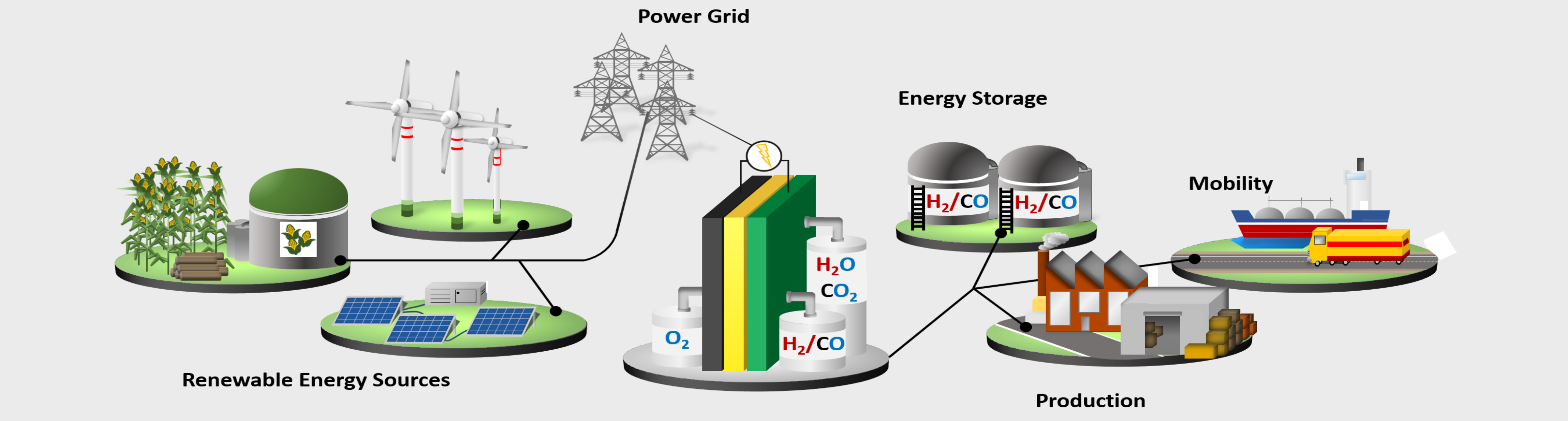


DEVELOPMENT OF PEROVSKITE-BASED ALTERNATIVE FUEL ELECTRODES FOR SOLID OXIDE ELECTROLYSIS CELLS (SOECs)

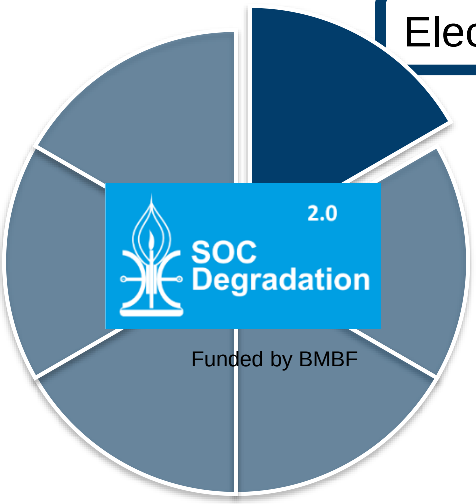
18th International Symposium on Solid Oxide Fuel Cells (SOFC-XVIII)

05/31/23 I F. Winterhalder, Y. A. Farzin, A. Weber, N. H. Menzler

Figure by Stephanie Wolf Forschungszentrum Jülich GmbH – IEK-9

SOC DEGRADATION 2.0

Improving service life of solid oxide cell (SOC) stacks / components



Electrolysis (SOEC) and reversible (rSOC) operation

- Investigation of degradation mechanisms of state-of-the-art materials adopted from SOFCs:
  e.g. Ni cermet fuel electrode, 8YSZ electrolyte, LSC/LSCF oxygen electrode
- Substitution of state-of-the-art materials

8YSZ = 8 mol% Y_2O_3 stabilized ZrO_2, LSC/LSCF = La-Sr-Co(-Fe) oxide

GEFÖRDERT VOM
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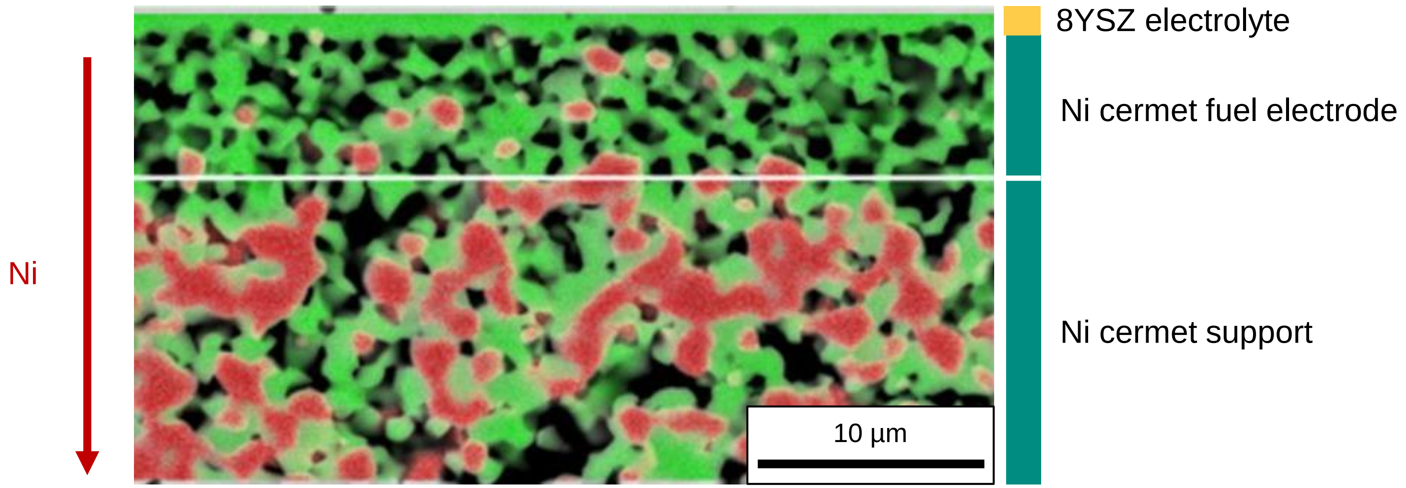
DEGRADATION MECHANISMS OF THE FUEL ELECTRODE DURING HIGH-TEMPERATURE ELECTROLYSIS OPERATION

Degradation mechanisms

- Ni migration
- Ni agglomeration/coarsening
- Segregation of impurities



Ni migration away from the electrolyte/ fuel electrode interface after SOEC operation [a]

* a: Carolin E. Frey et al., J. Electrochem. Soc., 165 (2018)

