Detailed Study of Degradation Behavior of Solid Oxide Cells in Electrolysis and Co-Electrolysis Mode

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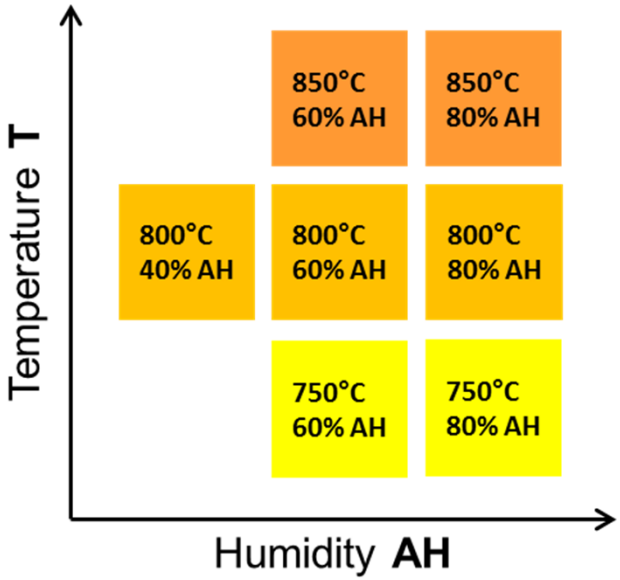
Outline

- Motivation and concept
- Cell manufacturing and characterization
- Degradation study and results from post-mortem analyses
- Conclusion

Present Work – Motivation and Concept

Systematic study: Operating parameter → Degradation

- Temperature (T): 750, 800, 850 ° C
- Fuel gas humidity (AH): 40%, 60%, 80% AH
- Current density (i): OCV, 0.5, 1.0, 1.5 A/cm^2



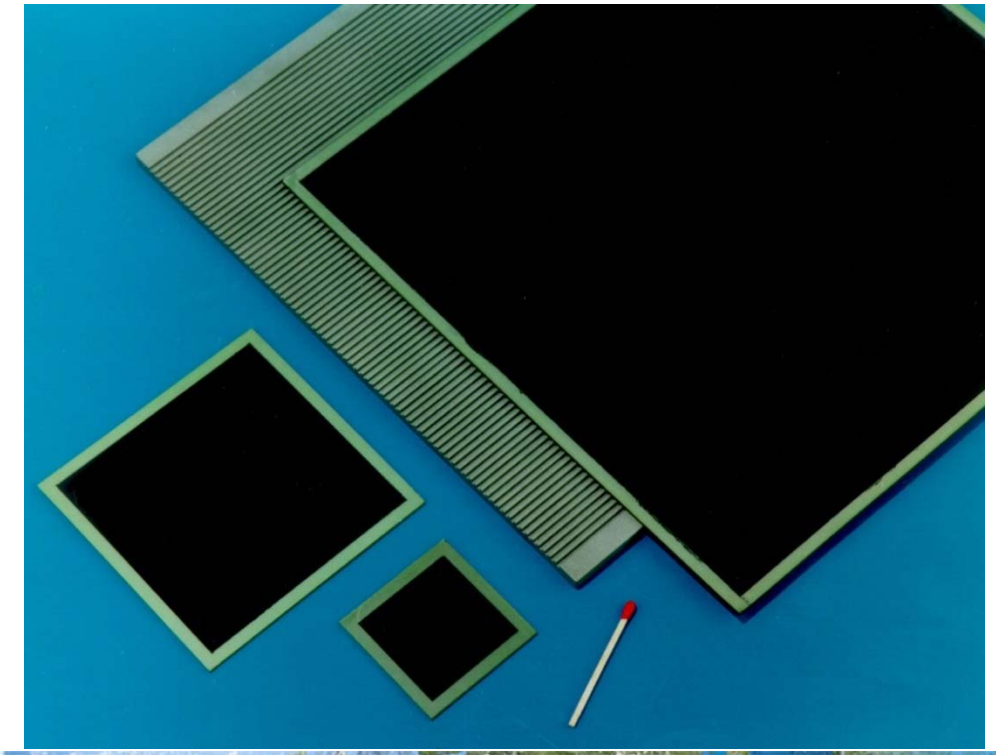
Experimental concept:

- 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 (16 cm^2)
  → Ni-8YSZ support | Ni-8YSZ | 8YSZ | CGO | LSCF

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



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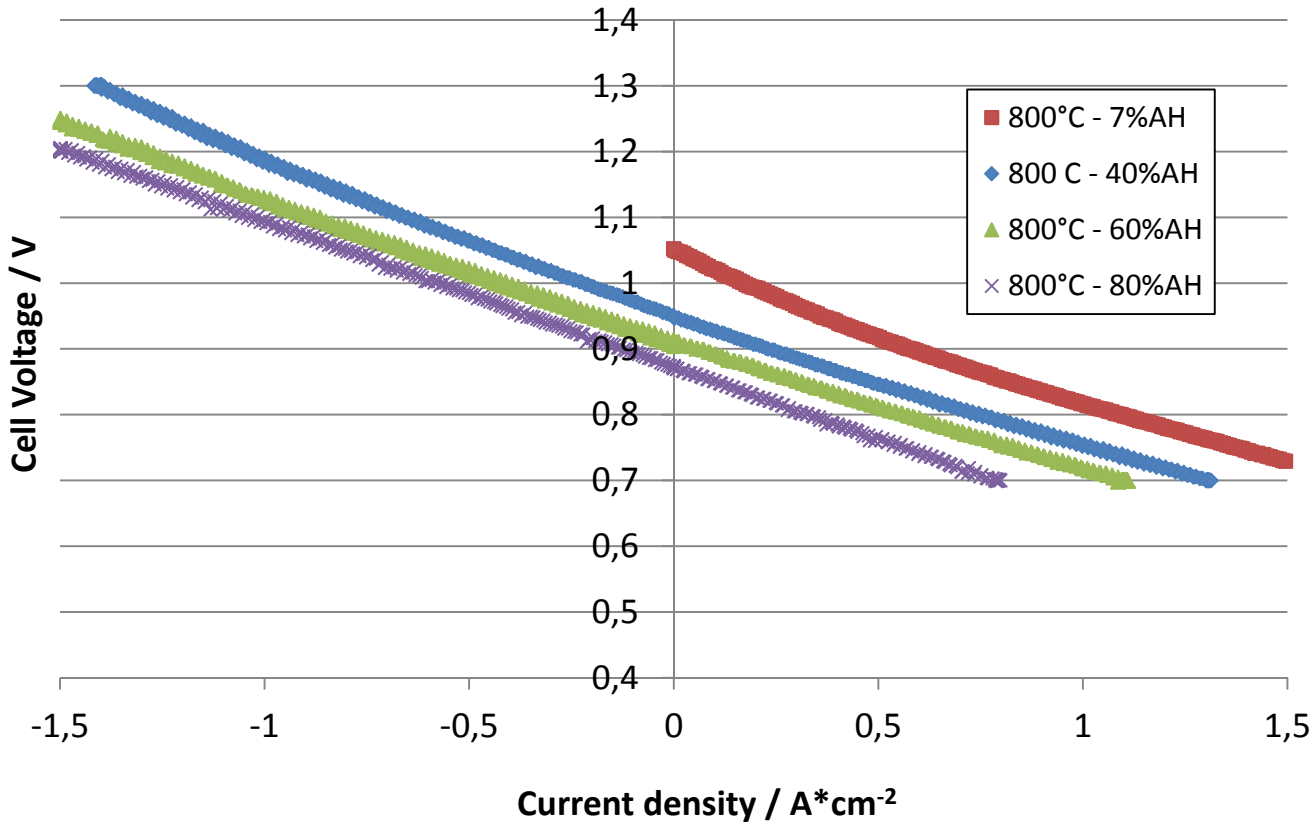
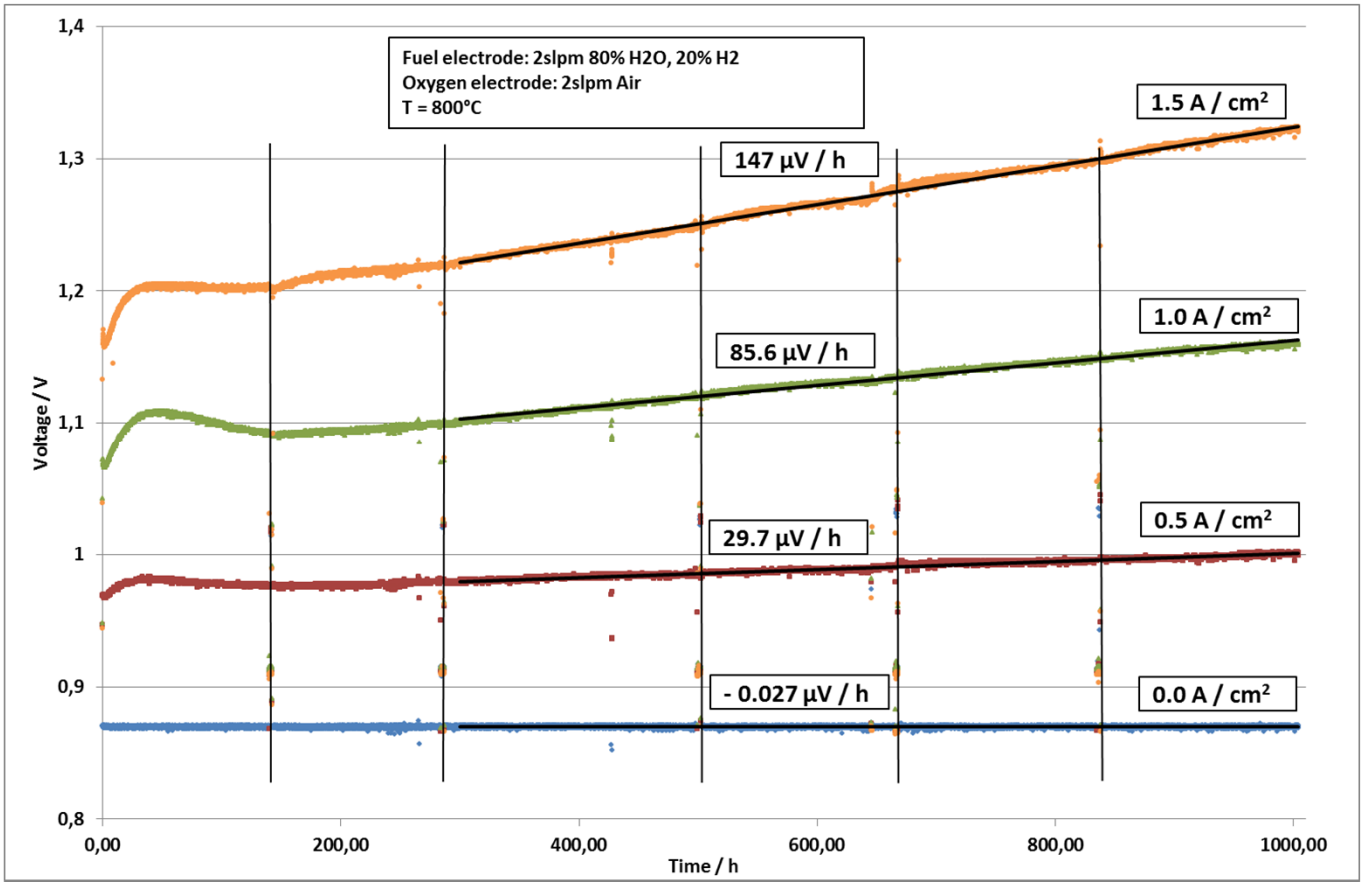
I-V Curves at 800 ° C as a Function of Steam Content

