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PROSPECTS ON PROTONIC CERAMIC CELLS
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# Effect of sintering conditions on the phase and microstructure features of $Ba_{1.015}Zr_{0.8-x}Ce_{0.2}Y_xO_{3-\delta}$ proton conducting cell components

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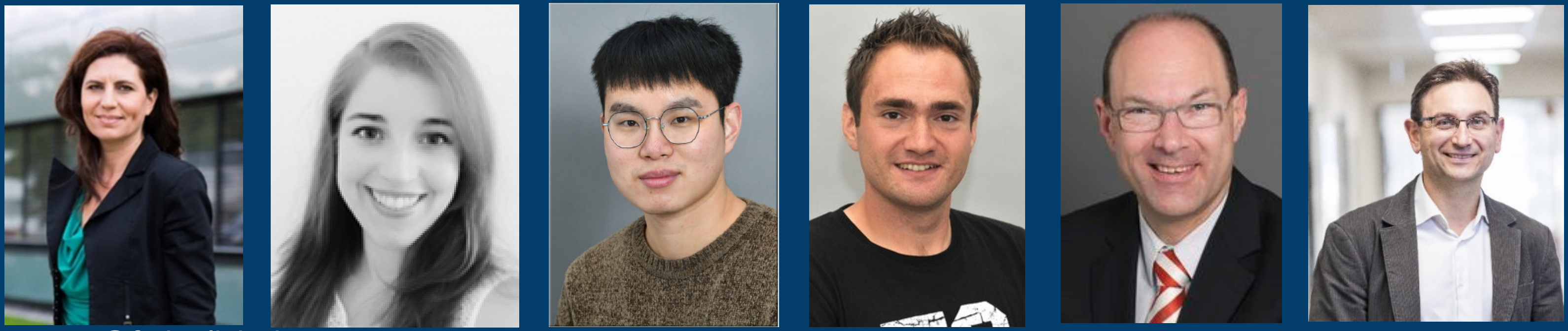
Norbert H. Menzler[1,2], Olivier Guillon[1,2,3]



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# OUTLINE

- Introduction
- SoA (ref): Strategies
- This work: bulk vs layer configuration (air side, 15 µm)
- Conclusive remarks

# INTRODUCTION

- BZCY: PCC used in development of electrochemical devices; electrolyte, constituent of supporting structure

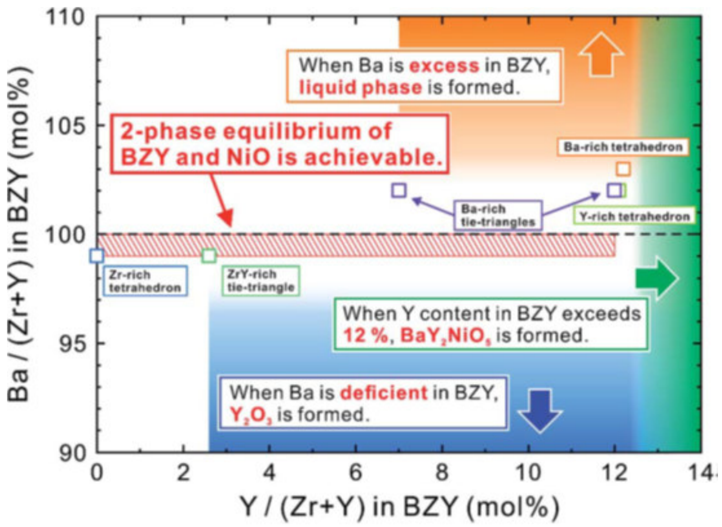
- NiO dual use: i) sintering aid for BZCY and ii) component of the fuel electrode with high activity for the $H_2$ Evolution Reaction (HER);

- Co-sintering at elevated temperatures

- ○ Ba evaporation, Ni diffusion, Ni incorporated in BZCY lattice compromises its hydration behaviour and conductivity;
- ○ Formation of secondary phases, e.g. $BaY_2NiO_5$, insulating ($Y_2O_3$) or $O^{2-}$ - conducting (CYO, ZYO);
- ○ (Ni) Electronic pathways across the electrolyte;
- ○ Compromised performance: conductivity drop, electronic leakage, thermochemical-mechanical problems;

**Important:** Strategy to improve the phase compatibility between the BZCY and NiO in a thin electrolyte layer configuration (Note: reference sources often report about bulk electrolyte specimens, not µm-range layers).

# SoA (Ref): STRATEGIES



[K. Ueno et al., *Thermodynamic maximum of Y doping level in barium zirconate in co-sintering with NiO,* J. Mater. Chem. A, 2019, 7, 7232–7241]

Proposed as efficient: for bulk material (pellets)
Either BZY+NiO (SA) or BZY:60-70%NiO composite

- Co-sintering of BZY with NiO, at 1500°C:

i) Y-rich BZY (Y > 12 mol.%): $BaY_2NiO_5$ +LP ($BaNiO_2$)
ii) Ba-excess: LP
iii) Ba-deficiency: $Y_2O_3$
Bi-phase equilibrium, no SP > $Ba_{1(-0.01)}Zr_{0.88}Y_{0.12}O_{3-\delta}$

- Improved compositional homogenization of BZY by increased sintering T (1300°C→1600°C) +
- Manipulating BaO activity at 1500°C > higher BaO activity (embedded sintering) > single phase material (no $Y_2O_3$ or traces of Ni as residues of $BaY_2NiO_5$ decomposition). Y, Ni incorporated in the BZY crystal lattice.

[D. Han et al., *Strategy to improve phase compatibility between proton conductive BZY20 and NiO*, RSC Adv. 2016, 6, 19288-19297]

- Manipulation of sintering profile (BZY+4 mol.% NiO (SA)

Control of Y and Ba content might be more efficient tool for enhanced performance than preventing Ni incorporation

[D. Fagg group at UAVR (PT), personal communication]

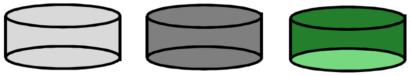
Limited reports on thin supported PCC electrolyte layers
BZ with Y in the support being crucial for $BaY_2NiO_5$ LP formation and electrolyte densification

[W. Deibert et al., *Fabrication of multi-layered structures for proton conducting ceramic cells*, J.Mater.Chem.A, 2022, 10, 2362 (2022)]

[K. Leonard et al., Processing ceramic proton conducting membranes for use in steam electrolysis, Membranes 2020, 10, 339-357]

# BULK vs LAYER CONFIGURATION

## Bulk samples (P.)



$Ba_{1.015}Zr_{0.8-x}Ce_{0.2}Y_xO_{3-\delta}$ (x = 0.175; 0.24) + 0.5 wt.% NiO

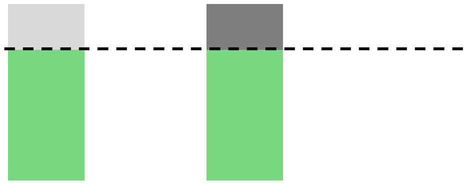
E1> x = 0.175
E2> x = 0.24

$Ba_{1.015}Zr_{0.8-x}Ce_{0.2}Y_xO_{3-\delta}$ (x = 0.175) + NiO (40:60 wt.%)

S> (not considered currently)

*versus*

## ESA



$Ba_{1.015}Zr_{0.8-x}Ce_{0.2}Y_xO_{3-\delta}$ (x = 0.175; 0.24) + 0.5 wt.% NiO

$Ba_{1.015}Zr_{0.8-x}Ce_{0.2}Y_xO_{3-\delta}$ (x = 0.175) + NiO (40:60 wt.%)

ESA1> x = 0.175
ESA2> x = 0.24

Looking at the pellet top / the electrolyte side in ESA configuration > the side exposed to air during the (co-)sintering.