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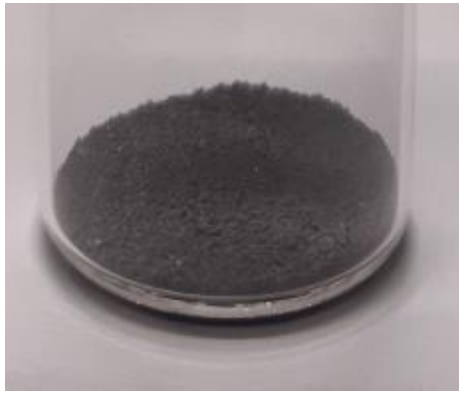
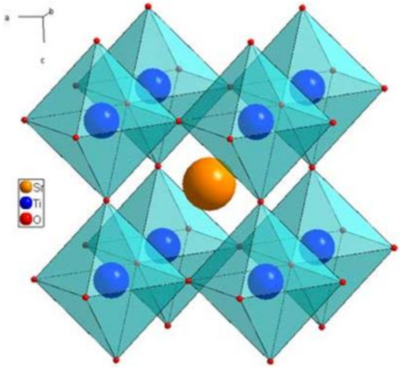
PEROVSKITES AS BASE FOR ALTERNATIVE FUEL ELECTRODES

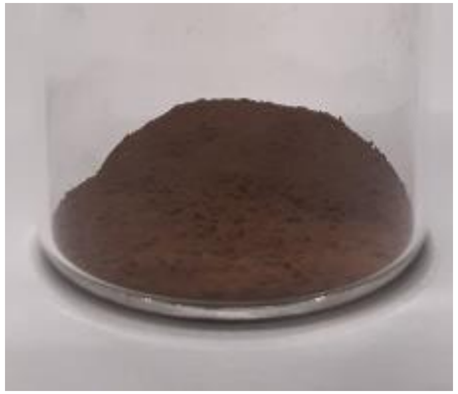
$La_{0.35}Sr_{0.63}TiO_{3-\delta}$ (LST)

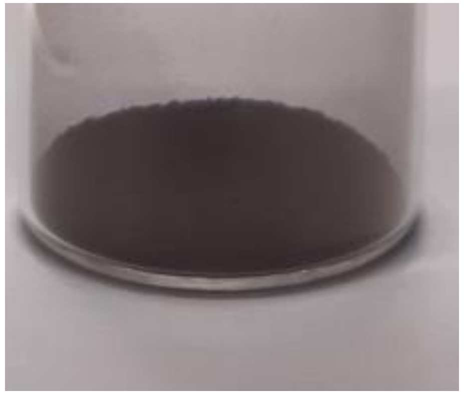


$La_{0.6}Sr_{0.38}Fe_{0.8}Mn_{0.2}O_{3-\delta}$ (LSFM)



$Sr_{1.98}FeNbO_{6-\delta}$ (SFN)





$Sr_{0.98}Ti_{0.7}Fe_{0.3}O_{3-\delta}$ & $Sr_{0.98}Ti_{0.5}Fe_{0.5}O_{3-\delta}$

(3STF & 5STF)

Figure: https://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html -22.05.22

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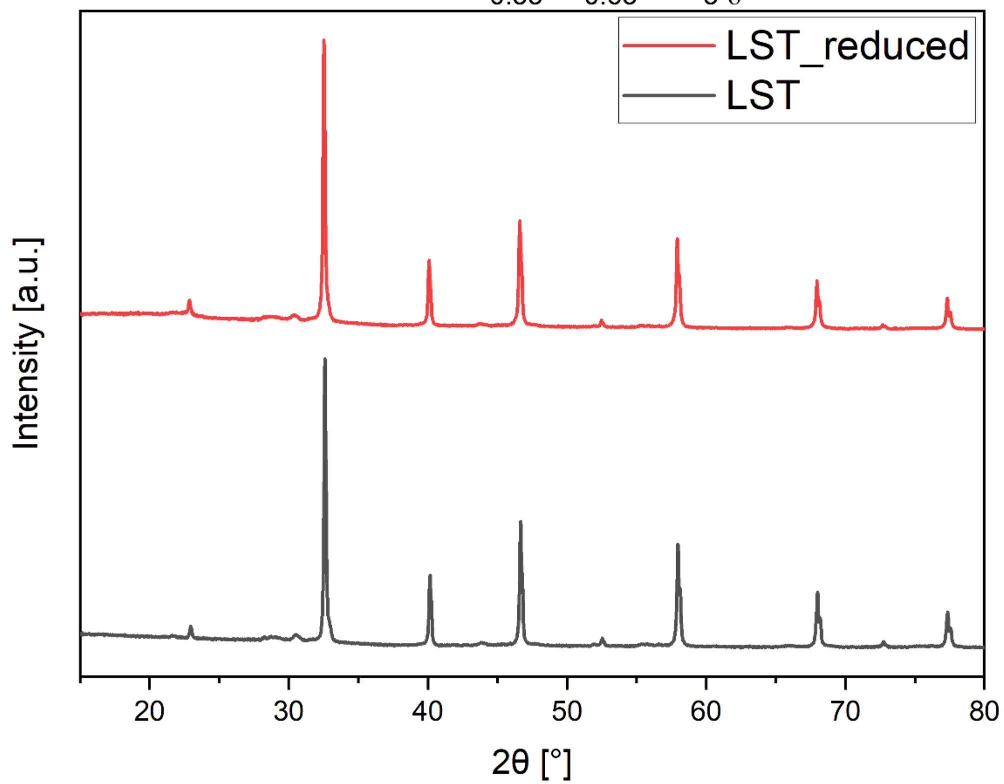
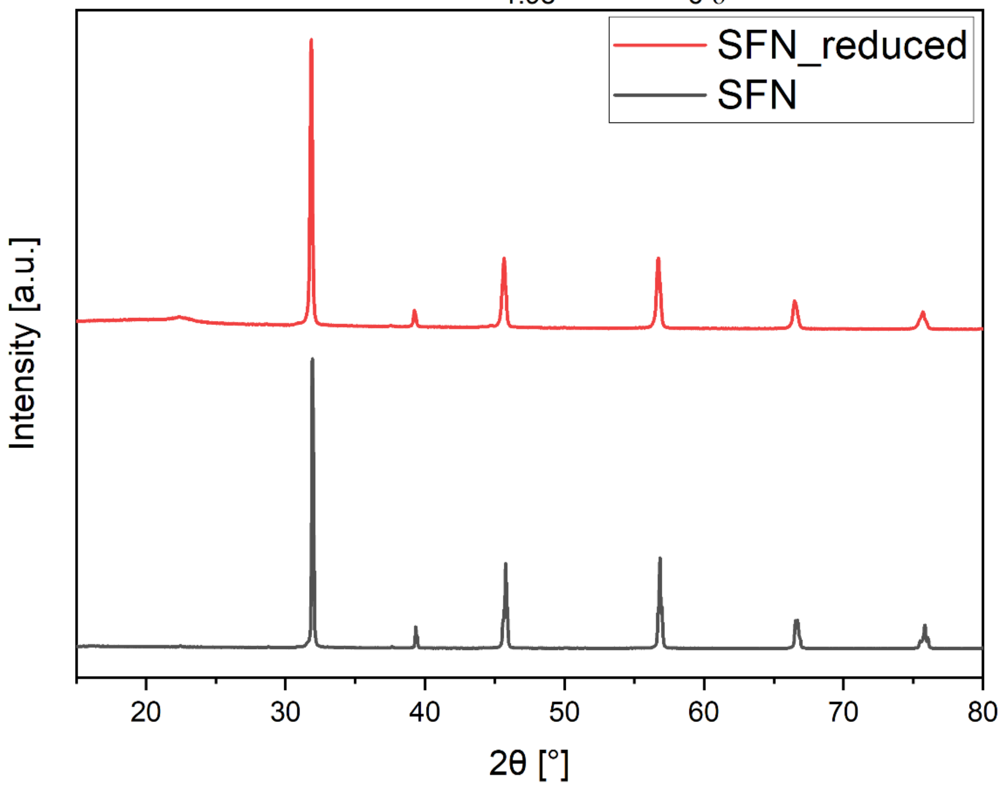
CHEMICAL STABILITY IN 2.9% H_2/Ar @ 850 °C FOR 5 h

