Study of Detailed Degradation Behavior of Solid Oxide Electrolyzer Cells (SOEC)

Günter Schiller[1], Michael Hörlein[1], Frank Tietz[2], K.A. Friedrich[1]

[1]German Aerospace Center (DLR),
Institute of Engineering Thermodynamics, Stuttgart, Germany

[2]Forschungszentrum Jülich (JÜLICH)
Institute for Energy and Climate Research
Materials Synthesis and Processing (IEK-1)

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Outline

- Introduction: Need for energy storage
  Principle of solid oxide electrolysis
- Motivation and concept
- Cell manufacturing and characterization
- Degradation study and results from post-mortem analyses
- Conclusion

Storage of Electricity from Renewable Energy Sources

- Need for energy storage
  → Increasing fluctuating power generation
  → Mobile applications

- Electrical energy difficult to store
  → Conversion to chemical energy

- Water electrolysis: $H_2O + W_{el} \rightarrow H_2 + ½ O_2$

- Solid oxide electrolysis is one possible conversion technology

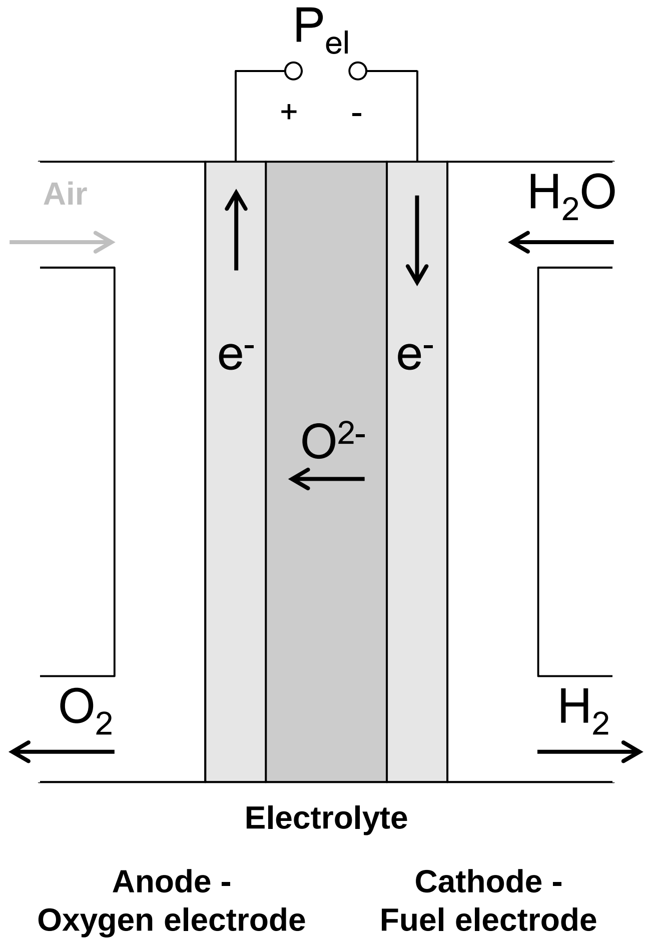
Principle of Solid Oxide Electrolysis

Advantages:

- High temperature (600 - 900° C)
  - Fast reaction kinetics
  - Low overvoltage
  - High efficiency & high current densities
- No noble metals as catalysts
- Fuel versatility: CO_2 electrolysis
  - → Co-electrolysis of H_2O/CO_2 possible
  - → Syn-gas production
  - → External (or internal) hydrocarbon formation

Problem:

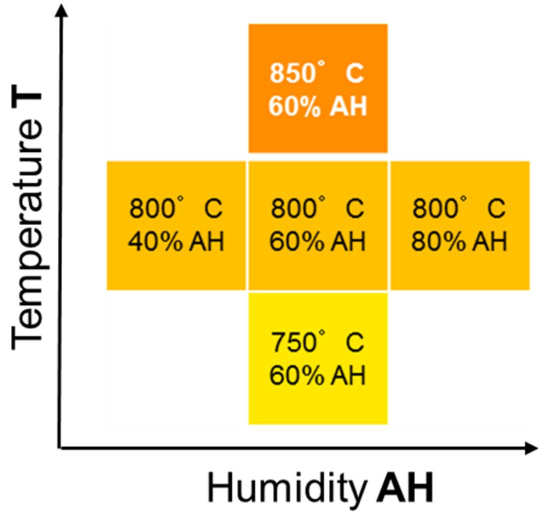
Low longevity - Degradation



Present Work – Motivation and Concept

Systematic study: operating parameter → degradation

- Temperature (T)
- Fuel gas humidity (AH)
- Current density (i)



Experimental concept:

- Degradation experiments for 1000 h
- Test rig – quadruple cell measurement

  → Identical temperature, gas supply (and also incidents)

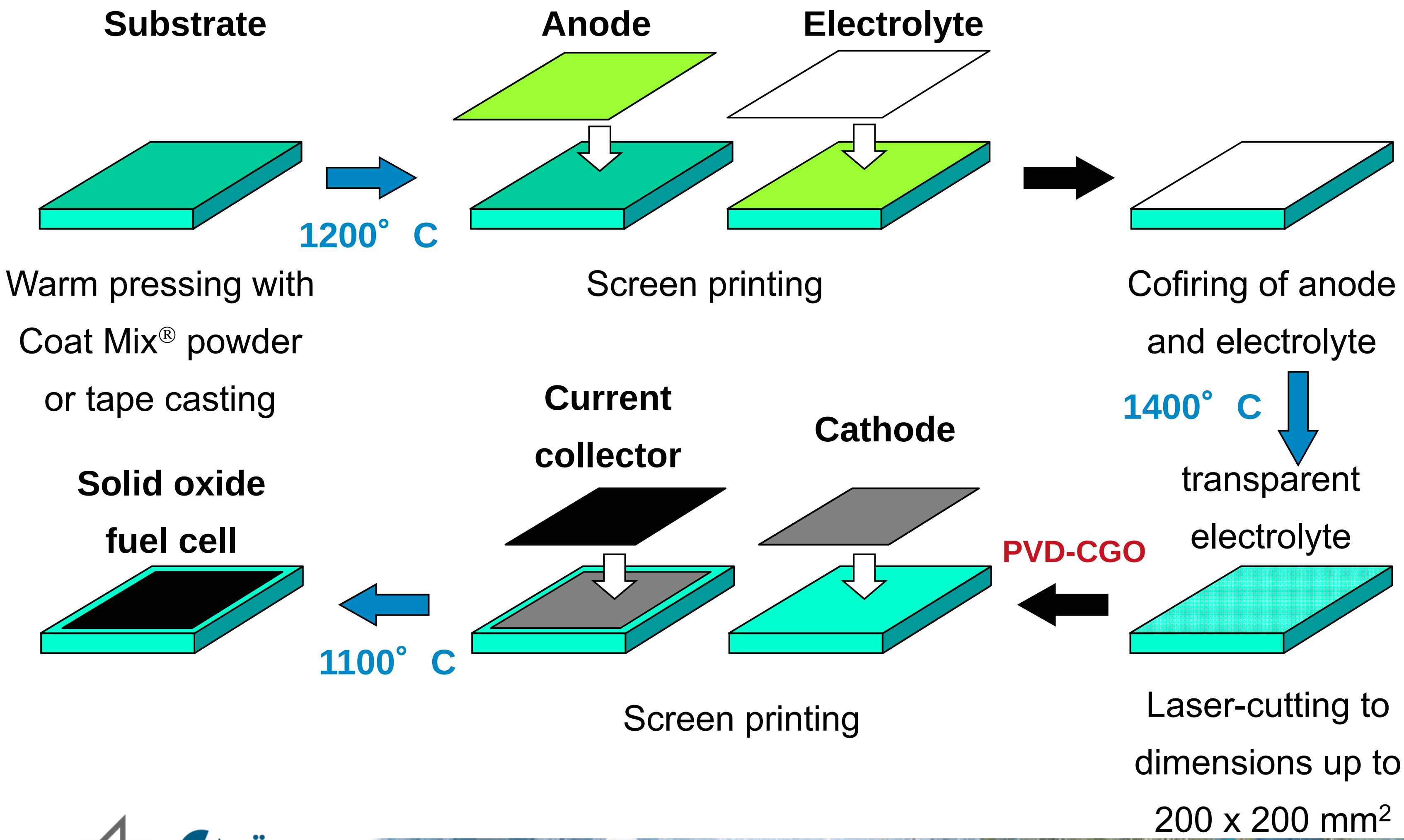
  → Four different current densities simultaneously
- Fuel electrode supported cells from FZ Jülich and CeramTec

  → Ni-8YSZ support | Ni-8YSZ | 8YSZ | CGO | LSCF

Objectives

- To gain fundamental understanding of degradation processes
  - → Distinguish between degradation processes
  - → Identify degradation mechanisms
  - → Correlate them with operating parameters
- To optimize cells for electrolysis operation
- To adapt operating parameters for low degradation

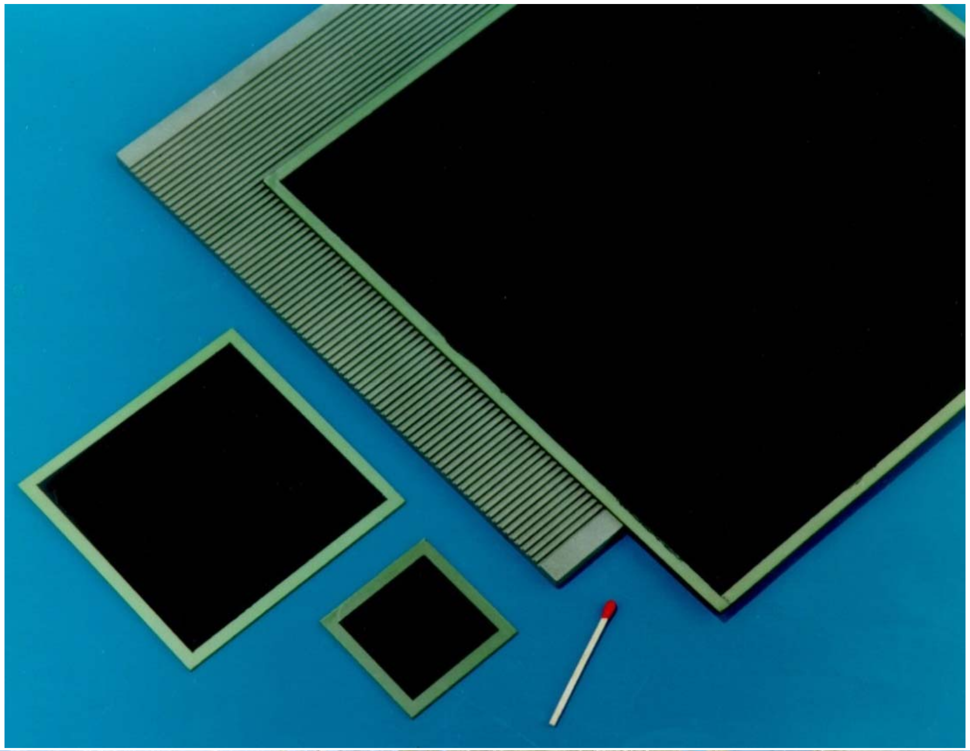
Manufacturing Steps of SOFC Anode-Supported Cells