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



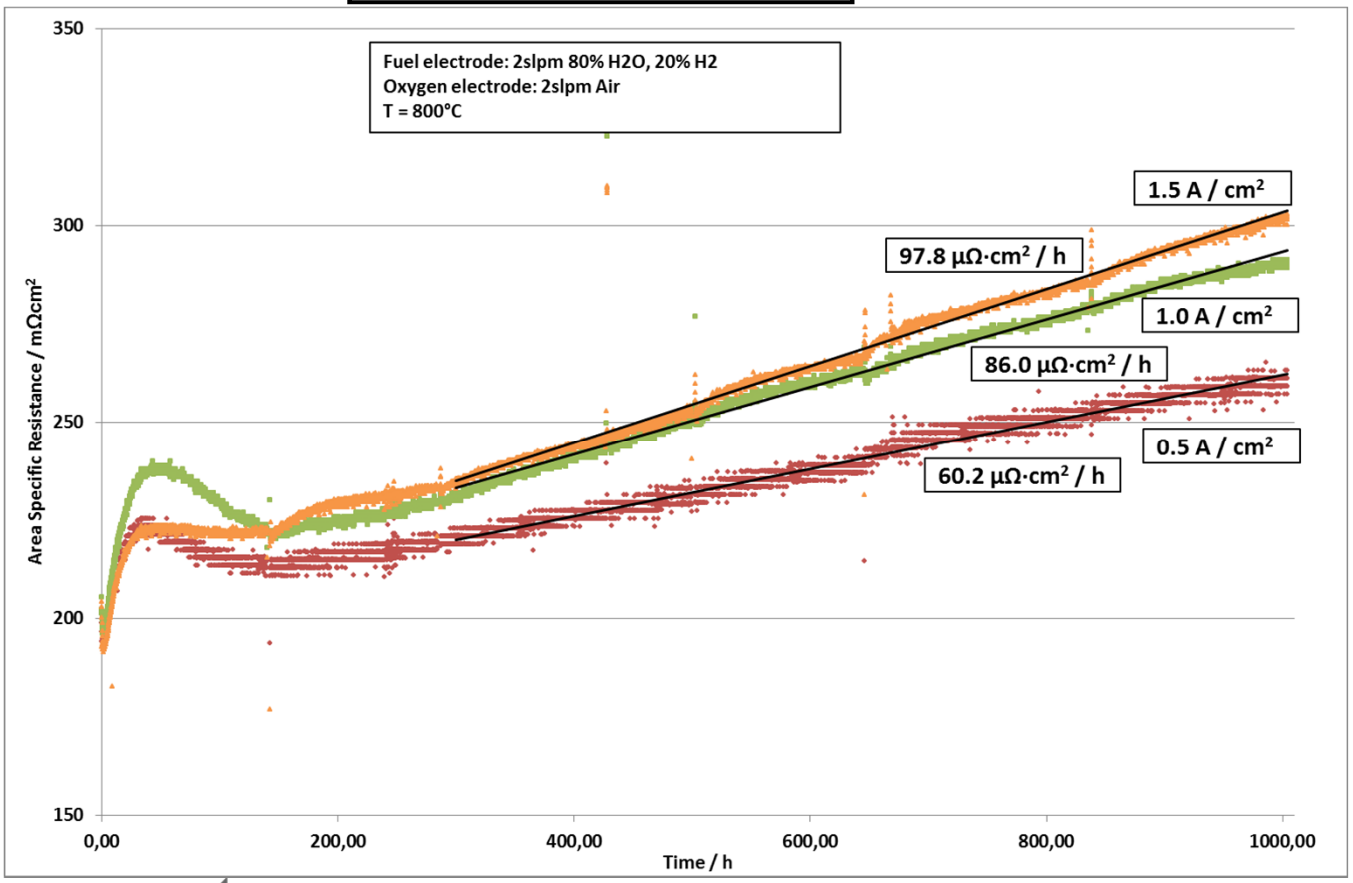
Degradation Experiment and Impedance Data Interpretation



- 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

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

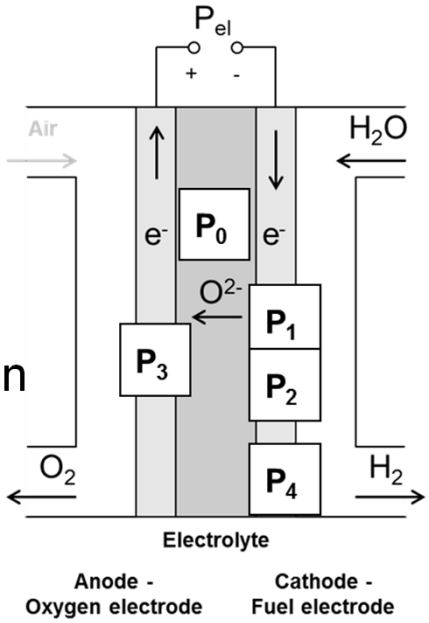


- Degradation rate at 1.5 A/cm^2 only 13 % higher than at 1.0 A/cm^2
- Degradation rate at 0.5 A/cm^2 significantly lower
- ASR degradation rate about 30% compared to 3% voltage degradation (per 1000 h @ 0.5 A/cm^2)

