
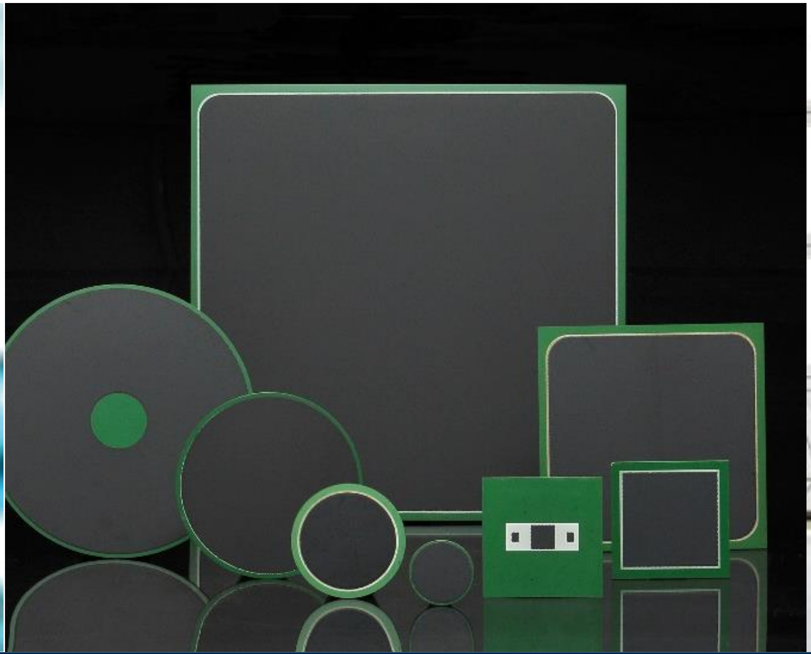


Interdiffusion in Multi-Layer Electrolytes for Solid Oxide Cells: Co-Firing and Rapid Densification Techniques

MAY 20TH, 2025 | CHRISTIAN LENSER,[1] DENISE RAMLER,[1,2] ALEXANDER SCHWIERS,[1] NORBERT H. MENZLER[1,2] AND O. GUILLON[1,2,3]

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(3) Jülich Aachen Research Alliance – Energy (JARA), Jülich/Germany;

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Wandel gestalten

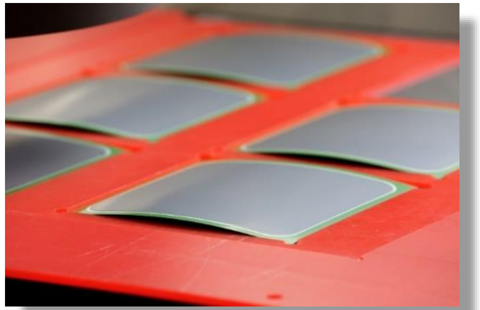
Overview

- Motivation: Ni migration in Ni-YSZ cathodes
- Substitution of YSZ by GDC in cermets – challenges and advantages
- Co-firing of multilayer electrolytes - effects of interdiffusion
- Rapid sintering techniques –the way forward?

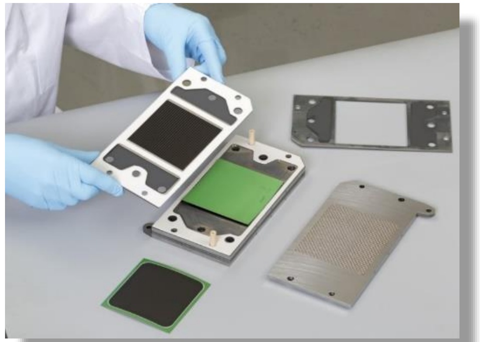
Solid oxide cells @ Jülich

Raw materials

Single cells

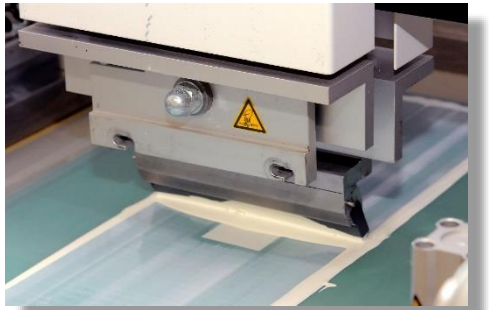


Single repeating unit (SRU)



Short / power stacks

Processing techniques



Screen printing

Tape casting

Wet powder spraying

Atmospheric plasma spraying

Dip coating

Physical vapour deposition

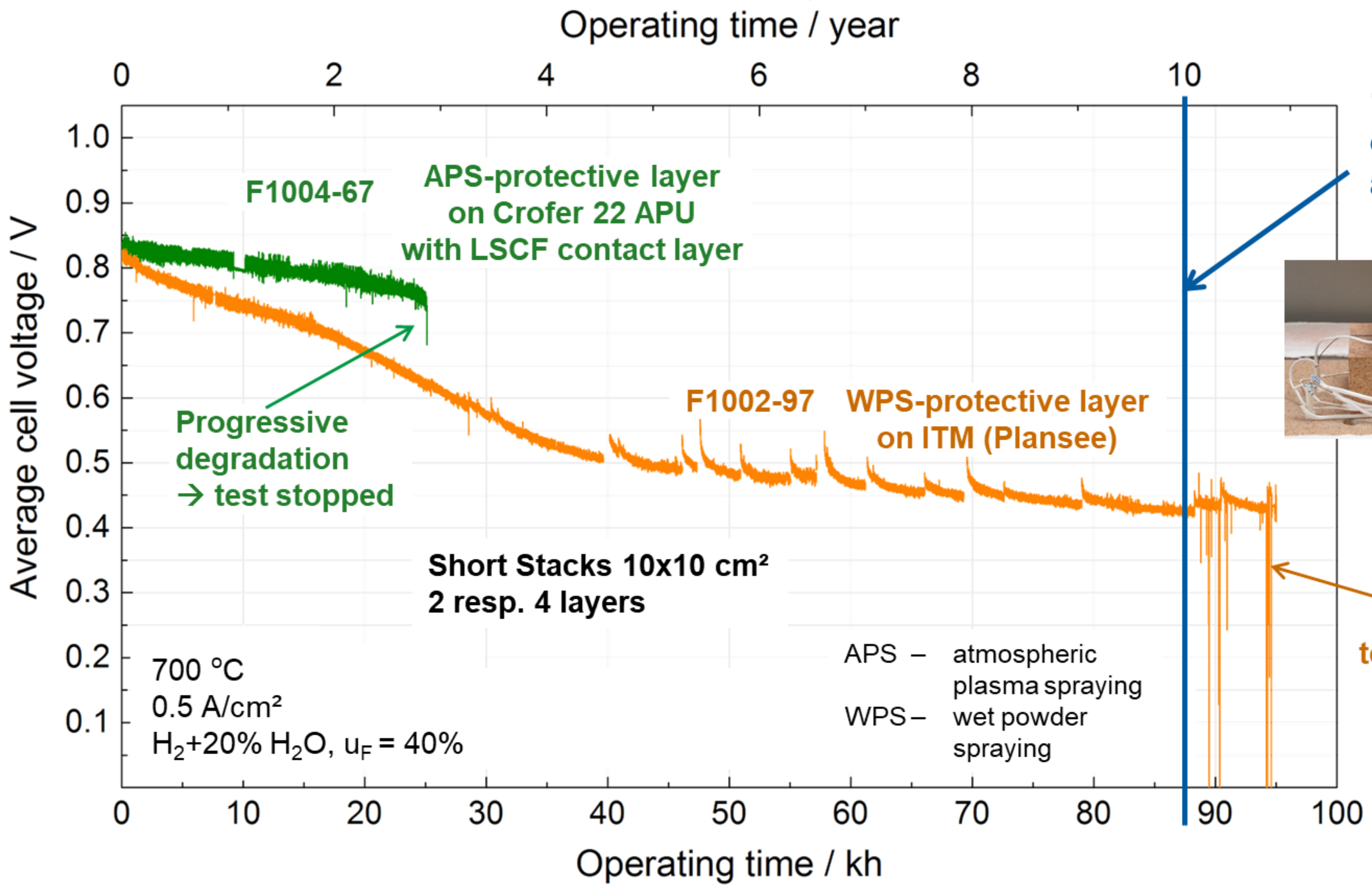
Spin coating

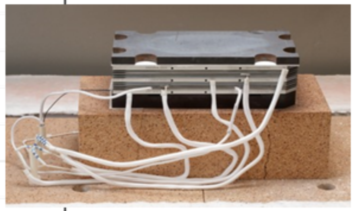
Research highlight – long-term testing

Operating time under load

93,000 h @ 0.55 %/kh
25,000 h @ 0.25 %/kh

Degradation rate

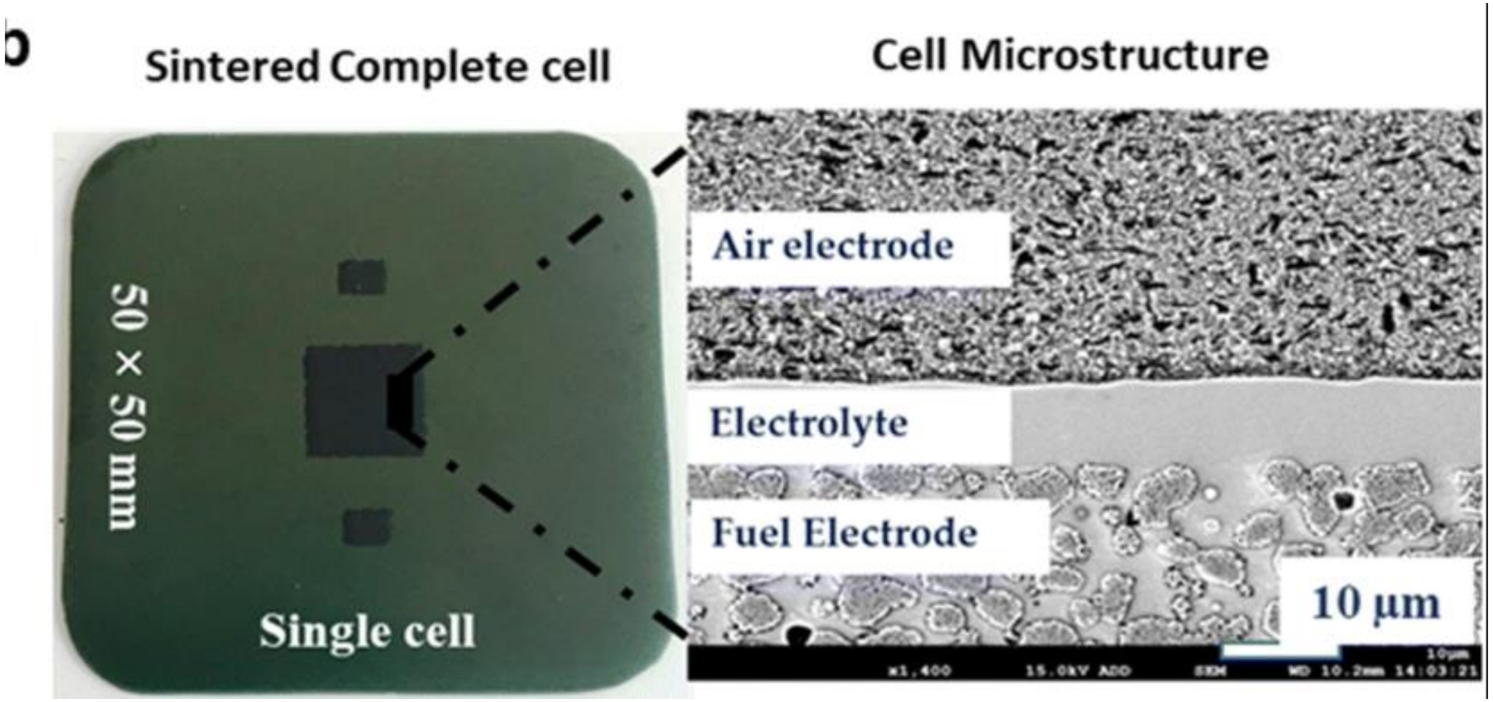




Q. Fang, L. Blum, D. Stolten, ECS Transactions, 91 (2019) 687-696.

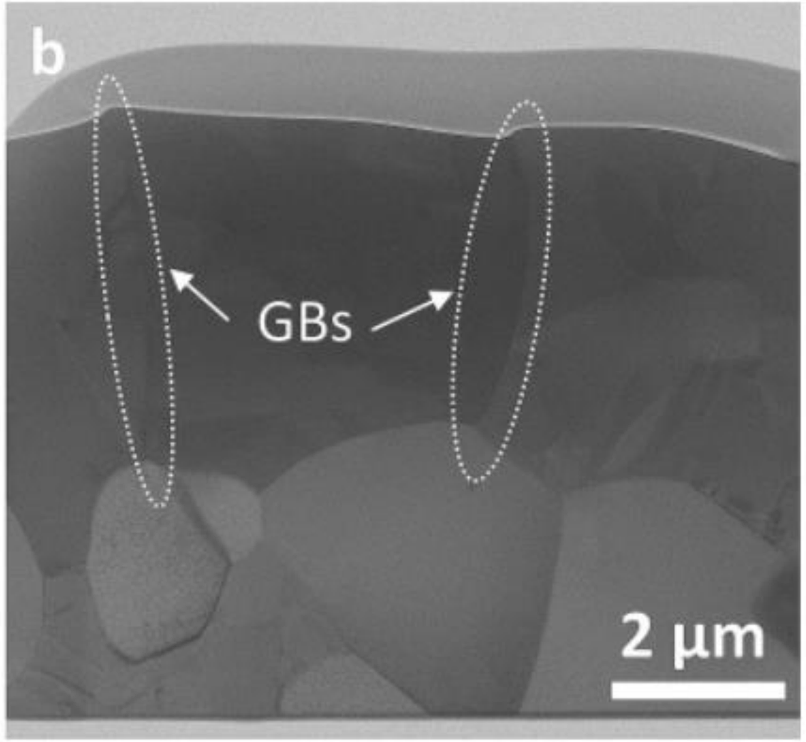
N. H. Menzler, D. Sebold, Y. J. Sohn, S. Zischke, Journal of Power Sources, Volume 478, 2020, 228770

Research highlights - PCCEL



- PCC made by sequential tape-casting
- Use a $SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$ support to sinter at 1300 °C

- PCC with thin electrolyte using wet powder spraying (WPS)



L. Kwati, et al., ***Mater. Adv.***, 2025,**6**, 3253-3263
Y. Zeng, et al., Materials Science and Engineering: B, Volume 319, 2025, 118340,

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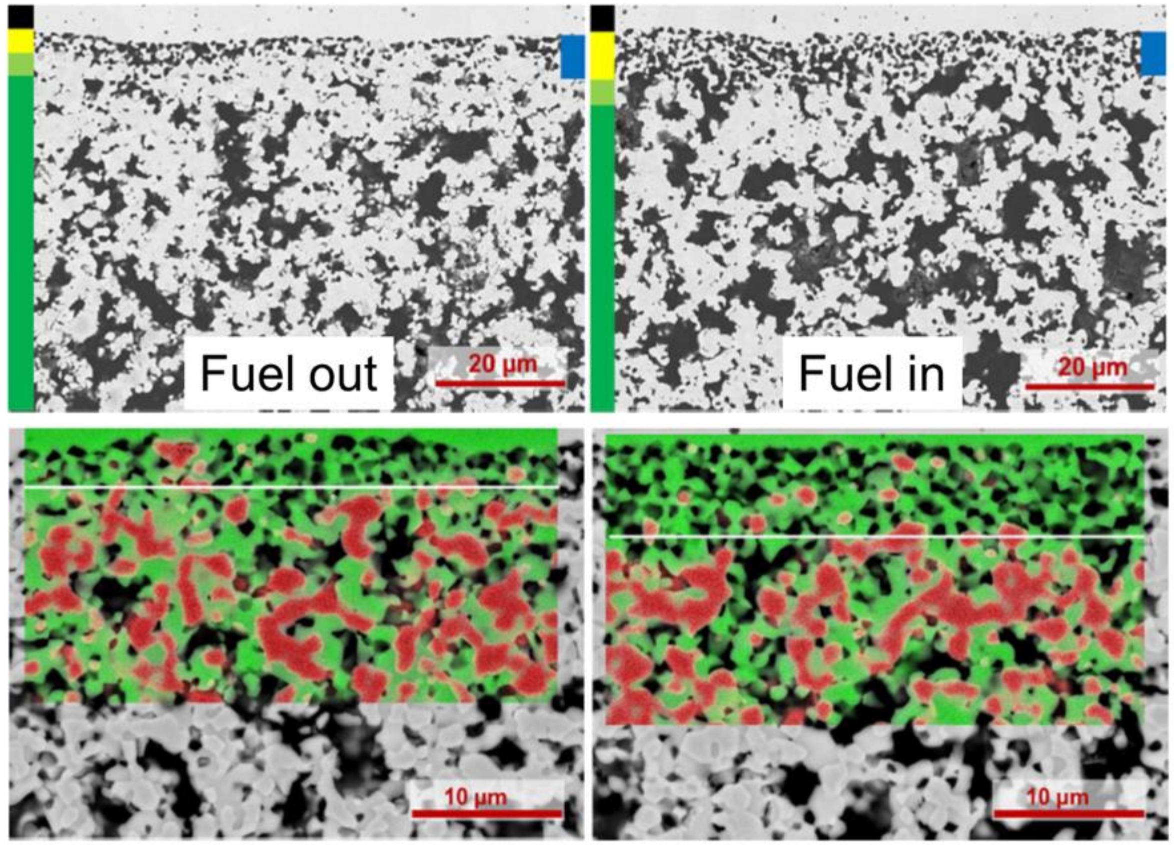
Motivation: Ni migration in Ni-YSZ



Ni depletion in fuel electrode after 20.000 h of electrolysis operation

C. Frey, et al., *J. Electrochem. Soc.* (2018);165:F357-F64.
Q. Fang, et al., *J. Electrochem. Soc.* (2018);165:F38-F45.

- Voltage / ASR degradation of 0.6 / 8.2% / kh
- Ni migration as the primary degradation mechanism
- Can Ni-GDC cathodes solve this problem?