Solid Oxide Electrolyser Cells: Planar Design

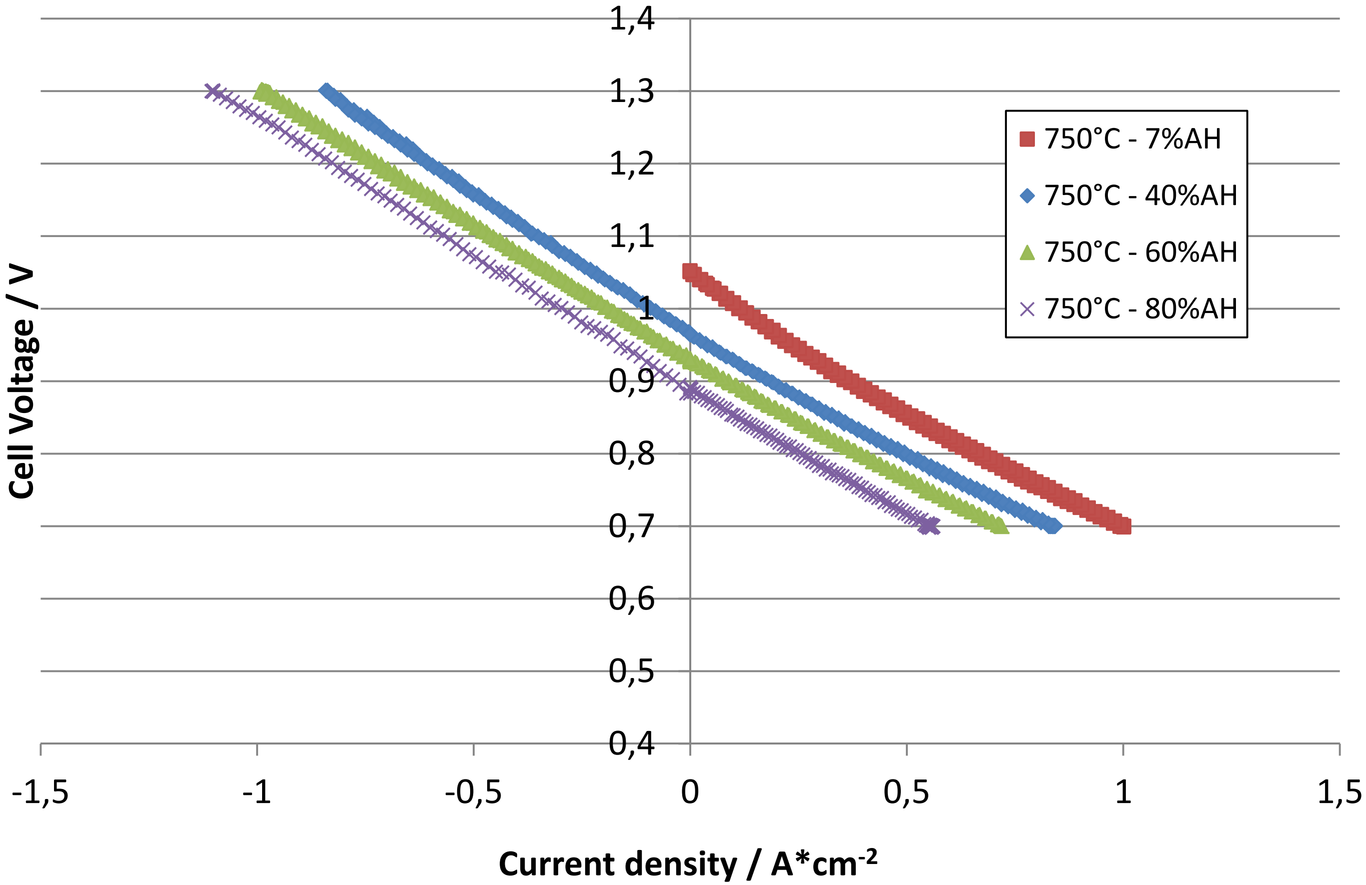
Materials

Anode:	$(La,Sr)(Fe,Co)O_3$
Diffusion barrier:	CGO – 1-5 µm
Electrolyte:	8YSZ – 5-10 µm
Cathode:	Ni/YSZ
Cathode Substrate:	Ni/YSZ



I-V Curves at 750 ° C as a Function of Steam Content

(Flow rates: 2 l/min H_2/H_2O, 3 l/min air)



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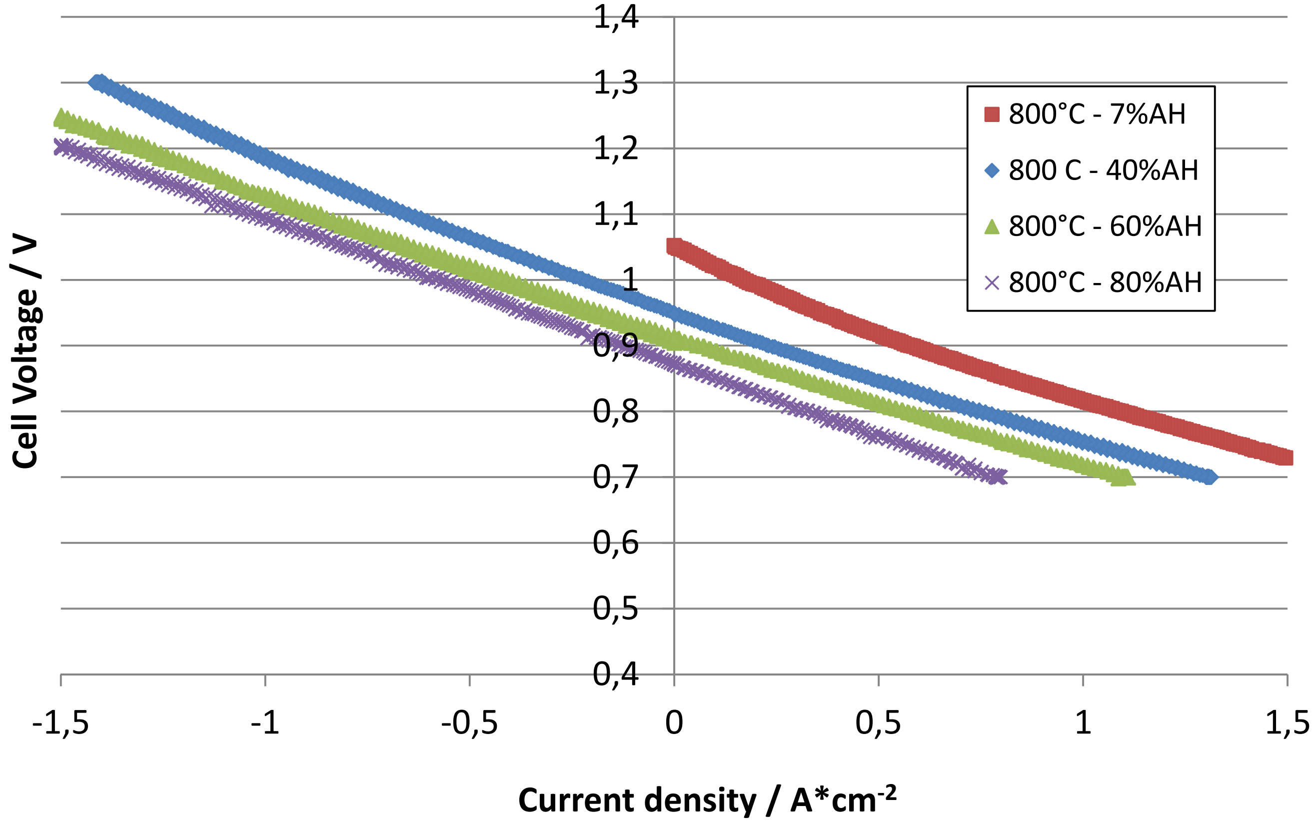
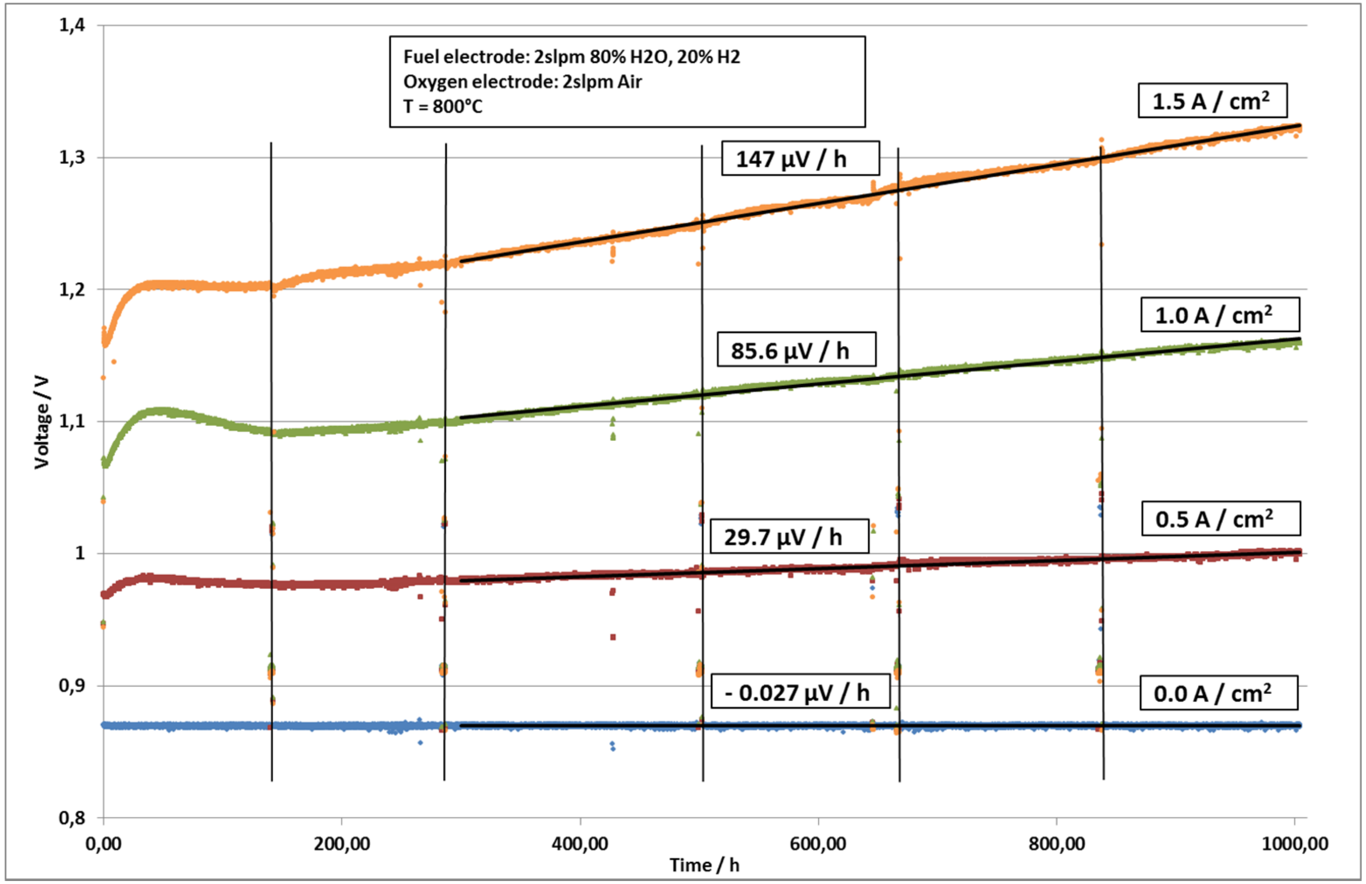
I-V Curves at 800 ° C as a Function of Steam Content
(Flow rates: 2 l/min H_2/H_2O, 3 l/min air)