LST = $La_{0.35}Sr_{0.63}TiO_{3-\delta}$



SFN = $Sr_{1.98}FeNbO_{6-\delta}$



- No apparent change in the XRD pattern of LST after the reduction
- No apparent change in the peak position; slight changes in the shape of the peak tips of SFN after the reduction

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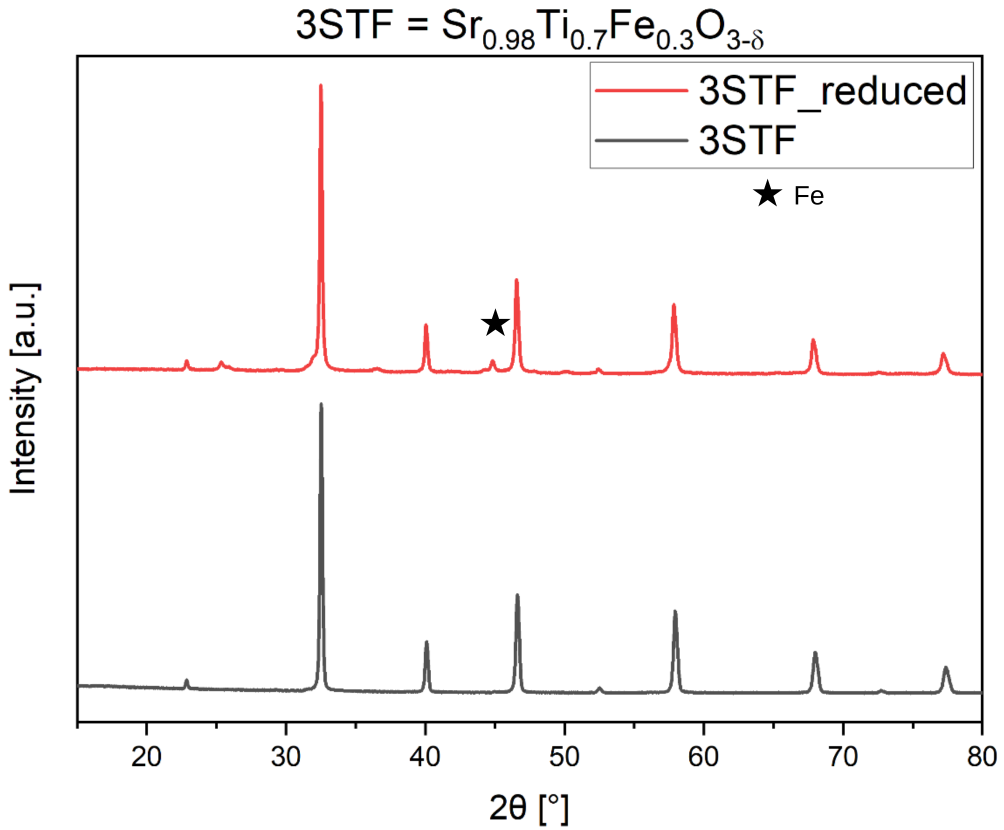
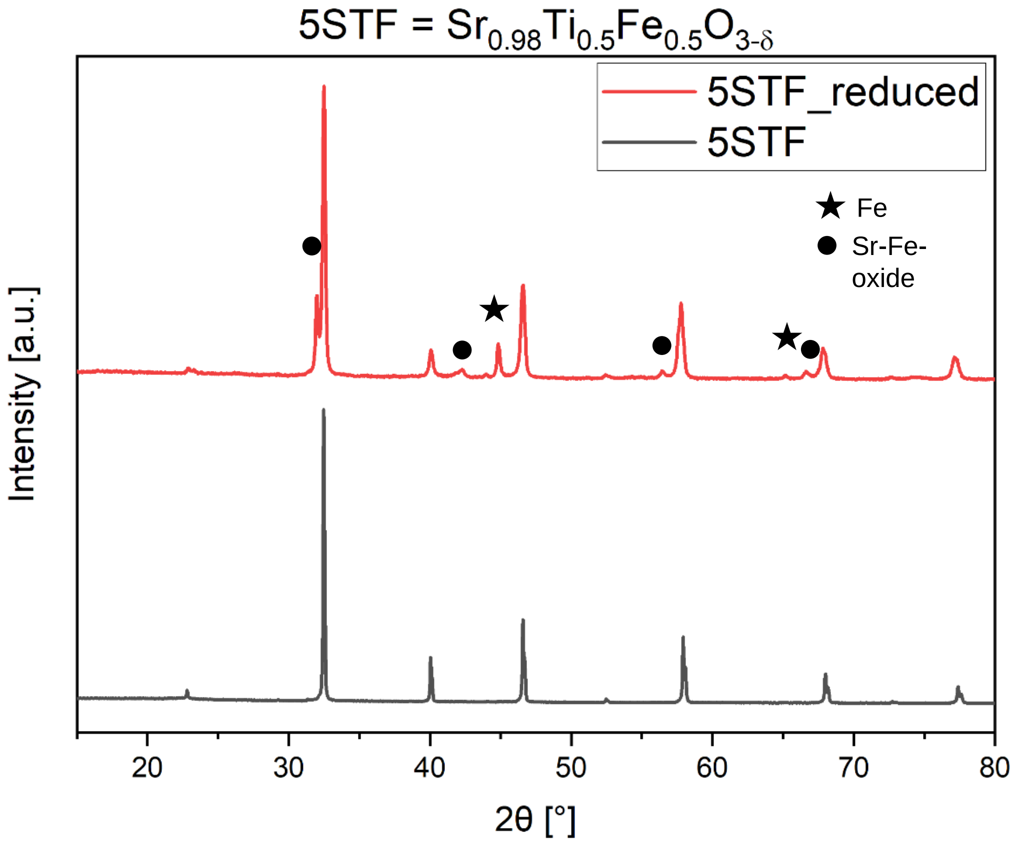
CHEMICAL STABILITY IN 2.9% H_2/Ar @ 850 °C FOR 5 h