# STARTING POINT PROTOMEM

## BZCY

**Ce:**

- Zr/Ce to be kept balanced: higher ratio better stability but compromised conductivity

**Y:**

- required for generation of oxygen vacancies, i.e. proton defects, maximal possible content

### 1. Solubility ranges for Ce, Y in $BaZrO_3$

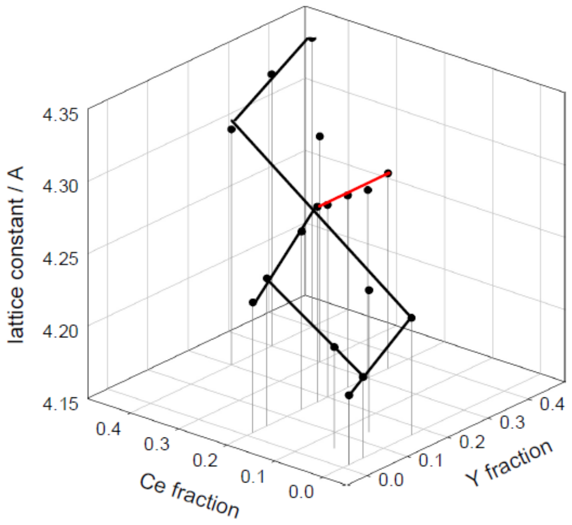
- ○ Pronounced solubility for Ce than for Y
- ○ Ce to be kept up to 20 mol.% (stability) and Y up to 25 mol.% (solubility)
- ○ $BaZr_{1-x}Ce_zY_yO_{3-y/2}$ with $y,z \leq 0.45$

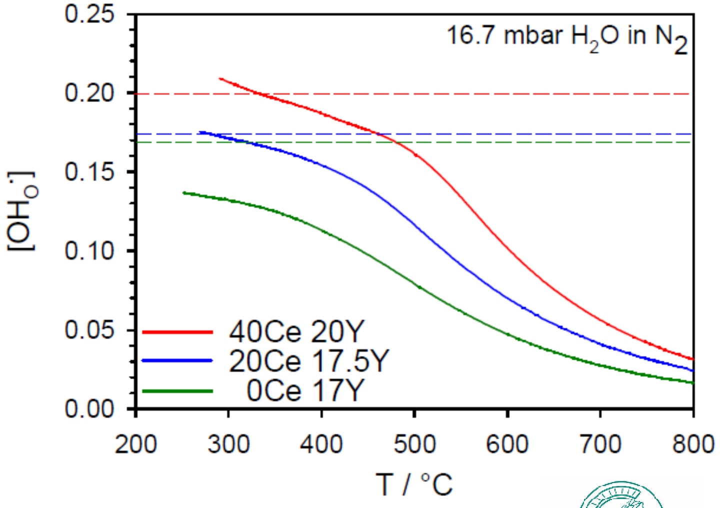
### 2. Effect of Ce, Y amounts on BZCY hydration

- ○ Hydration TD more favorable with Ce content increasing

$BaZr_{1-x}Ce_zY_yO_{3-y/2}$ with $y,z \leq 0.45$, e.g. $BaZr_{0.56}Ce_{0.2}Y_{0.24}O_{3-\delta}$

$BaZr_{0.625}Ce_{0.2}Y_{0.175}O_{3-\delta}$

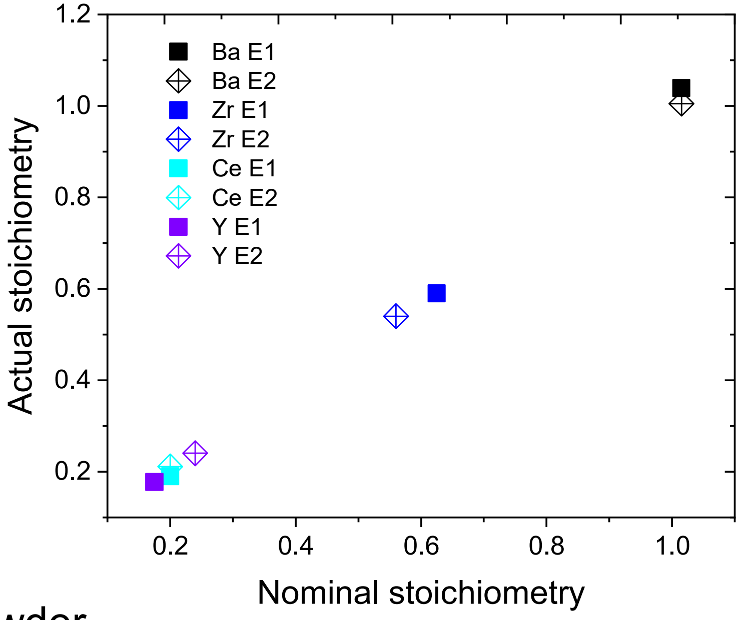




# SAMPLES PREPARATION

## Powders (Pwd.)

- Mixing stoichiometric amounts of $BaCO_3$, $ZrO_2$, $CeO_2$, $Y_2O_3$
- E1, E2> milled, calcined 1100°C/8h, x 3 times
- S> milled, calcined 1300°C/6h
- Addition of NiO, homogenization
  - ➢ as sinter-aid, 0.5 wt.% to E1, E2 powders
  - ➢ as cermet forming phase, 60 wt.% to S powder



## Bulk samples (P)

- Shaping> iso-static pressing D =13 mm, L = 2-3mm

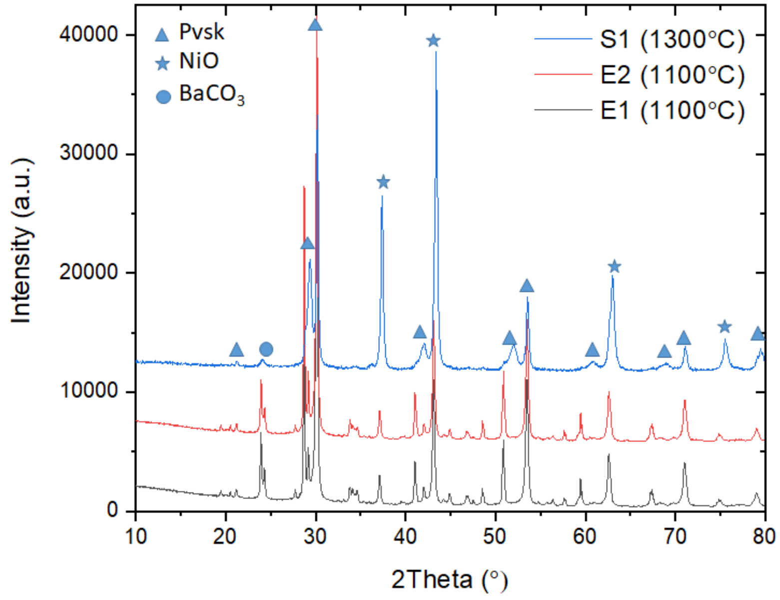
## ESA

- Ceramic suspensions
- Tape casting
- Shaping samples,10x10 mm

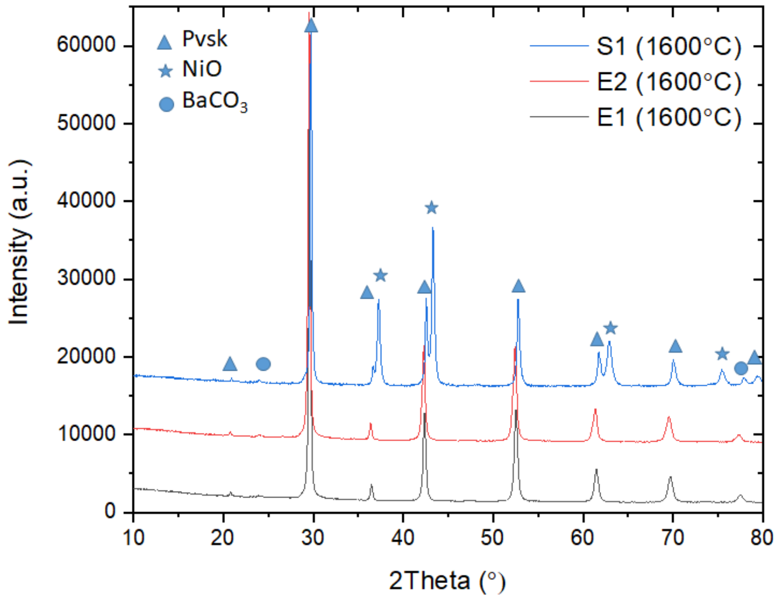
Sintering: 1450°C/6h; 1500°C/3h; 1550°C/3h, 2 K/min, air, MgO