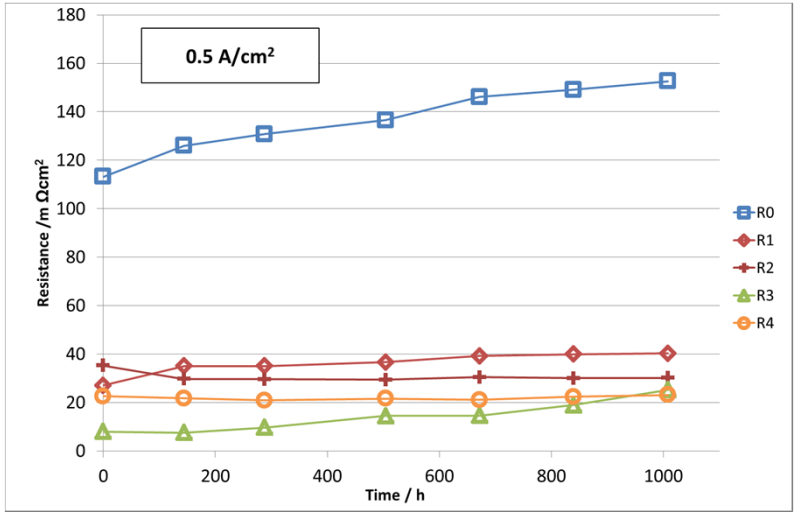
Degradation Experiment and Impedance Data Interpretation

Impedance data revealed 5 rate limiting processes:

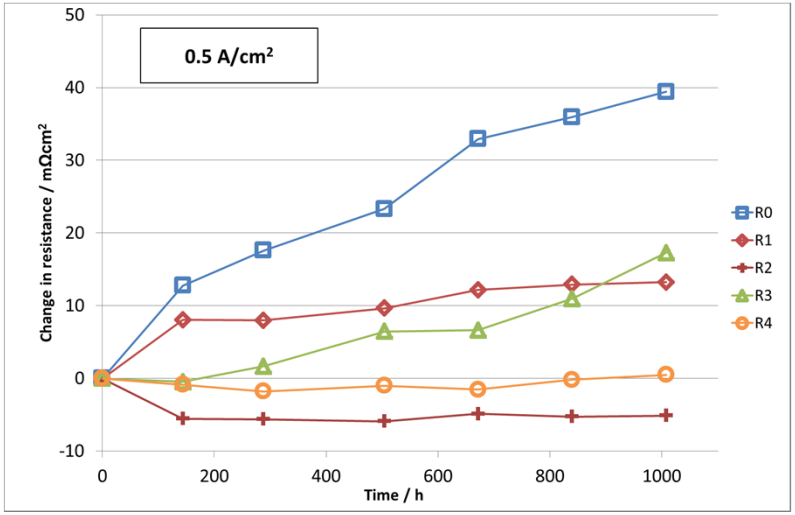
- P_0: Ohmic resistance (> 10^5 Hz)
- P_1: Fuel electrode process A (~ 10^4 Hz)
  Charge transfer reaction at TPB coupled with ionic transport in porous electrode geometry
- P_2: Fuel electrode process B (~ 10^3 Hz)
  Charge transfer at TPB
- P_3: Oxygen Electrode Process (~ 10^2 Hz)
- P_4: Fuel electrode mass transport limitation (~ 10^1 Hz)
  Diffusion through FE-support along with gas conversion



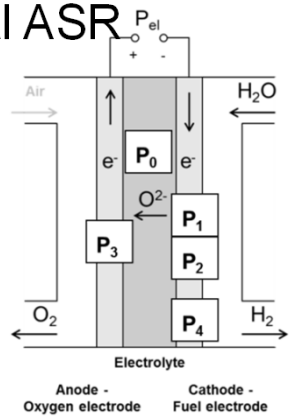
Influence of Current Density on Degradation



ΔR

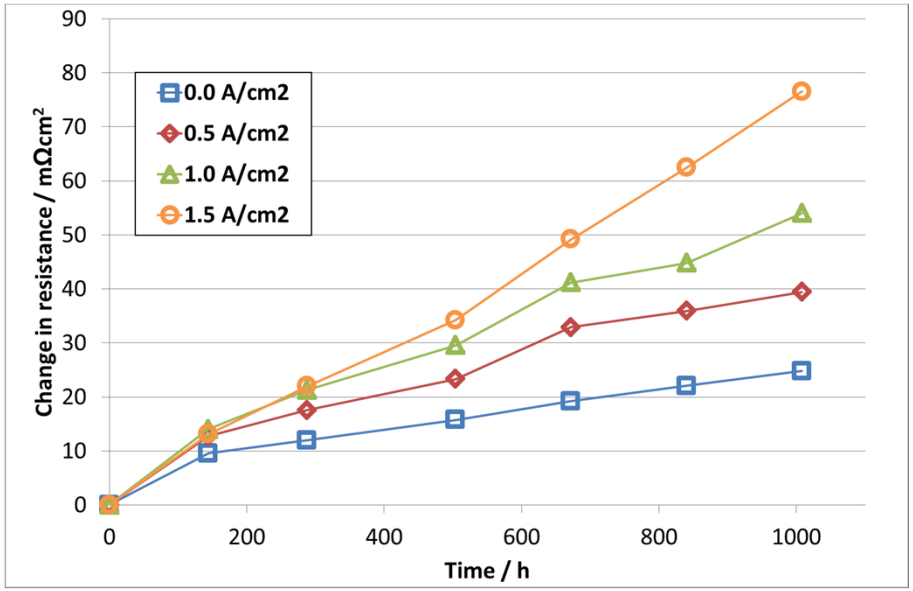


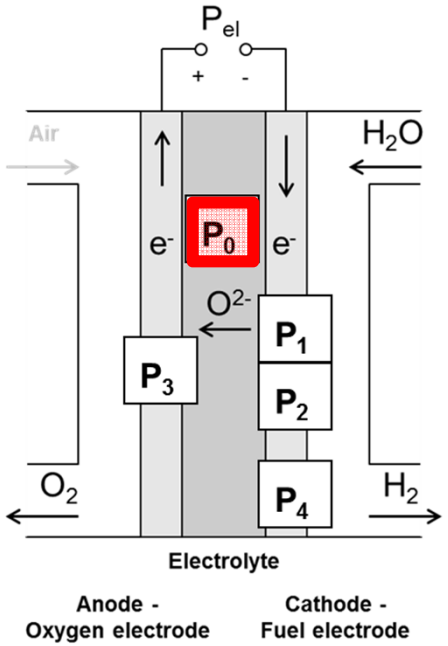
- Ohmic resistance contributes more than 50% of total ASR