- Formation of peaks matching Fe and few other secondary phases after the reduction of 3STF
- Formation of peaks matching mostly Fe and Sr-Fe-oxide secondary phases after the reduction of 5STF

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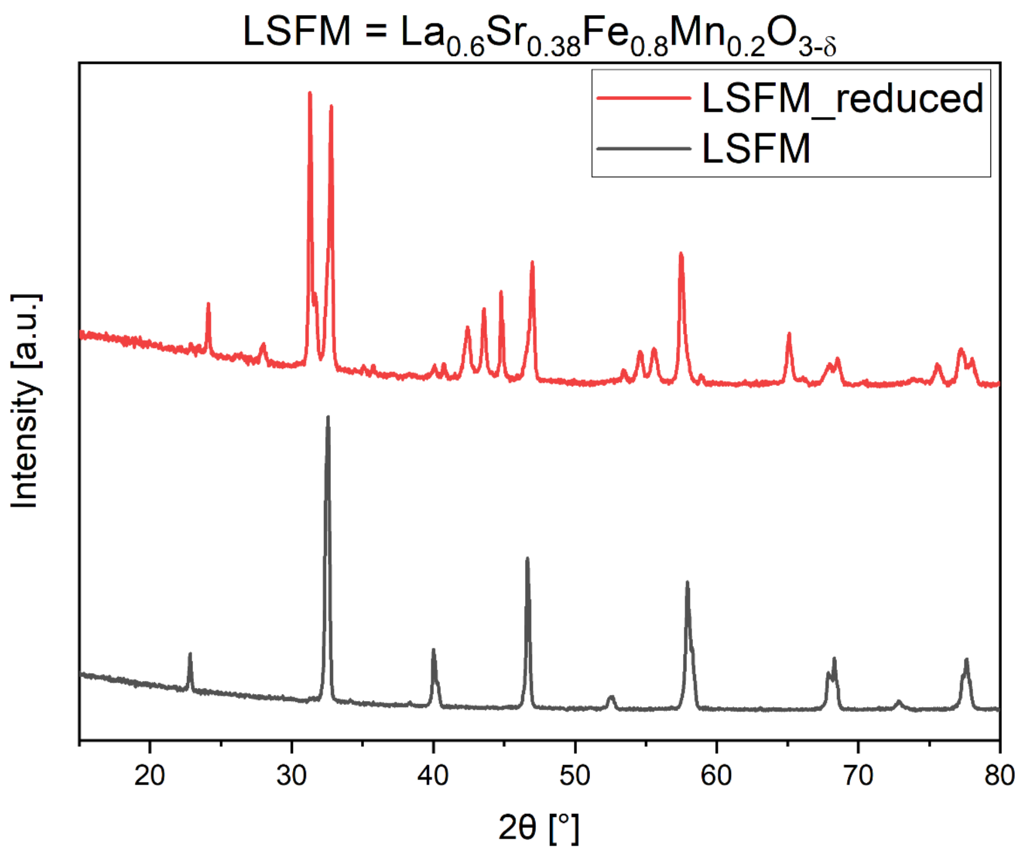
CHEMICAL STABILITY IN 2.9% H_2/Ar @ 850 °C FOR 5 h



- Significant changes after the reduction of LSFM; formation of Fe-Mn, Sr-La-Fe-oxide and layered Sr-La-Mn-oxide secondary phases; loss of original perovskite phase

- **LST** & **SFN** show the **highest chemical stability** under the tested conditions
- **Exsolution** of **metallic Fe** particles on the electrode´s surface might be beneficial regarding the performance of the material

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COMPATIBILITY TESTING BETWEEN THE PEROVSKITES AND 8YSZ

Imitation of manufacturing process of electrode-supported cells using 8YSZ as electrolyte material

1. Mixing of perovskite + 8YSZ electrolyte material (50:50)
2. → Pressing of powder mixtures (uniaxial, samples Ø 10 mm)
3. → Sintering of samples @ 1400 °C for 5 h
4. → SEM analysis of sintered samples
5. → Evaluation of SEM results → secondary phases formed ?

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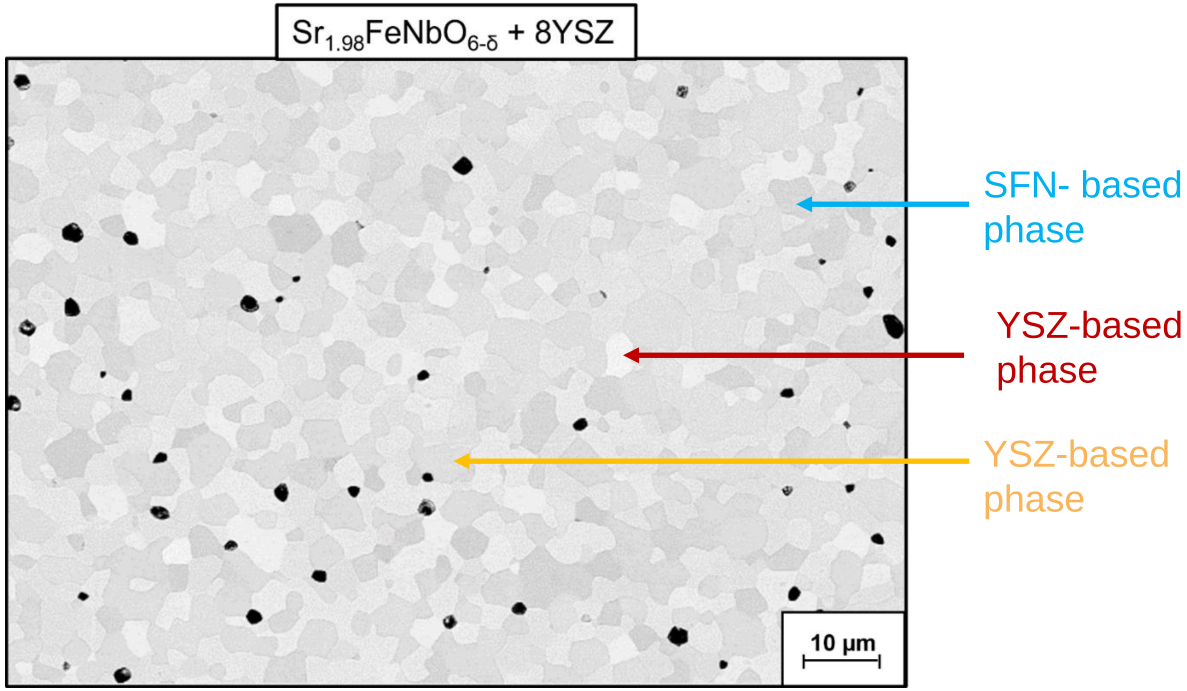
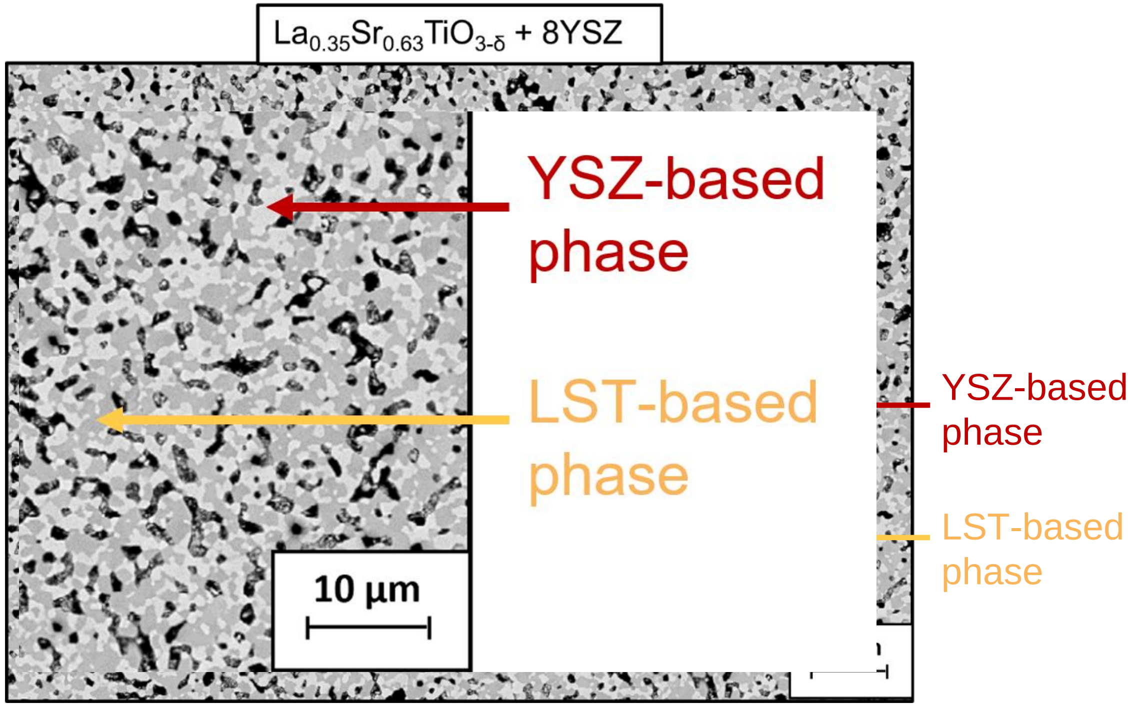
COMPATIBILITY TESTING BETWEEN THE PEROVSKITES AND 8YSZ