# POWDER SAMPLES, SSRS, RT

SSRS mixture developed for tape casting



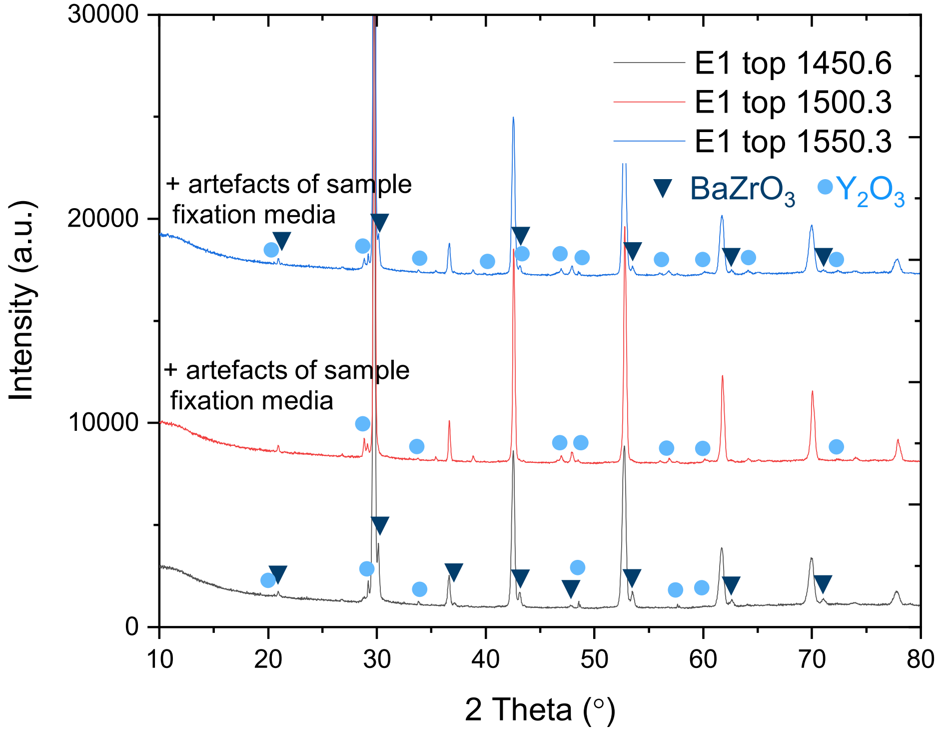
SSRS mixture sintered @ 1600°C/10h, Air



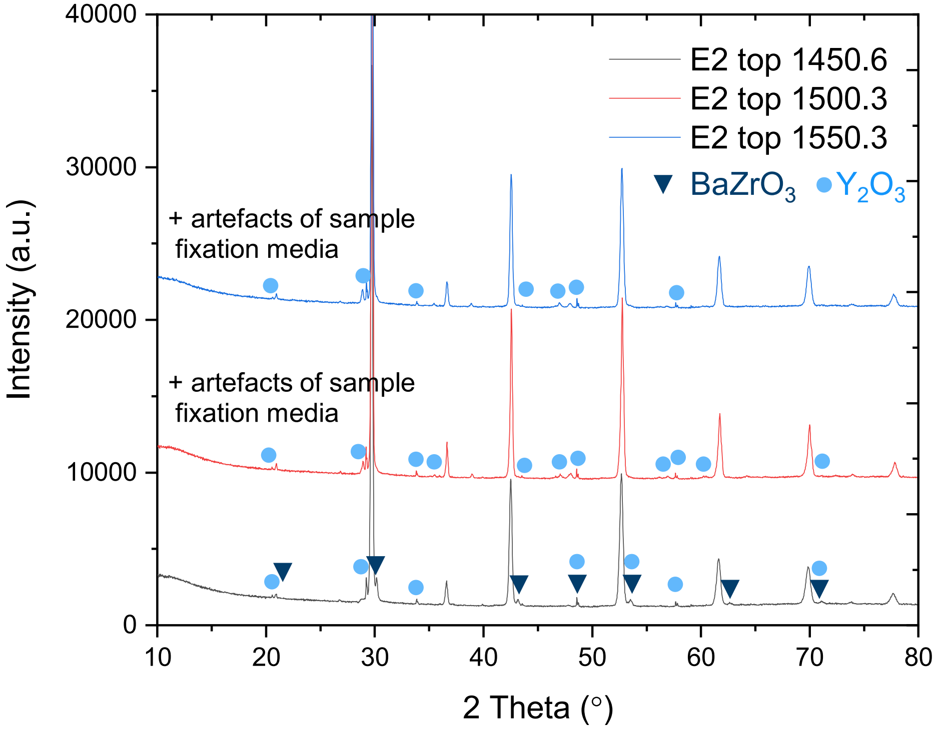
Used both for P and ESA

# **BULK SAMPLES** Air side, RT

$Ba_{1.015}Zr_{0.8-x}Ce_{0.2}\mathbf{Y_{0.175}}O_{3-\delta}$ + **0.5 wt.% NiO**



$Ba_{1.015}Zr_{0.8-x}Ce_{0.2}\mathbf{Y_{0.24}}O_{3-\delta}$ + **0.5 wt.% NiO**

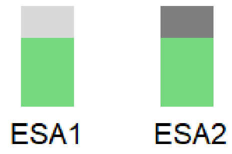


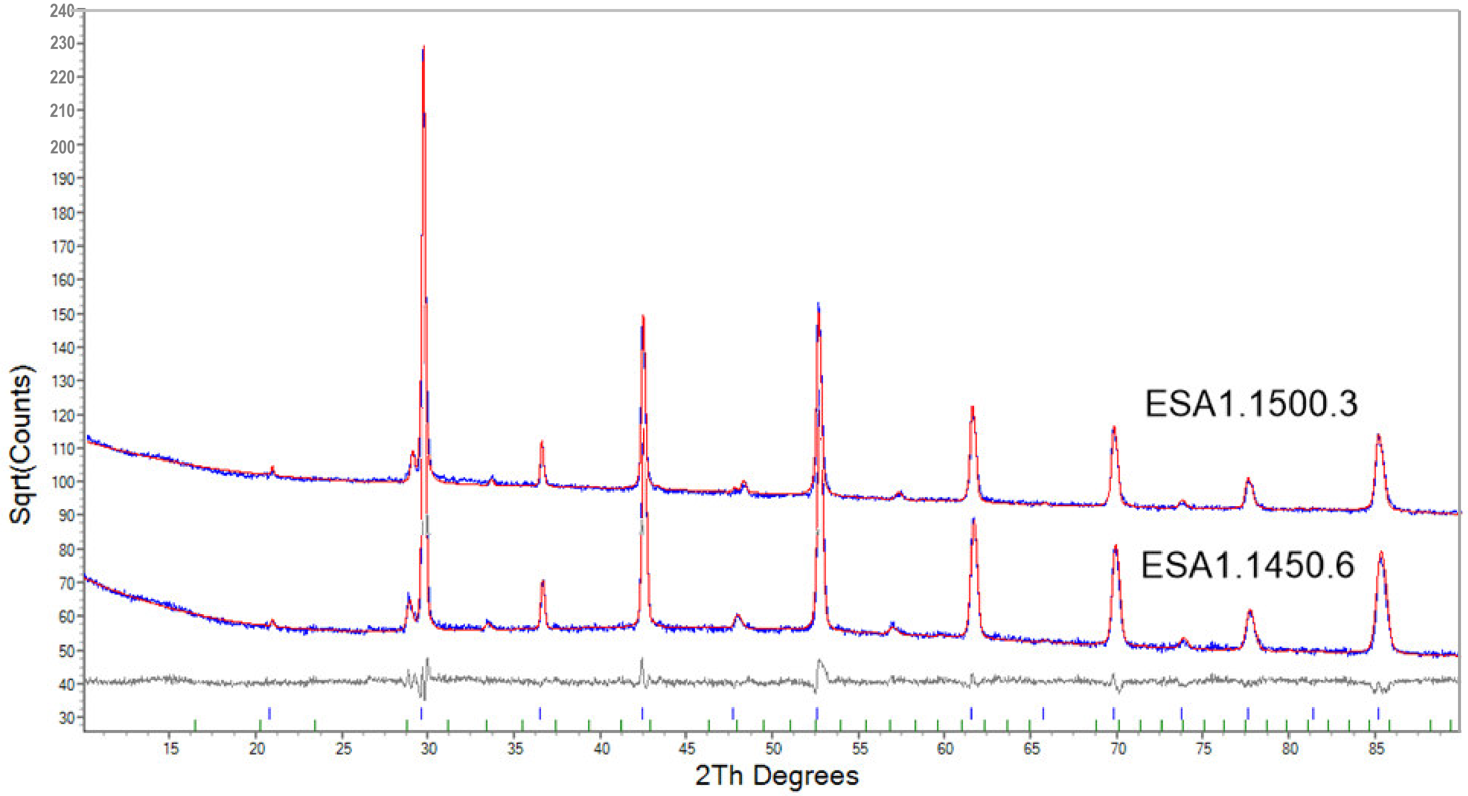
1450.6: BZCY 92%; BZ 6%; $Y_2O_3$ 2%
1500.3: BZCY 99%; $Y_2O_3$ 1%
1550.3: BZCY 94%; BZ 5%; $Y_2O_3$ 1%

1450.6: BZCY 95%; BZ 3%; $Y_2O_3$ 2%
1500.3: $BZCY_1$ 49%; $BZCY_2$ 49%; $Y_2O_3$ 2%
1: a=4.250(2)Å; 2: a=4.258(24)Å;
1550.3: BZCY 99%; $Y_2O_3$ 1%