Overview

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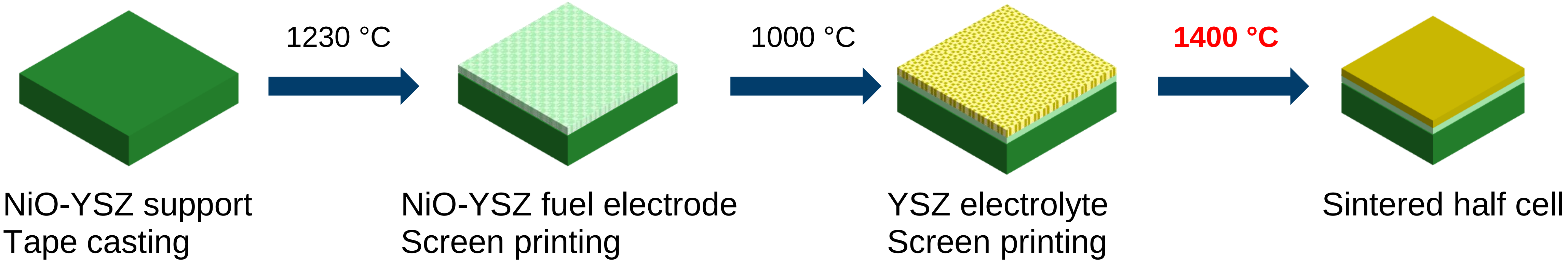
- Substitution of YSZ by GDC in cermets – challenges and advantages
- Co-firing of multilayer electrolytes - effects of interdiffusion
- Rapid sintering techniques –the way forward?

Material challenge - Integration of Ni-GDC into FESCs

- Ni-GDC fuel electrode is common in metal-[1,2] or electrolyte-supported[3,4] cell designs
- Very rarely encountered in fuel electrode-supported cells
- The problem can be located in the manufacturing route:



[1] D. Udomsilp et al., Cell Reports Physical Science, 1 (2020) 100072.
[2] C. Bischof et al., International Journal of Hydrogen Energy, 44 (2019) 31475-31487.
[3] N. Trofimenko et al., ECS Transactions, 78 (2017) 3025-3037.
[4] M. Kusnezoff et al., Materials, 9 (2016) 906.

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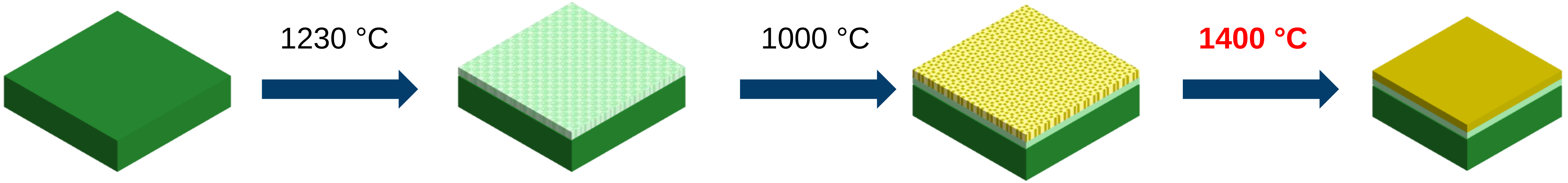


NiO-YSZ support
Tape casting

NiO-**GDC** fuel electrode
Screen printing

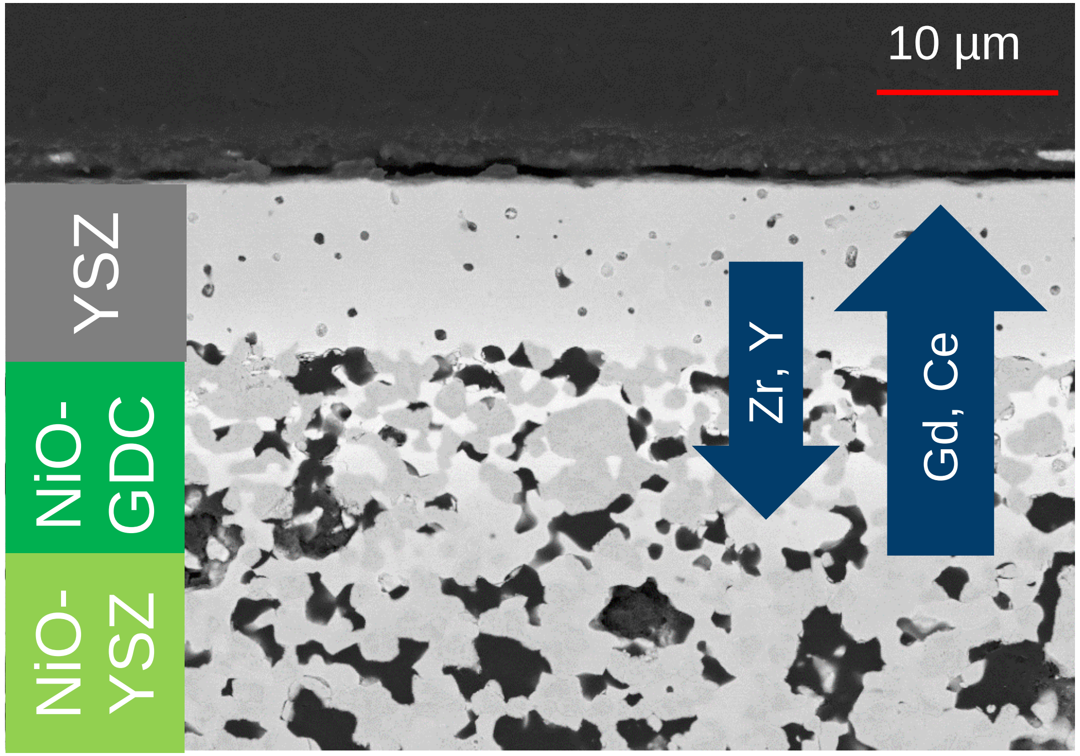
YSZ electrolyte
Screen printing

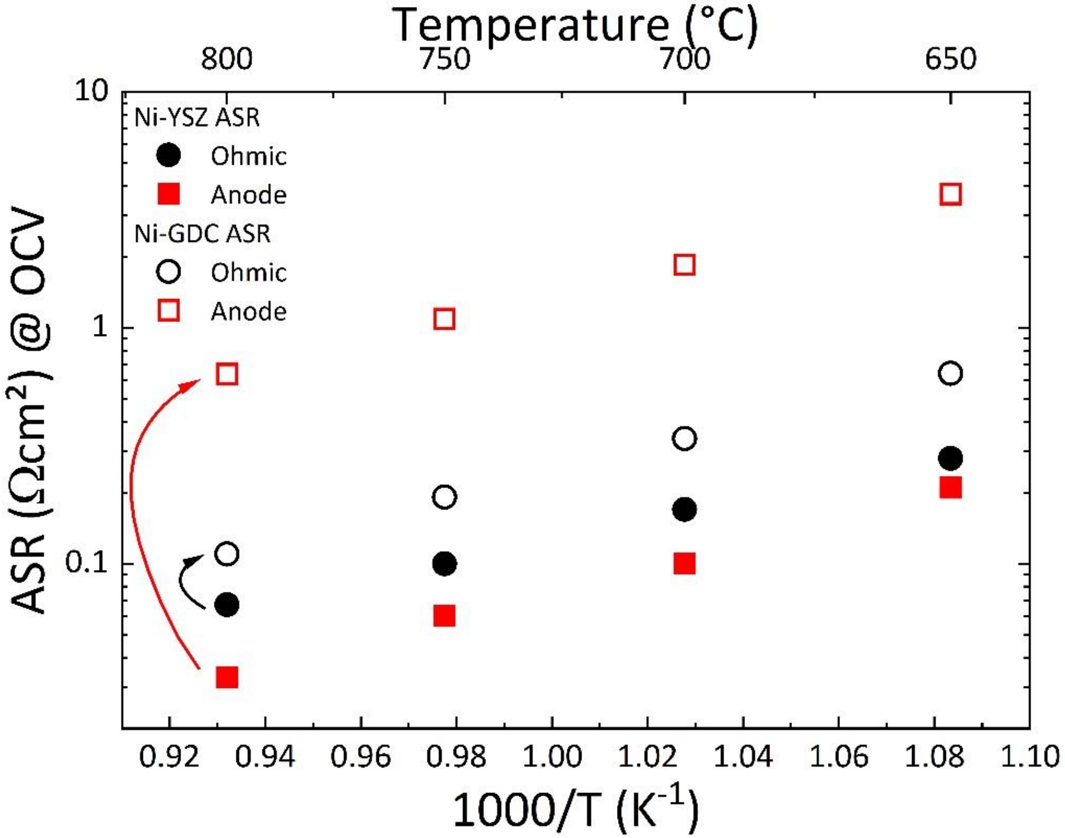
Sintered half cell
Strong interdiffusion

[1] D. Udomsilp et al., Cell Reports Physical Science, 1 (2020) 100072.
[2] C. Bischof et al., International Journal of Hydrogen Energy, 44 (2019) 31475-31487.
[3] N. Trofimenko et al., ECS Transactions, 78 (2017) 3025-3037.
[4] M. Kusnezoff et al., Materials, 9 (2016) 906.

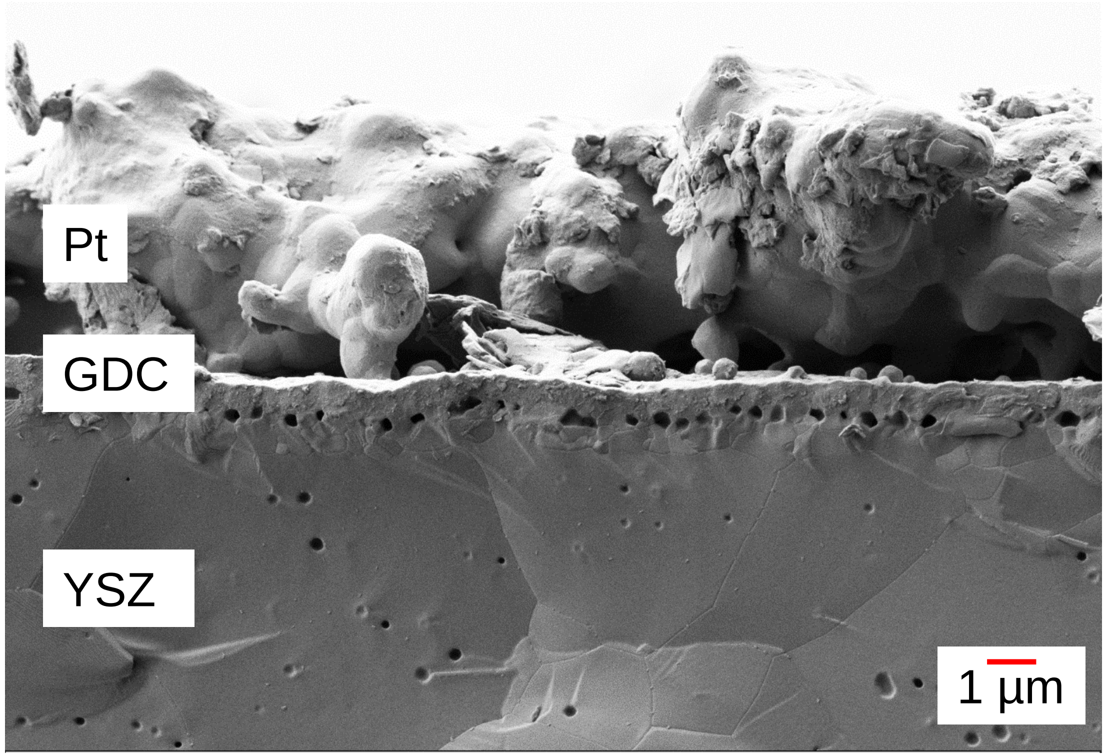
Reduced performance due to interdiffusion

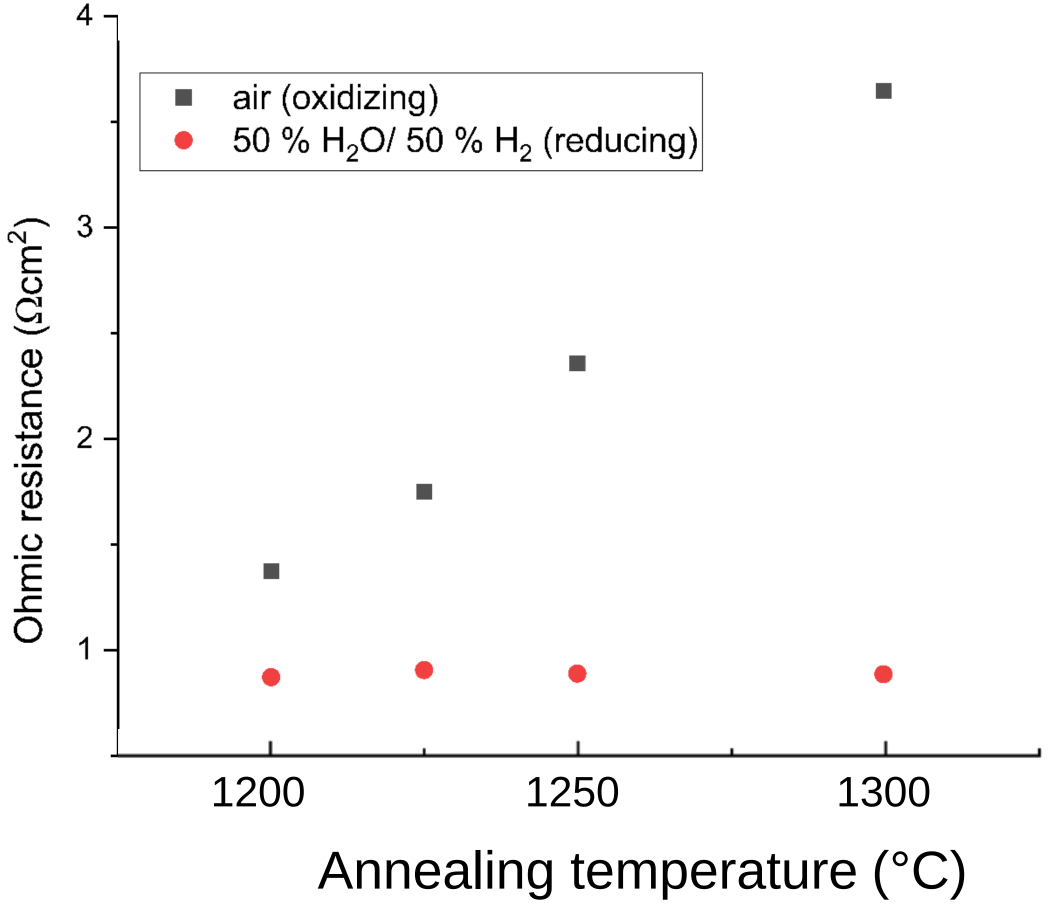
- Substitution of NiO-YSZ by NiO-GDC in FESC manufacturing route → decreased performance
- Well-known: decreasing conductivity, less well-known: Kirkendal porosity





Effect of interdiffusion as a function of pO_2

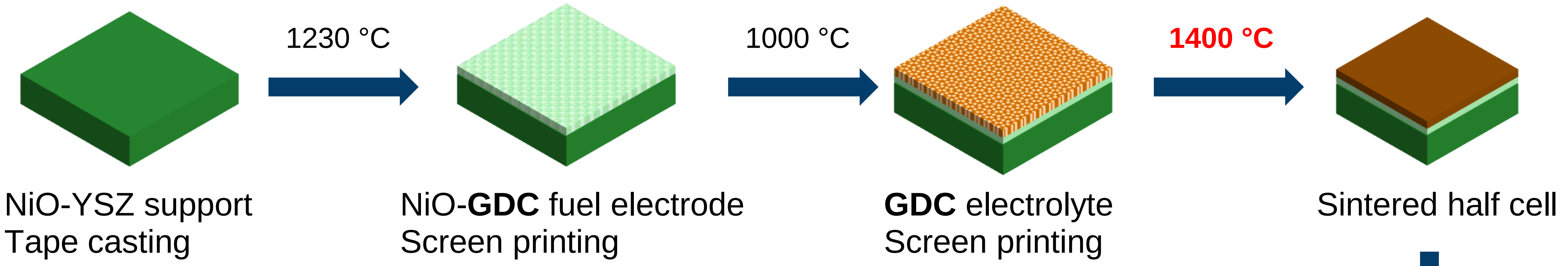


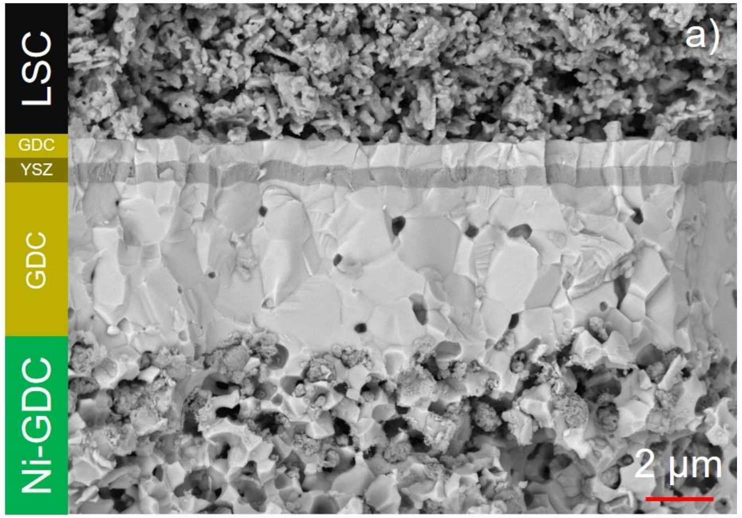


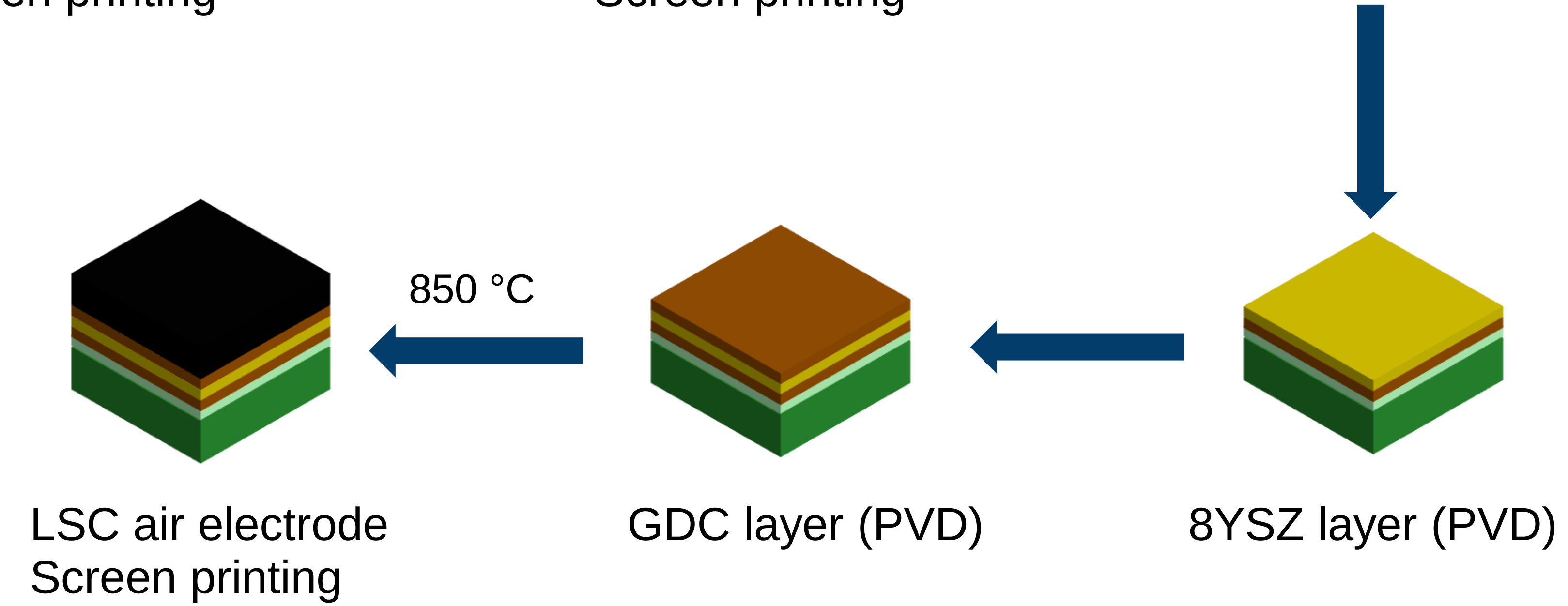
- Interdiffusion at GDC-YSZ model interface
- R_{ohm} in air, R_{pol} in H_2