- Minor reaction in form of interdiffusion (Fe, Sr, Zr)

- Minor reaction in form of interdiffusion (Y, La, Sr, Ti)

SEM images by Dr. D. Sebold (FZ Jülich, IEK-1).

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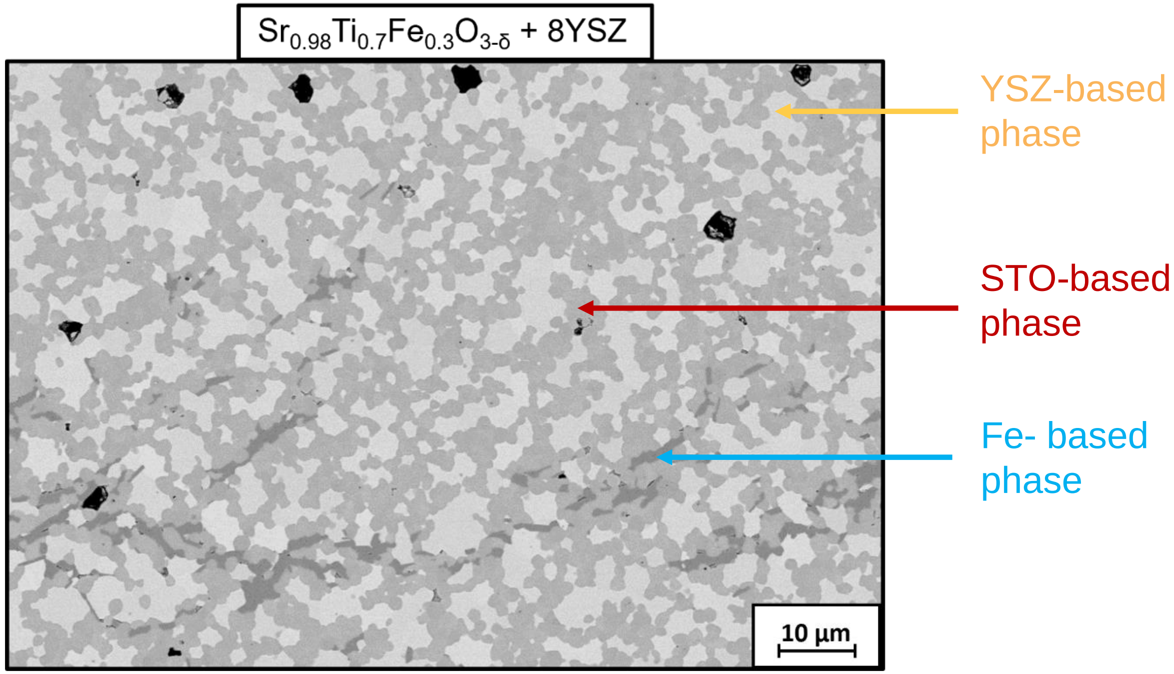
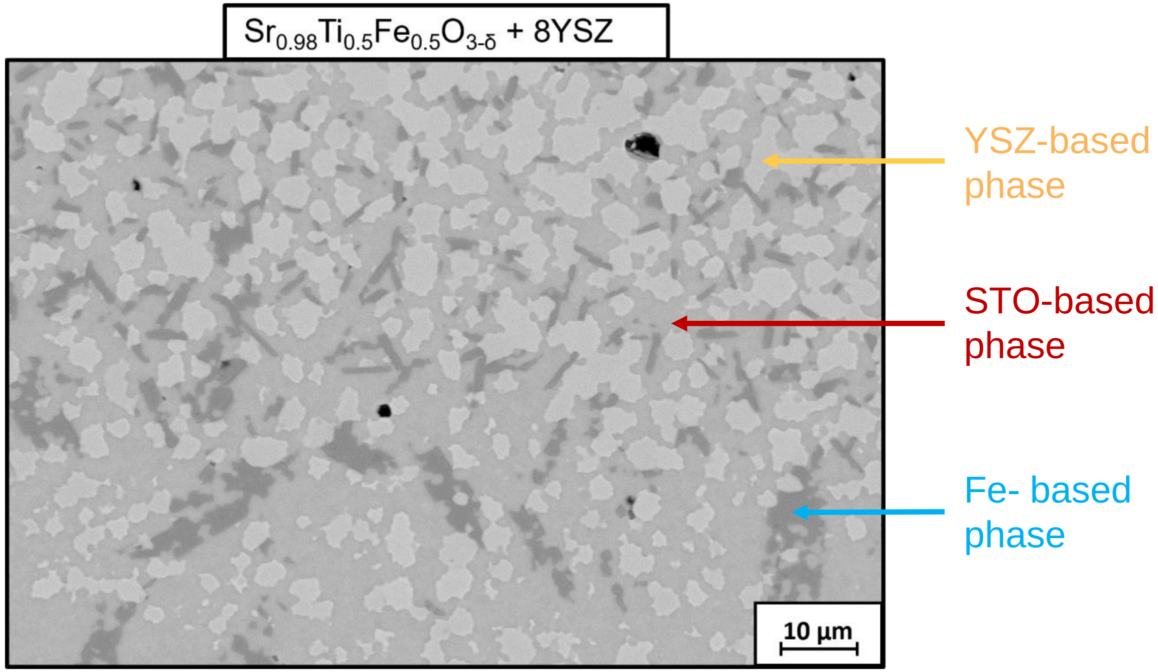
COMPATIBILITY TESTING BETWEEN THE PEROVSKITES AND 8YSZ