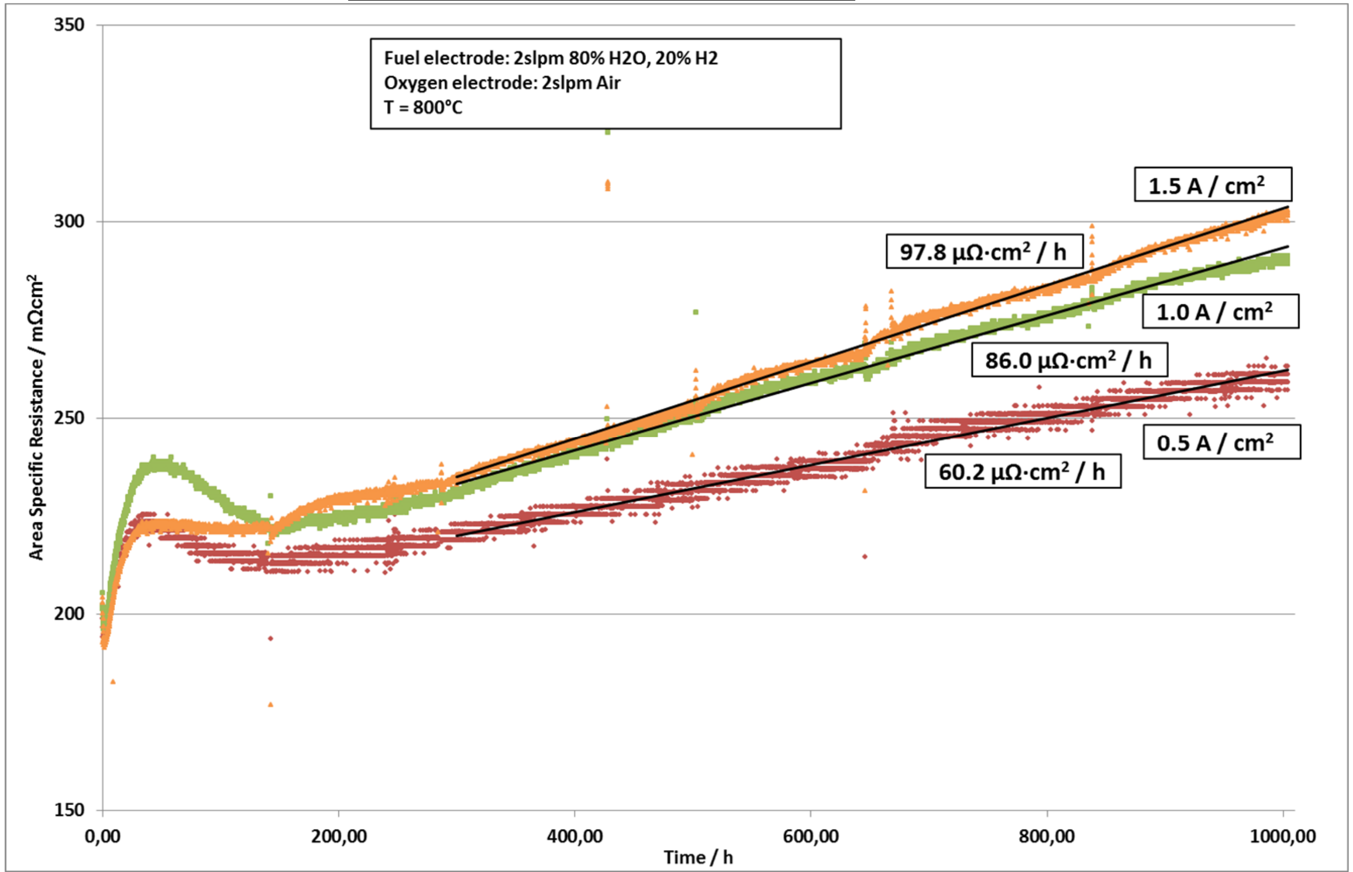
Degradation Experiment and Impedance Data Interpretation



- 4 cells measured simultaneously at different current densities
- Linear degradation after initial phase
- Be careful with interpretation of voltage degradation rate

Degradation Experiment and Impedance Data Interpretation

$$ASR(t) = \frac{U(t) - OCV}{i(t)}$$

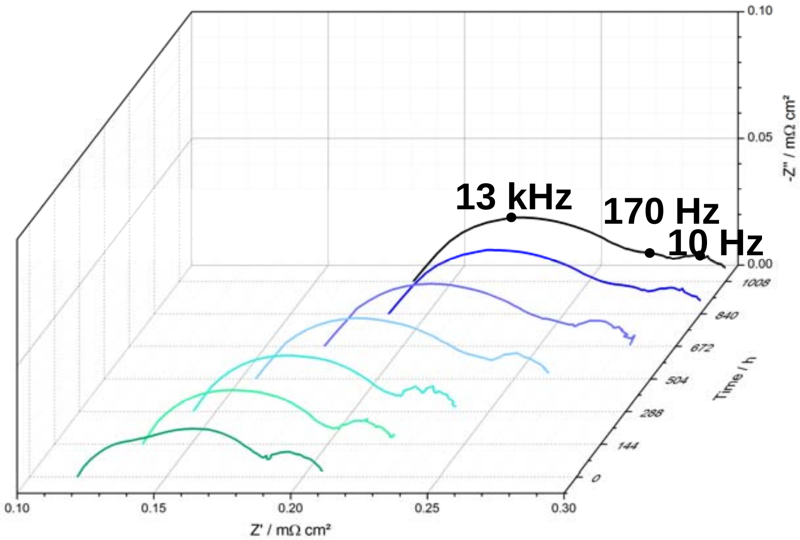


- Degradation rate at 1.5 A/cm² only 13 % higher than at 1.0 A/cm²
- Degradation rate at 0.5 A/cm² significantly lower
- ASR degradation rate about 30% compared to 3% voltage degradation (per 1000 h @ 0.5 A/cm²)

Degradation Experiment and Impedance Data Interpretation

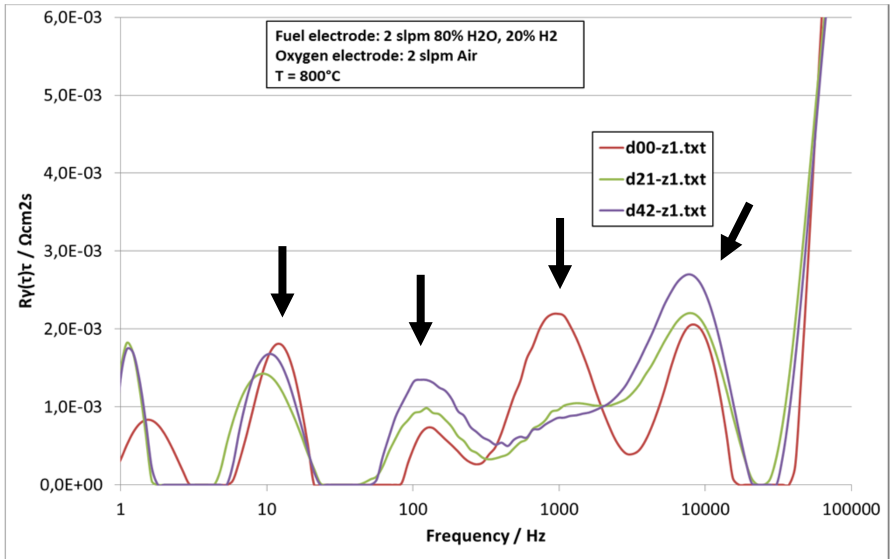
Method 1: DRT-Analysis with parameter variation

Impedance - Spectra



Levenberg-Marquardt algorithm

DRT-Spectra



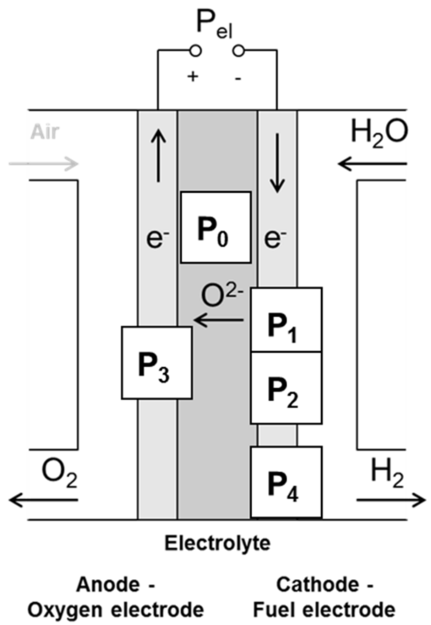
Information for improved CNLS fitting

Degradation Experiment and Impedance Data Interpretation

Method 2: Physico-chemical modelling

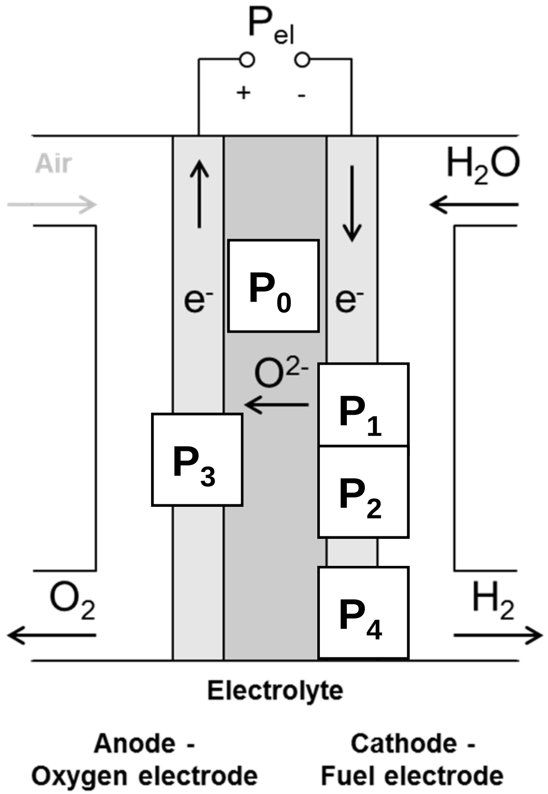
5 rate limiting processes:

- Ohmic contributions
- First Fuel Electrode (FE) Process: 1-2·10^4 Hz
  Charge transfer reaction at TPB coupled with ionic transport in porous electrode geometry
- Second Fuel Electrode (FE) Process: approx. 1·10^3 Hz
  Charge transfer coupled at TPB
- Oxygen Electrode Process: 1-2·10^2 Hz
- Mass transport limitation: 1-2·10^1 Hz
  Diffusion through FE-support along with gas conversion



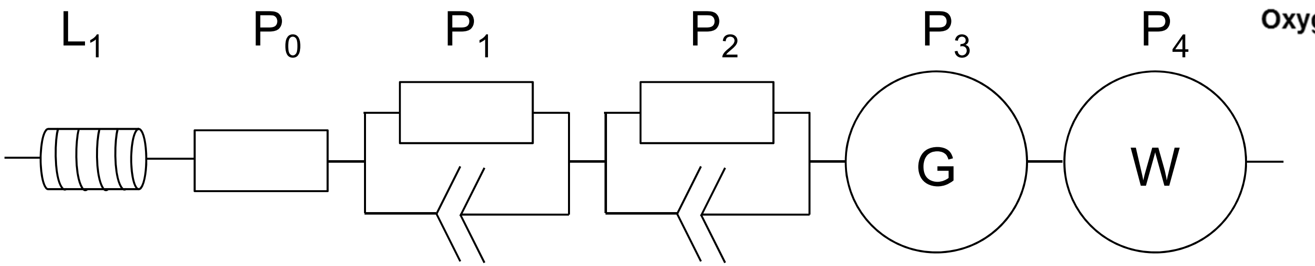
→ Both methods are in good agreement!

Degradation Experiment and In-situ Data Interpretation

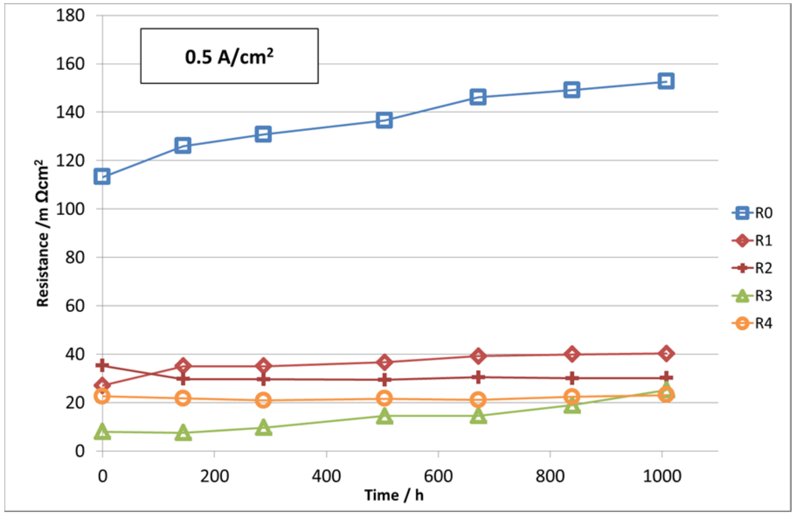


Equivalent circuit model

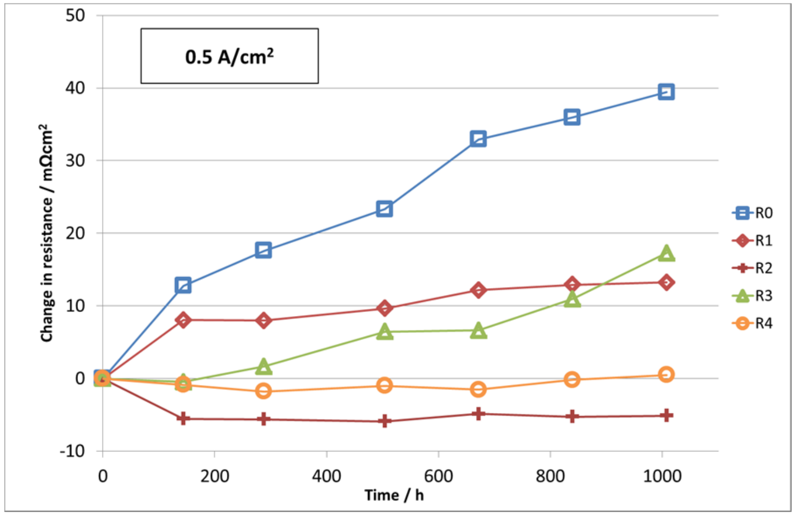
- L_1: High frequency induction
- P_0: Ohmic resistance (> 10^5 Hz)
- P_1: Fuel electrode process A (~ 10^4 Hz)
- P_2: Fuel electrode process B (~ 10^3 Hz)
- P_3: Oxygen electrode process (~ 10^2 Hz)
- P_4: Fuel electrode mass transport (~ 10^1 Hz)



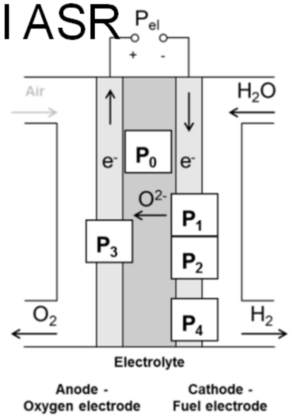
Influence of Current Density on Degradation



ΔR

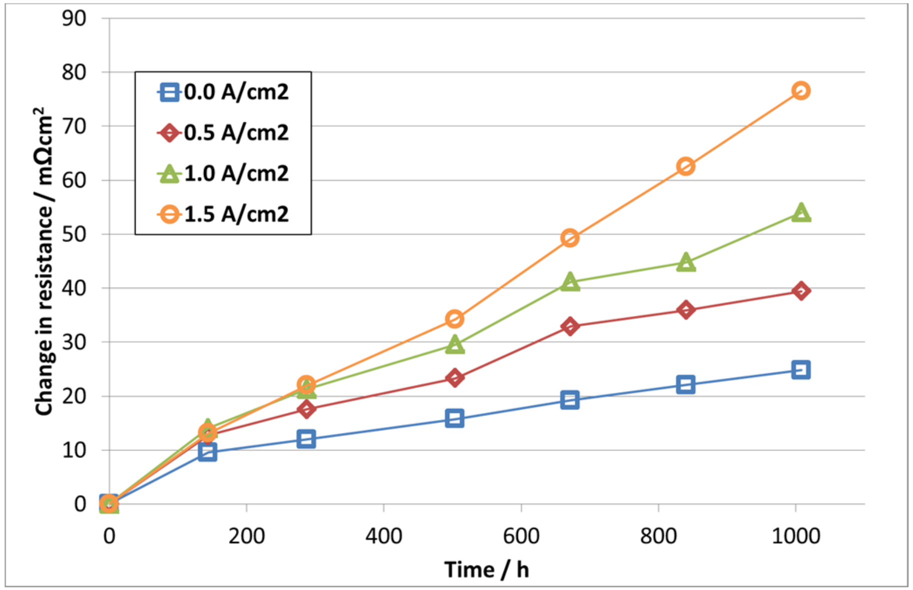


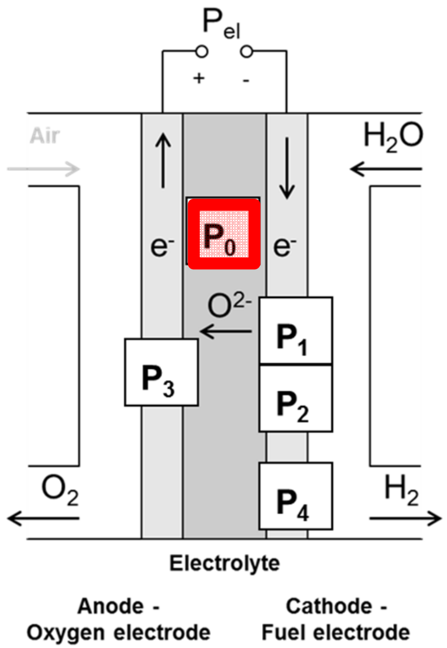
- Ohmic resistance contributes more than 50% of total ASR



- Degradation of ohmic resistance is most severe
- Oxygen electrode has small ASR but high contribution to degradation
- Fuel electrode process 1 degrades while process 2 improves performance