# ESA SAMPLES

Air side, RT

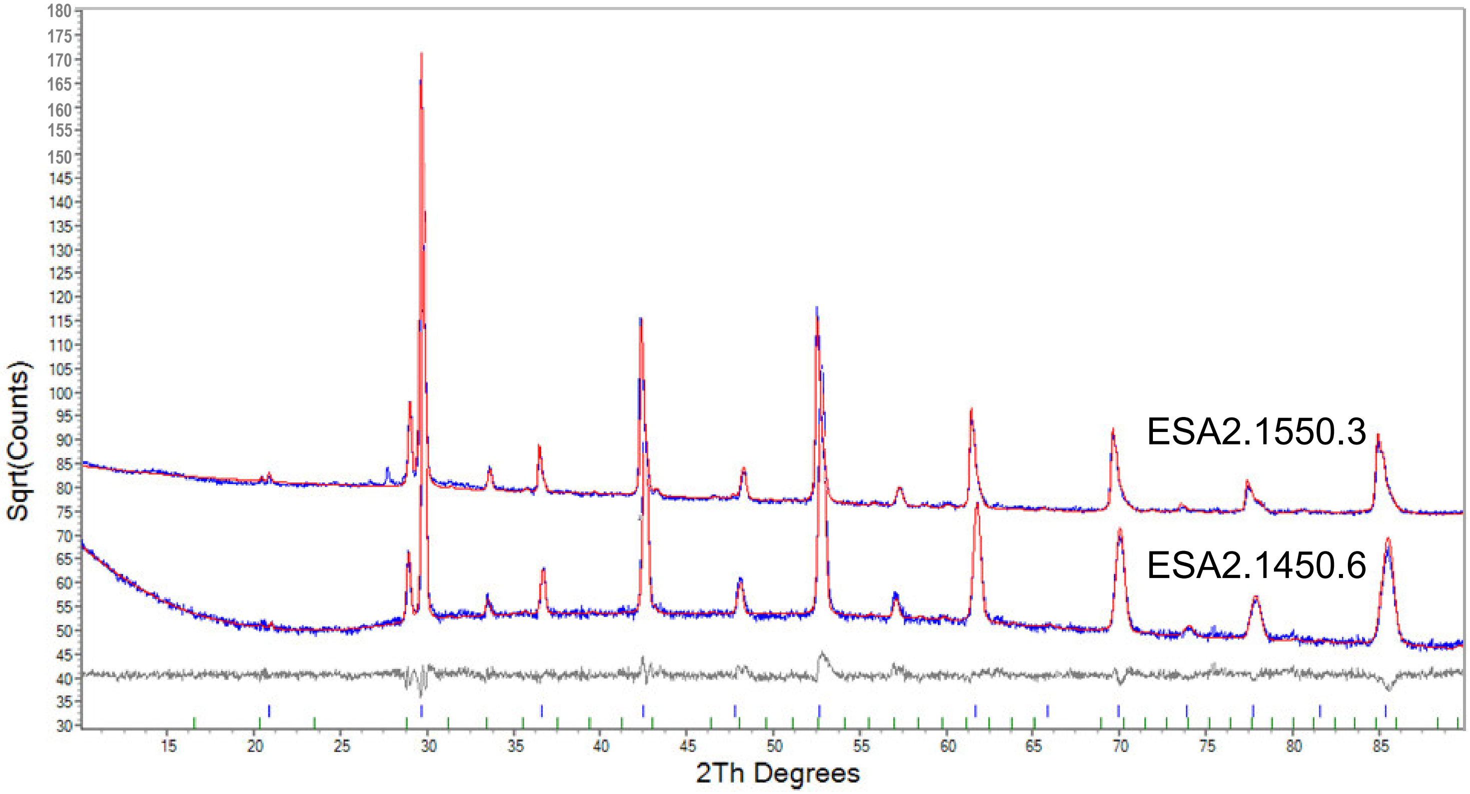




1450.6: BZCY 96%; $Ce_{0.375}Y_{0.625}O_2$ 4%
1500.3: BZCY 95%; $Ce_{0.2}Y_{0.8}O_2$ 5%
1550.3: t.b.d.

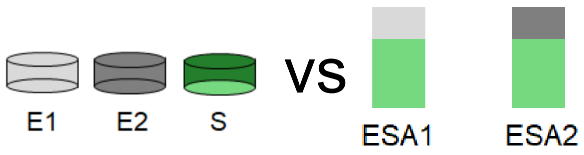
# ESA SAMPLES

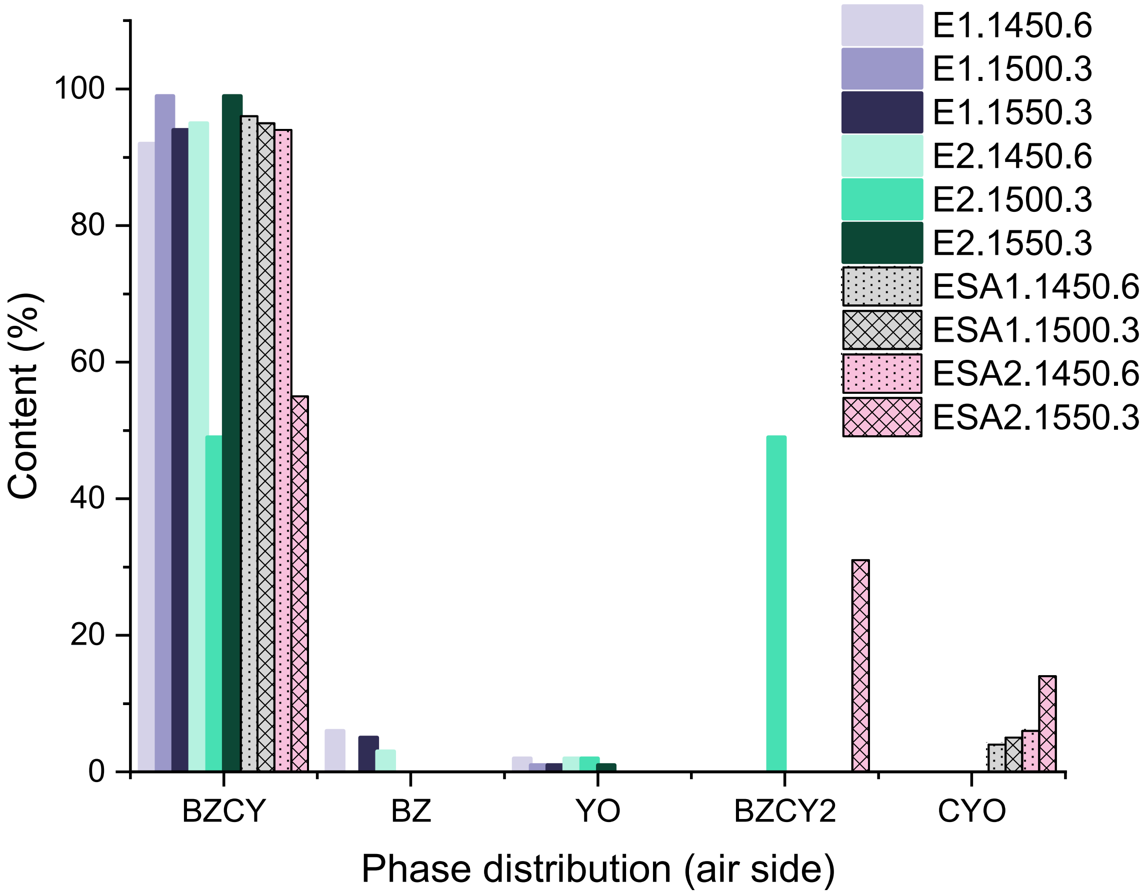
Air side, RT



1450.6: BZCY 94%; $Ce_{0.375}Y_{0.625}O_2$ 6%
1500.3: t.b.d.
1550.3: $BZCY_1$ 55%; $BZCY_2$ 31%;$Ce_{0.2}Y_{0.8}O_2$ 14%
1: a=4.271(2)Å; 2: a=4.25(2)Å;

