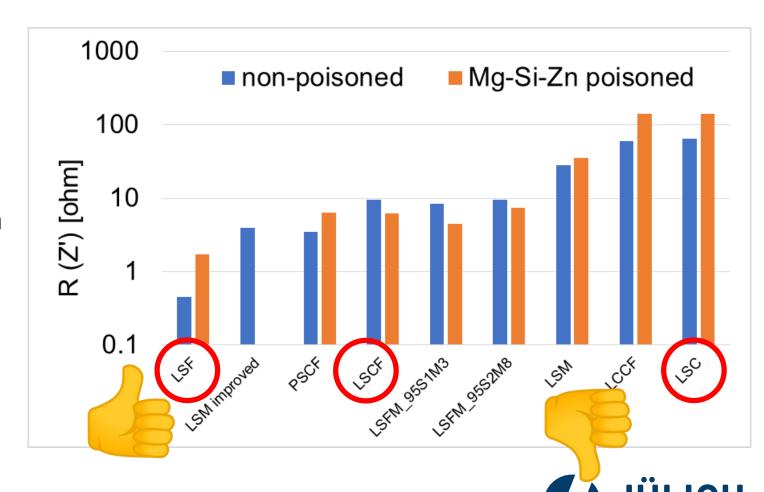








- LSF lowest polarization resistance, LSC the highest
- Unexpected poisoning effects
- Usually LSC and LSCF are high performance cathodes [1]
- Effect of microstructure?



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MICROSTRUCTURE

Introduction

Chemical interactions

Electrochemical performance

Microstructure

Co-sintering

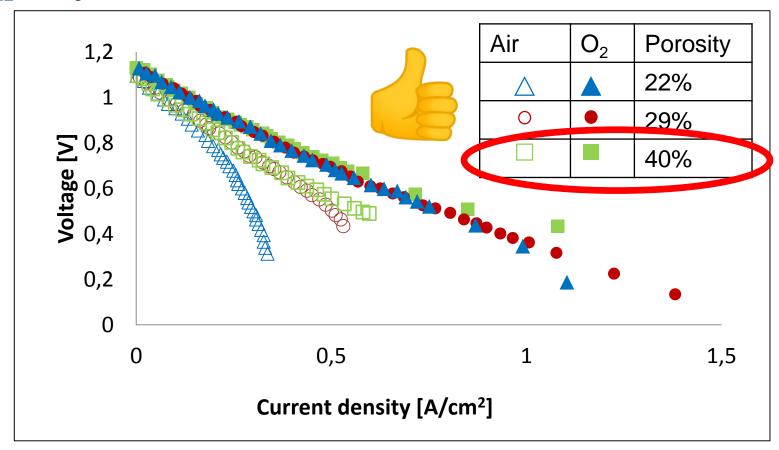
Summary





REQUESTED MICROSTRUCTURAL POROSITY

For La_{0.8}Sr_{0.2}MnO₃+8YSZ cathode



Best cathode performance found at 40% porosity [1]

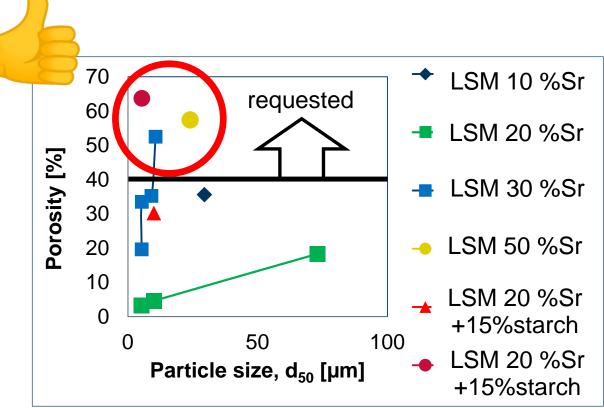




EVALUATION OF MICROSTRUCTURAL PARAMETERS

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 d₅₀: LA-950 V2 Retsch Horiba

[5] Takeda et al., Material Research Bulletin, 1991.



^[1] Roosmalen et al., Solid State Ionics, 1993. [2] Wolfenstine et al., Solid State Ionics, 1996.

^[3] Wolfenstine et al., Journal of Materials Research, 1996. [4] Palcut, Journal of Physical Chemistry C, 2007.

CO-SINTERING

Introduction Chemical Electrochemical Microstructure Co-sintering Summary



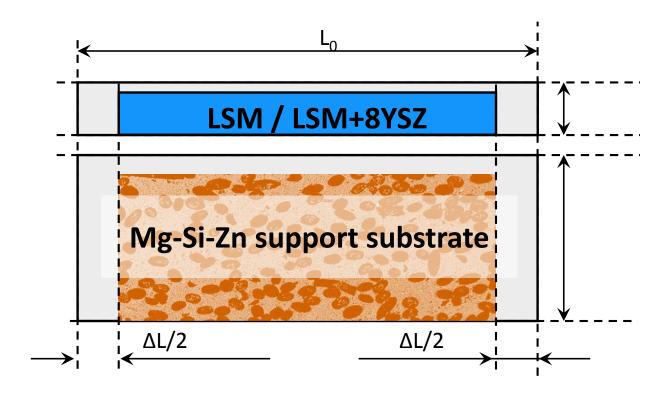
FREE SINTERING: LSM+8YSZ CATHODE, SUPPORT SUBSTRATE

Free sintering strain behavior depends on:

- Powder (paste) properties
- Temperature

Material optimization:

- Matching of time and temperature dependant strain rate $\dot{\epsilon}_{\mathsf{T}}$ or
- Adaptation of rheological properties



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



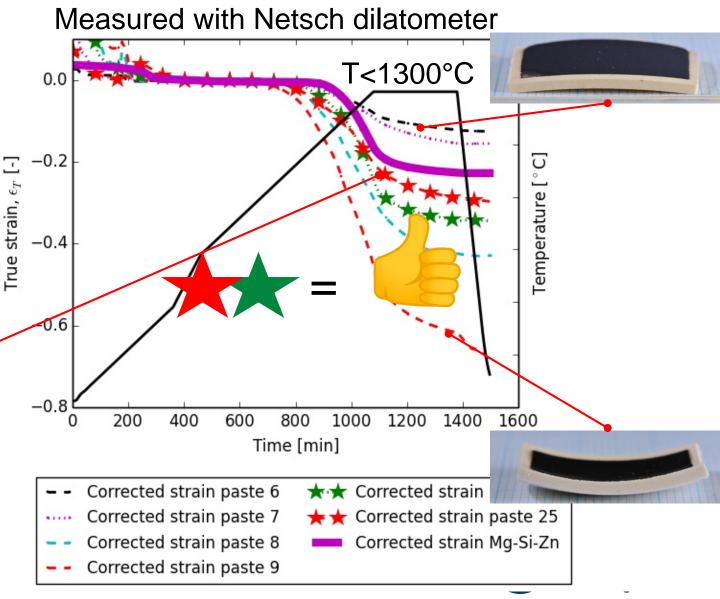
CO-SINTERABILITY PREREQUISITE

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



SUMMARY

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



Succesful

with LSM

ACKNOWLEDGMENT

A special thanks to MSc Fabian Grimm for conducting measurements

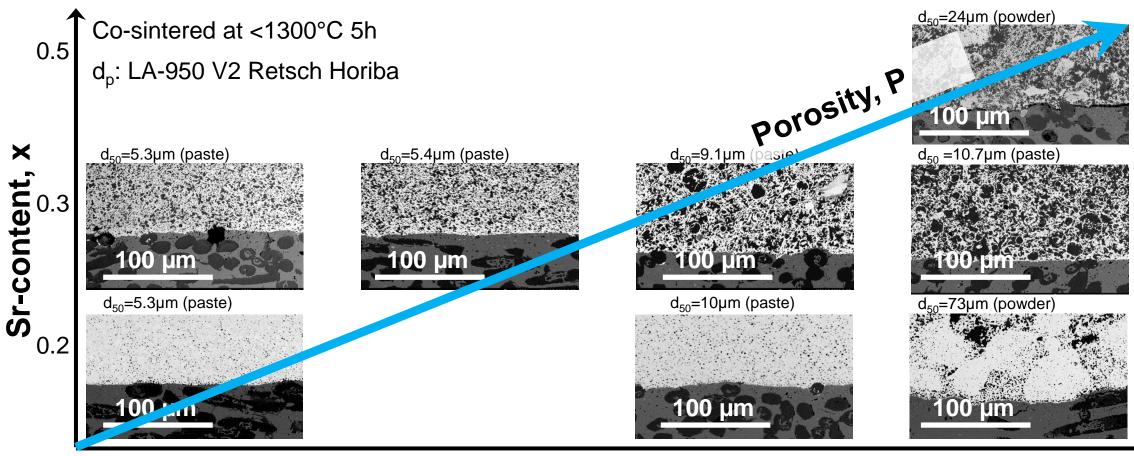




Colleagues at Forschungszentrum Jülich for support in investigations

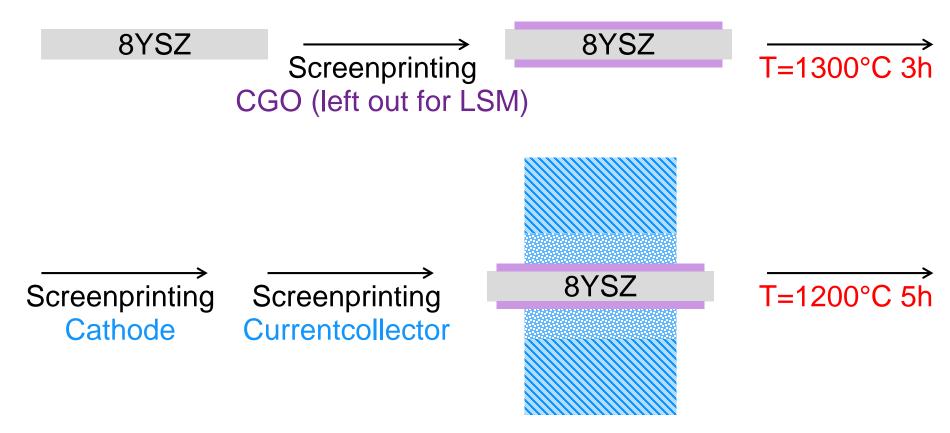


IMPACT OF PARTICLE SIZE AND Sr-CONTENT ON SINTERED MICROSTRUCTURE (La_{1-x}Sr_x)_yMnO₃



Powder particle size





Impedance-measurements samples: symmetric cells