- 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

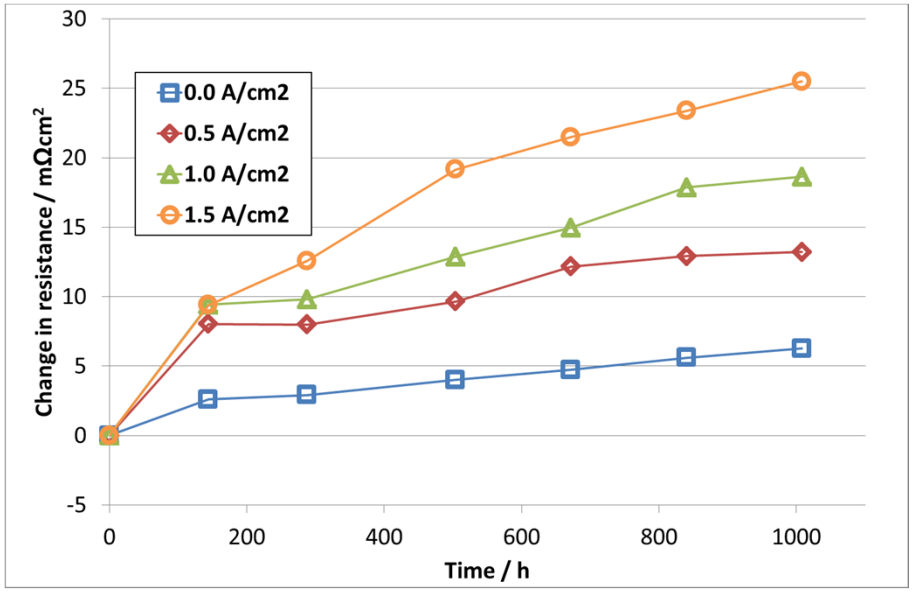


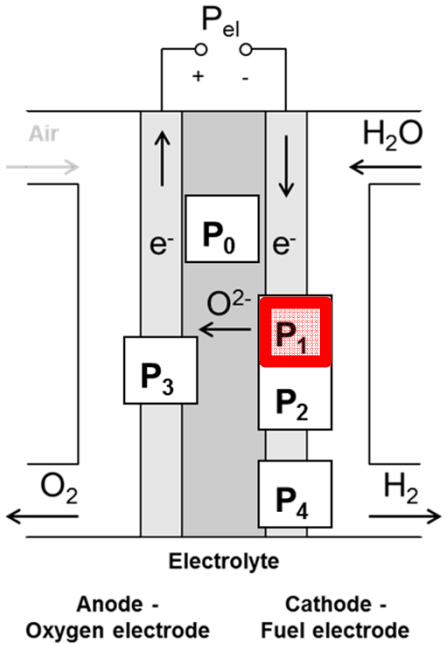


P_0: Ohmic resistance

- Obvious correlation with current density
- Linear degradation with time

Influence of Current Density on Degradation

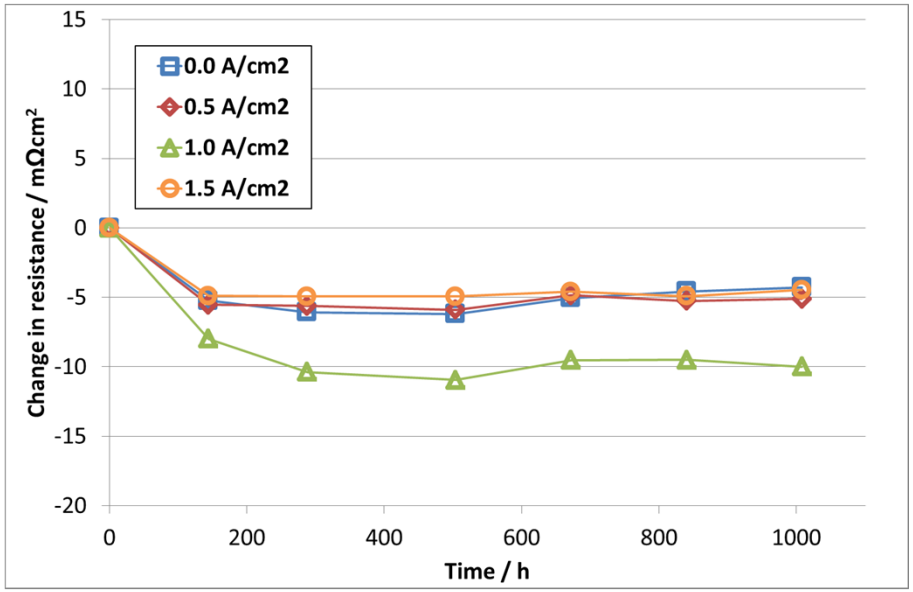


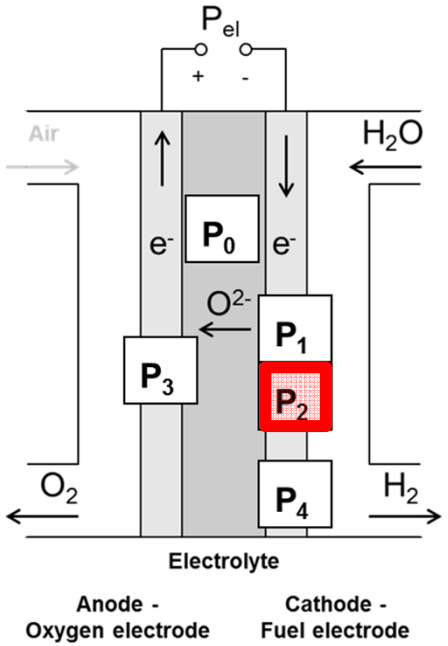


P_1: Fuel electrode process 1

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

Influence of Current Density on Degradation

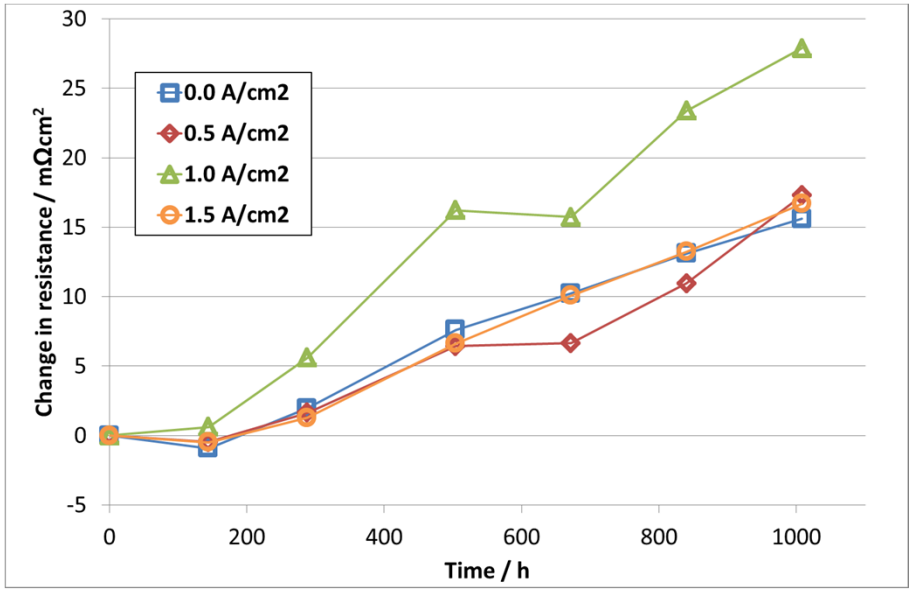


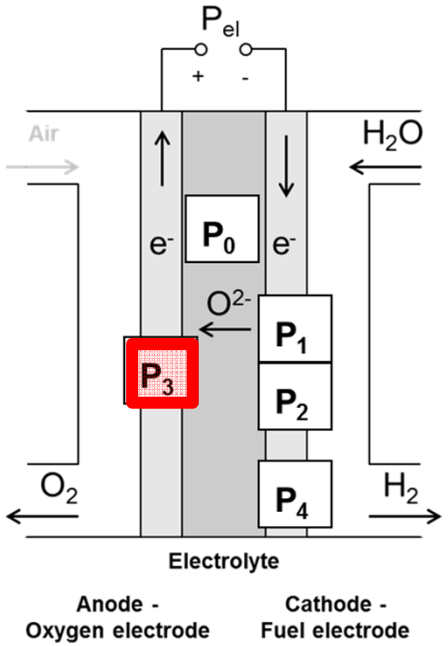


P_2: Fuel electrode process 2

- 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