- Minor reaction in form of interdiffusion (Fe, Ti, Zr, Y, Sr) & formation of Fe-based secondary phase
- Minor reaction in form of interdiffusion (Y, Zr, Sr, Ti) & formation of Fe-based secondary phase

Left SEM image by Dr. D. Sebold (FZ Jülich, IEK-1).

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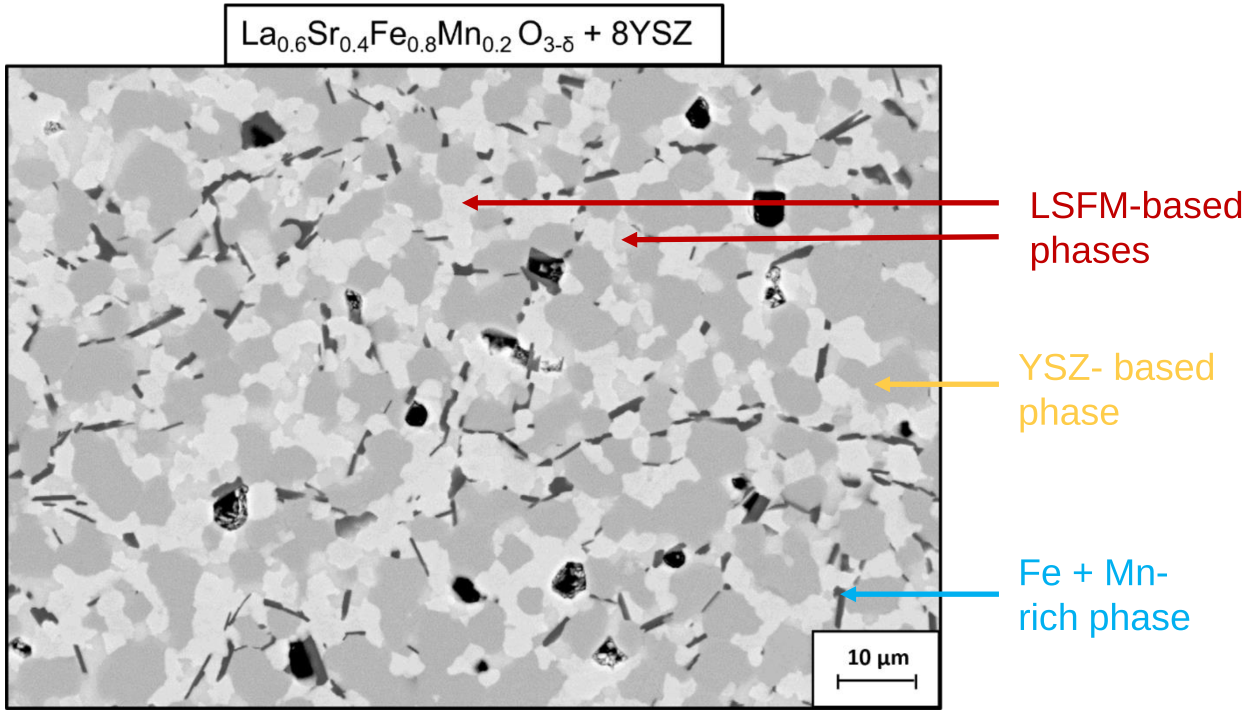
COMPATIBILITY TESTING BETWEEN THE PEROVSKITES AND 8YSZ



- Reaction in form of interdiffusion (Mn, Zr, Y, Fe, Sr, La) & formation of Fe+ Mn-based secondary phase

- (Minor) chemical reactions for all 5 powders with 8YSZ electrolyte @ 1400 °C
- Use of a barrier layer between electrolyte and electrode necessary

SEM image by Dr. D. Sebold (FZ Jülich, IEK-1).

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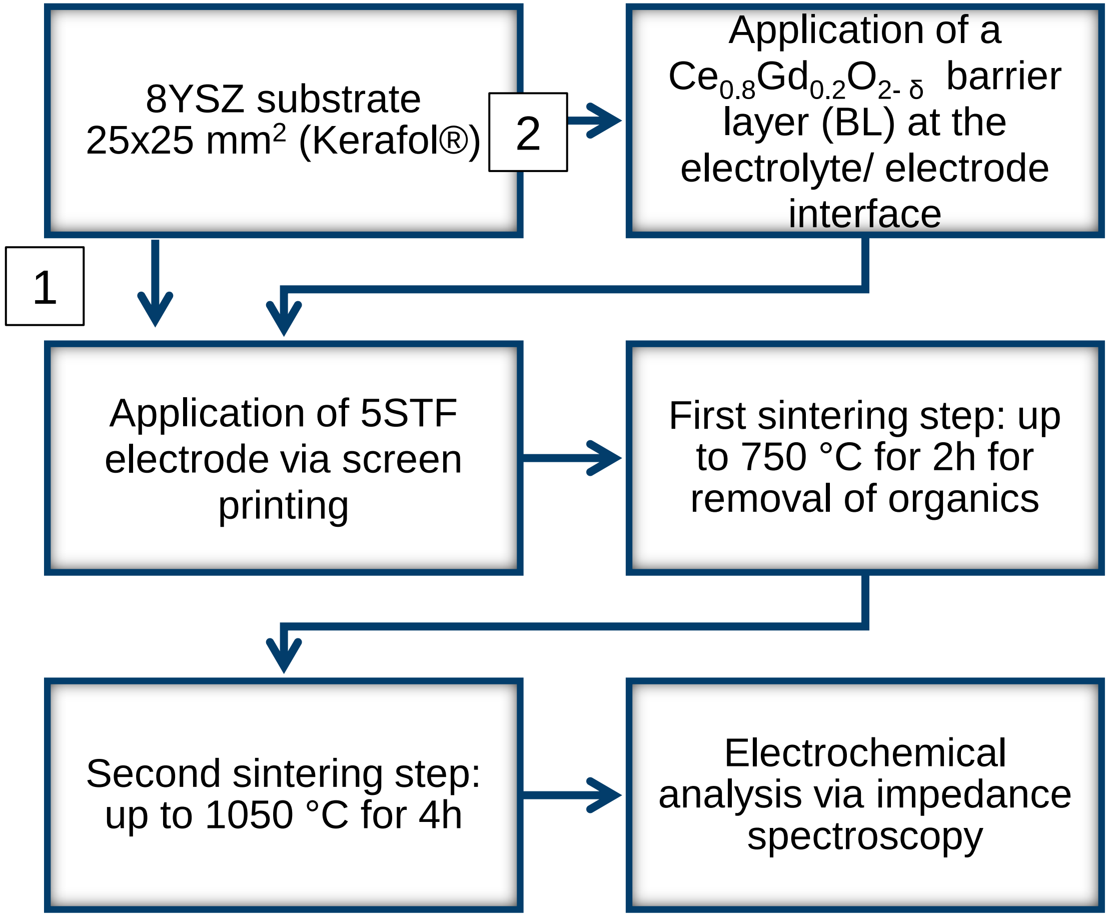
ELECTROCHEMICAL ANALYSIS OF SYMMETRICAL ESCs USING 5STF AS ELECTRODE MATERIAL