Albert Lopez de Moragas, et al, in preparation

How to avoid interdiffusion





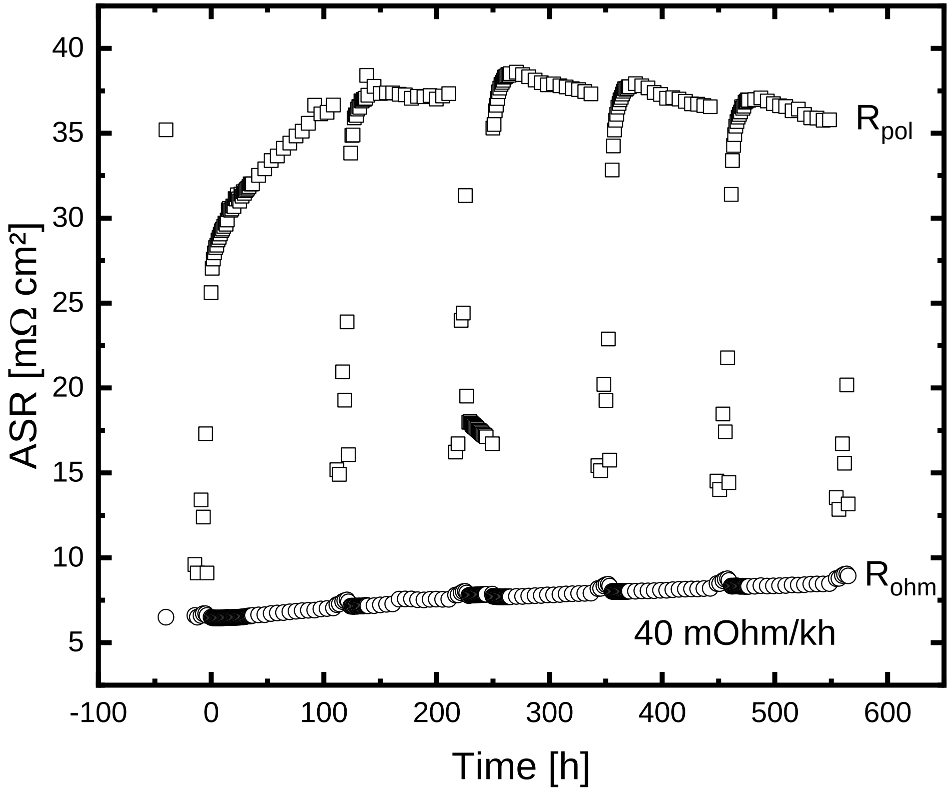


[1] J. Zhang, C. Lenser, N. Russner, A. Weber, N.H. Menzler, O. Guillon, Journal of the American Ceramic Society, 106 (2022) 93-99.

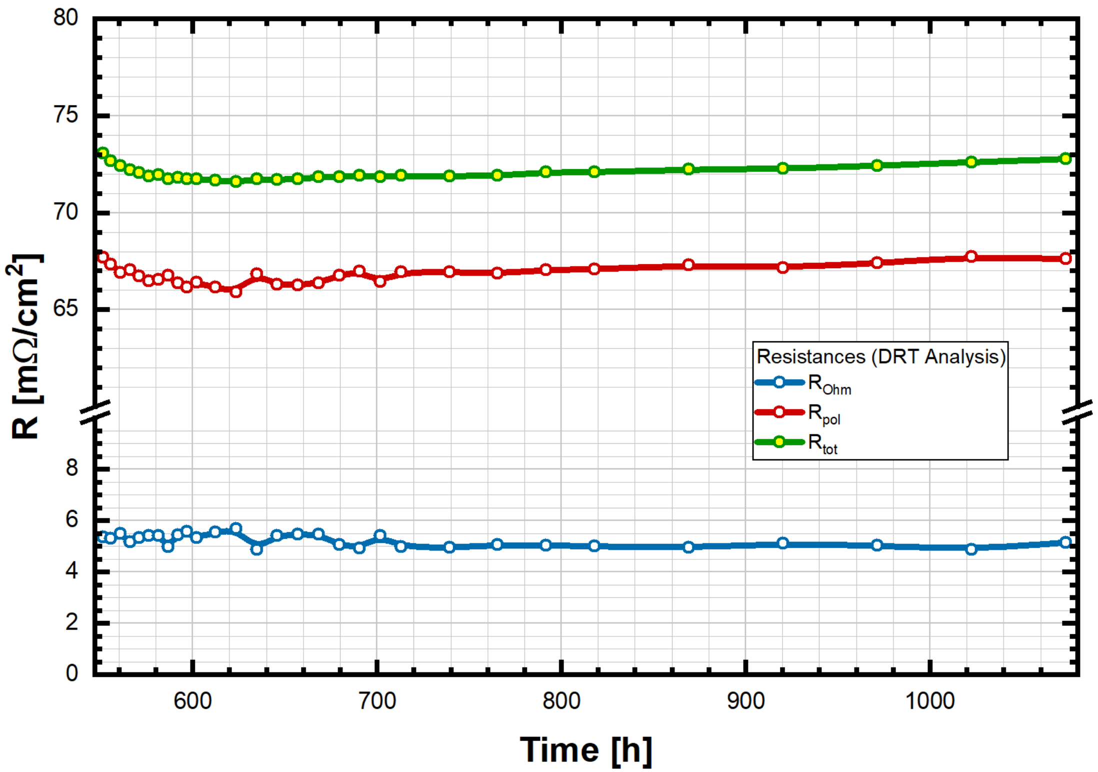
Stability of Ni-GDC and Ni-YSZ

800 °C, 50/50 H_2/H_2O, 1.5 A/cm²

Ni-YSZ cathode (Jülich standard cell)



Ni-GDC cathode



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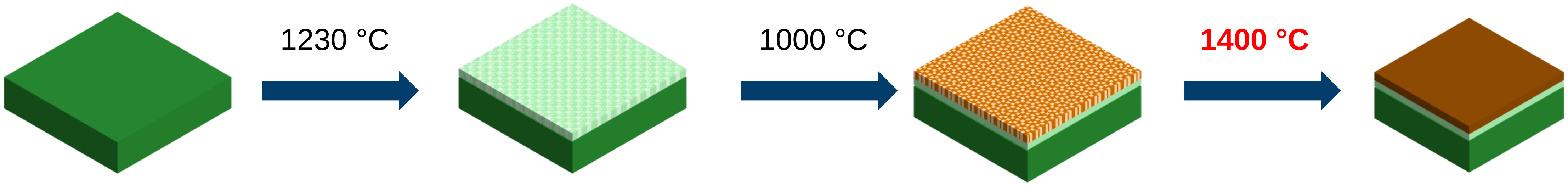
Screen-printing a three-layer electrolyte



NiO-YSZ support
Tape casting

NiO-**GDC** fuel electrode
Screen printing

GDC / YSZ / GDC electrolyte
Screen printing

Sintered half cell

- Fabrication of a three-layer electrolyte by co-sintering
- Layers must be matched in shrinkage during sintering and adapted to support
- Paste rheology must be controlled to achieve uniform and defect-free layers

- But we know what we are doing – right?

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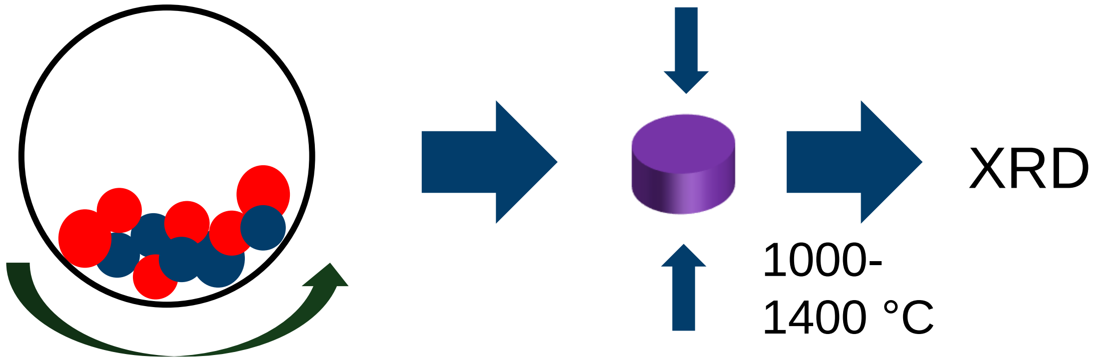
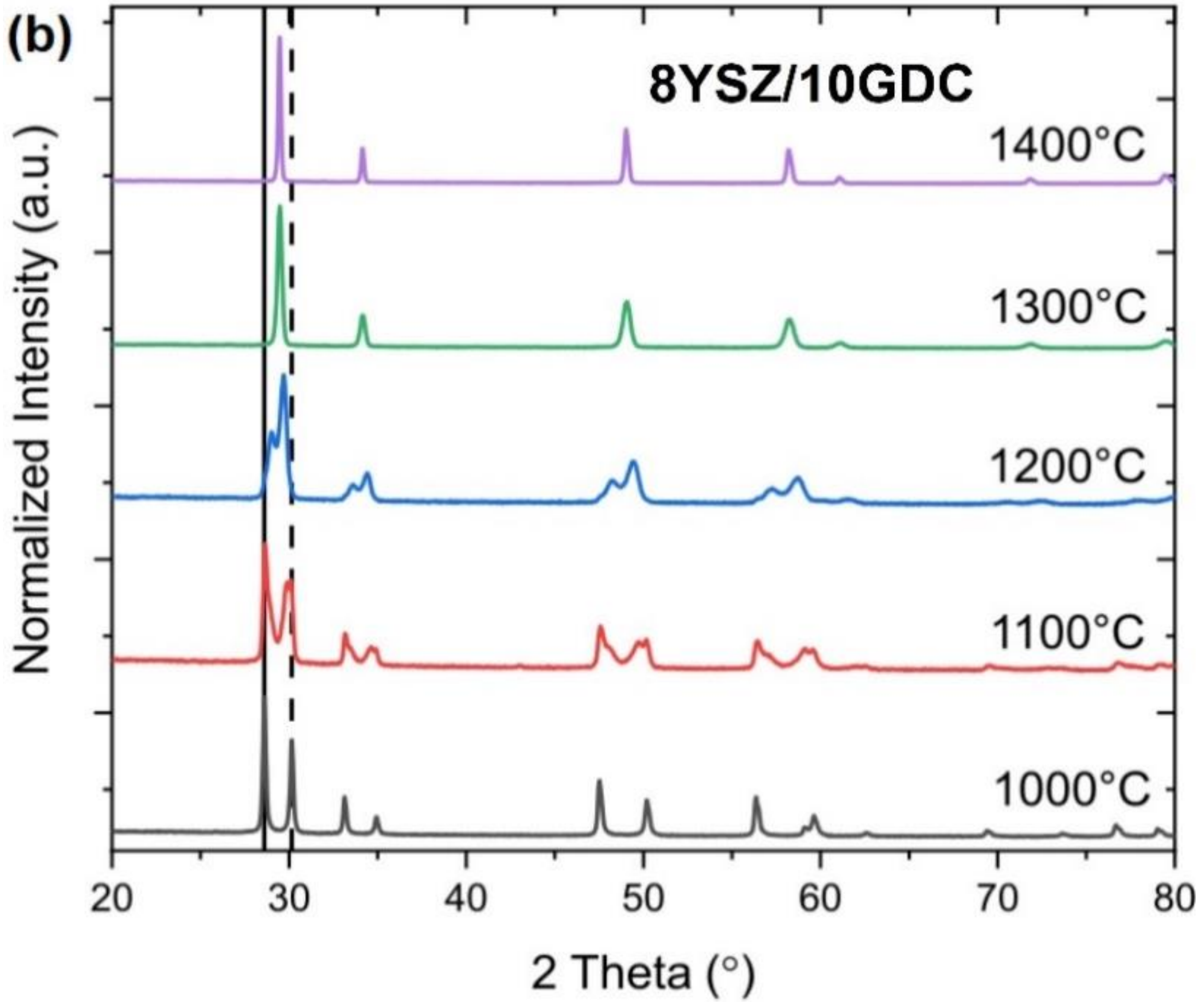
Interdiffusion experiments

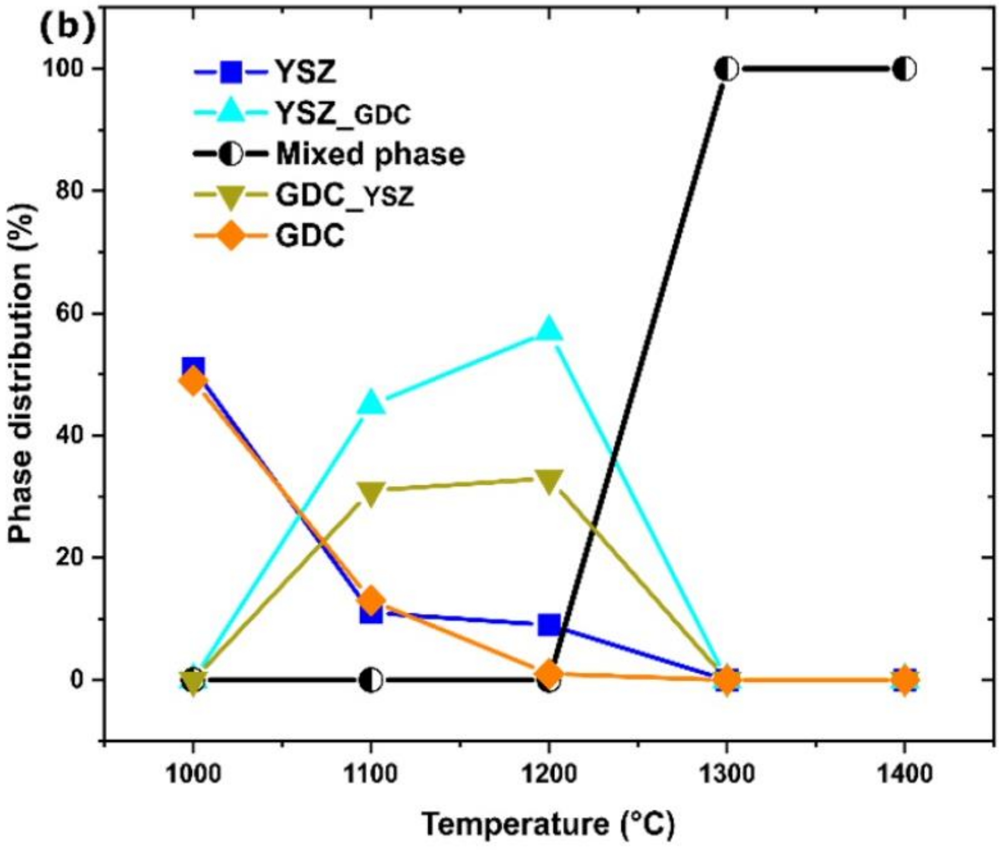
- Started these experiments in 2018
- Sinter well mixed powders
  - GDC: d_{50} = 0.1 µm
  - YSZ: d_{50} = 0.48 µm
- Crush pellets + phase analysis via XRD

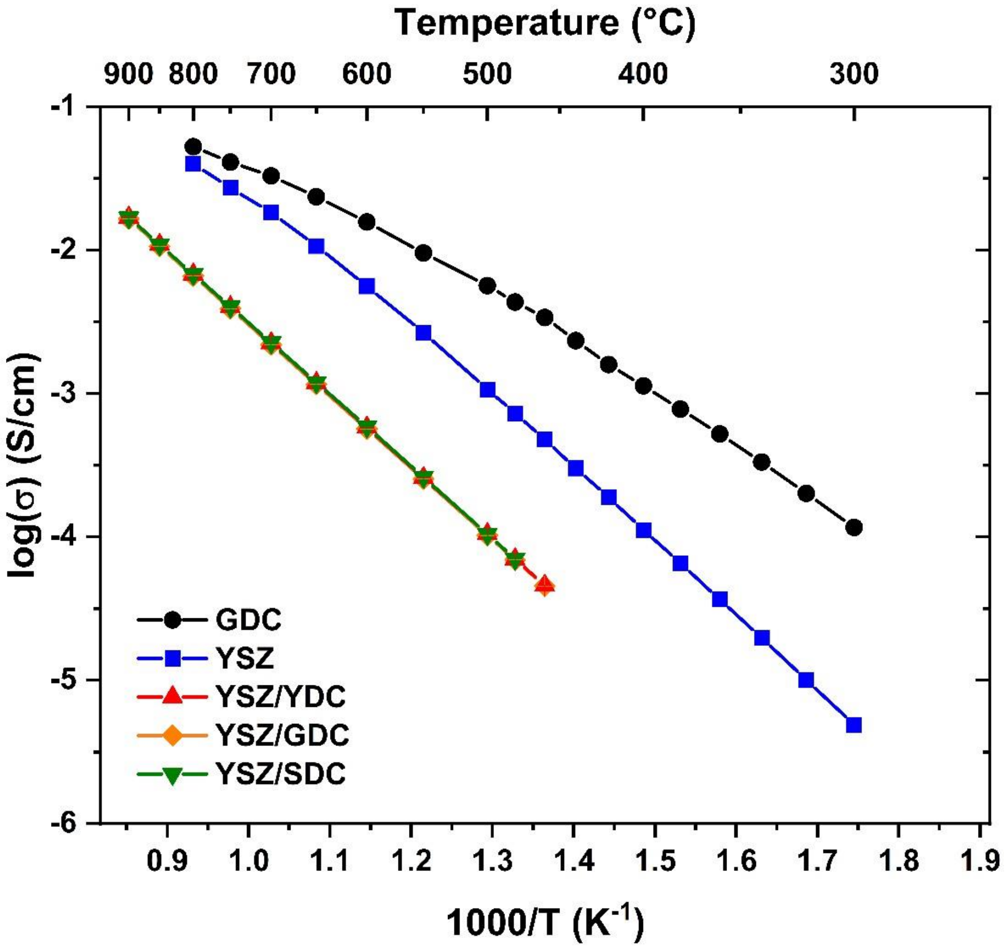




A. Schwiers, C. Lenser, O. Guillon and N. H. Menzler J. Eur. Ceram. 2023, 43, **14**, Pages 6189-6199
DOI: https://doi.org/10.1016/j.jeurceramsoc.2023.06.015