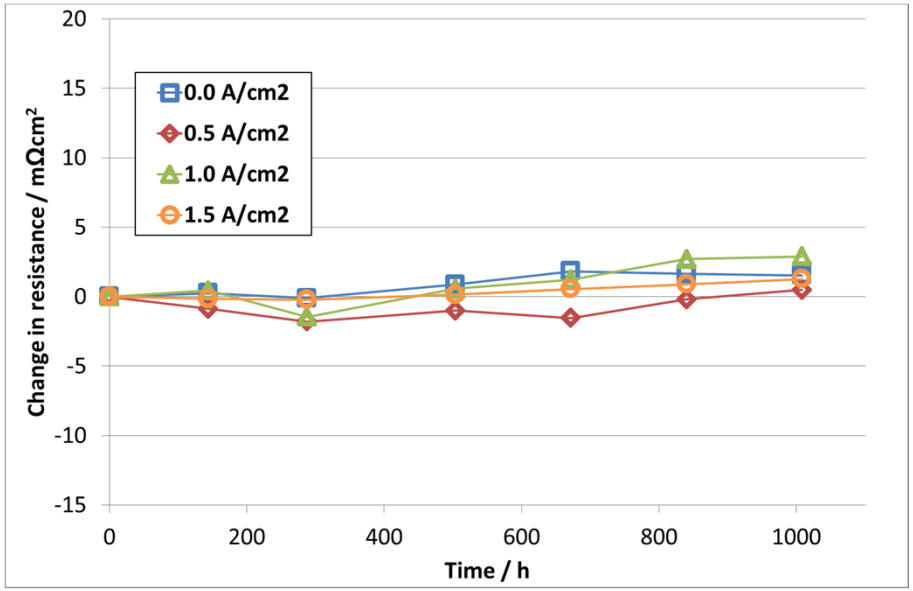


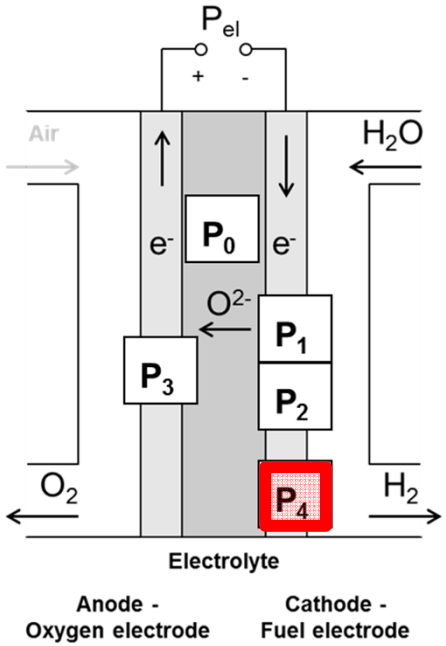


P_3: Oxygen electrode process

- Shift shown by 1.0 A/cm² 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

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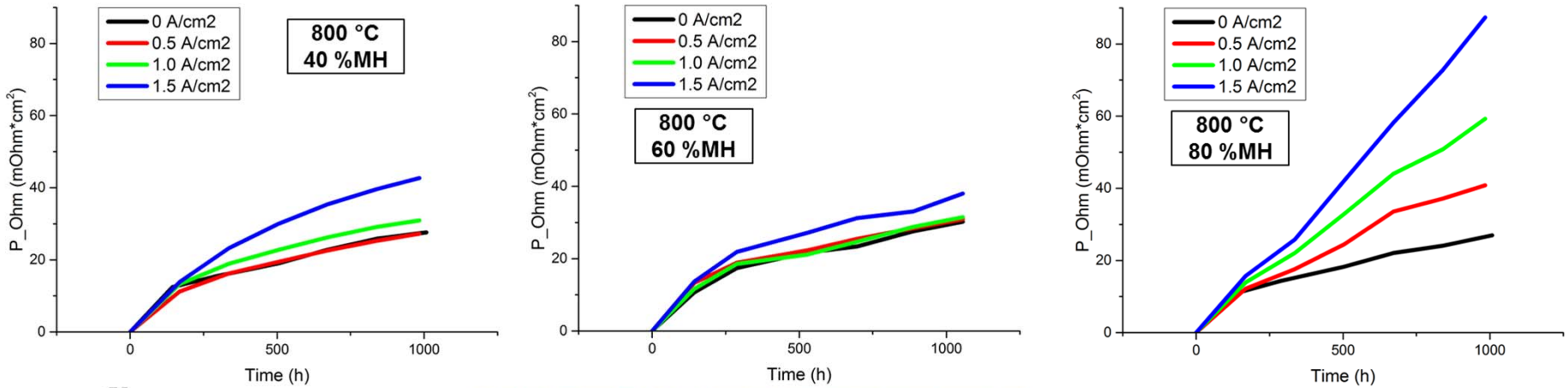
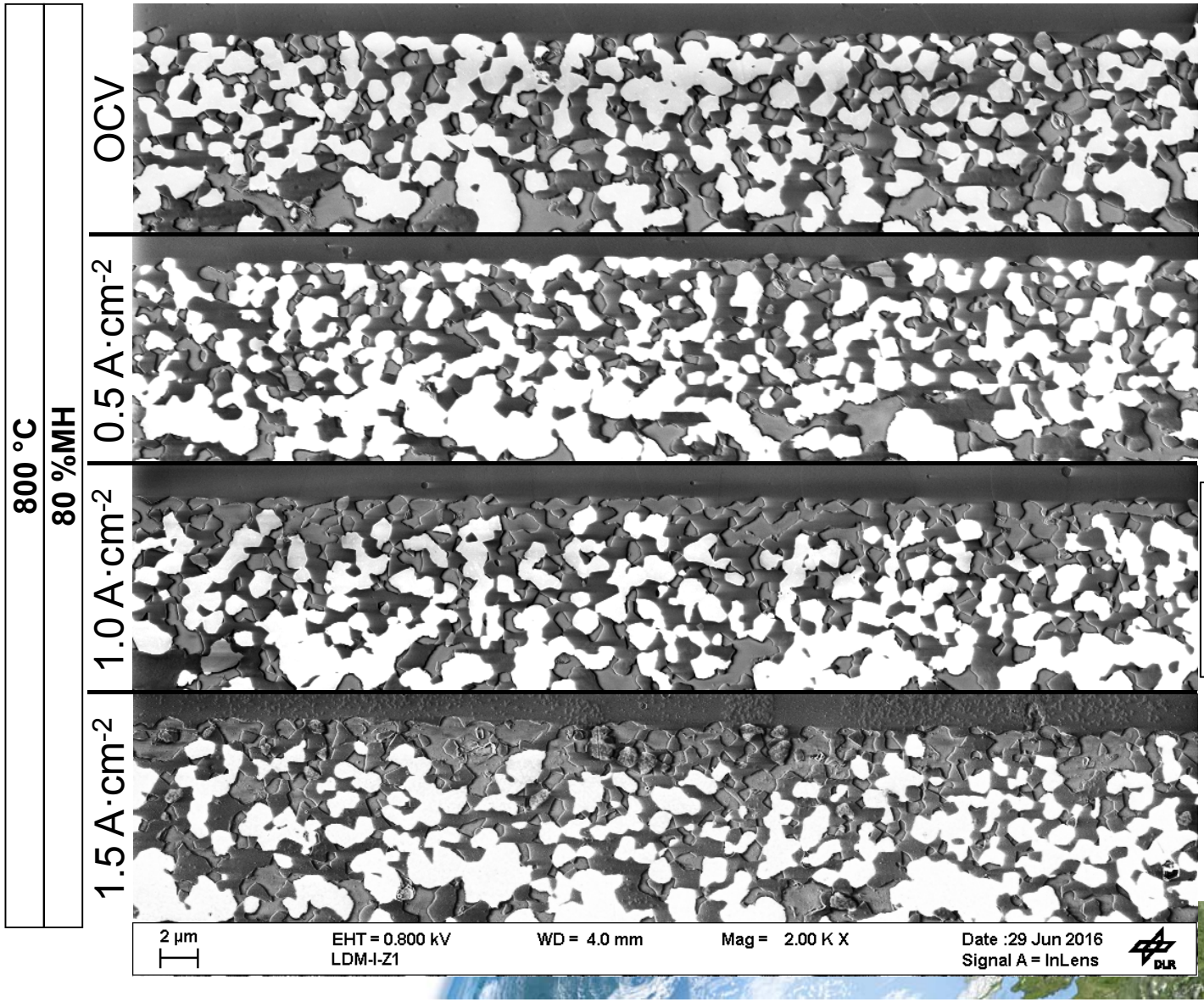
Degradation Results: Ohmic Resistance

40 % MH and 60 % MH	80 % MH
▪ Degradation of ohmic resistance at all current densities	▪ Influence of current density much stronger
▪ Influence of current density only at high current densities	▪ Current density has effect even at low current densities