Influence of Current Density on Degradation

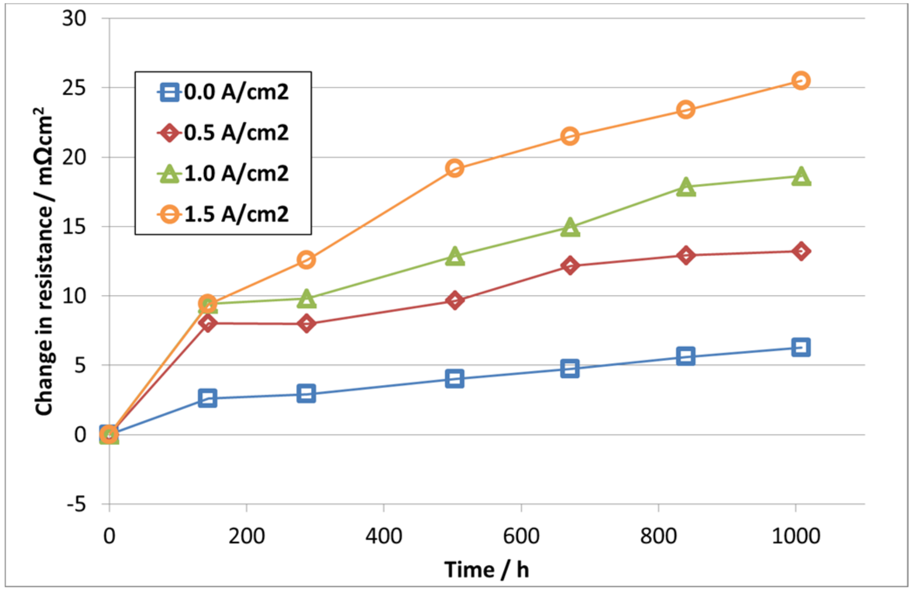


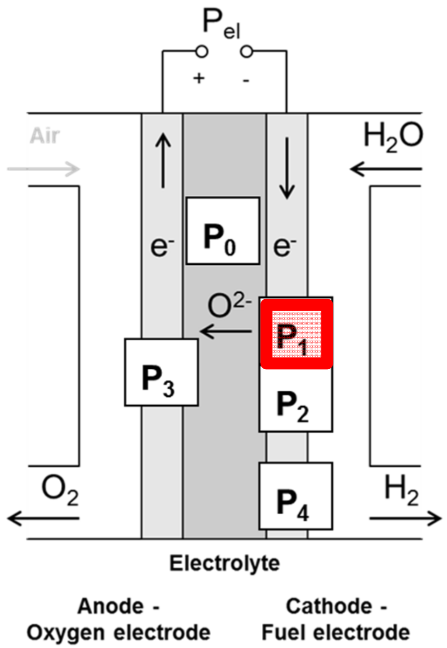


P_0: Ohmic resistance

- Obvious correlation with current density
- Linear degradation with time

Influence of Current Density on Degradation

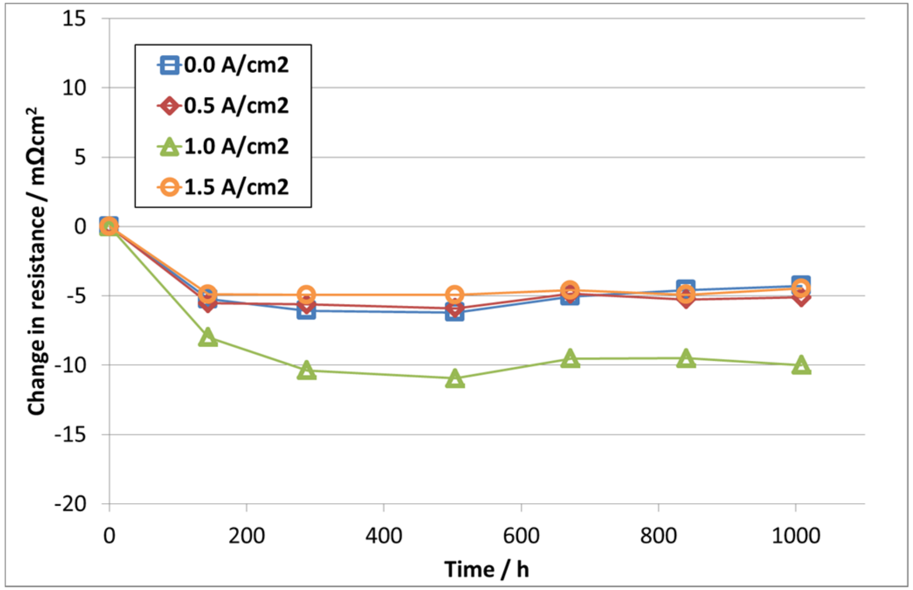


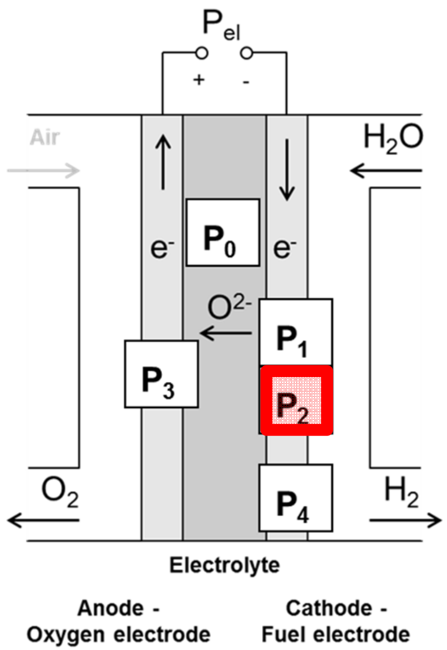


P_1: Fuel electrode process 1

- Also obvious correlation with current density
- Degradation initially fast but slowing down with time

Influence of Current Density on Degradation

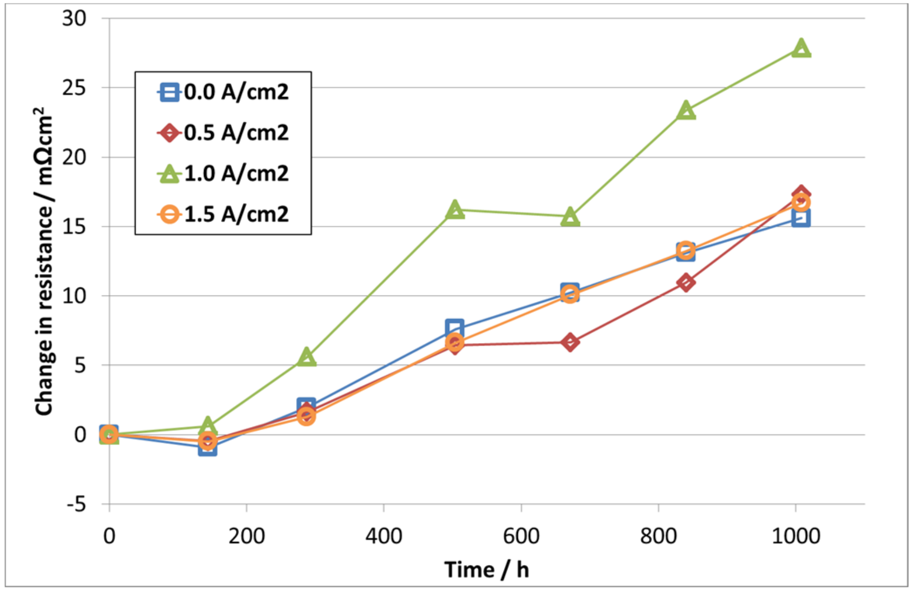


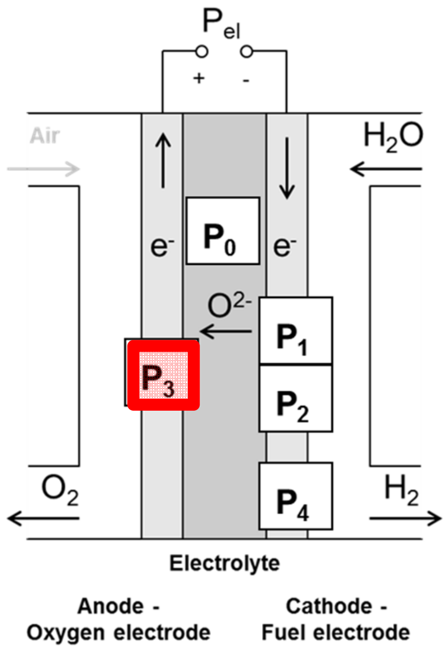


P_2: Fuel electrode process 2

- Offset of 1.0 A/cm² curve is likely artifact (compare process 3)
- Degradation independent of current density
- Initial improvement of performance
- Very stable after initial change

Influence of Current Density on Degradation

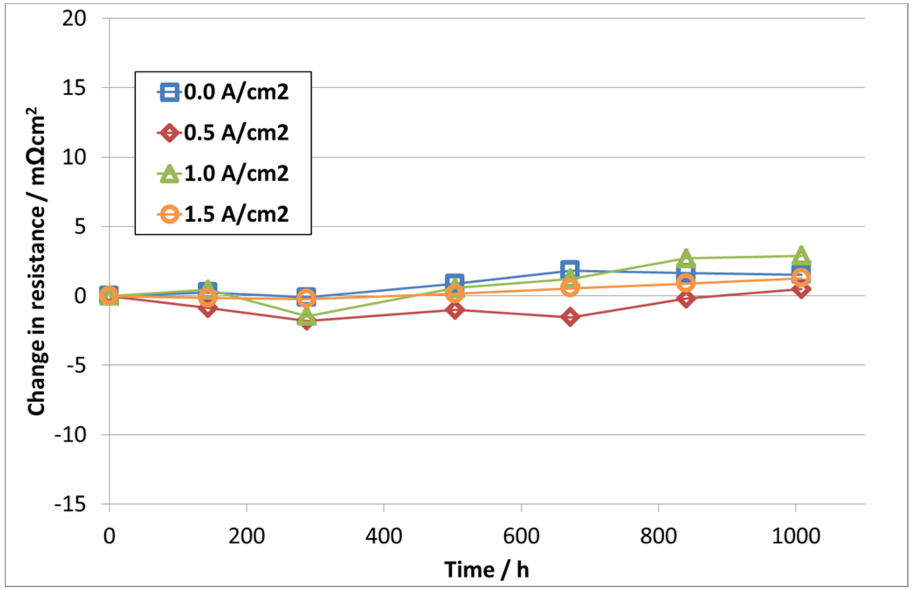


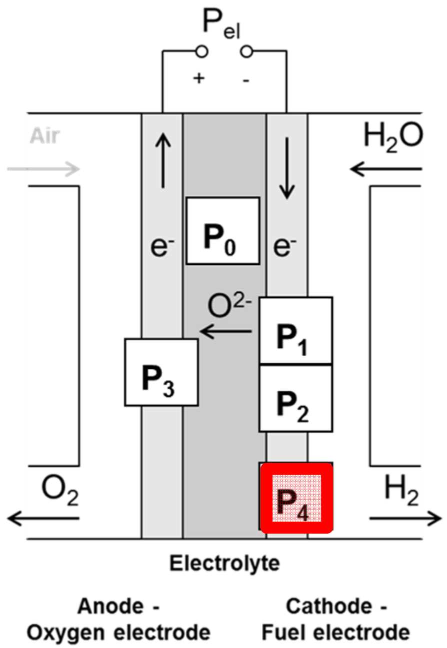


P_3: Oxygen electrode process

- Shift shown by 1.0 A/cm^2 curve is likely artifact (compare process 2)
- Initially stable → afterwards linear degradation
- Degradation independent of current density