Interdiffusion – phase composition





- Complete mixing after 1400 °C, 5h
- Decreased conductivity as reported in literature

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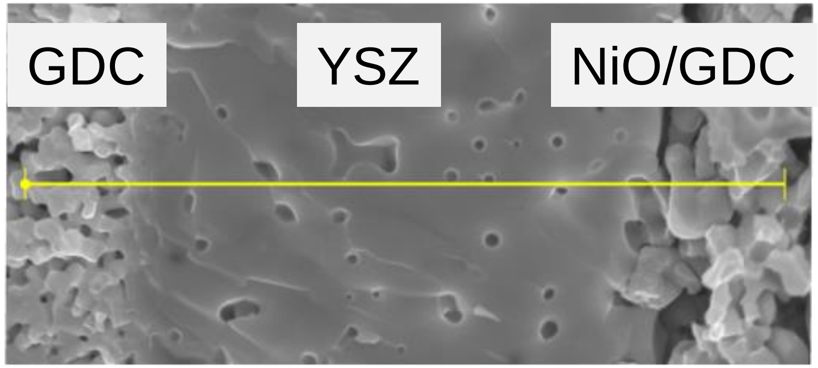
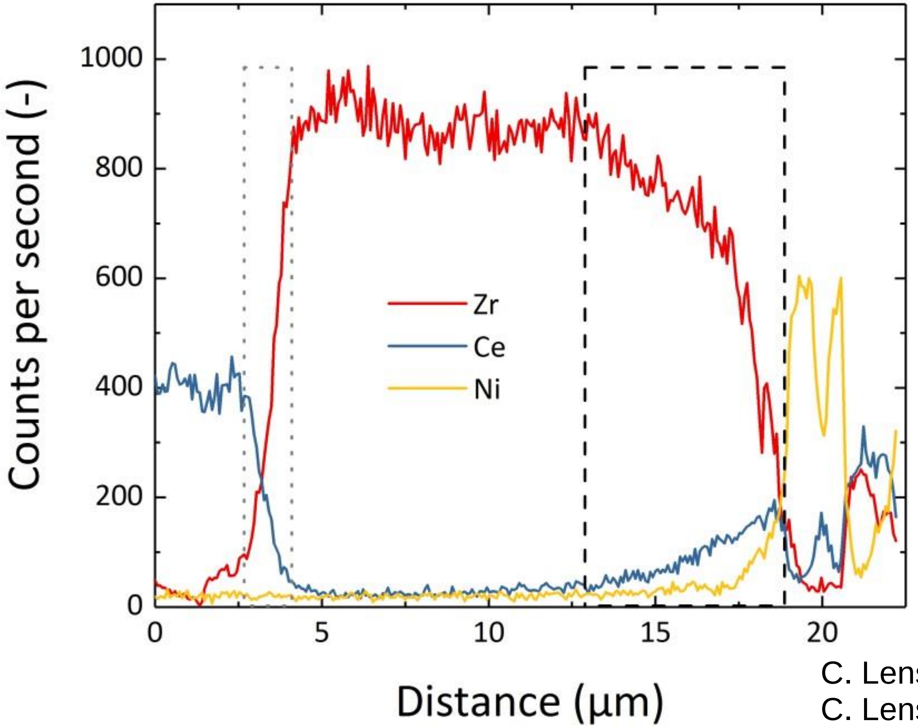
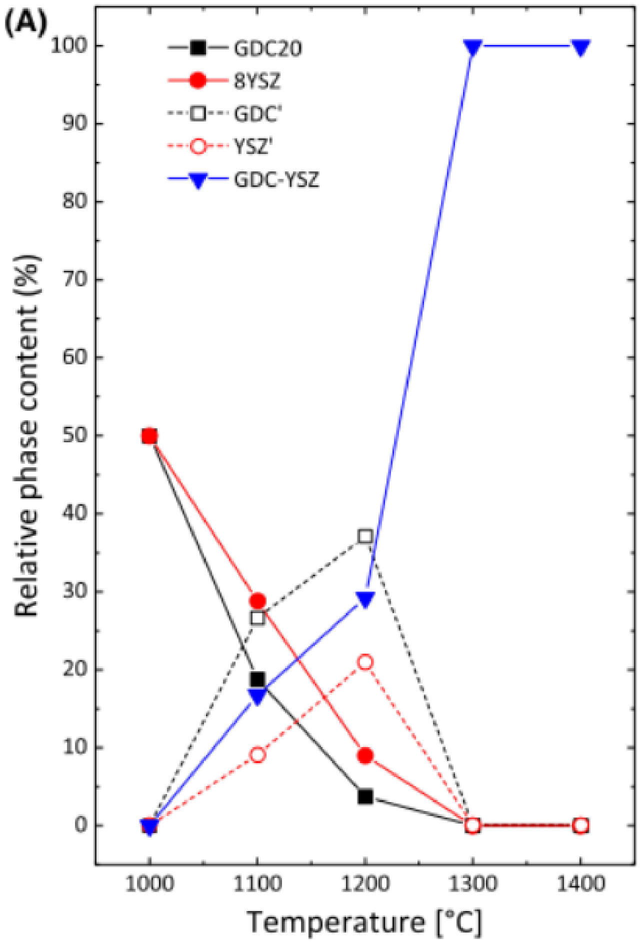
Interdiffusion - the role of NiO

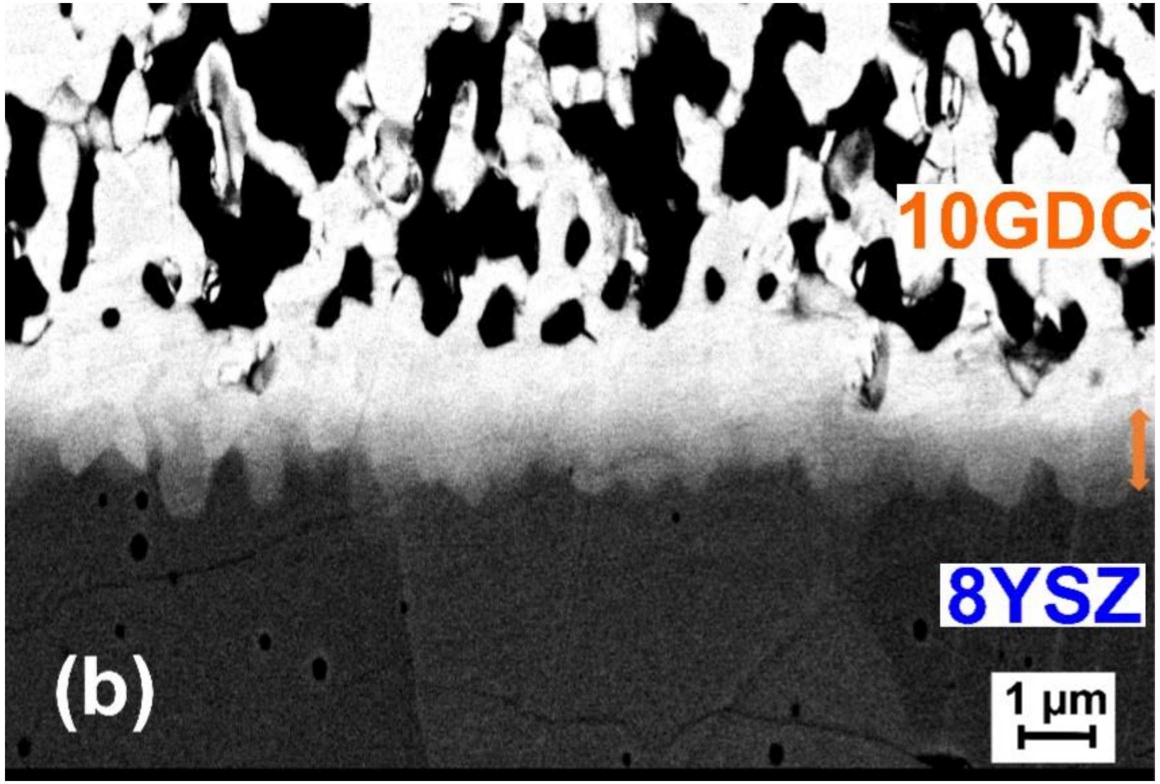


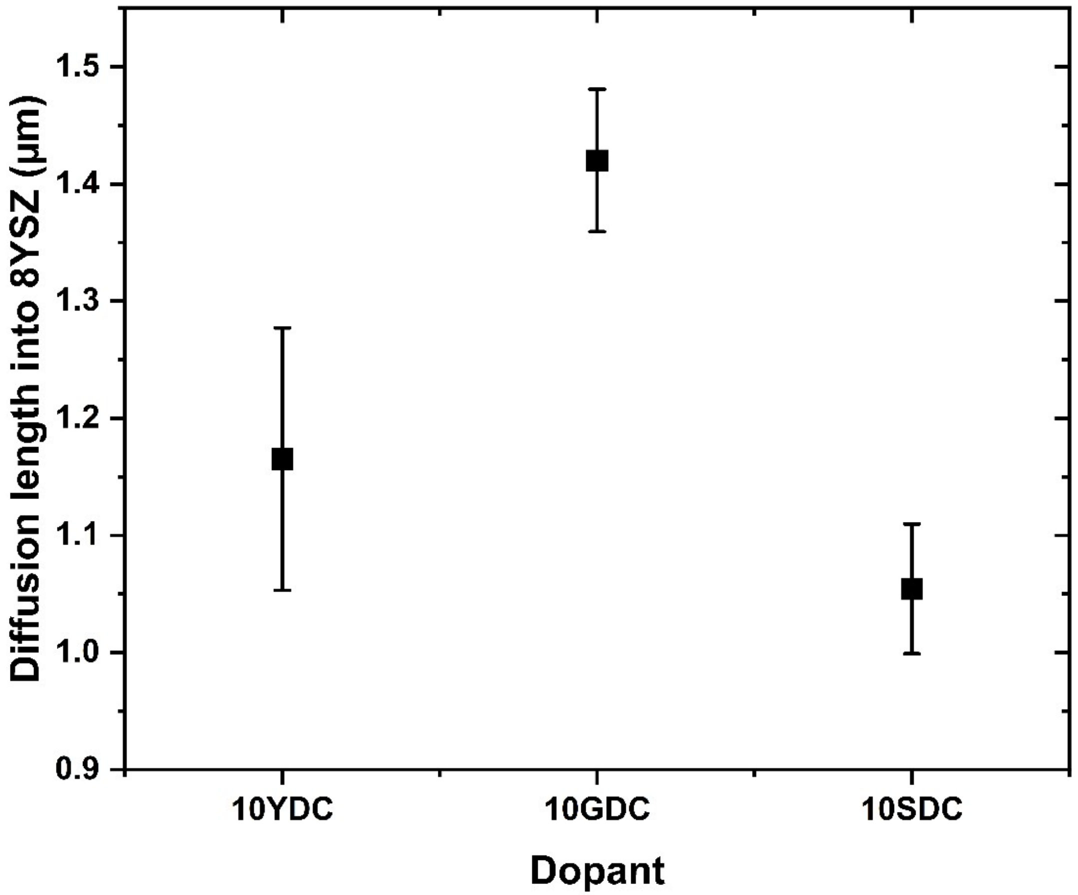




C. Lenser et al., Journal of the American Ceramic Society, 101 (2017) 739-748.
C. Lenser, N.H. Menzler, Solid State Ionics, 334 (2019) 70-81.

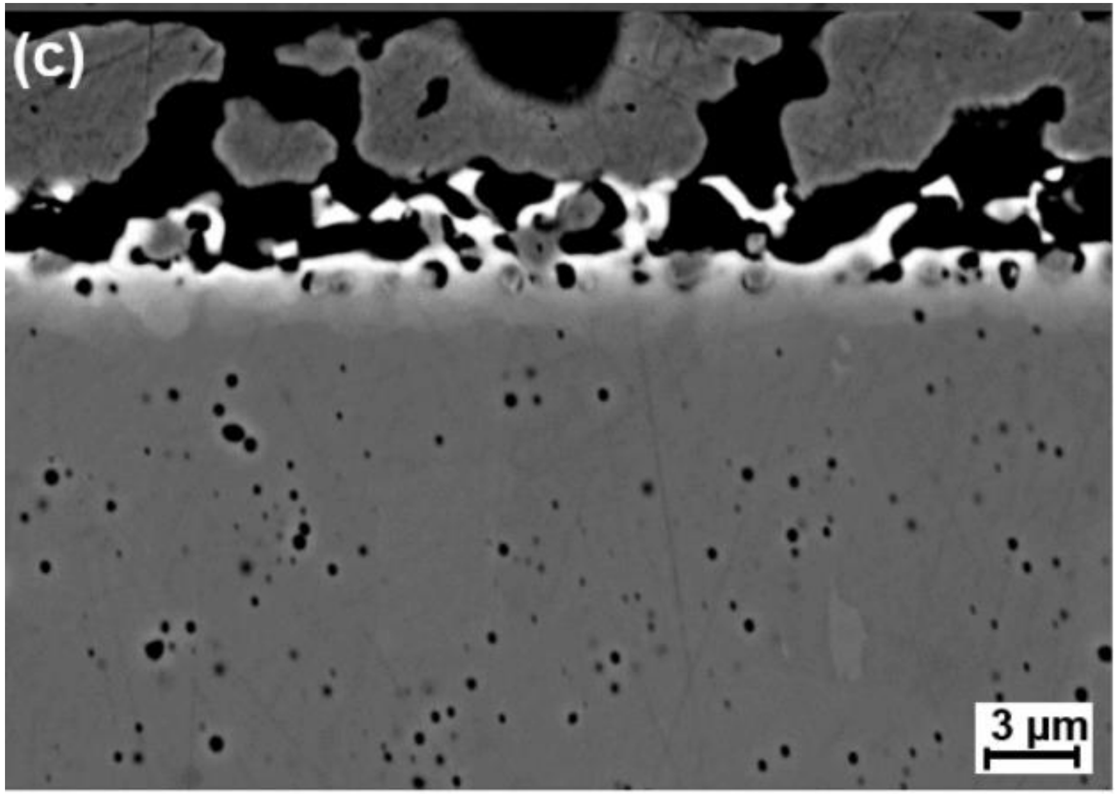
Interdiffusion length – GDC on YSZ

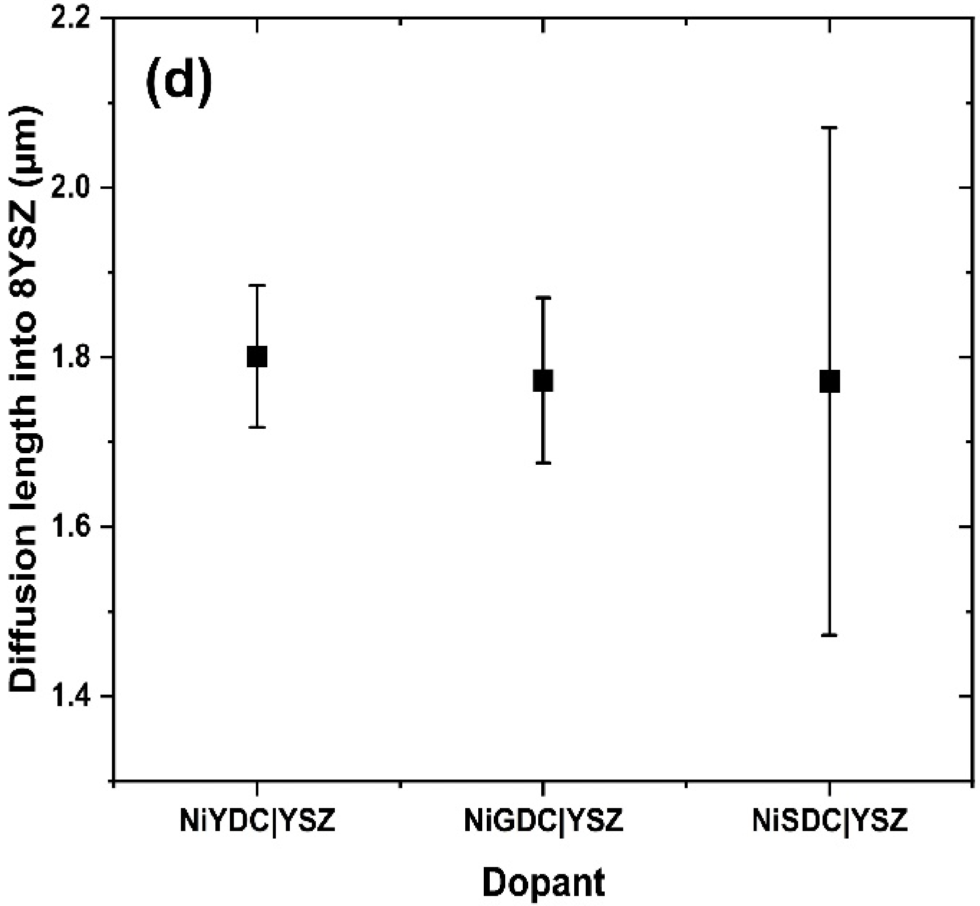




- Printed layers on densified ceramic
- SEM analysis using Z-contrast show interdiffusion length 1 – 1.5 µm