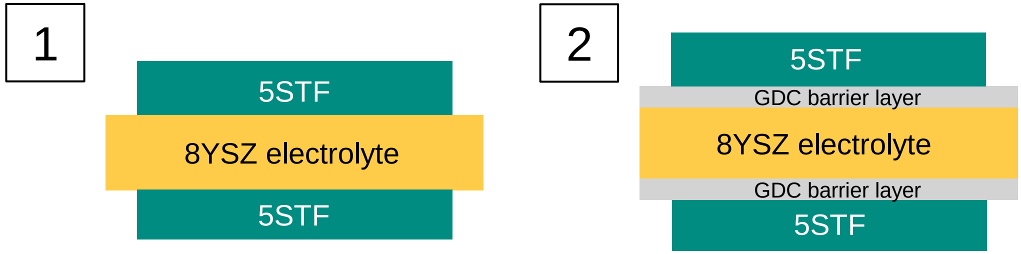


Impedance parameters

OCV condition @ 800 °C

Frequency: 0.01 Hz to 1 MHz

Atmospheres: 50% H_2 + 50% H_2O & 97% H_2 + 3% H_2O



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SOC Degradation 2.0

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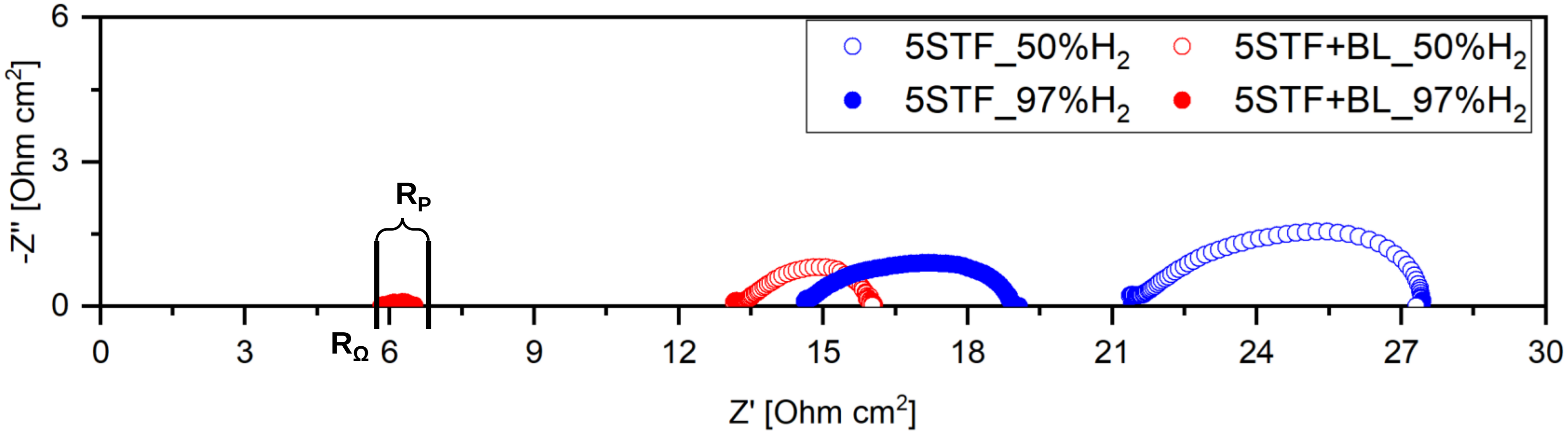
INFLUENCE OF OXYGEN PARTIAL PRESSURE ON CELL RESISTANCES

Nyquist-plot of pre-reduced symmetrical ESCs with and without a GDC barrier layer (BL), measured at OCV at 800 °C



Pre-reduced = heated up + holding time at 800°C in 97% H_2 before measurement

5STF = $Sr_{0.98}Ti_{0.5}Fe_{0.5}O_{3-\delta}$

GDC = $Ce_{0.8}Gd_{0.2}O_{2-\delta}$

Cell type	R_P @ 50%H_2/H_2O	R_P @ 97%H_2/H_2O
With BL	≈2.90 $\Omega\cdot cm^2$	≈0.70 $\Omega\cdot cm^2$
Without BL	≈6.00 $\Omega\cdot cm^2$	≈4.40 $\Omega\cdot cm^2$

Electrochemical testing by Dr. Y. Farzin (KIT, IAM-ET).

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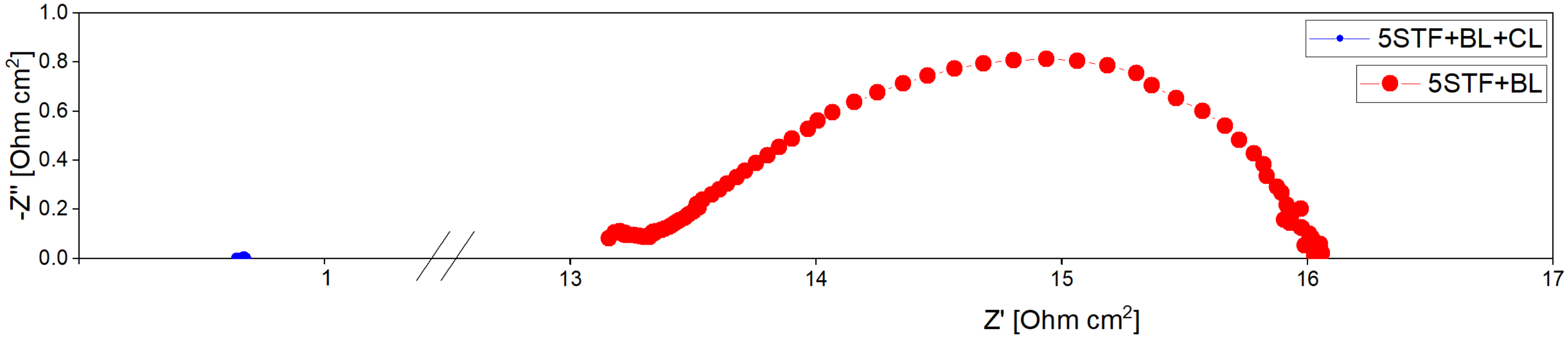
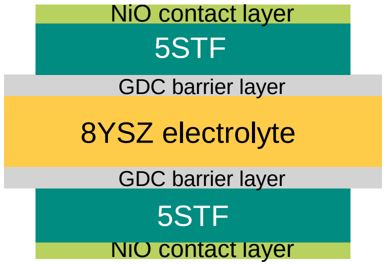
INFLUENCE OF A NiO CONTACT LAYER ON CELL RESISTANCES