Degradation caused by a combination of current density and high humidity



Degradation Results: Ohmic Resistance

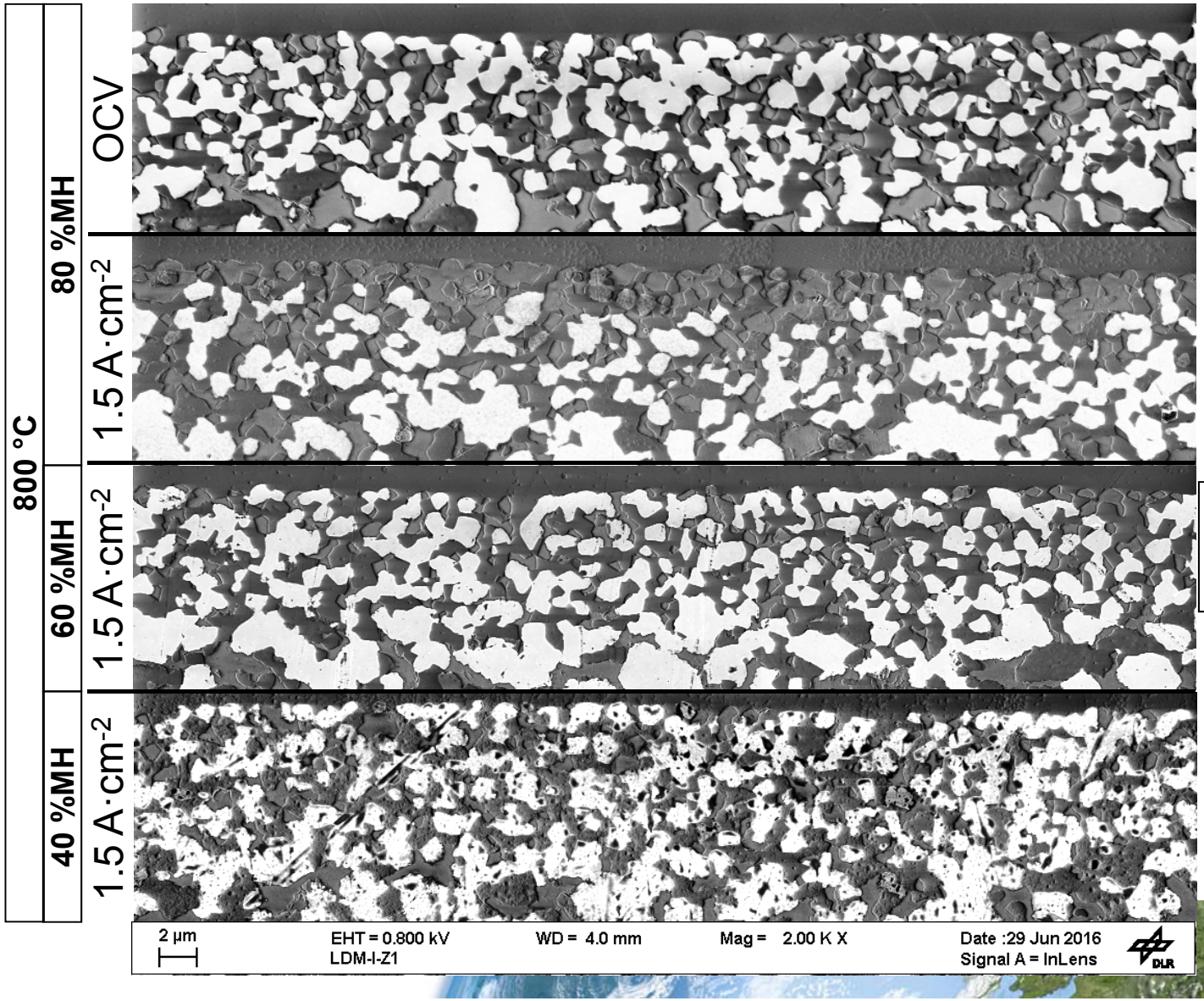


Ni depletion at electrode|electrolyte interface

→ Effectively increasing electrolyte thickness

Direct correlation between Ni depletion and current density

Degradation Results: Ohmic Resistance

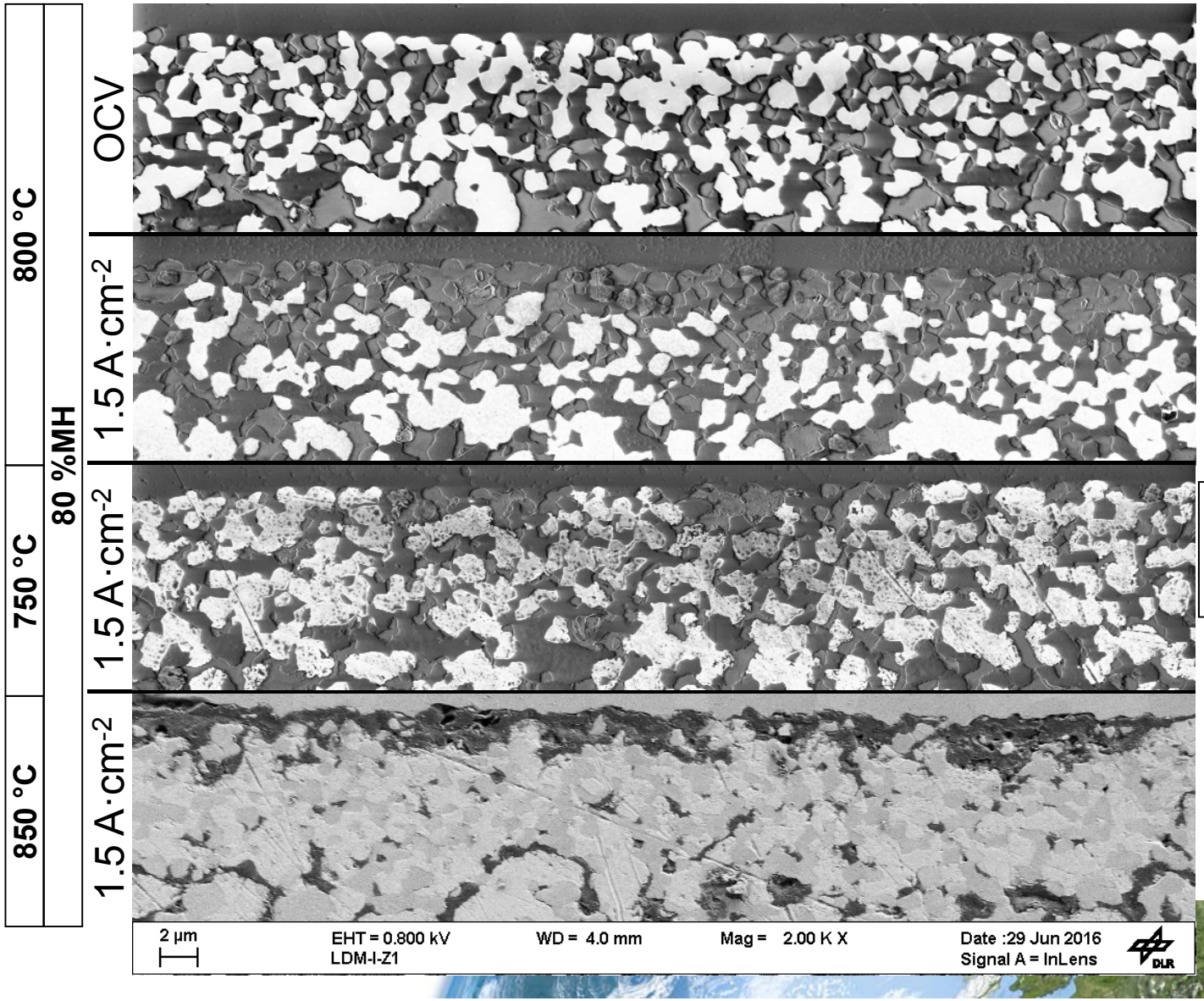


Ni depletion at electrode|electrolyte interface

→ Effectively increasing electrolyte thickness

No Ni depletion at lower humidity

Degradation Results: Ohmic Resistance



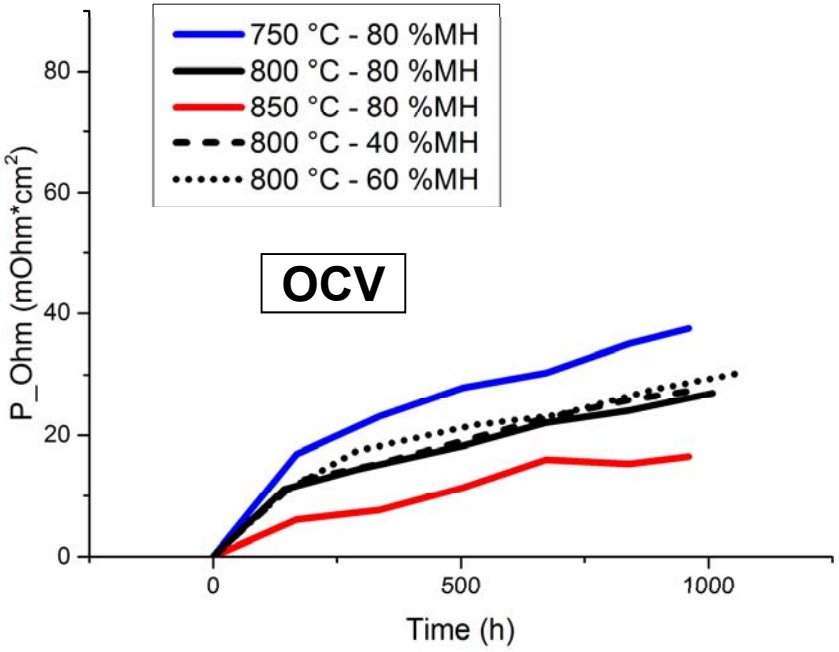
Ni depletion at electrode|electrolyte interface