Interdiffusion length – NiO-GDC on YSZ

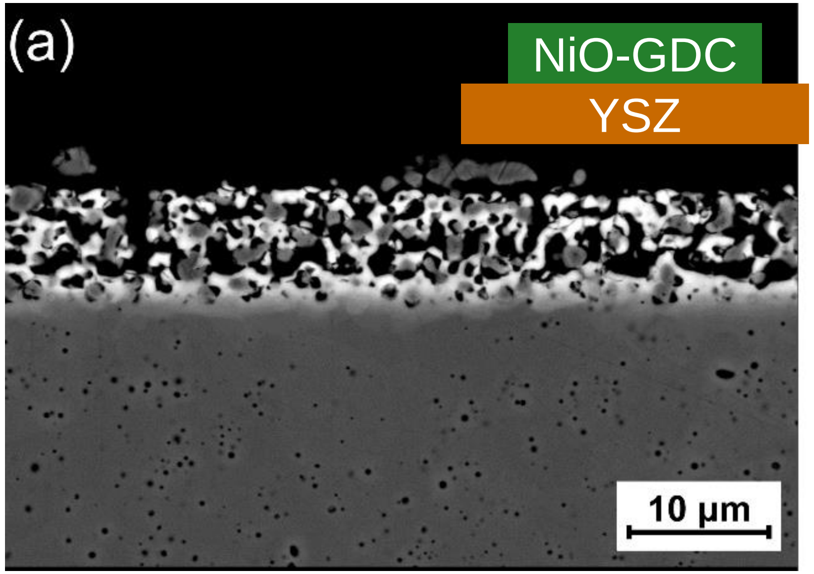


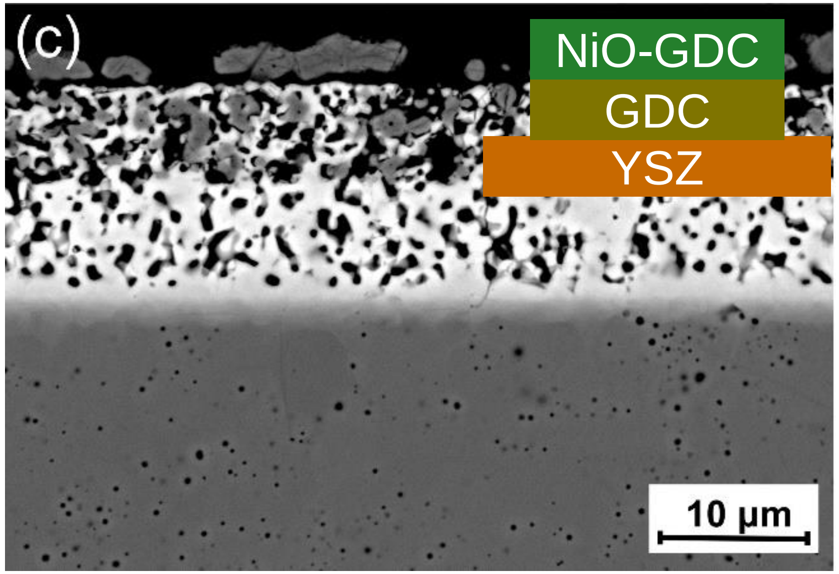


- Printed layers on densified ceramic
- SEM analysis using Z-contrast show higher interdiffusion length ~ 1.8 µm
- Notable porosity is formed at interface

Interdiffusion – sintering sequence

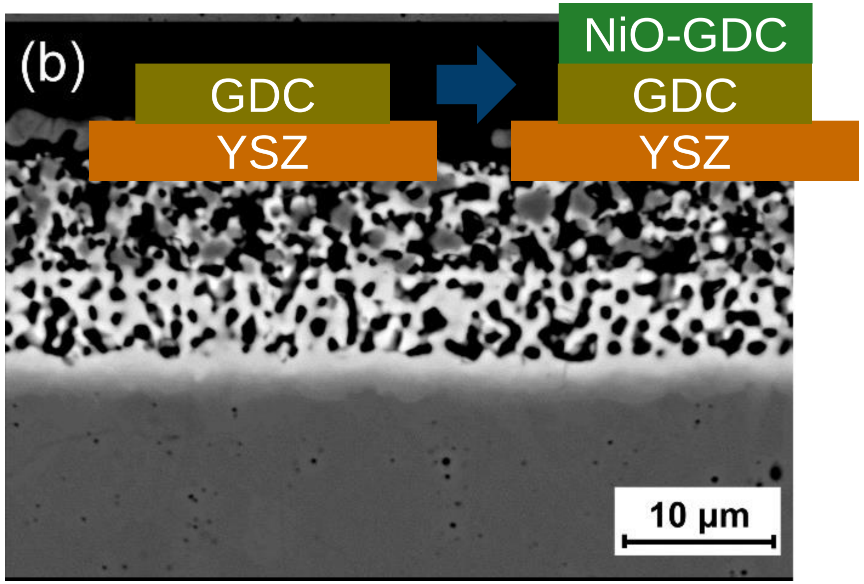
1.8 µm





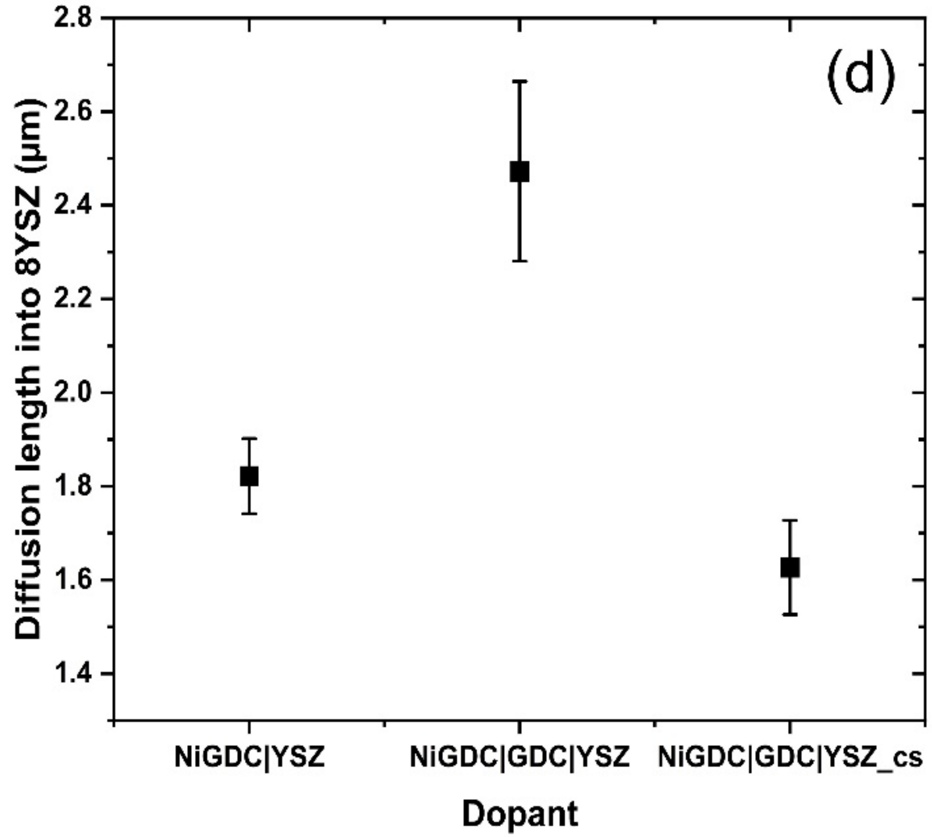
1.6 µm

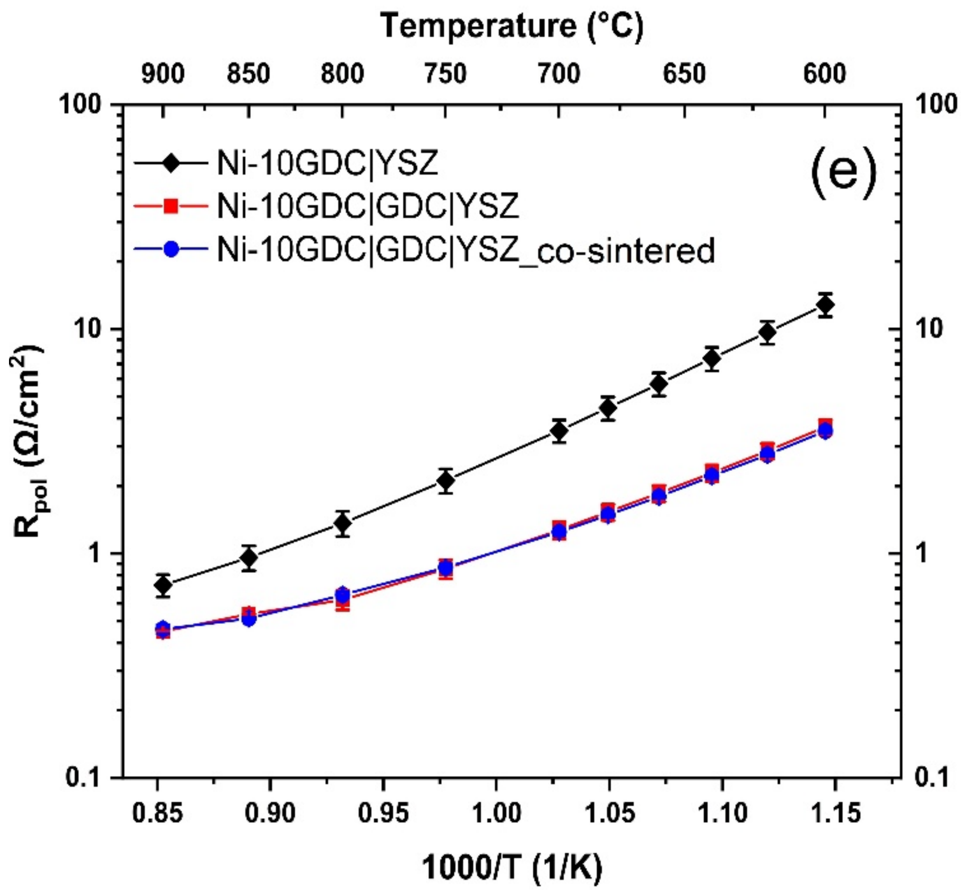
2.5 µm



- Printed layers on dense YSZ ceramic
- Interdiffusion length scales with sintering T and duration
- Porosity at NiO-GDC; <u>not</u> at GDC-YSZ interfaces

Interdiffusion – electrochemical impedance spectroscopy





- Increased R_{pol} for NiO-GDC sintered on YSZ
- Lower R_{pol} when GDC interlayer is used
- Not correlated to interdiffusion length, but to formation of porosity!

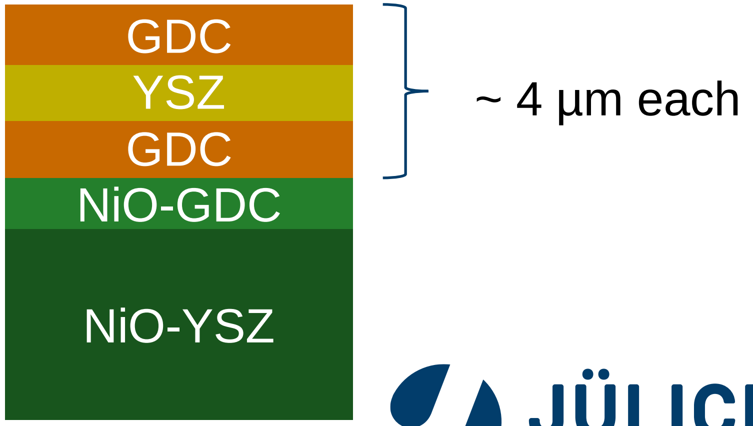
Co-firing strategy

- Previous work shows:
  - Interdiffusion at NiO-GDC / YSZ leads to strongly increased cell resistance
  - Interdiffusion at GDC / YSZ interfaces only leads to small ohmic increases
  - Interdiffusion length during 1400 °C, 5h is smaller than 2 µm

Hypothesis:

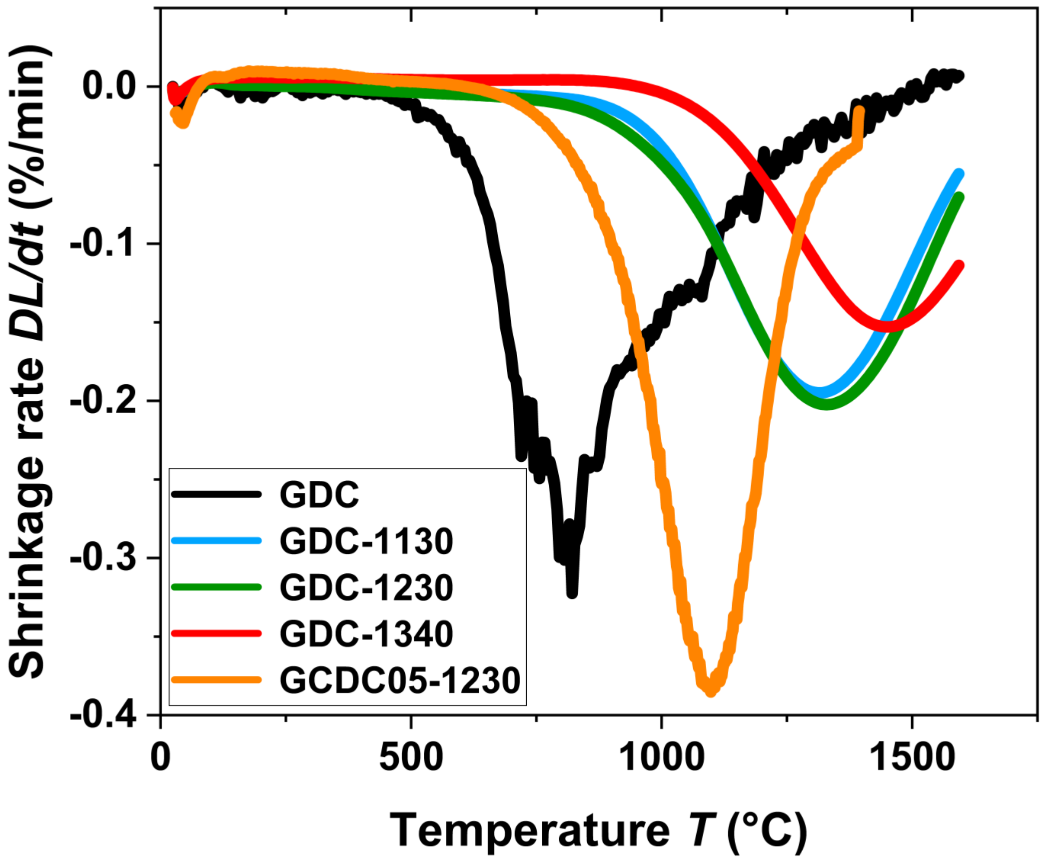
1) interdiffusion located inside the electrolyte should lead to acceptable performance losses!

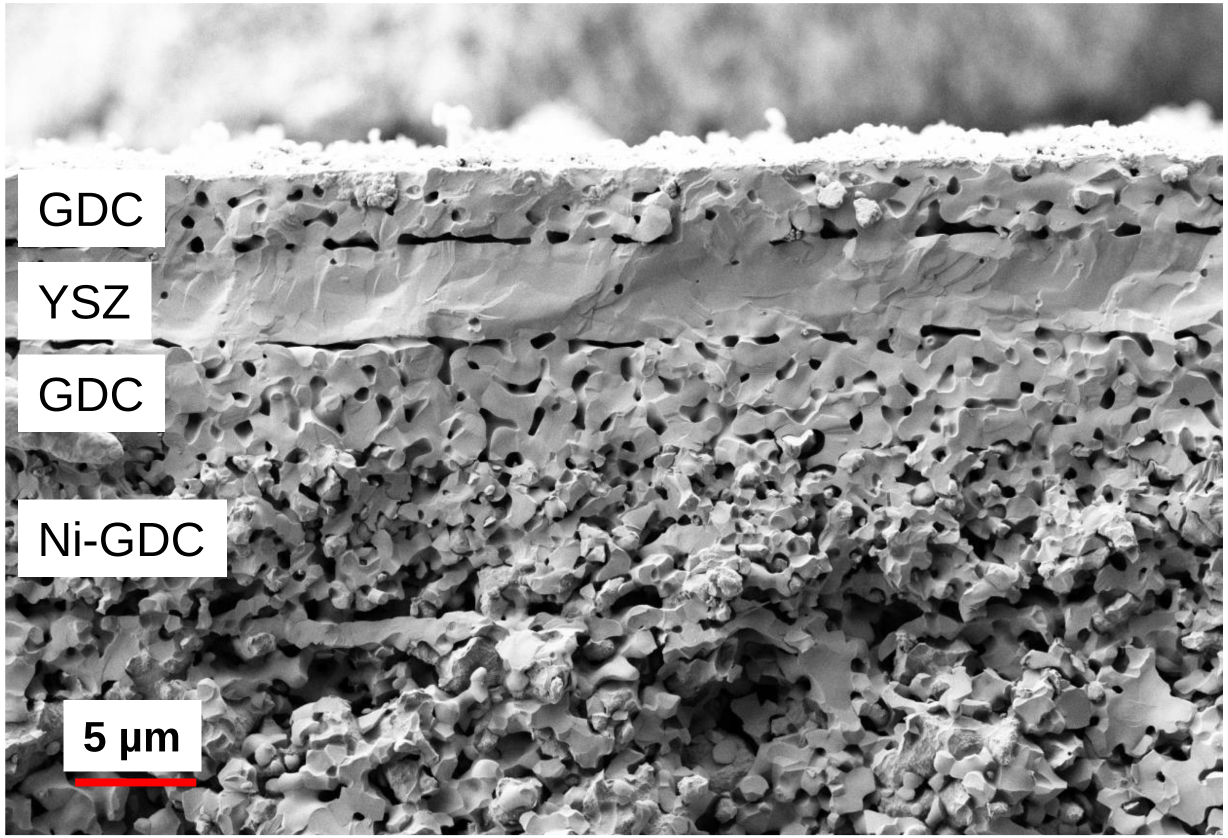
2) a YSZ thickness of 4 µm should be sufficient.