Influence of Current Density on Degradation

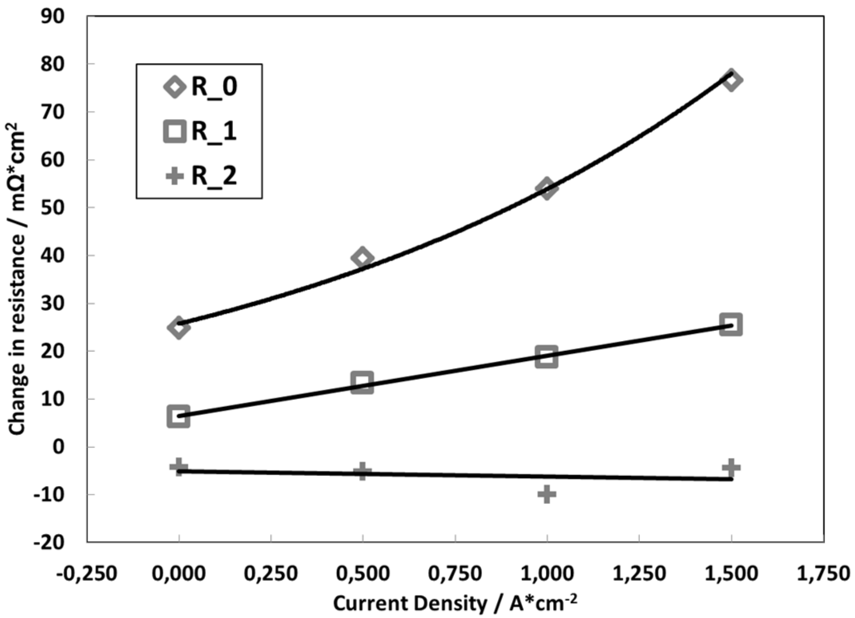


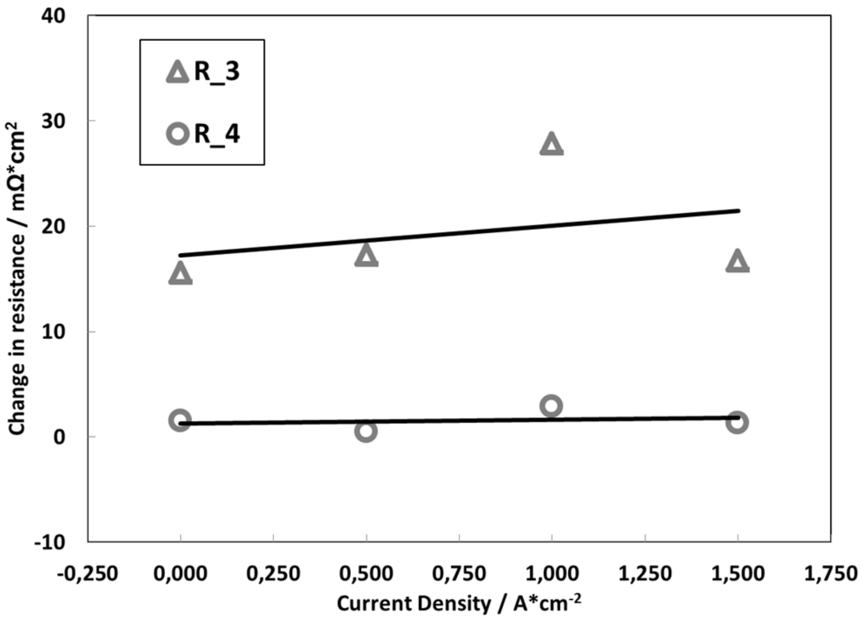


P_4: Fuel electrode mass transport

- Very little degradation
- Independent of current density

Influence of Current Density on Degradation

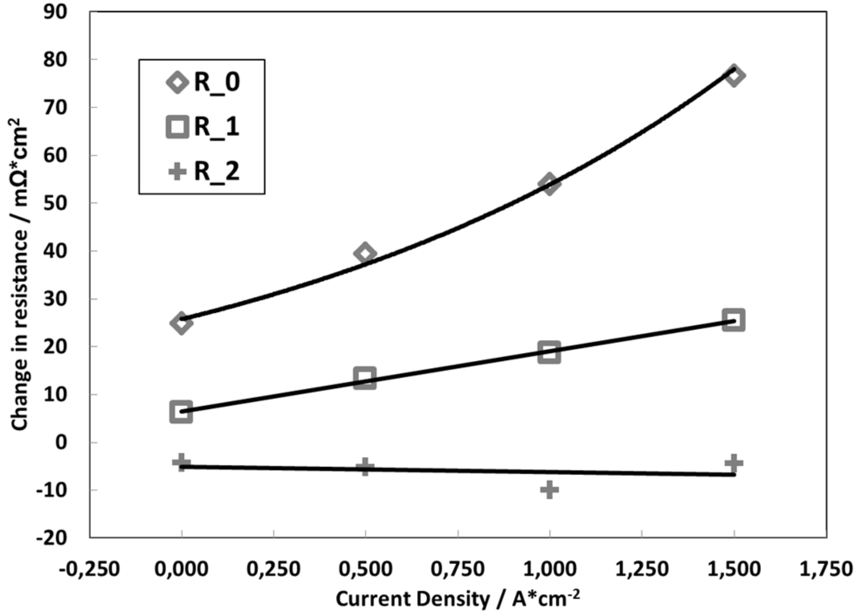


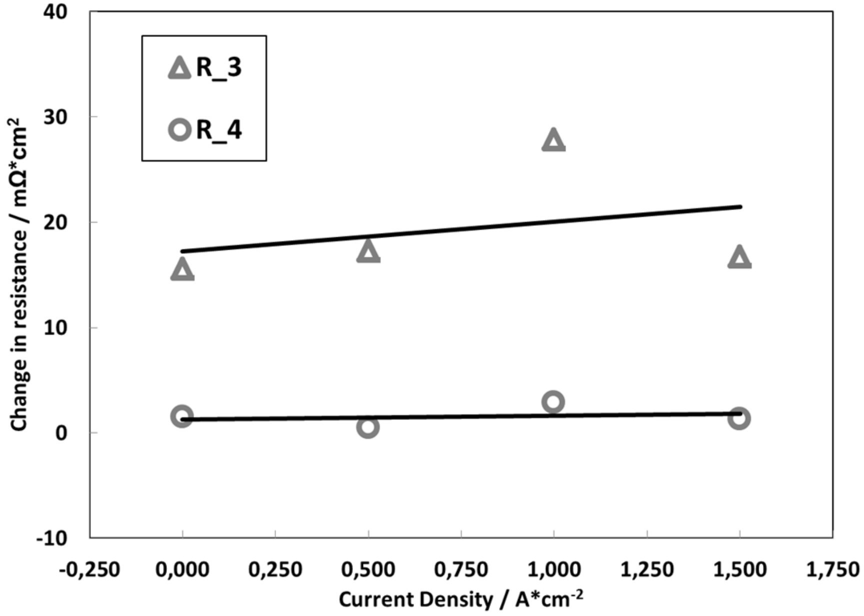


<u>Degradation after 1000 h</u>

- Ohmic resistance: strong dependence on current density
  Dependence possibly exponential

Influence of Current Density on Degradation

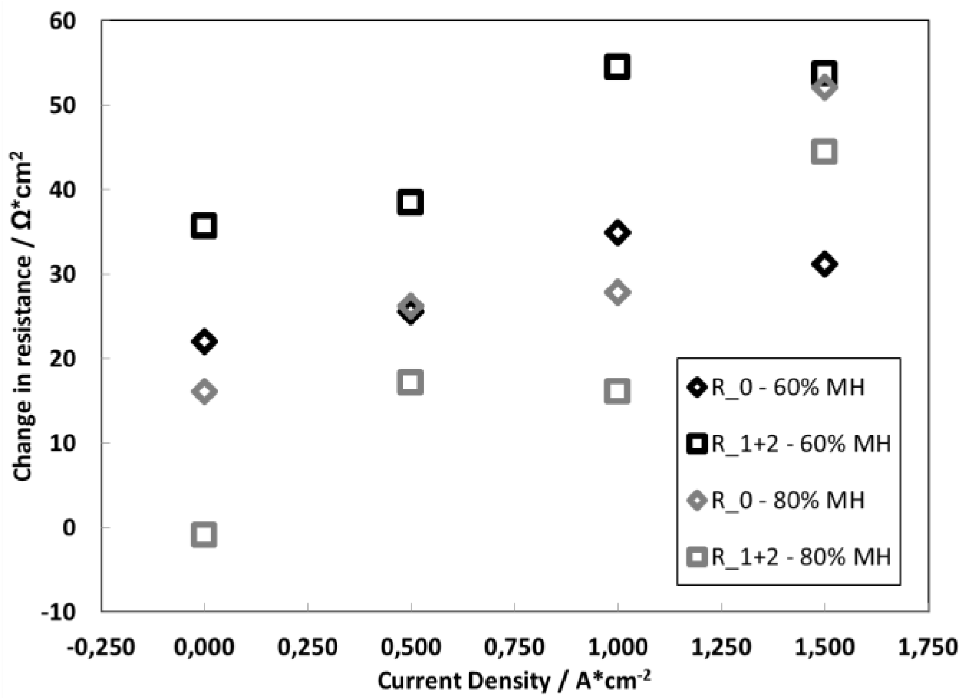




Degradation after 1000 h

- Fuel electrode process 1: clear linear dependence on current density
- Other three processes: no current dependency

Humidification



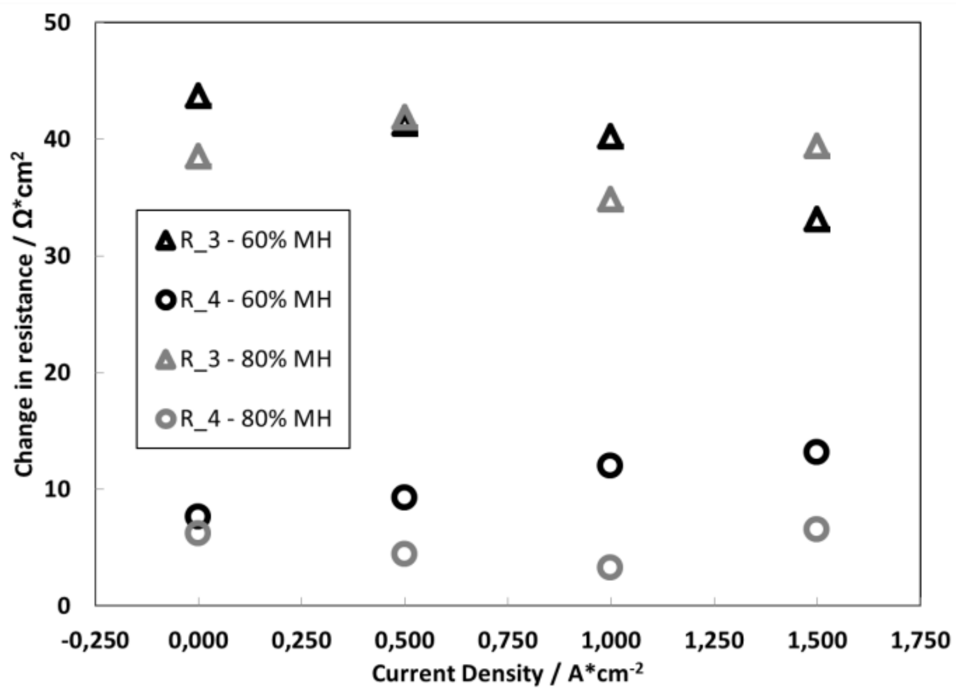
Ohmic resistance (R_0):

- Dependent on current density

Fuel electrode polarization (R_1+2):