→ Effectively increasing electrolyte thickness

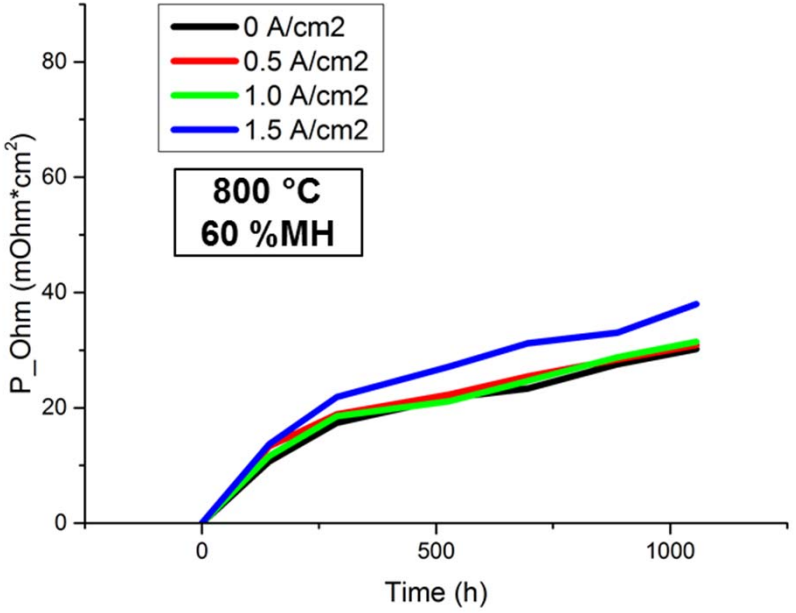
Less Ni depletion at lower temperature

Degradation Results: Ohmic Resistance

"Underlying" Degradation:



- Higher temperature leads to lower degradation
- Independent of humidity
- Little influence of current density



Degradation Results: Ohmic Resistance - Summary

Two major degradation processes

Ni Depletion:

- Direct correlation between current density and Ni depletion
- Minimum humidity (above 60 %MH) required
- Temperature facilitates process

"Underlying" Degradation:

- Temperature dependence: higher temperature → lower degradation
- No influence of humidity

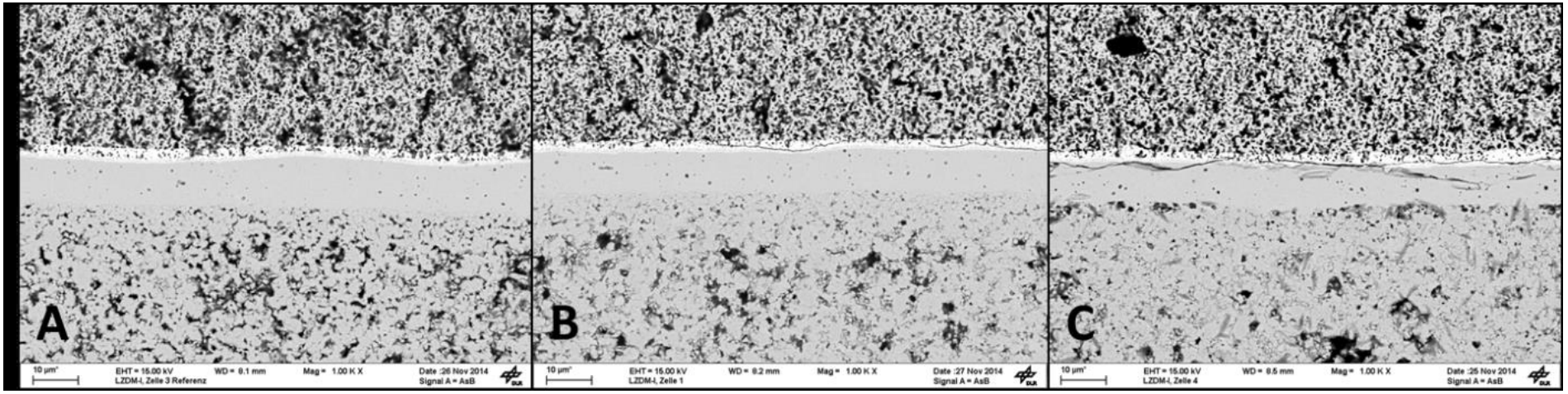
Deterioration of YSZ integrity

- Weakening of YSZ structure at high current densities

Not observed

- Correlation between YSZ deterioration and significant increase in ohmic resistance
- $SrZrO_3$ formation

Post-mortem Analysis – Electrolyte

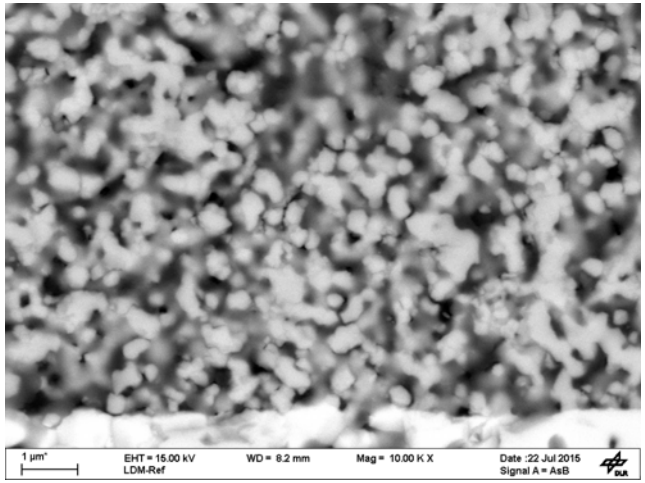


Reference | 1000 h @ OCV | 1000 h @ 1.5 A/cm^2

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



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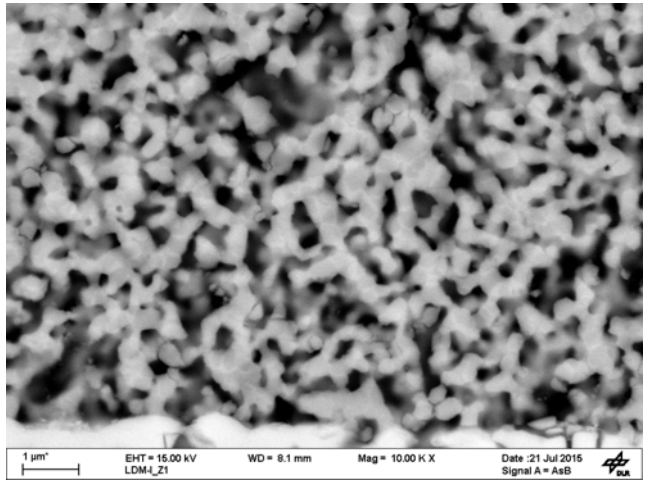
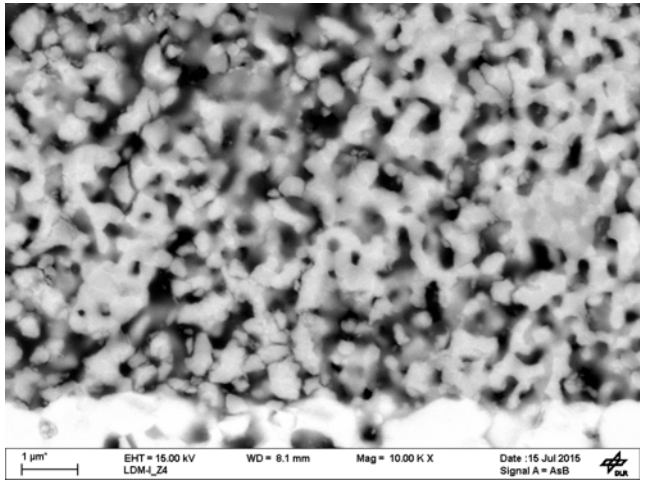
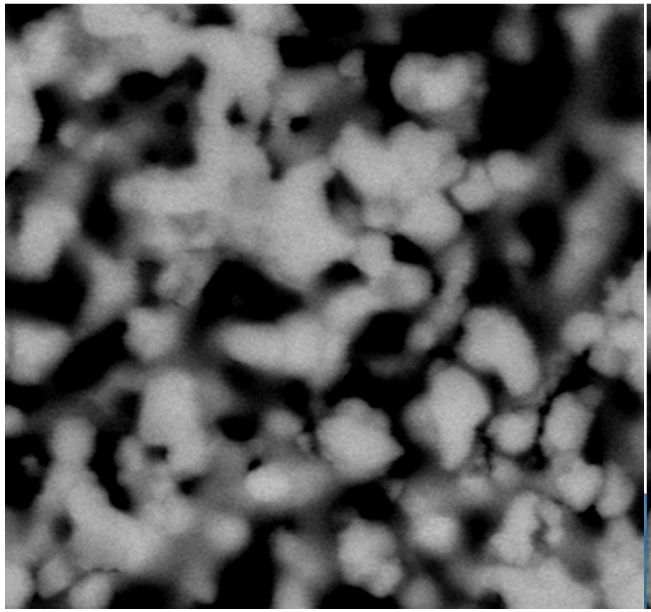
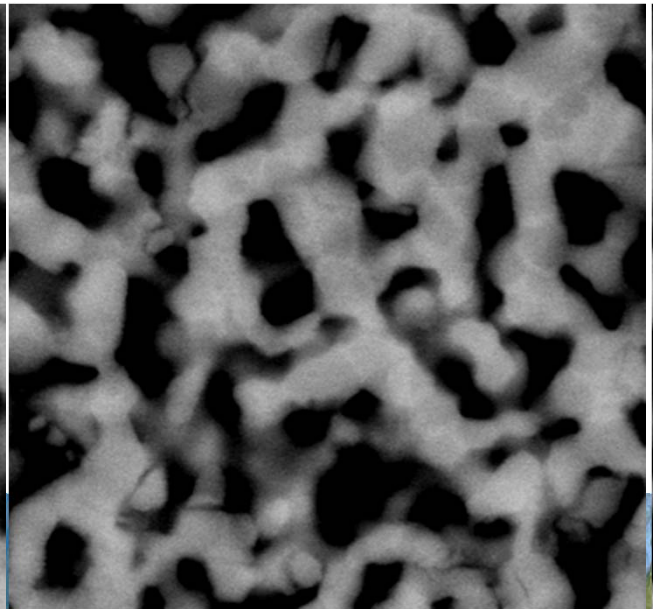