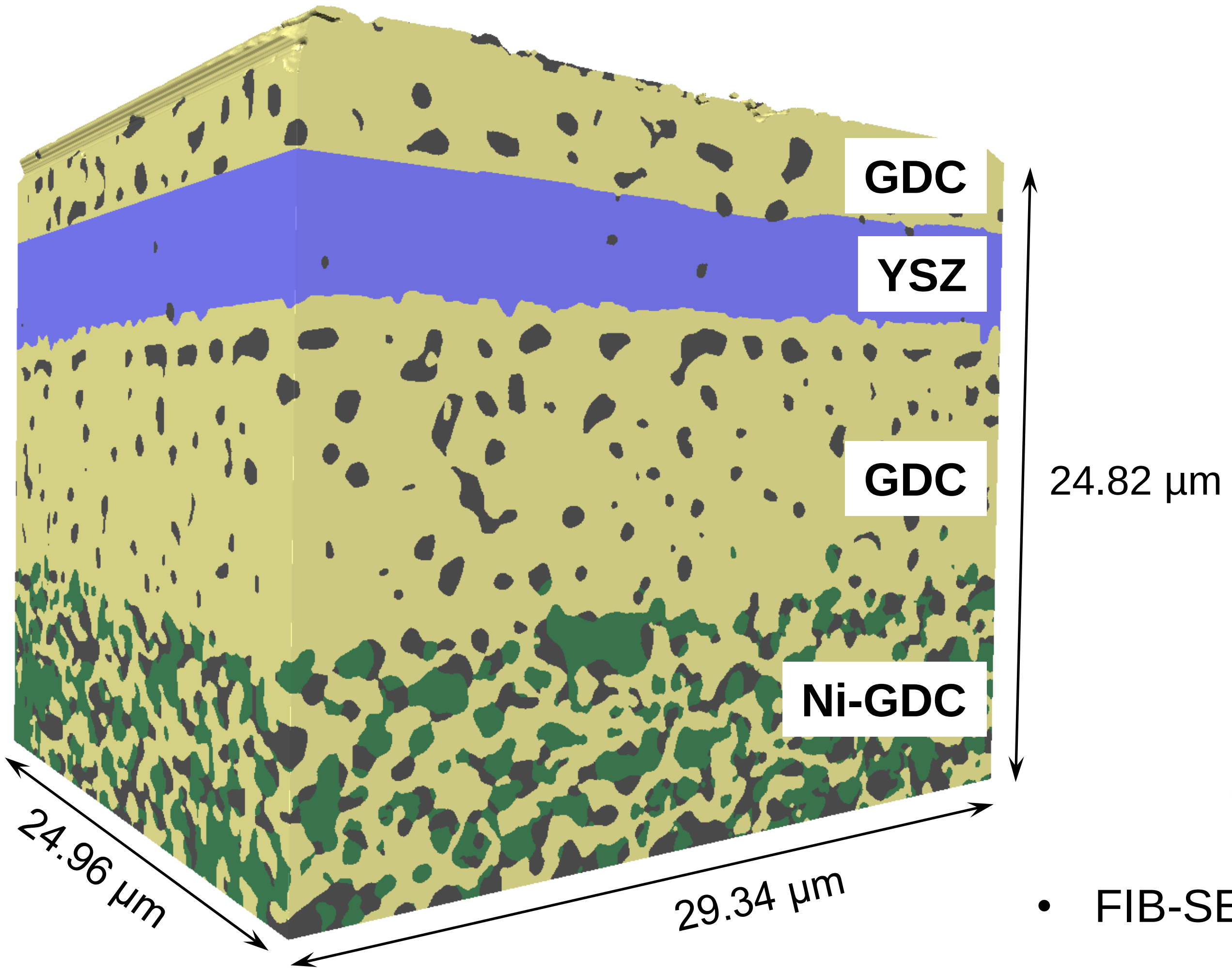
Screen-printing a three-layer electrolyte

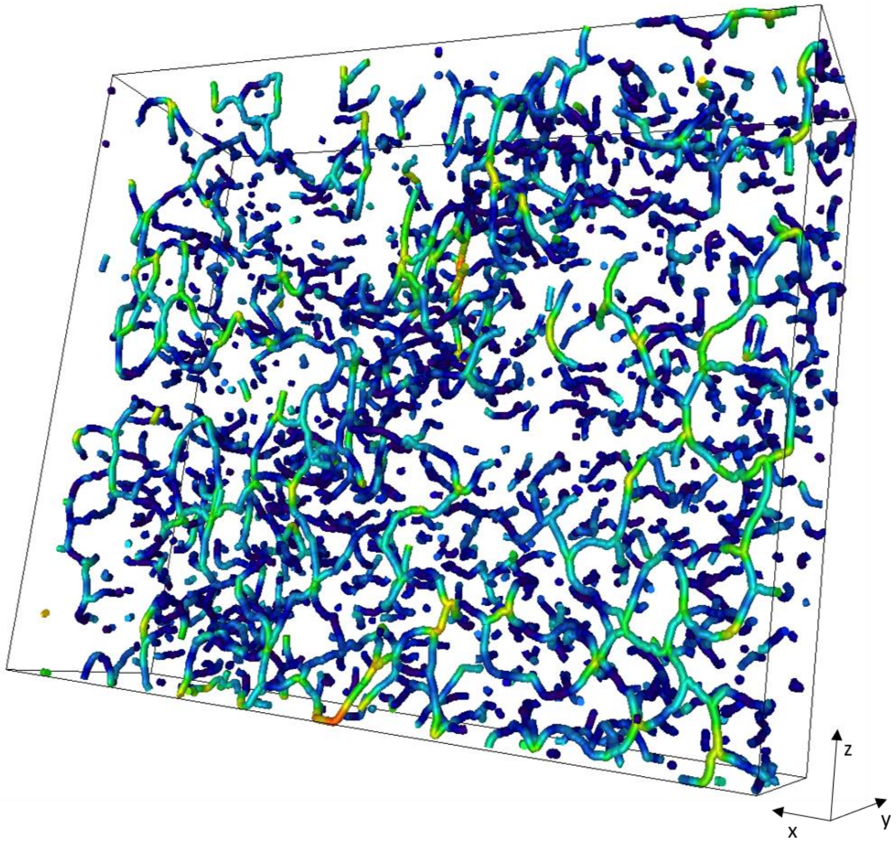
- Adjusting shrinkage rate by powder calcination
- First results show complex sintering behavior – very dense YSZ, porous GDC





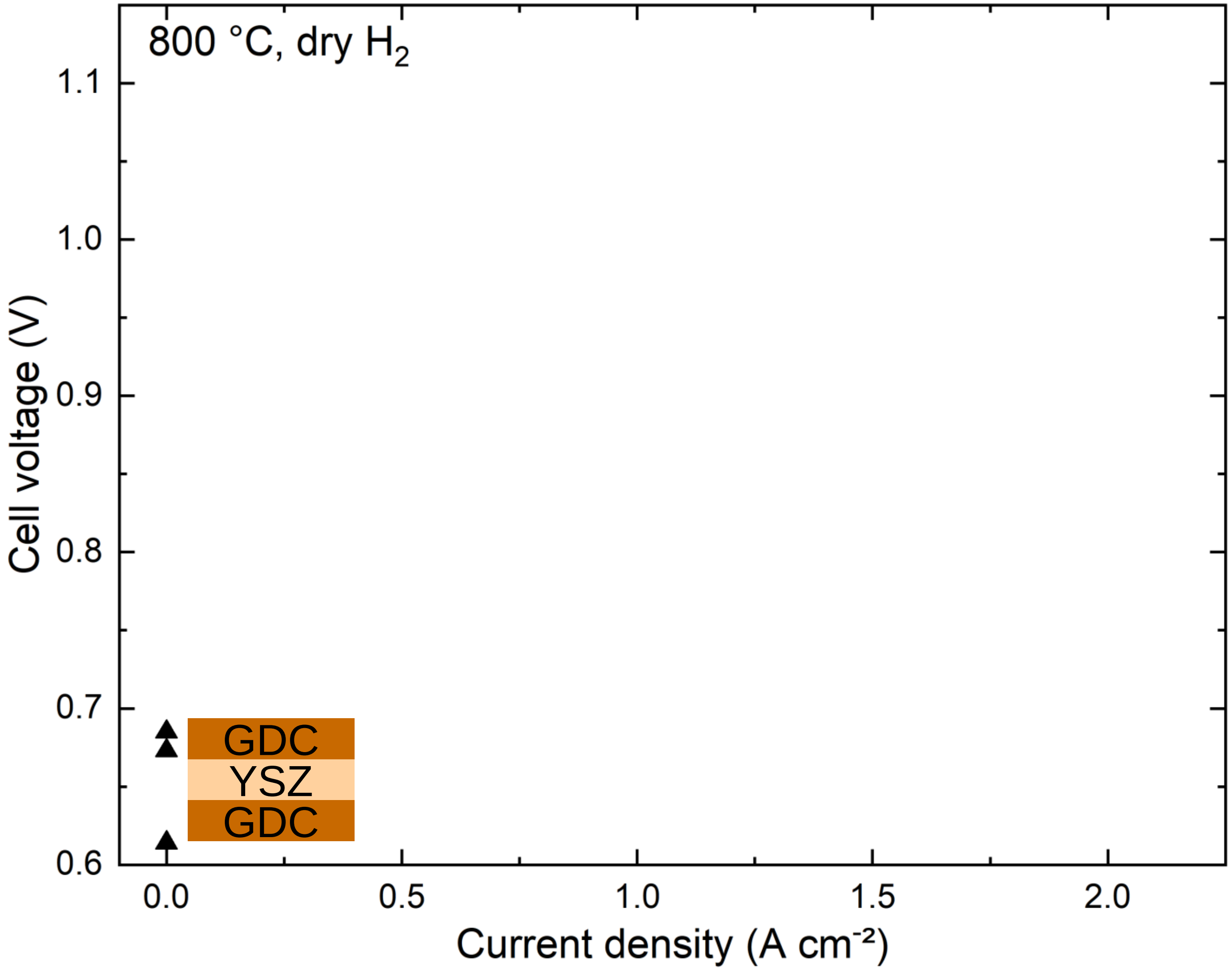
Ordered porosity after sintering





- FIB-SEM tomography confirms 2D connected pore network

Cell performance

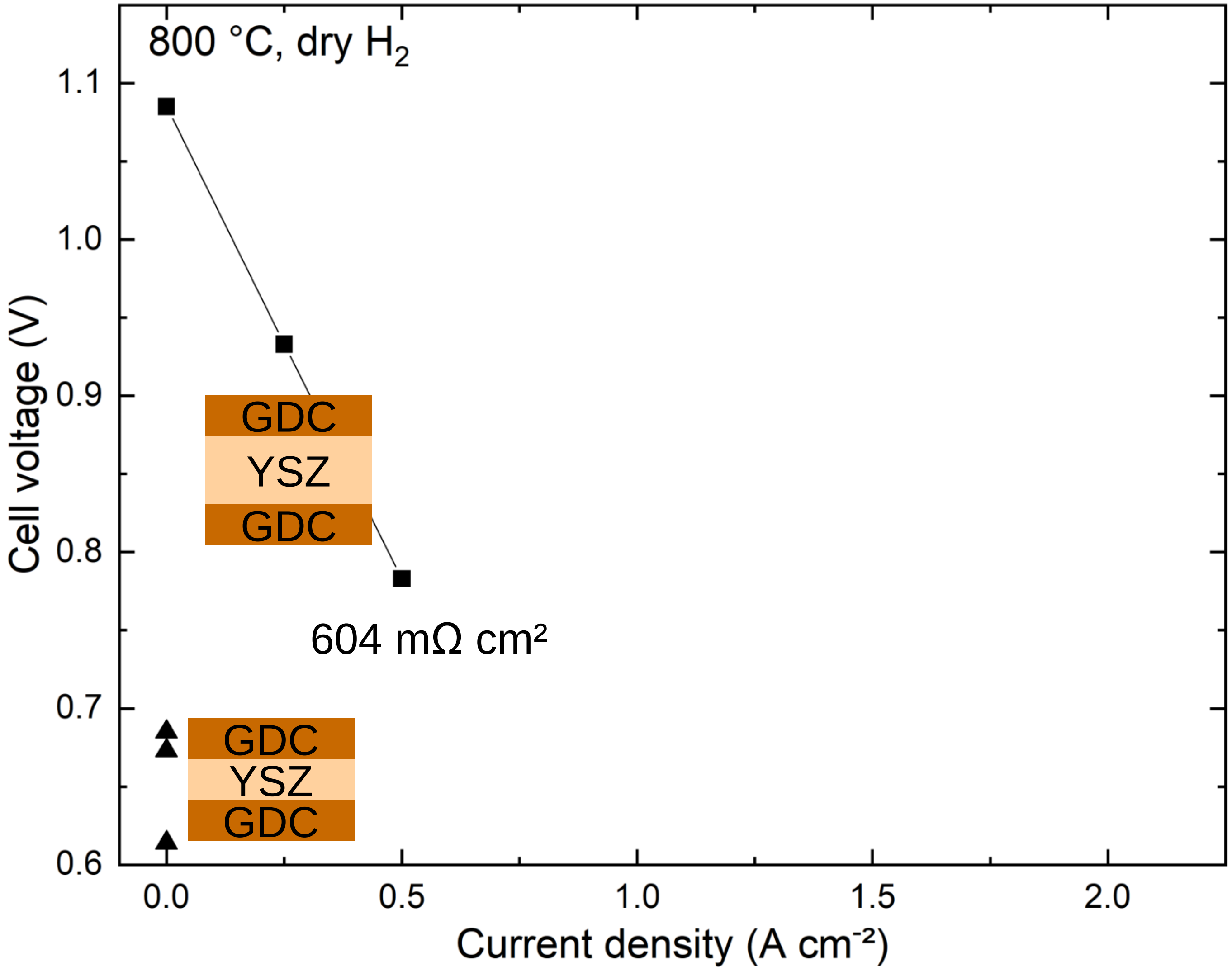


- Tested approx. 10 cells
- OCV values @ 800 °C, dry H_2 are between 0.6 and 0.7 V
- TEM investigations confirm that Ce diffuses through YSZ from both sides

➢ Current leakage

- Best result for SP-cells when top GDC layer is sintered separately

Cell performance



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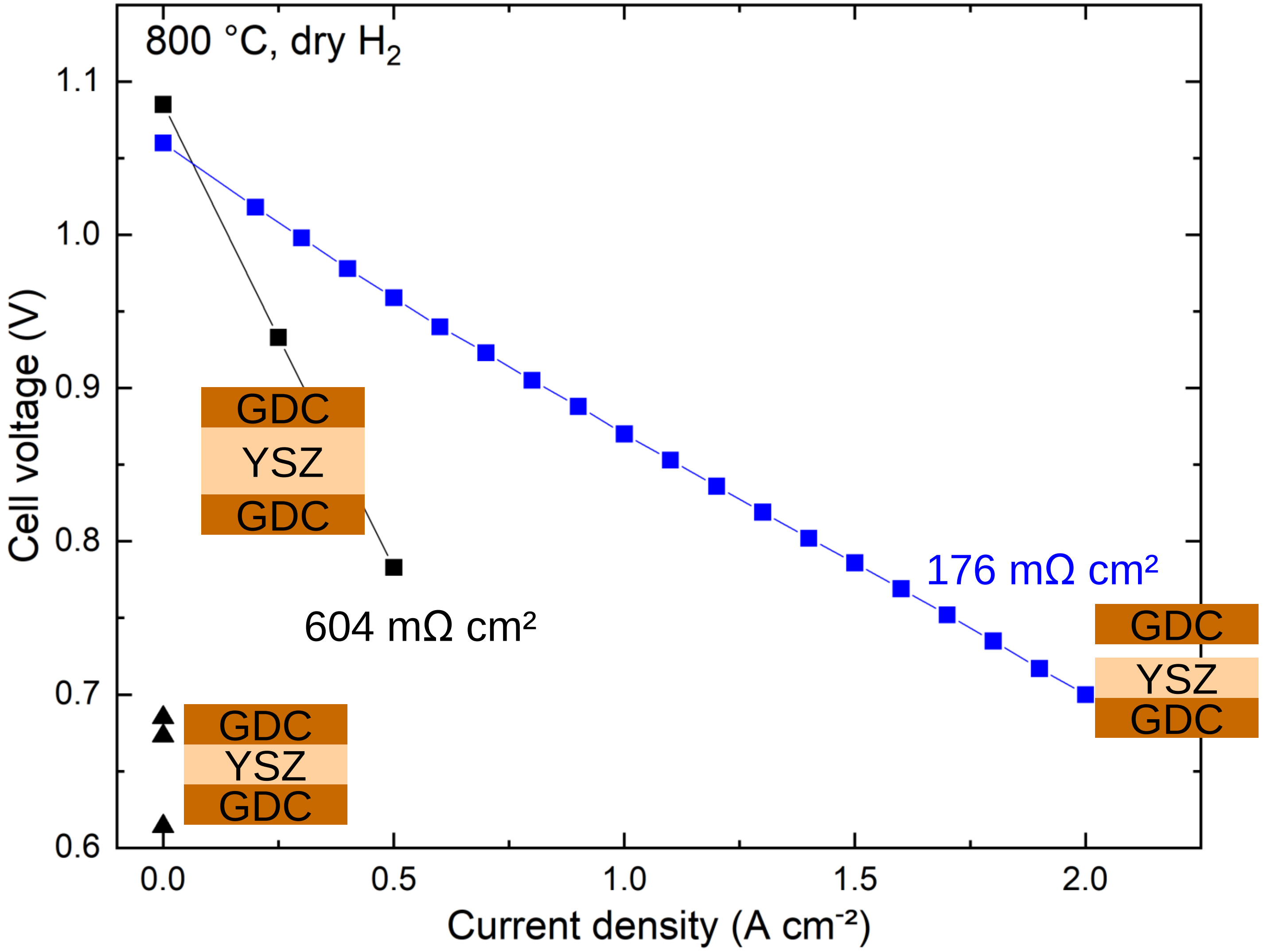