- Lower degradation rate at higher humidities…
- … but higher degradation dependence on current density

Humidification

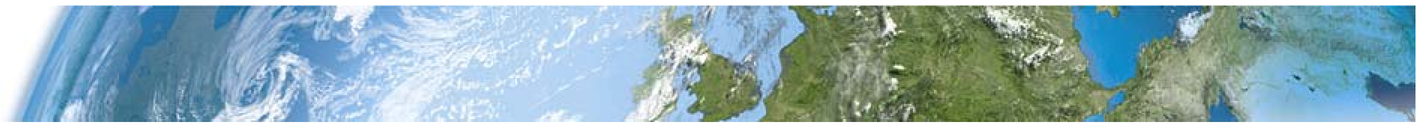


Oxygen electrode polarization (R_3):

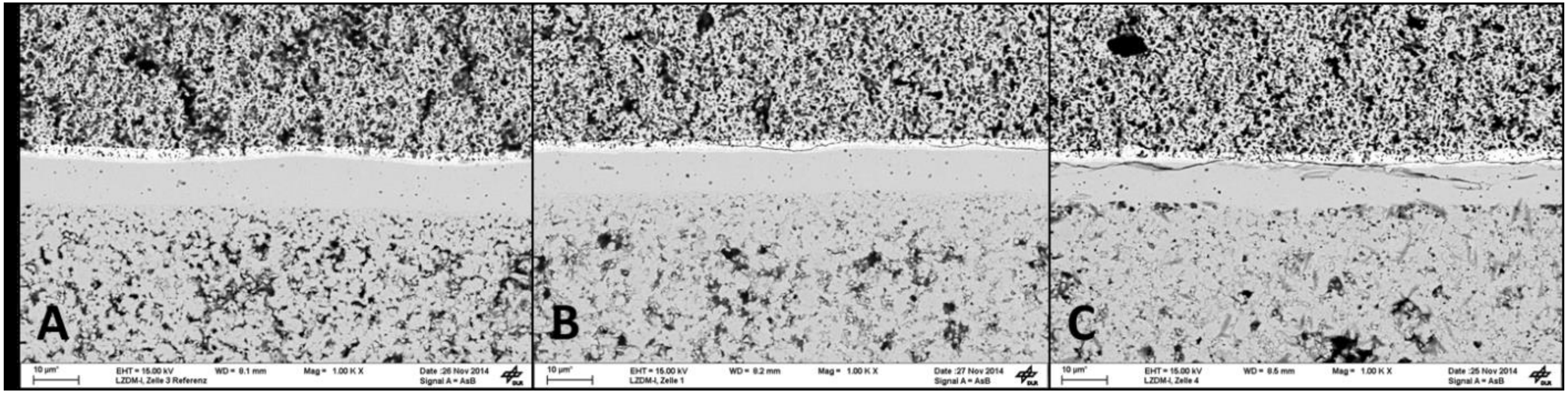
- Humidity has very little influence

Fuel electrode polarization (R_4):

- Generally small degradation
- Lower at higher humidity
- No obvious trend



Post-mortem Analysis – Electrolyte

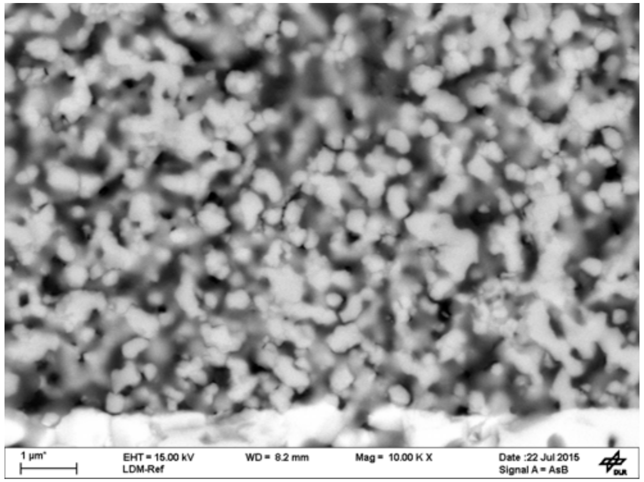


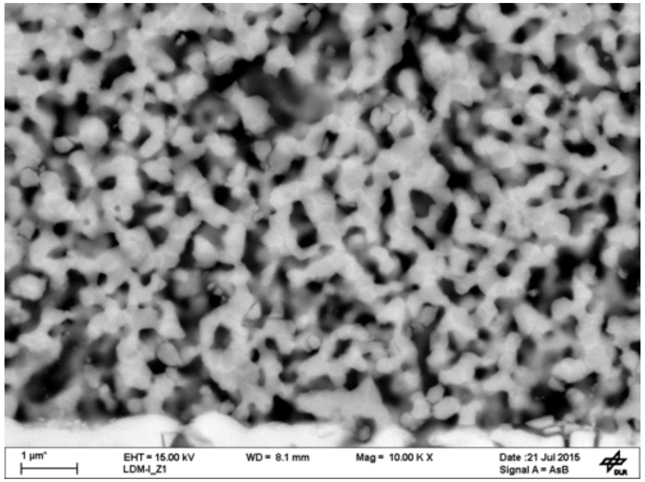
Reference 1000 h @ OCV 1000 h @ 1.5 A/cm^2

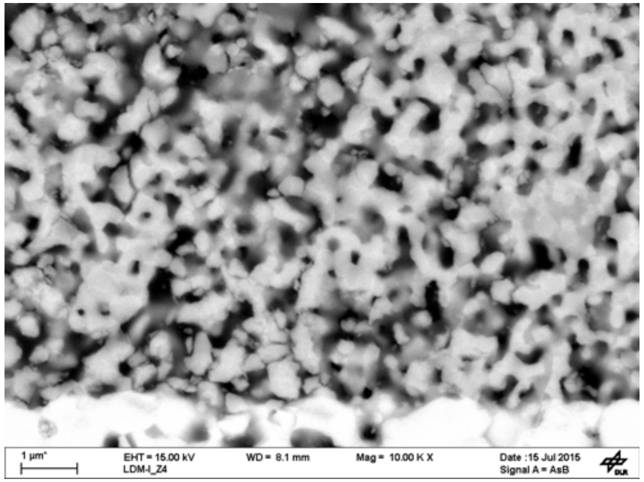
Ohmic resistance:

- Weakening of YSZ|CGO|LSCF interface → probably formation of cracks
- Visible cracks probably formed during sample preparation along weakened microstructure