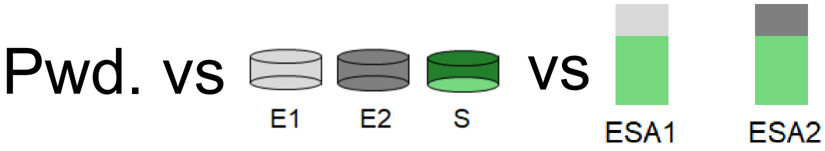
# QUANTIFICATION

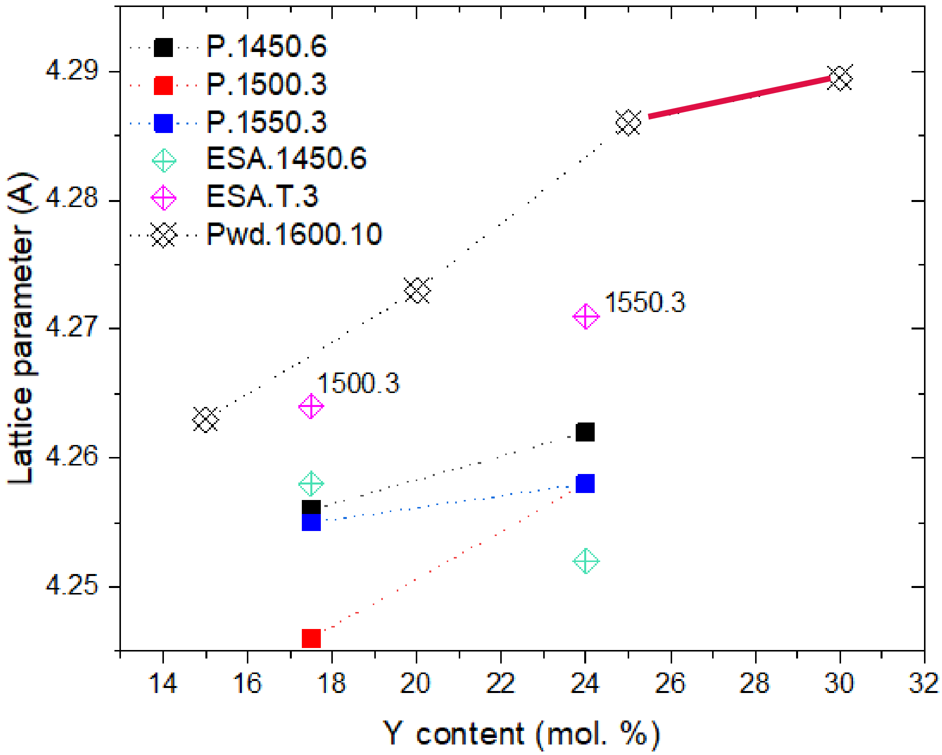




- **P vs T**: minor YO secondary phase amounts, surface effect at the oxidizing side; undoped/Y,Ce depleted BZ formed as a second phase;
- **ESA** (ca. 15-20 µm): T and Y increase leads to pronounced formation of secondary phases; Higher sintering T yielding more $BaY_2NiO_5$ in the electrolyte (increased diffusion of Ni from the support). $BaY_2NiO_5$ phase decomposes at HT; Ce solubility in LP; Ba, Ni evaporate, CYO formed.

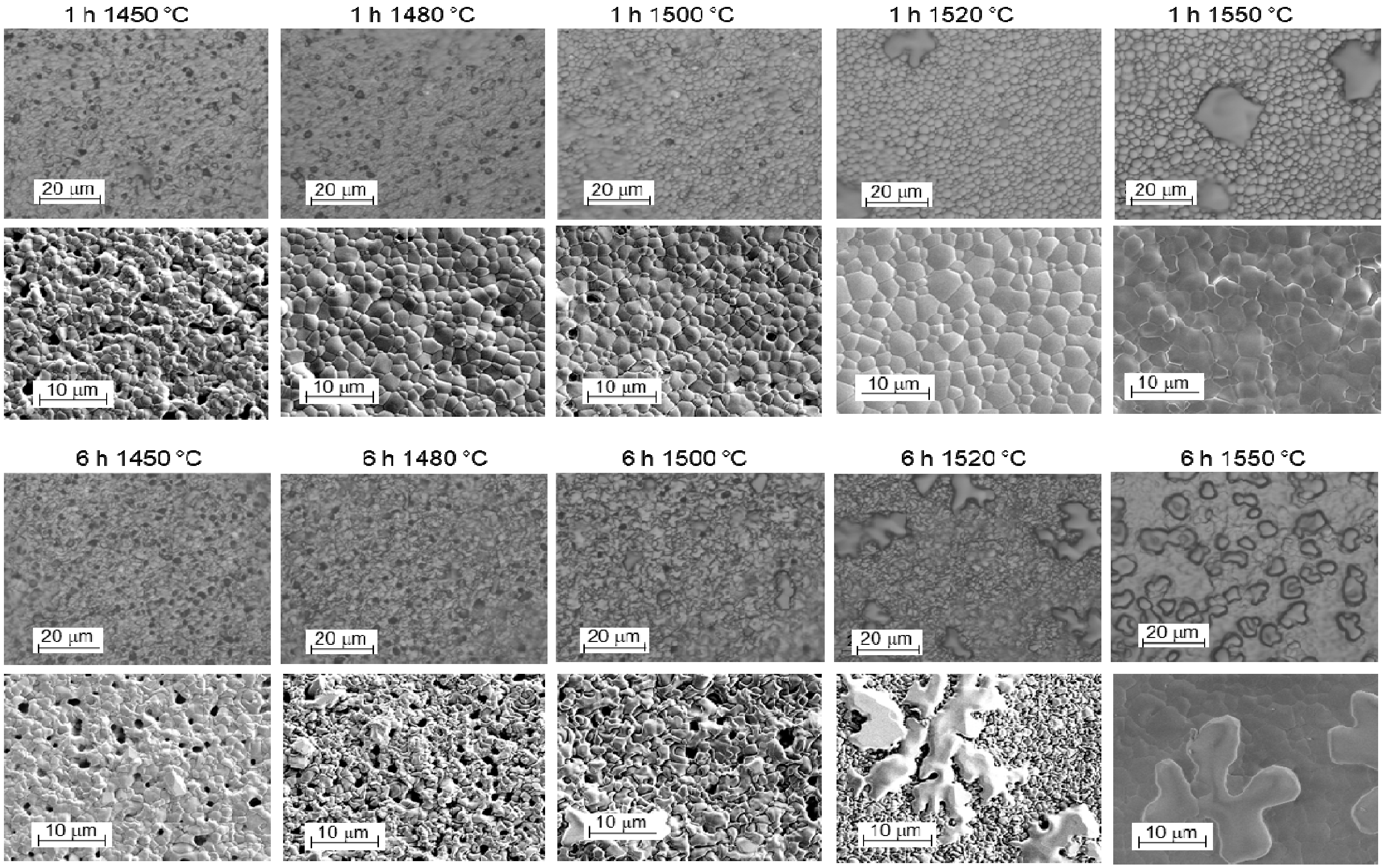
# LATTICE PARAMETER





- **Pwd**: single phase; reference series with Y15-30: deviation (red line) from the linear ***a*** increase with Y (Vegard's law, black line). Maximum Y solubility in BZCY at 1600 ºC > approx. 25 mol.%.
- **P**: with T increase ***a*** decreases; At the air side: oxygen incorporation; Y-rich secondary phases (SP) segregated: less acceptor dopant in the BZCY major phase; possible Ni additive incorporation in the lattice.
- **ESA** (ca. 15-20 μm): increase in lattice parameter (better homogenization of main phase; evtl. enhanced Y uptake in BZCY layer with increasing T despite SP formation);

# MICROSTRUCTURE: ESA1 (TOP)



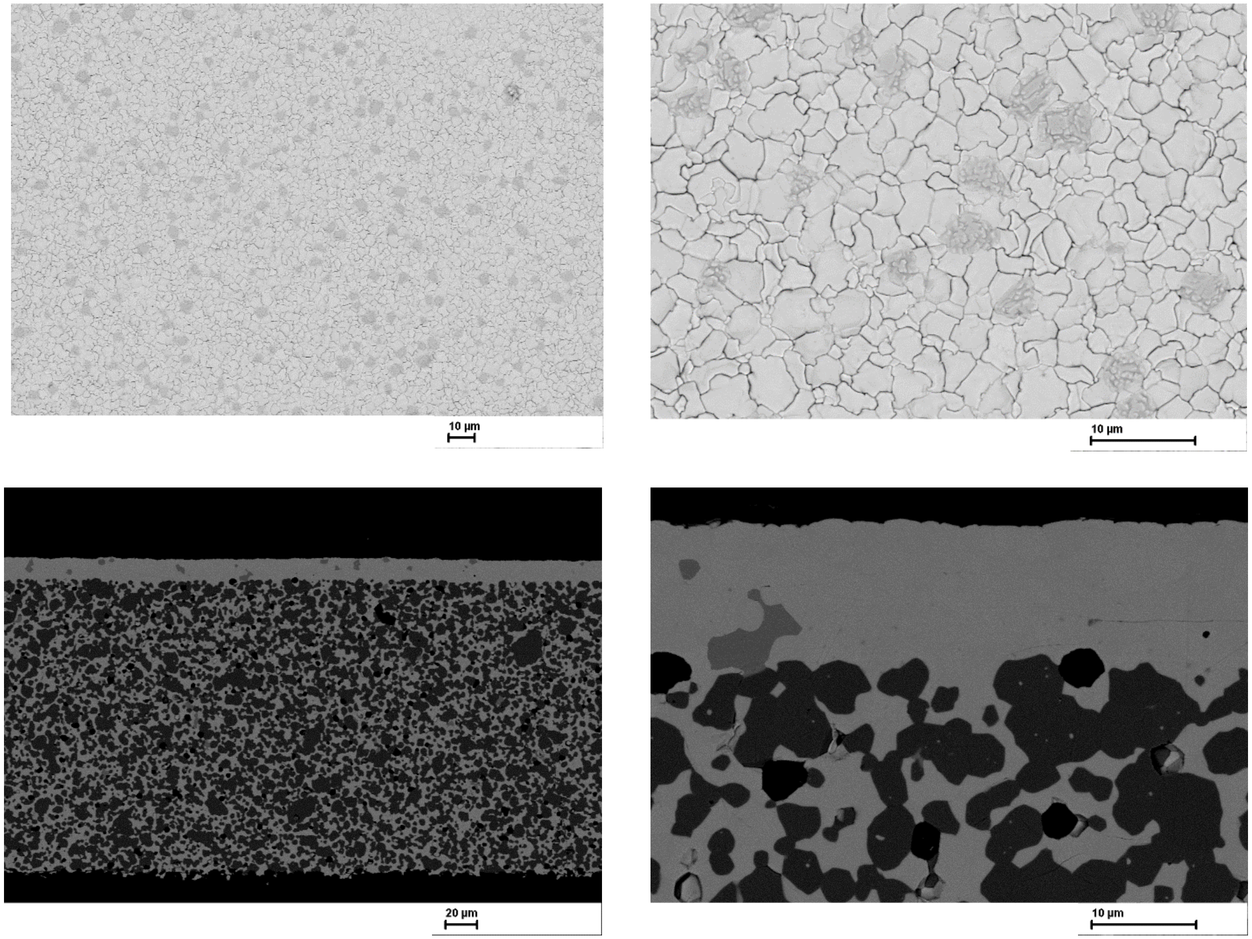
[W. Deibert, et al., *Fabrication of multi-layered structures for proton conducting ceramic cells,* J.Mater.Chem.A, 2022, 10, 2362 (2022)]