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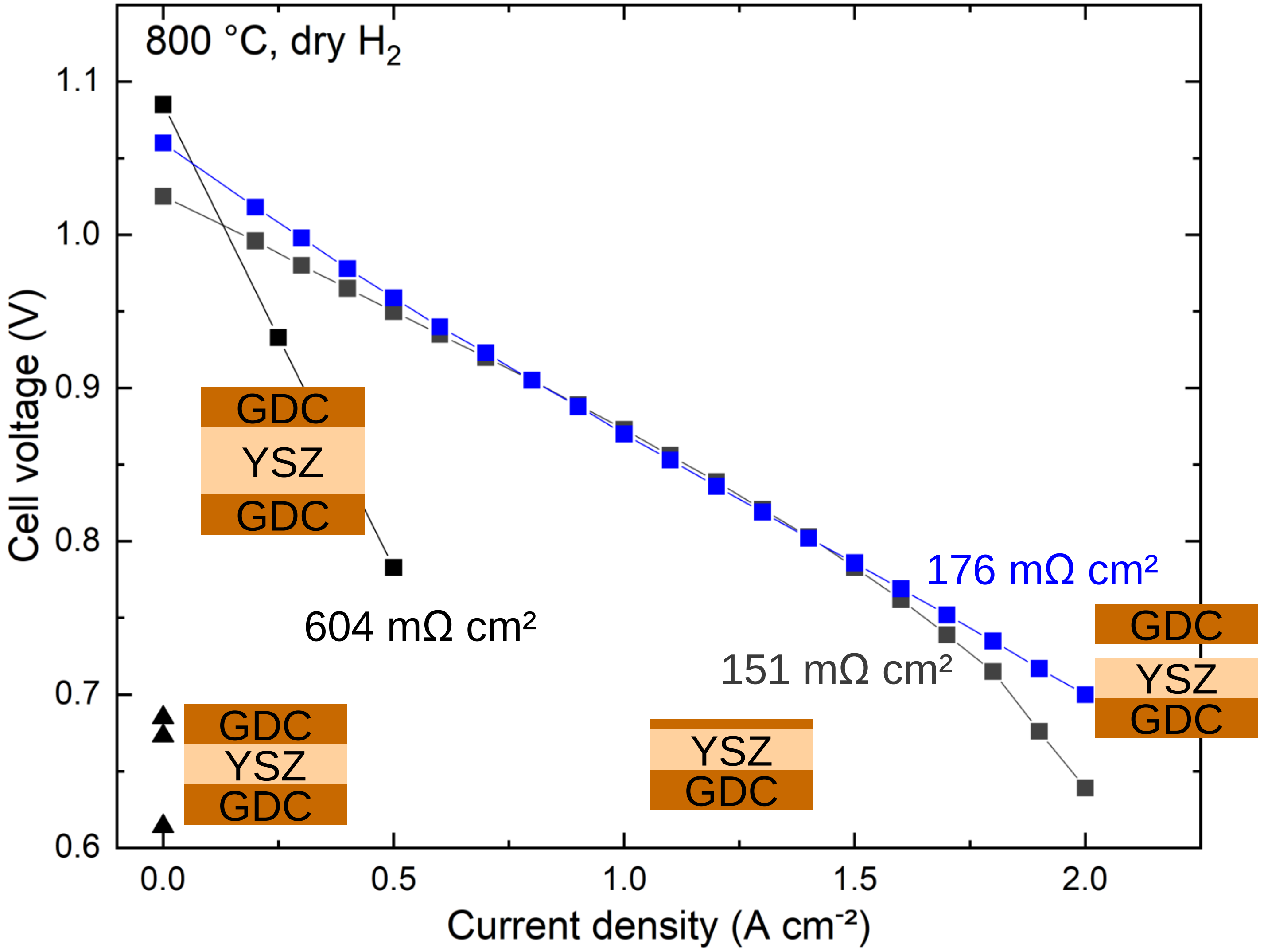

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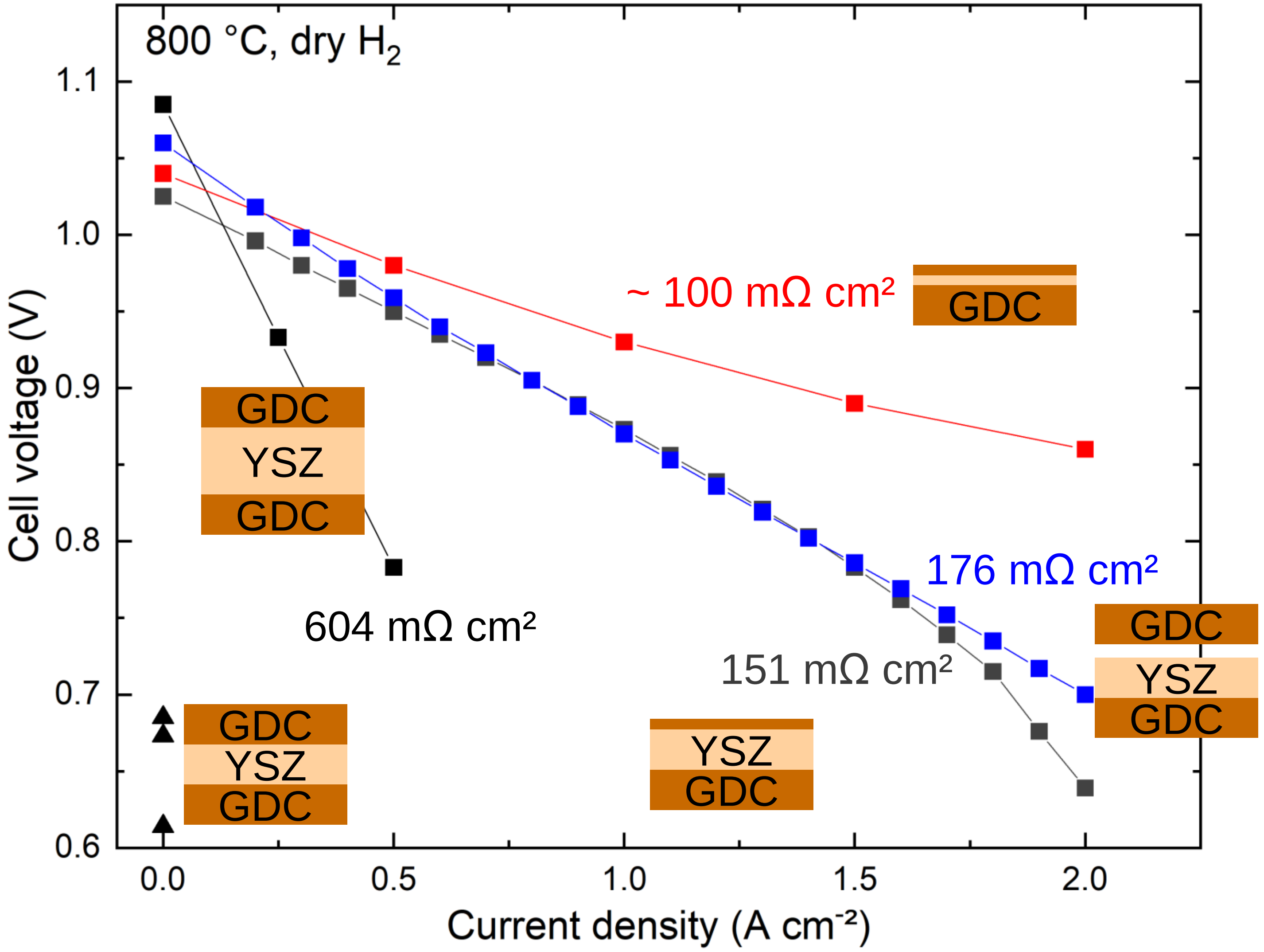

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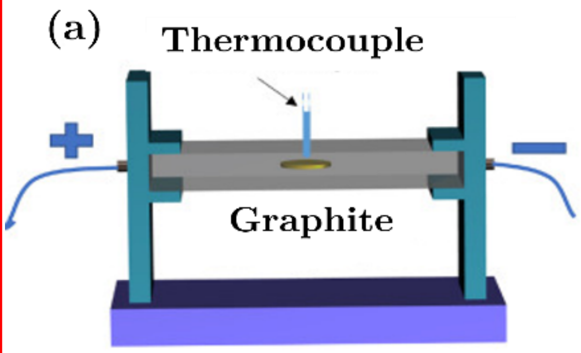
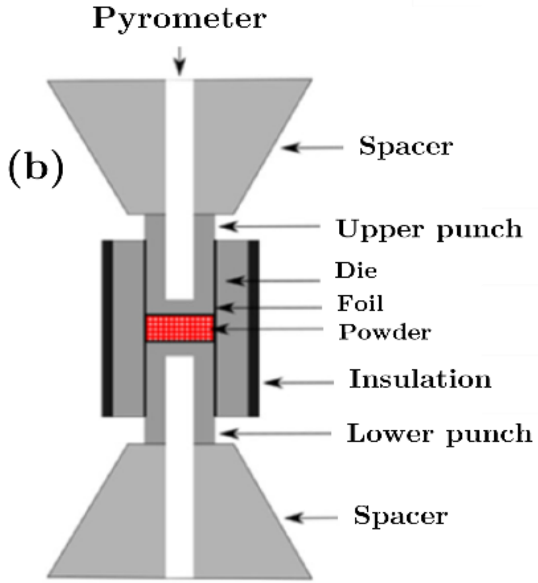
Rapid densification techniques

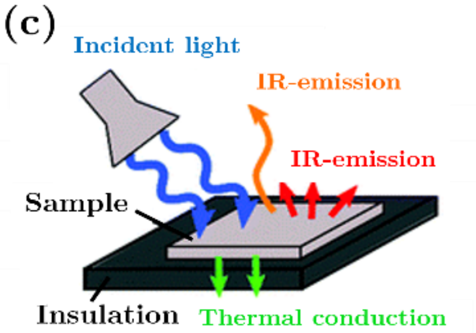
Ultrahigh temperature sintering (UHS)



Field-assisted sintering technique (FAST)



Blacklight sintering



1) J. Dong, Scripta Materialia 2021 Vol. 203

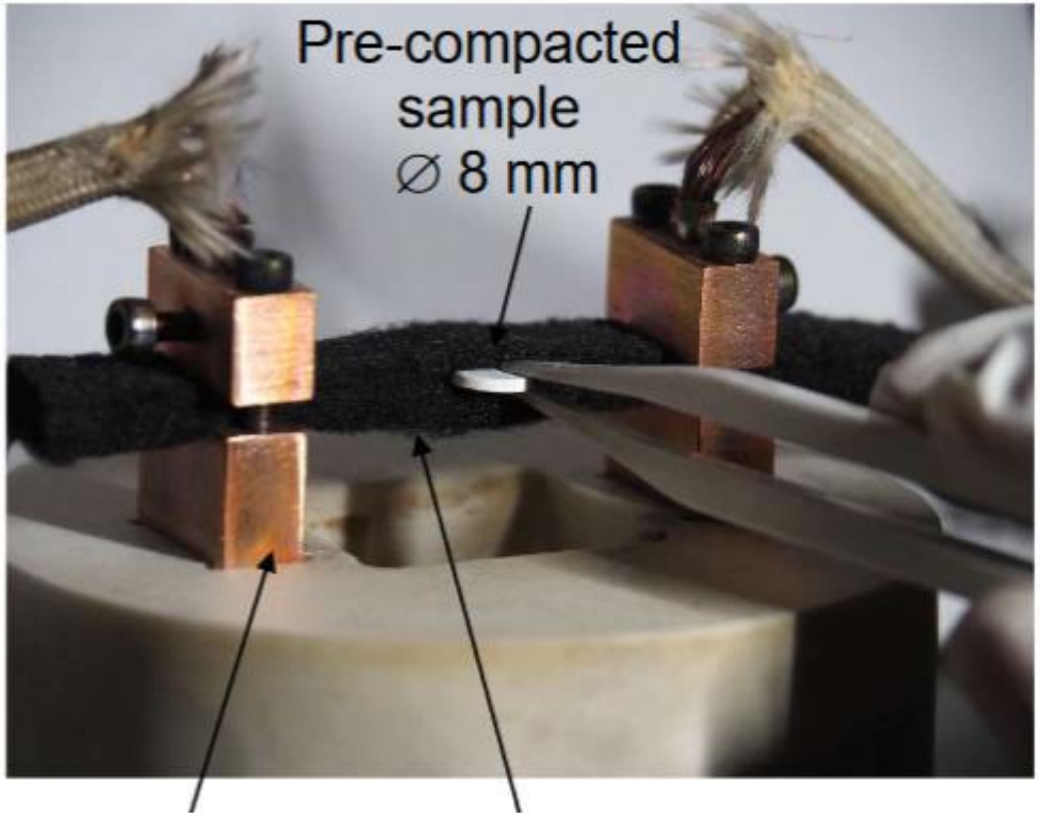
2) T. P. Mishra, et al.; Materials 2020 Vol. 13 Issue 14 Pages 3184

3) Porz, et al.; Materials Horizons 2022 Vol. 9 Issue 6 Pages 1717-1726

UHS - procedure

- Powder pressed uniaxially (120 MPa), followed by cold isostatic pressing (400 MPa
- Environment 1) vacuum and graphite felt
- Environment 2) Ar + Ta foil

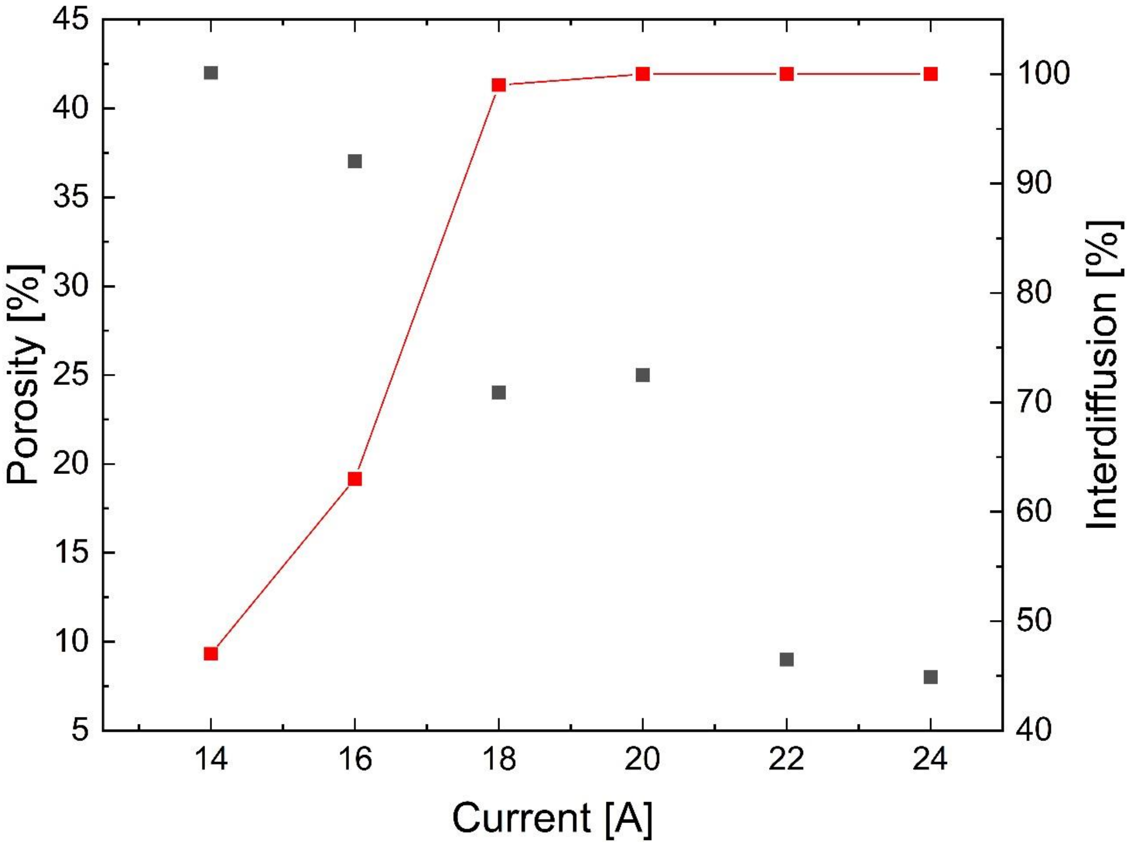
- Sintered density determined via Archimedes method
- Phase analysis of crushed pellets via XRD



UHS - interdiffusion

- Density increases with sintering current (~ temperature) for fixed hold time (10 s)
- Interdiffusion starts immediately
- Dense samples are completely interdiffused, showing GDC-YSZ solid solutions and a $Ce_2Zr_2O_7$-based pyrochlore structure
- The pyrochlore is a sign of strong carbothermal reduction