Post-mortem Analysis – Oxygen Electrode



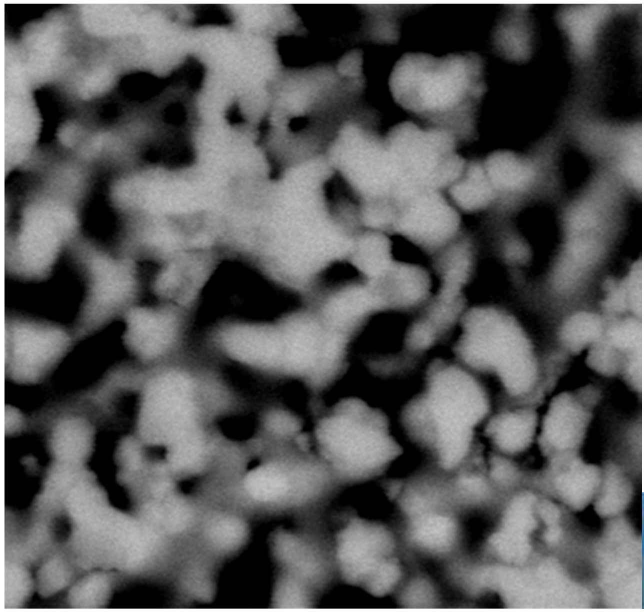


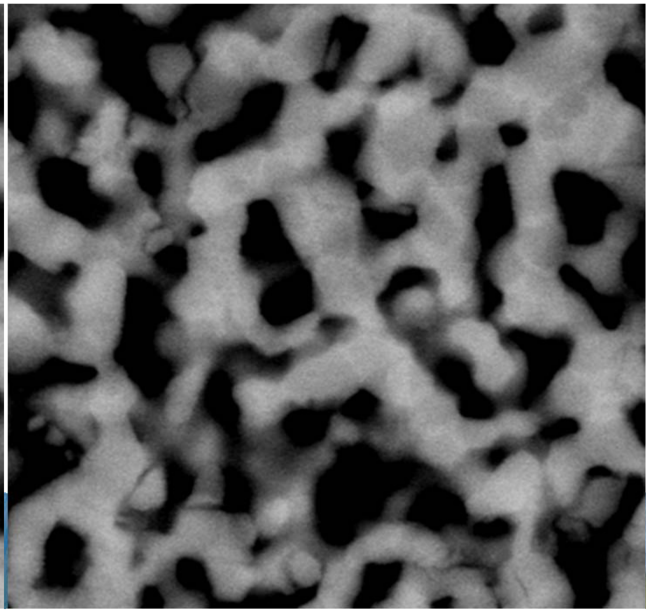


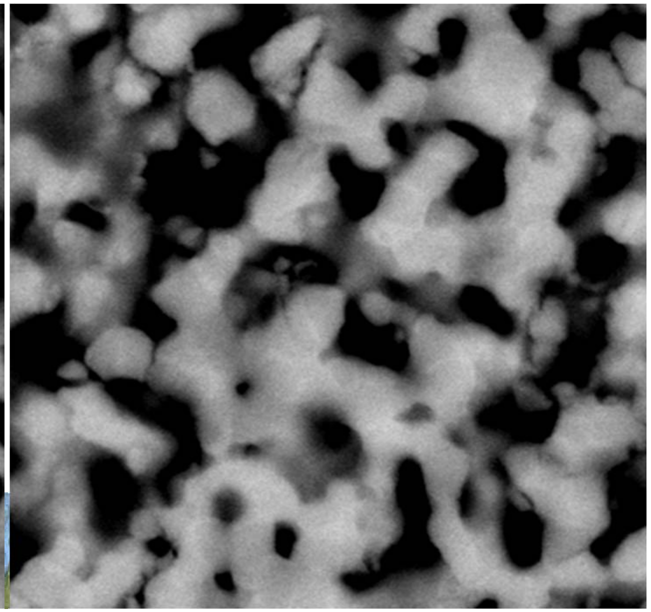
Reference

1000 h @ OCV

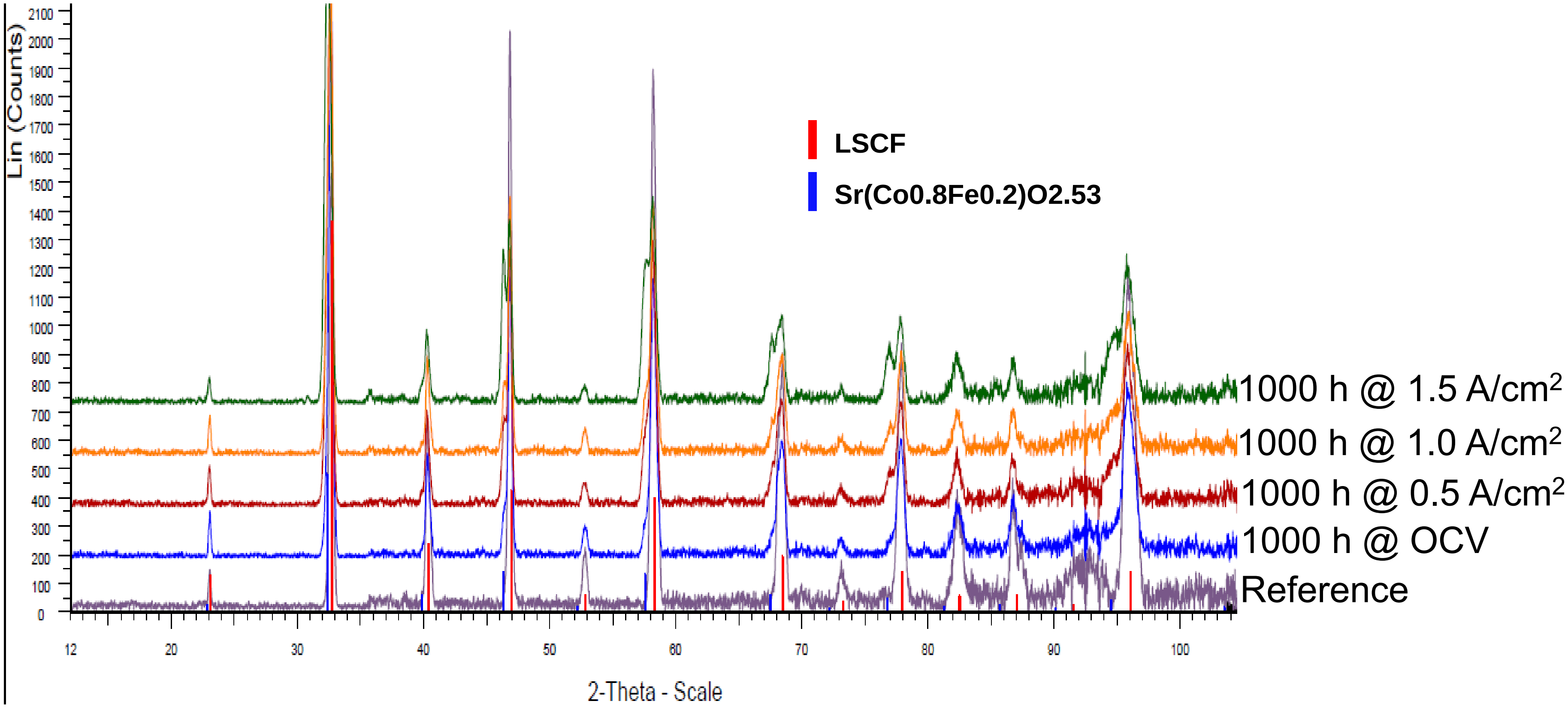
1000 h @ 1.5 A/cm^2





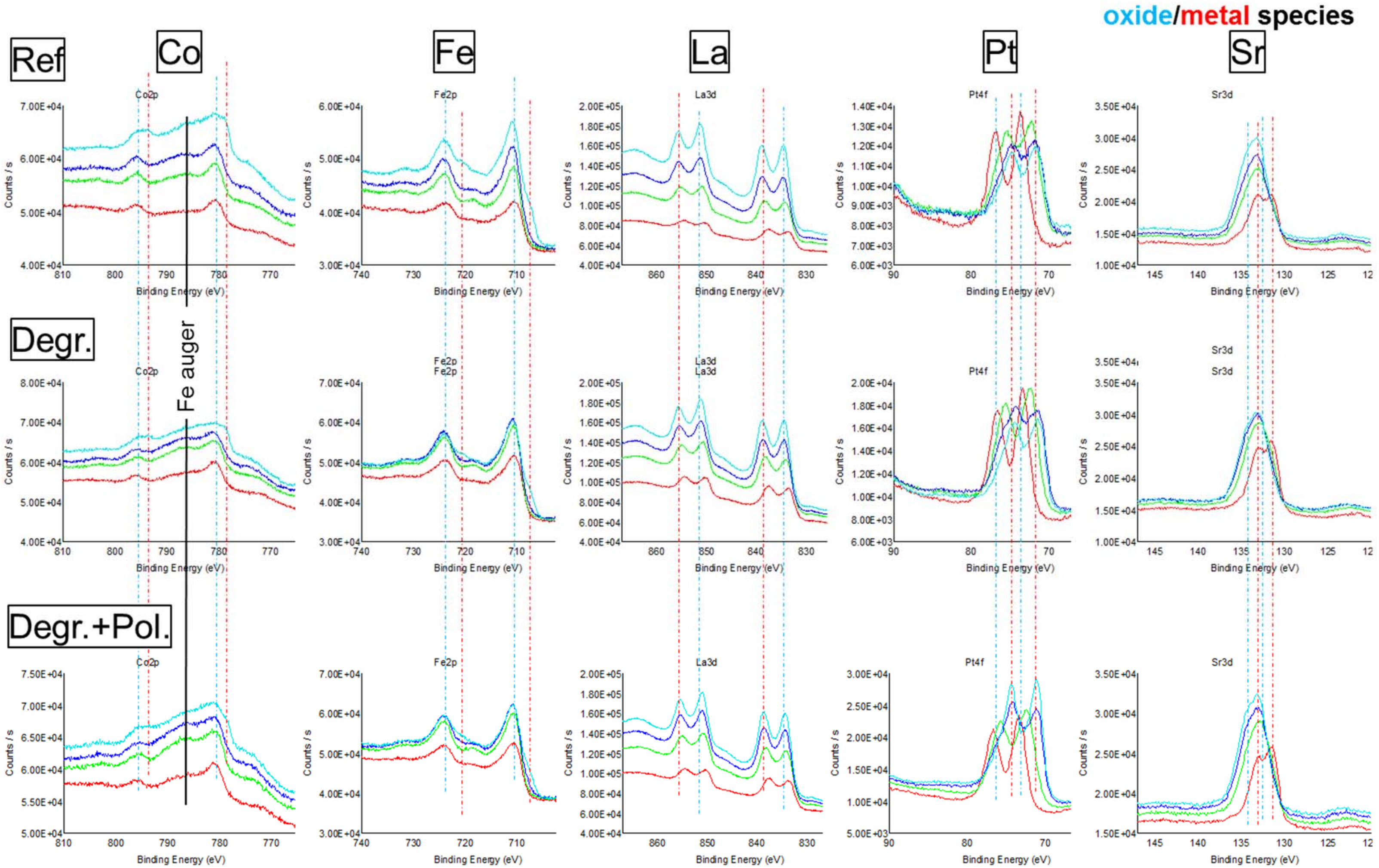


Post-mortem Analysis – Oxygen Electrode

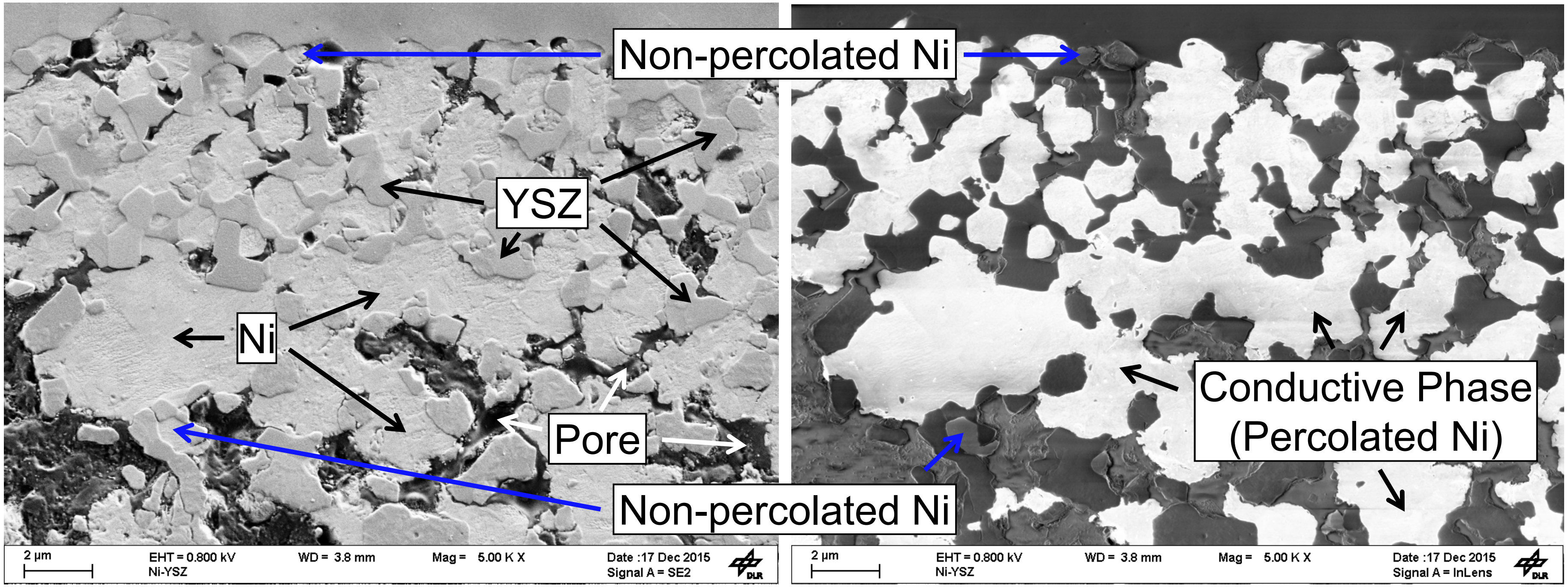


- Formation of a new crystalline compound
- Higher polarization → change more pronounced
- More detailed analyses necessary for reliable information on new phase

Post-mortem Analysis – Oxygen Electrode



Post-mortem Analysis – Fuel Electrode



1000 h @ 1.5 A/cm2, 850° C and 80% MH

Percolation

- Ni almost completely percolated
- Ni can be separated from percolation network in cross section

EDX measurement: no Ni depletion

Conclusion

- Correlation between degradation and current density has been investigated
- Ohmic resistance dominates degradation and increases with current density
- Oxygen electrode contributes significantly to degradation and is independent of current density
- Higher frequency fuel electrode process is significant for degradation and dependent of current density
- Lower frequency fuel electrode process is stable after initial activation and independent of current density
- No degradation in mass transport limitation
- Results of post-mortem analyses give further information and must be further evaluated

Acknowledgment

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Thank you for your attention

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