Nyquist-plot of pre-reduced symmetrical ESCs with GDC barrier layer with and without a NiO contact layer (CL), measured at OCV at 800°C





Pre-reduced = heated up + holding time at 800°C in 97% H_2 before measurement

Cell type	R_P	R_Ω
With BL	≈2.90 Ω·cm²	≈13.20 Ω·cm²
With BL + CL	≈0.06 Ω·cm²	≈0.60 Ω·cm²

5STF = $Sr_{0.98}Ti_{0.5}Fe_{0.5}O_{3-\delta}$

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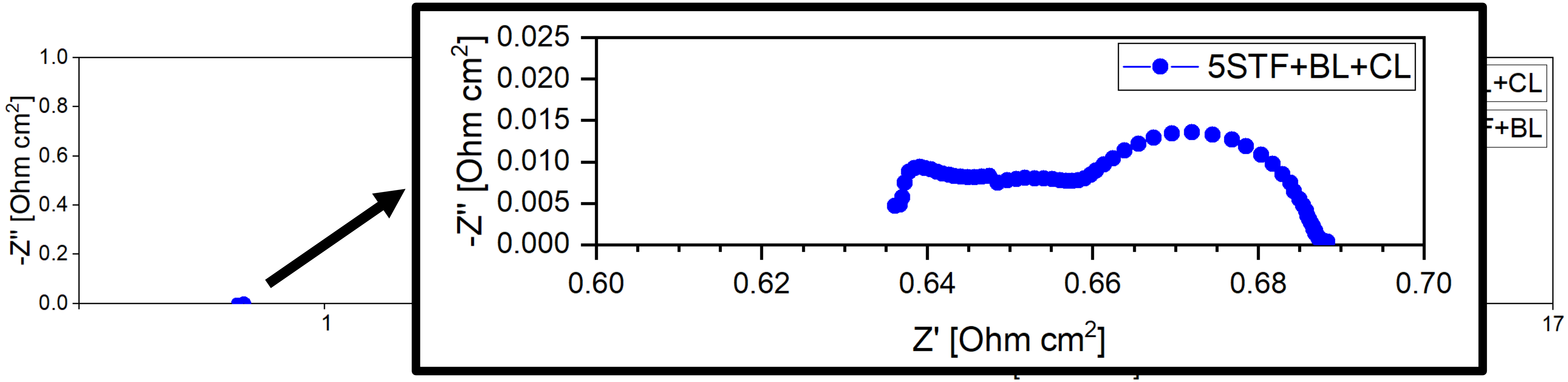

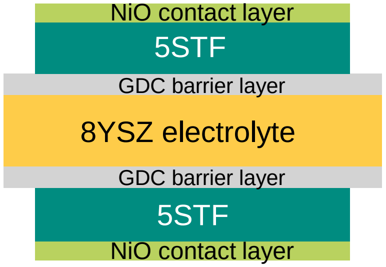

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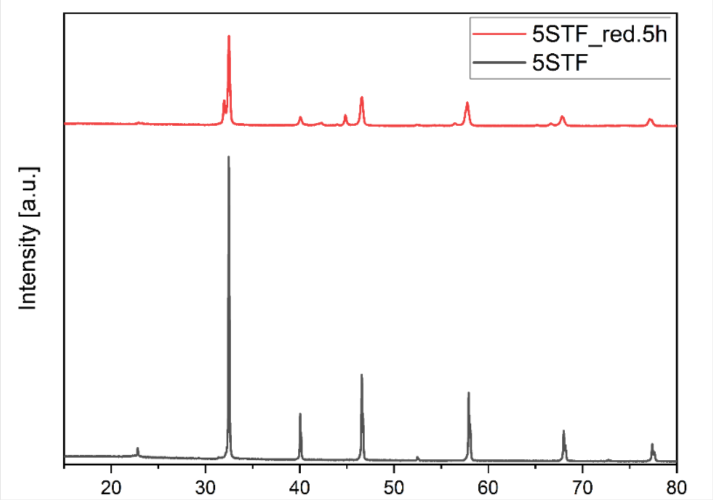
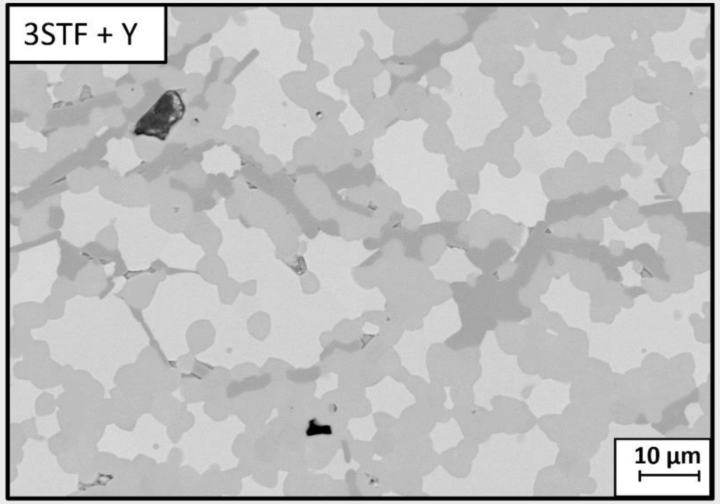
SUMMARY

Chemical stability under reduced conditions



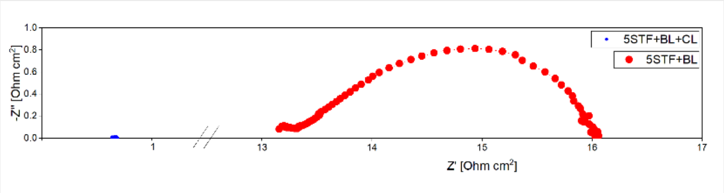
- LST & SFN chemical stable in tested conditions
- Exsolution of Fe → possible enhancement?

Compatibility with 8YSZ electrolyte



- Barrier layer between electrolyte and electrode necessary

Electrochemical measurements using a 5STF electrode



- Barrier layer between electrolyte and electrode necessary
- Contact layer between electrode and current collector necessary

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Funding by BMBF (SOC Degradation2.0)

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SOC Degradation 2.0

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