➢ Rapid sintering does not automatically reduce interdiffusion



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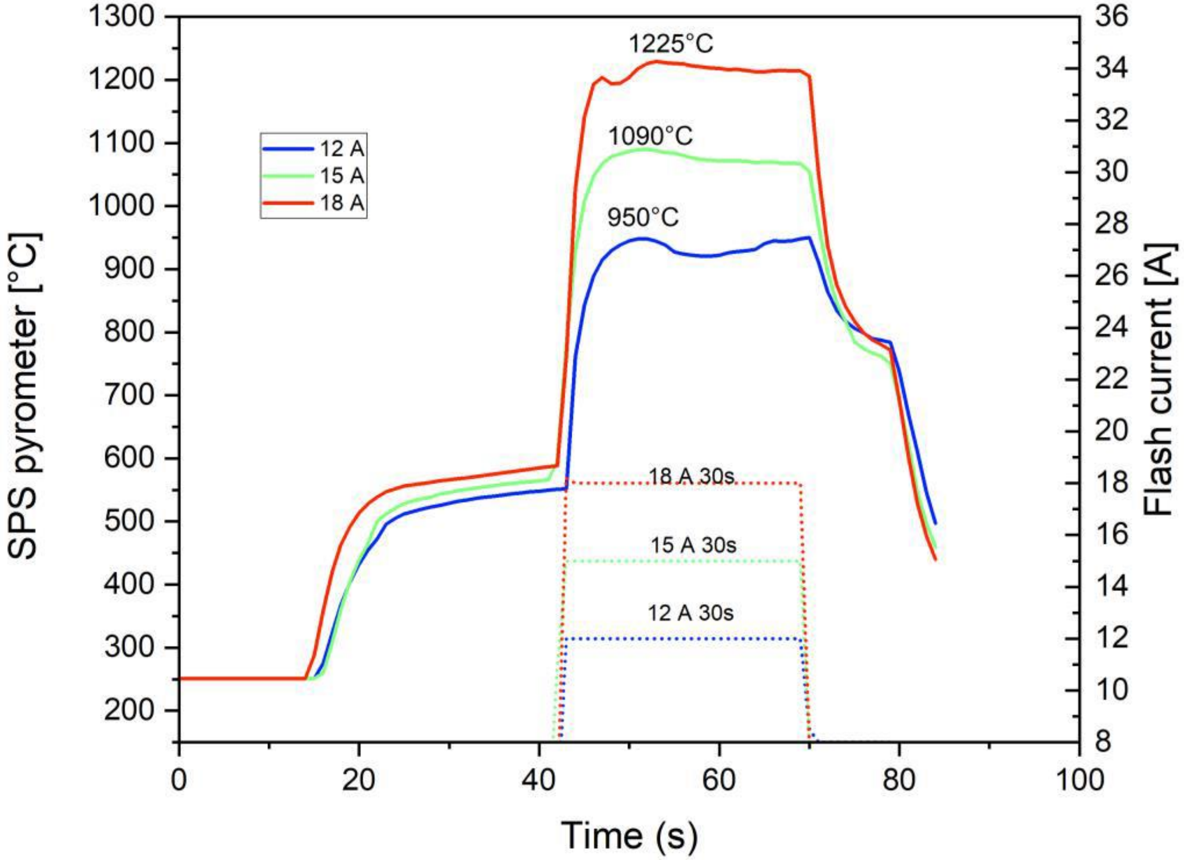
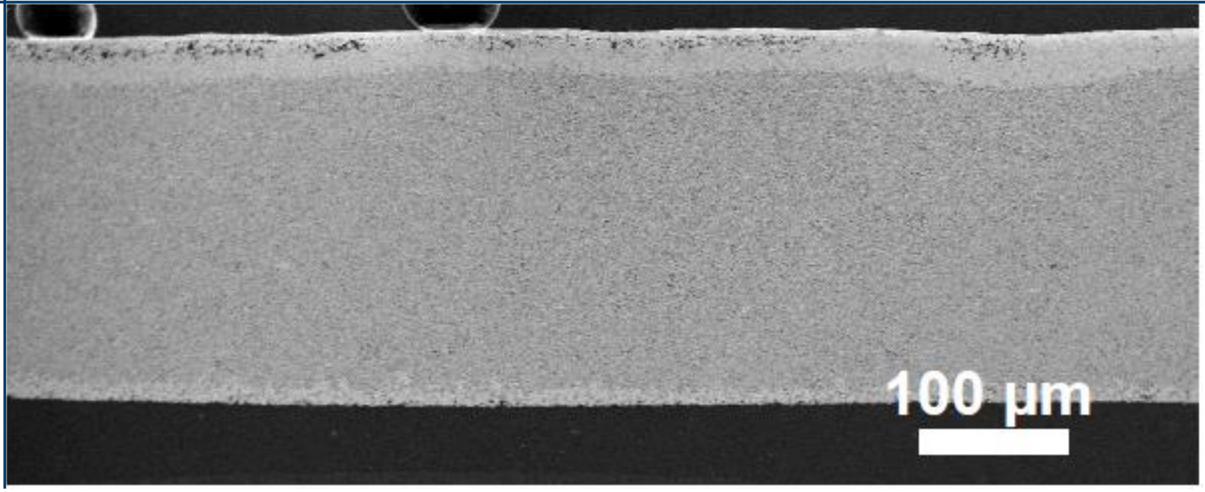
UHS – half cells

- Half-cells were produced with
  - NiO-YSZ support (tape cast)
  - NiO-GDC electrode (screen-printed)
  - GDC electrolyte (screen-printed)

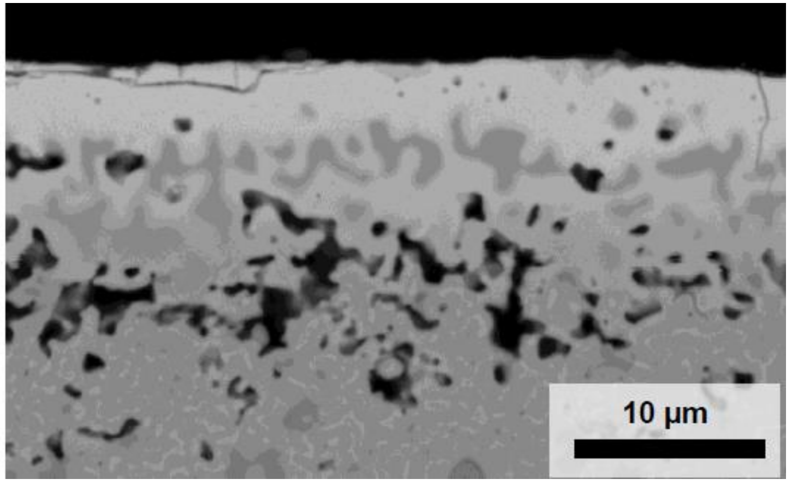
- 3 sintering profiles with increasing current
- T-control with pyrometer

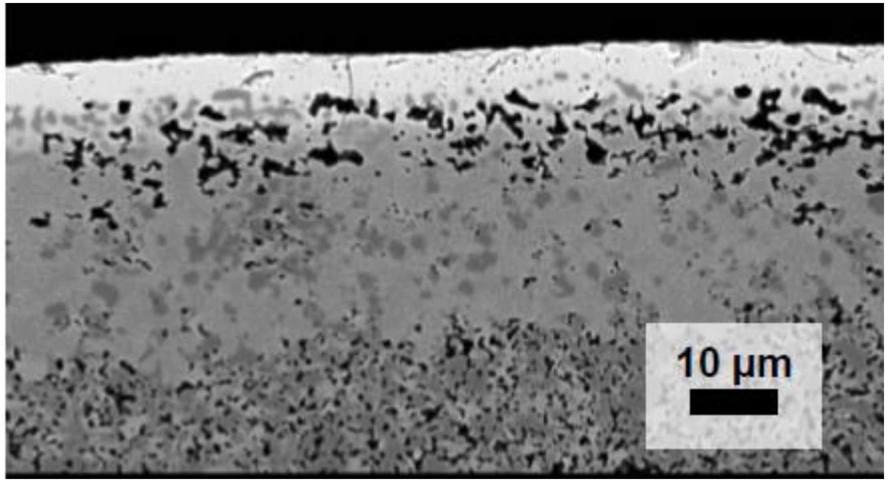


UHS – half cell 12 A / 30s



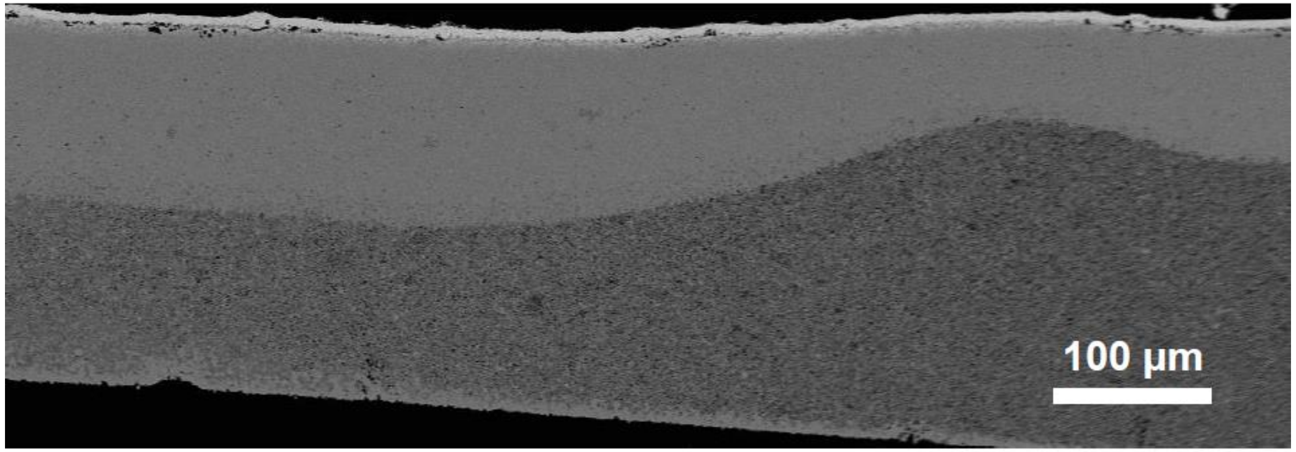
- Approx. 950 °C
- Distinct layer microstructure
- Densified electrolyte
- Support only densified at top & bottom
  - ➢ Heat transfer issues

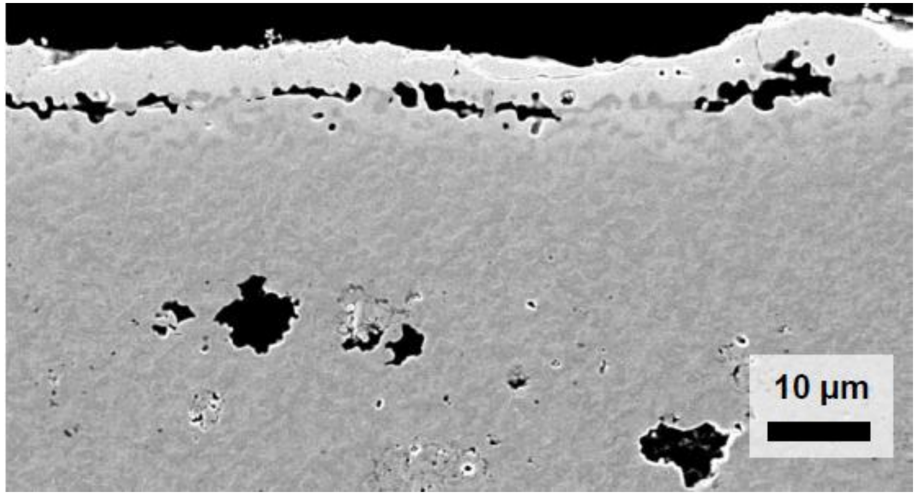


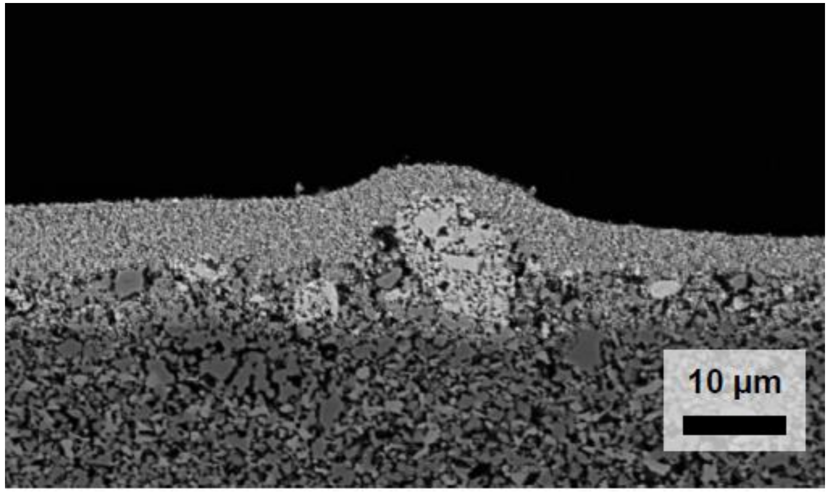


UHS – half cell 15 A / 30s

- Approx. 1090 °C
- More pronounced densification in support
- Pronounced porosity / electrolyte delamination
- inhomogeneous



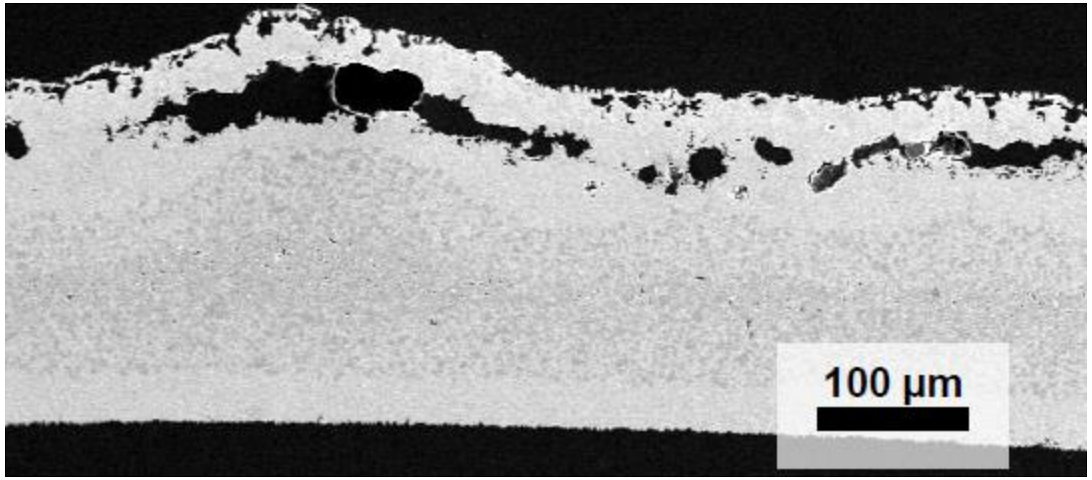


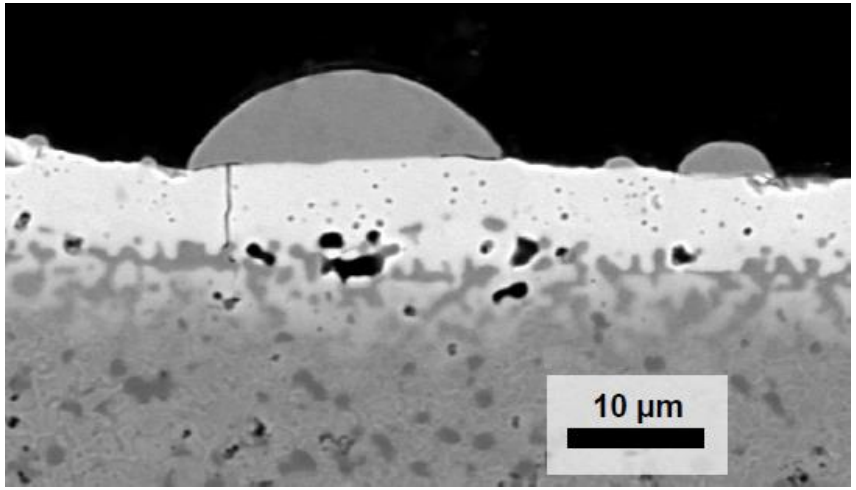


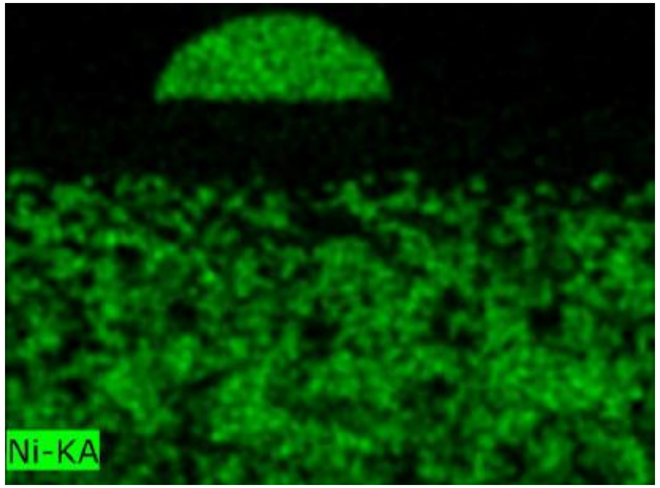
UHS – half cell 18 A / 30s

- Approx. 1225 °C
- Support almost dense
- Pronounced porosity / electrolyte delamination
- Very inhomogeneous
- NiO droplets found on top of electrolyte

➢ Partial melting?

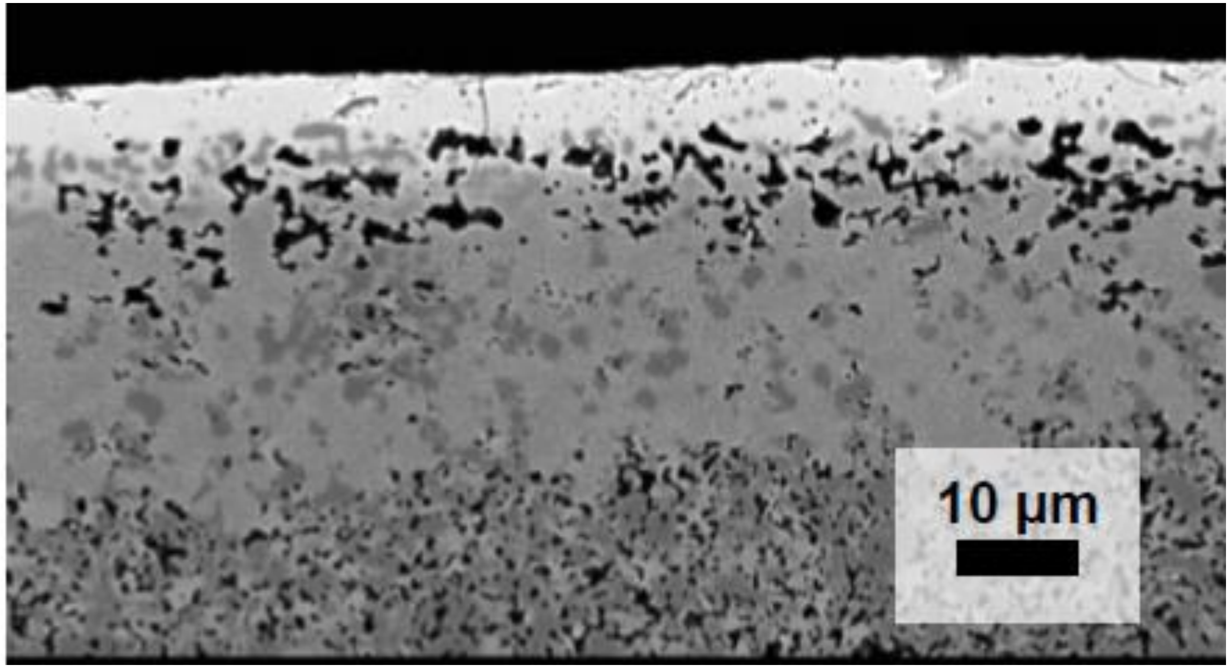






UHS – what does this all mean?

- Dense electrolyte ✓
- Porous electrode ✗
  - Interdiffusion?
- Porous support ✗
  - No NiO percolation
- Inhomogeneity ✗
  - Better process control necessary!



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Summary

Ni-GDC electrodes

- High stability in SOEC operation demonstrated
- Substitution for Ni-YSZ leads to interdiffusion during cell fabrication
- Ceria-based electrolyte needed to improve electrolyte / electrode interface

Co-fired electrolytes

- Simplify cell manufacturing
- Interdiffusion more severe during sintering, leads to short-circuit
- Good compromise may be co-firing of 2 layers with subsequent firing of GDC layer

Rapid densification

- Much shortes processing times
- Short time ≠ no interdiffusion
- Cells for rapid densification must be re-engineered to achieve densification in all components simultaneously