# MICROSTRUCTURE: ESA1 (TOP vs CS)

top

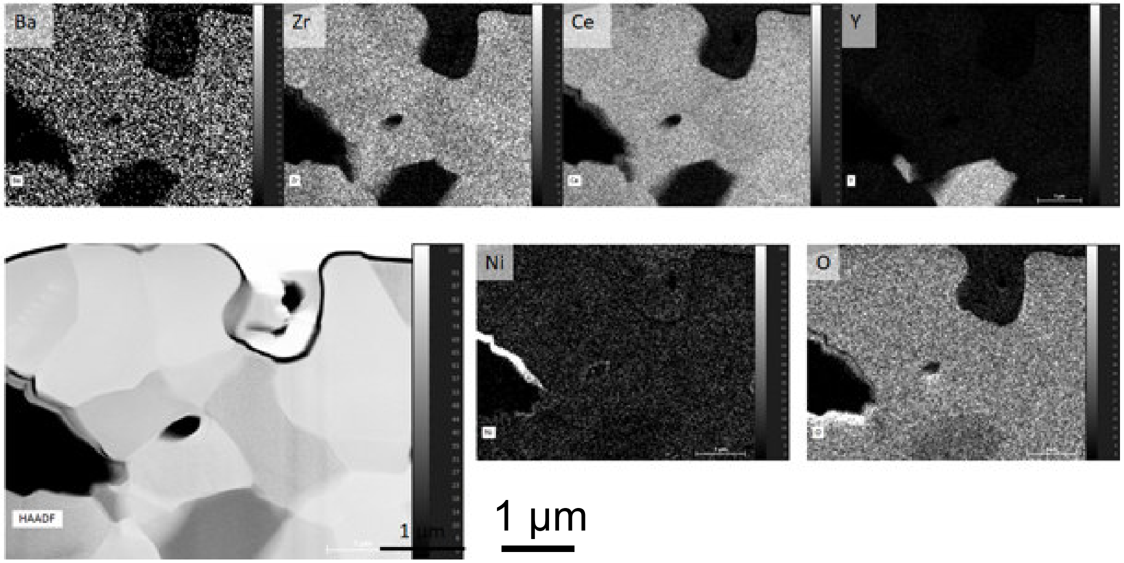
1550.3

CS

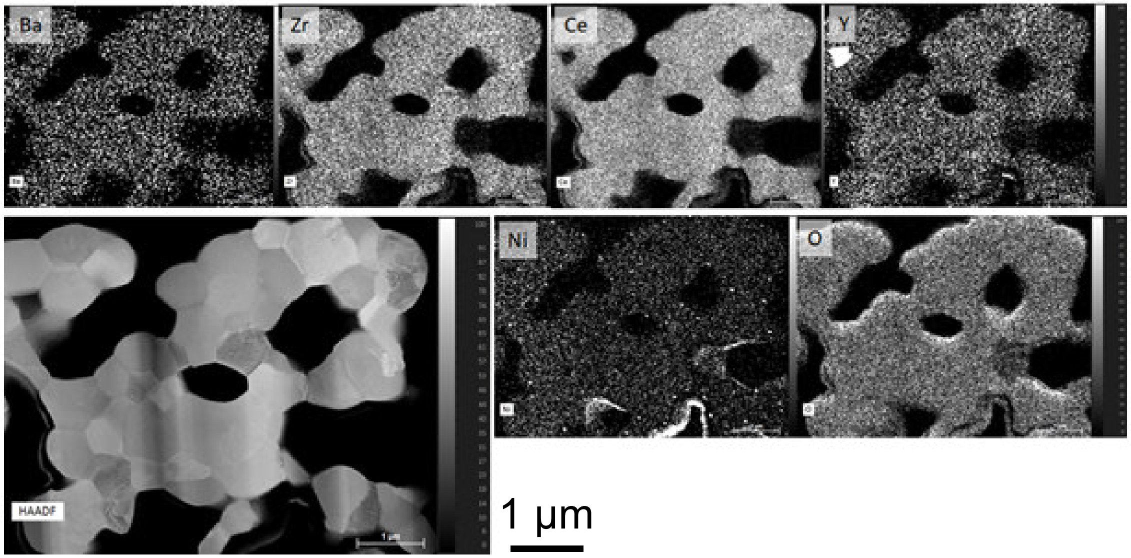


# STEM-HAADF (TOP)

ESA2.1450.6

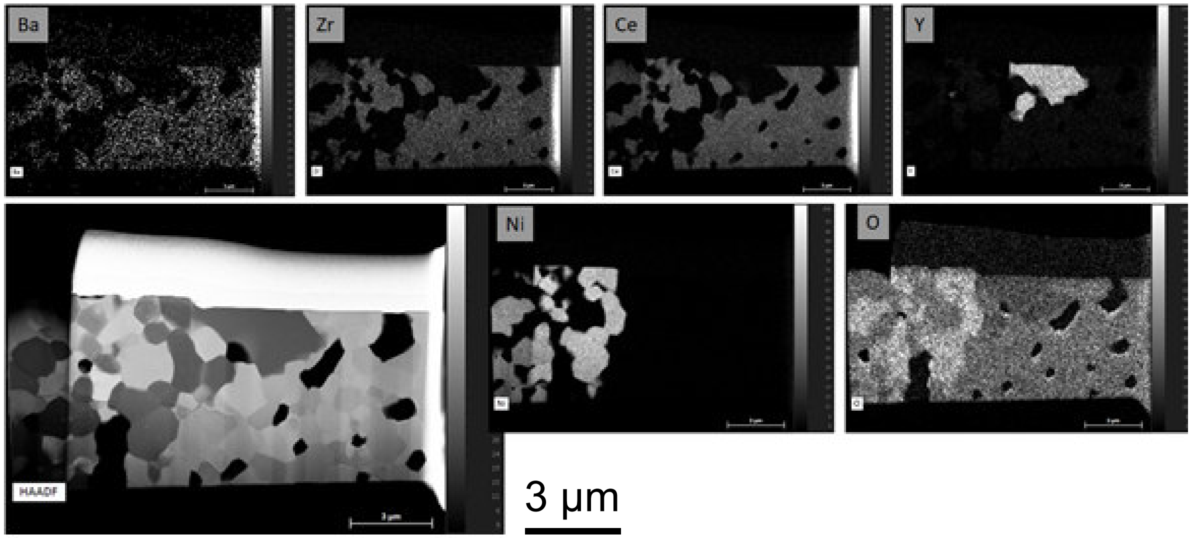


ESA2.1450.6
+ red 900.5

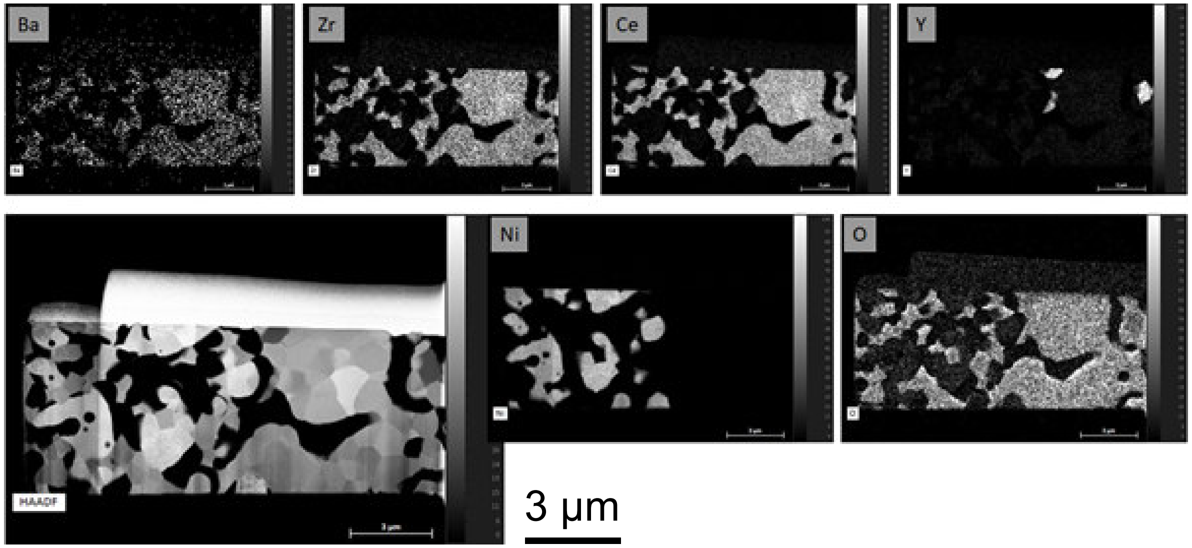


# STEM-HAADF (CS)

ESA2.1450.6

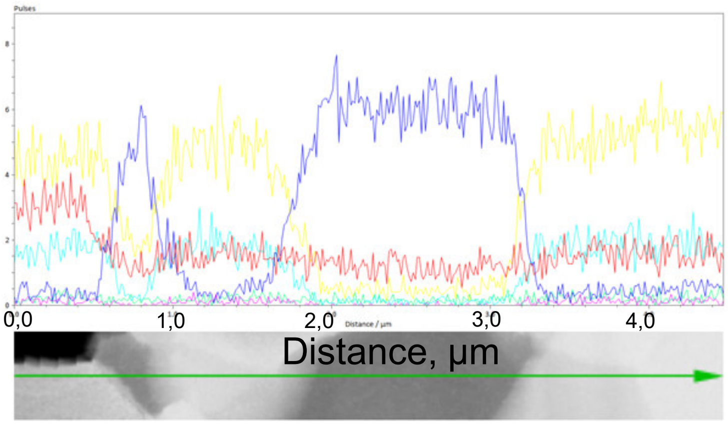


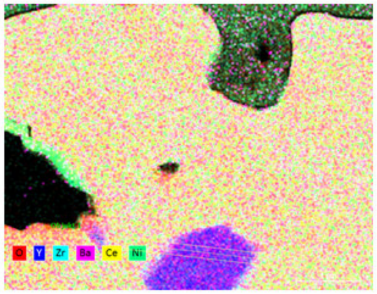
ESA2.1450.6
+ red 900.5

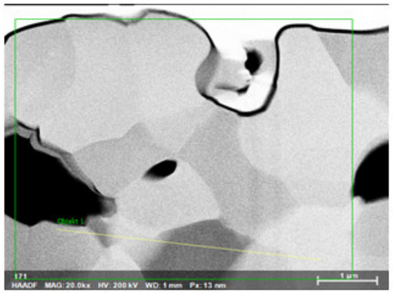


# CONCENTRATION PROFILES (TOP)

ESA2.1450.6

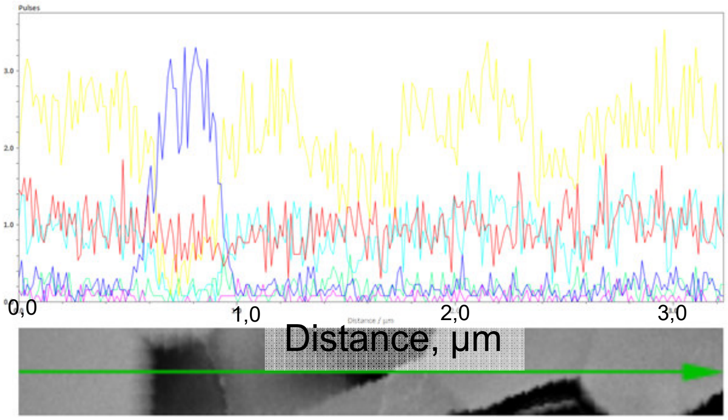


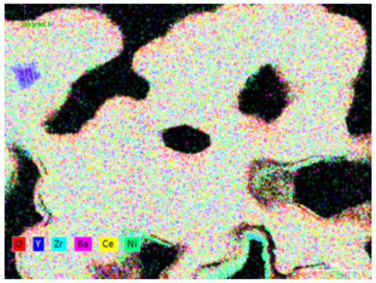


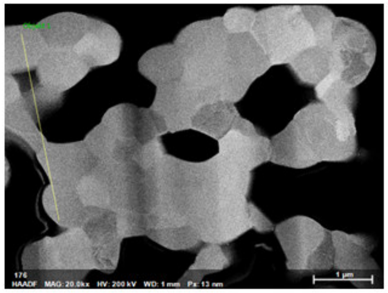


1 µm

ESA2.1450.6
+ red 900.5







1 µm

# CONSLUSIVE REMARKS

- Strategies to minimise SP in the PCC material proven to be efficient for bulk samples > not always transferrable to supported PCC electrolyte layer
- Most strategies demonstrated on BZY (both experimental and computational approaches) > scarce data about BZCY layers formed on NiO based cermet after co-firing at HT
- Ba deficiency not sufficiently addressed in the literature sources as a critical factor > in some ref $Ba_{(1-x)}$ considered as beneficial for PCC single phase formation
- Ba non-stoichiometry $Ba_{(1-x)}$ underpins the formation of defects > e.g. $(2Ni_i v_{Ba})^{\cdot\cdot}$ complex being considered TD favorable (DFT) but harmful for the electrolyte performance
- Slight Ba over-stoichiometry in the electrolyte was probed as a direct measure to address Ba loss in layers, for which covered/embedded sintering is not a practicable option > Ni incorporation in the lattice might be suppressed but BaO sink cannot be really counteracted;
- Y re-incorporation in the BZCY lattice suggested by an increase of the lattice parameter of ESA series
- Manipulation of the sintering profile applied to ESA to be tested as a next approach.

# ACKNOWLEDGEMENTS

## ProtOMem

Bundesministerium
für Bildung
und Forschung

FK: 03SF0537

- BMBF
- Duration 01.07.2016-30.06.2019
- Partners: **3** institutions
- Budget: total ~ **1.4 Mio Euro**

JÜLICH Forschungszentrum

for Solid State Research

StEM Stuttgart Center for Electron Microscopy

RWTH AACHEN UNIVERSITY

GFE

KERAFOL Keramische Folien GmbH

Morgan Advanced Materials

W. HALDENWANGER Technische Keramik GmbH & Co. KG

## INNOPOOL SOLAR H2

Bundesministerium
für Bildung
und Forschung

HELMHOLTZ
SPITZENFORSCHUNG FÜR
GROSSE HERAUSFORDERUNGEN

- BMBF and HGF

ENERGY RESEARCH FIELD
Materials and Technologies for the Energy Transition (MTET)

- Duration 01.01.2021-31.12.2023
- Partners: **17** institutes located in **6** HGF-research centers
- Budget: total ~ **6 Mio Euro** (~ 60% HGF, rest own contributions)

JÜLICH Forschungszentrum

KIT Karlsruher Institut für Technologie

HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

HZB Helmholtz Zentrum Berlin

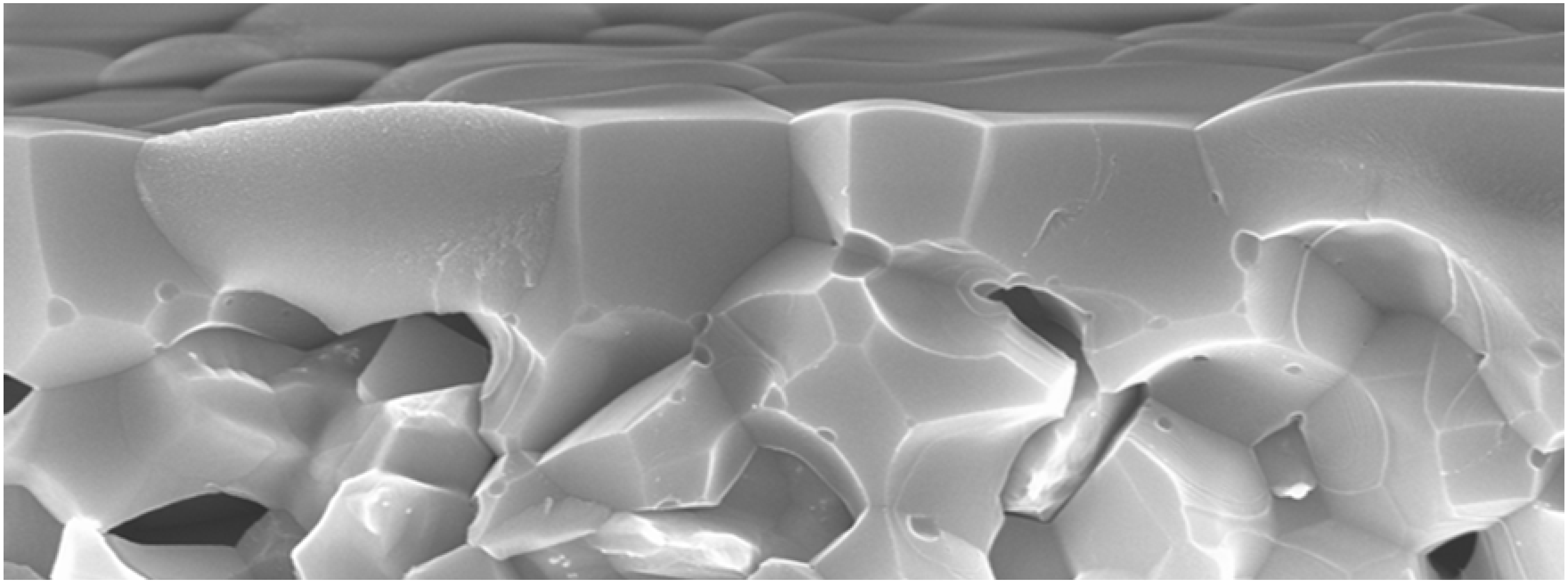
IPP Max Planck Institute for Plasma Physics

with own resources

DLR

# ACKNOWLEDGEMENTS

SOC DEPARTMENT



# THANK YOU!

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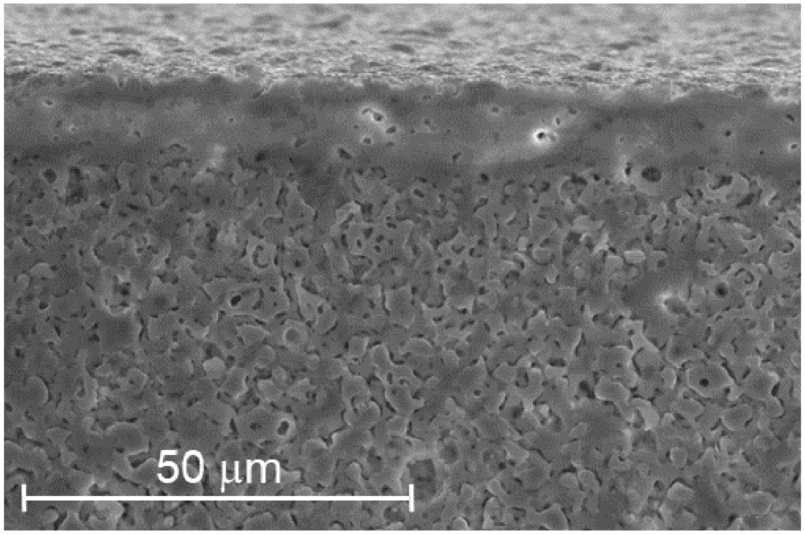
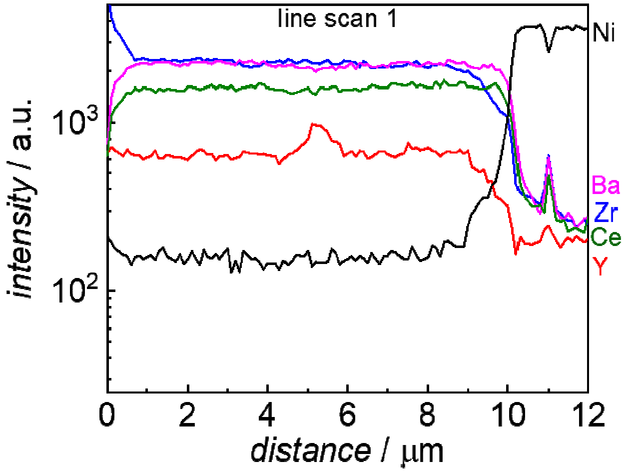
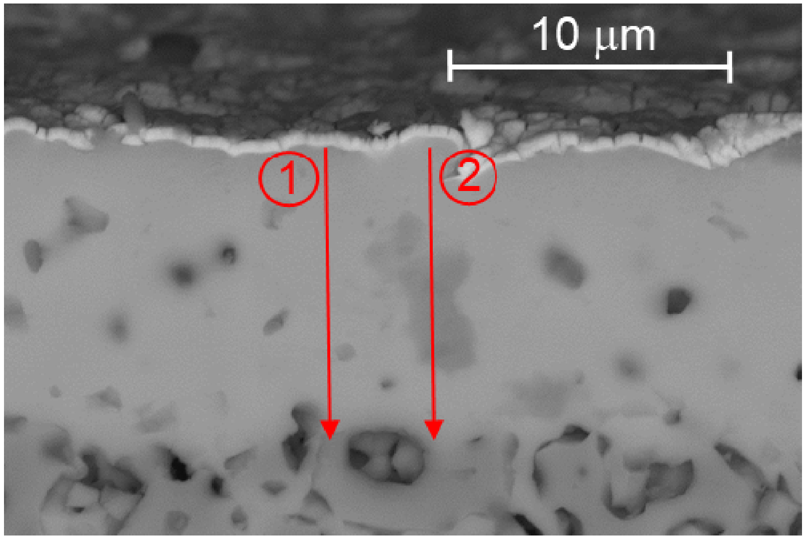
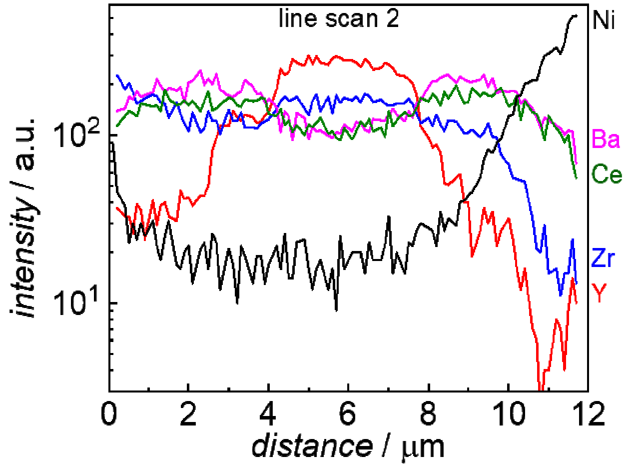
# ESA1-CS





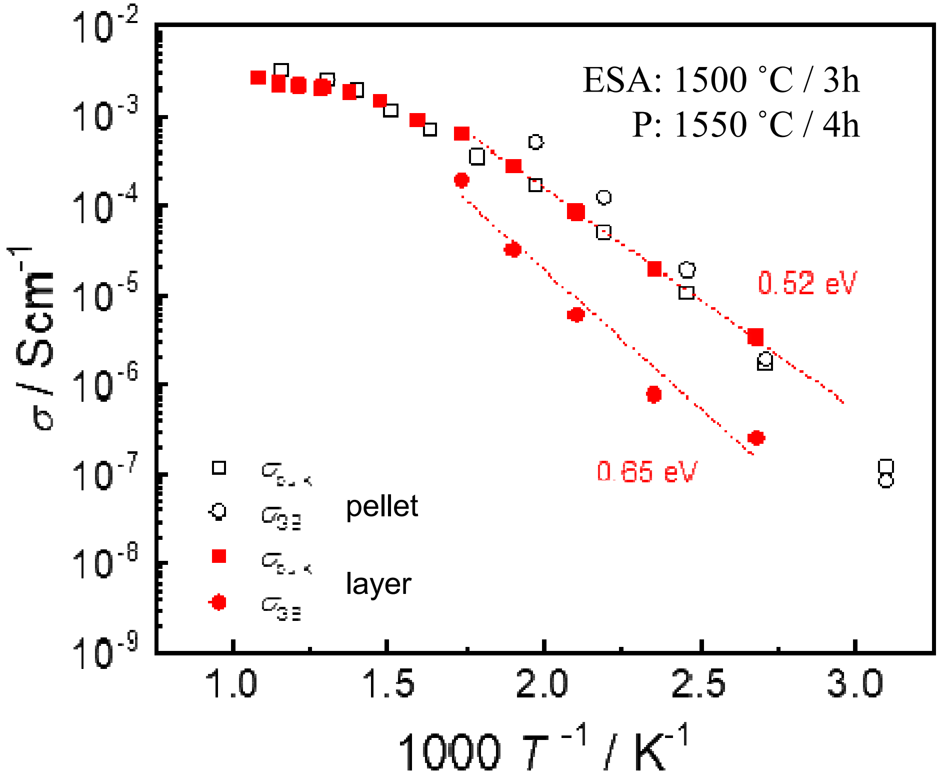




[W. Deibert, M. E. Ivanova, Y. Huang, R. Merkle, J. Maier, W.A. Meulenberg, *Fabrication of multi-layered structures for proton conducting ceramic cells,* J.Mater.Chem.A, 2022, 10, 2362 (2022)]

# CONDUCTIVITY

Max-Planck-Institut
für Festkörperforschung



- ESA1

✓ reduced specimens

✓ Measured in wet $H_2$ ($p_{H2O}$ = 20 mbar)

- Pellets

✓ Measured in wet $N_2$ (700 ˚C- 400 ˚C) and wet 2% $H_2$ at lower T

[W. Deibert, M. E. Ivanova, Y. Huang, R. Merkle, J. Maier, W.A. Meulenberg, *Fabrication of multi-layered structures for proton conducting ceramic cells,* J.Mater.Chem.A, 2022, 10, 2362 (2022)]