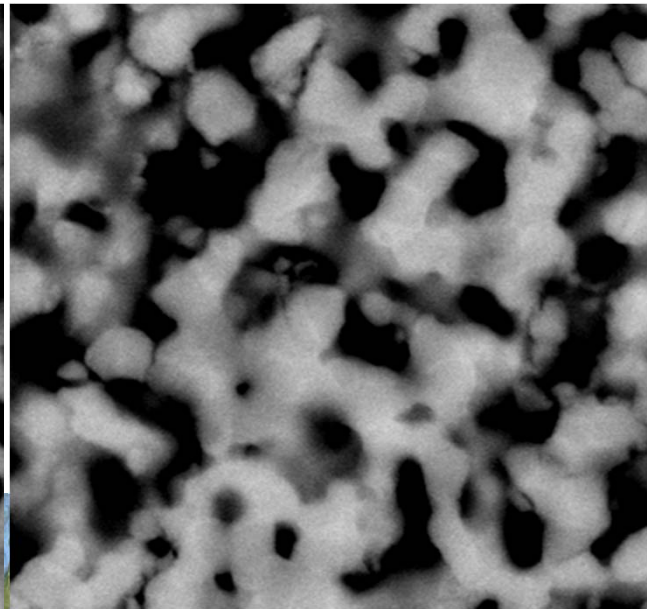
1000 h @ OCV



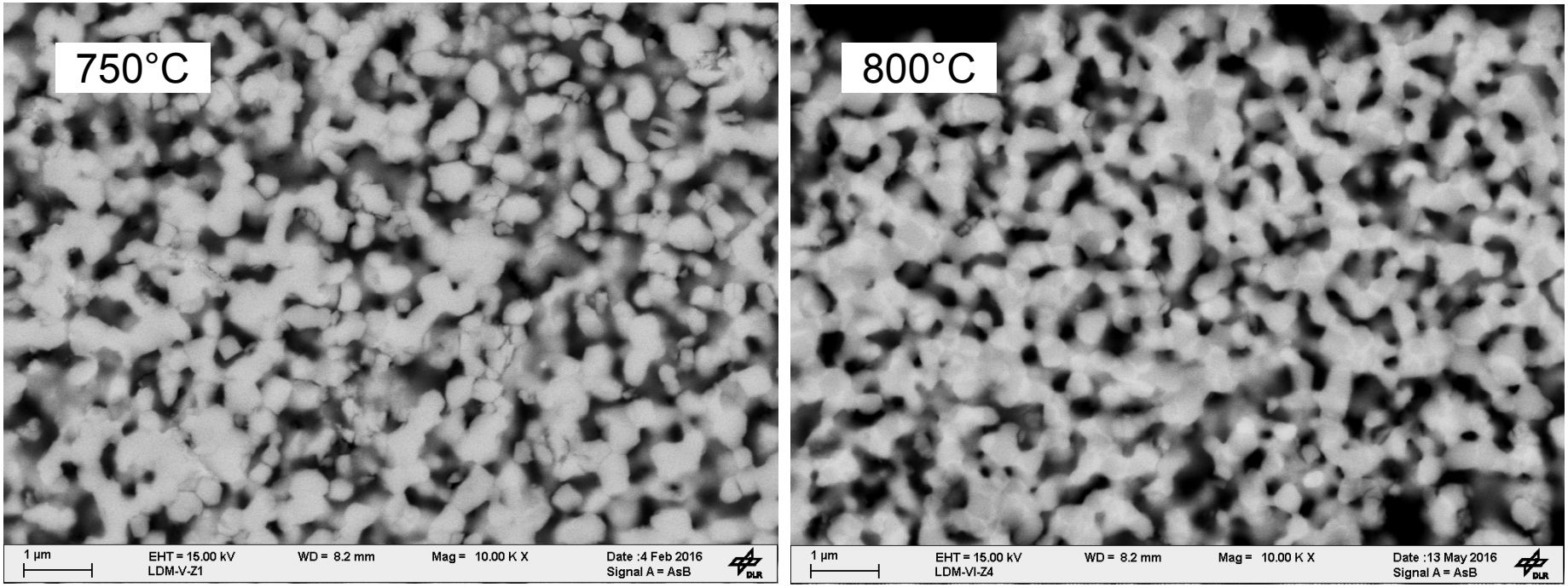
1000 h @ 1.5 A/cm^2





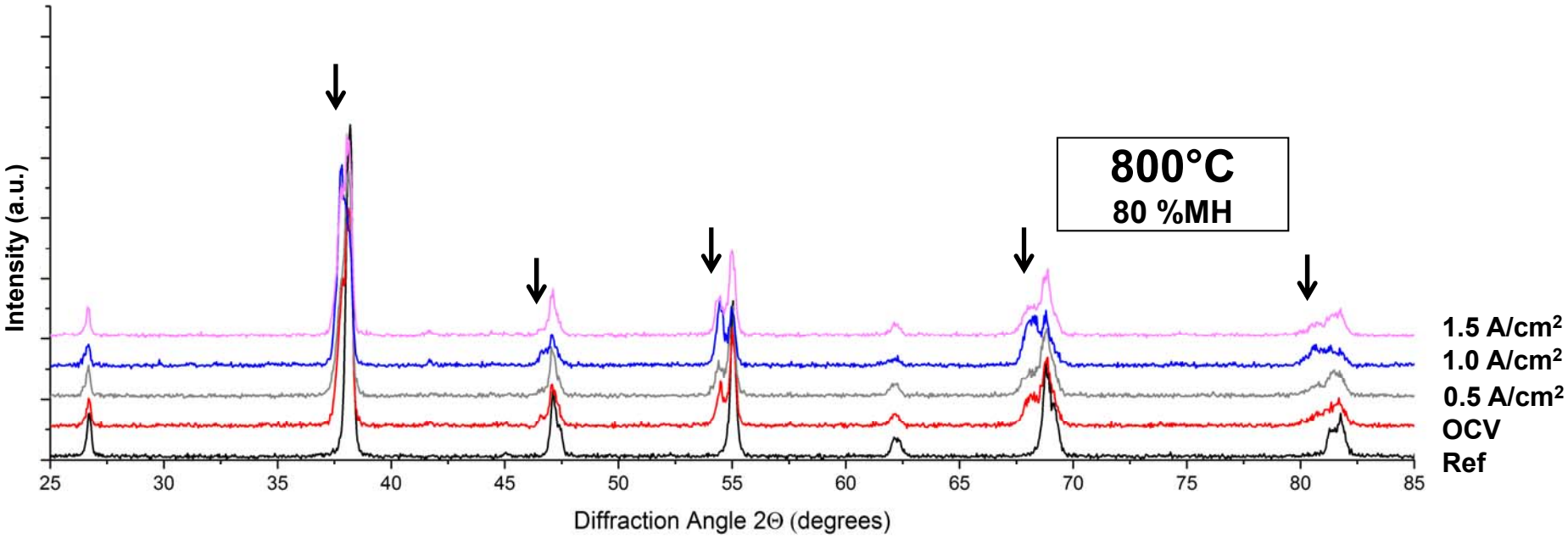


Degradation Results: Oxygen Electrode



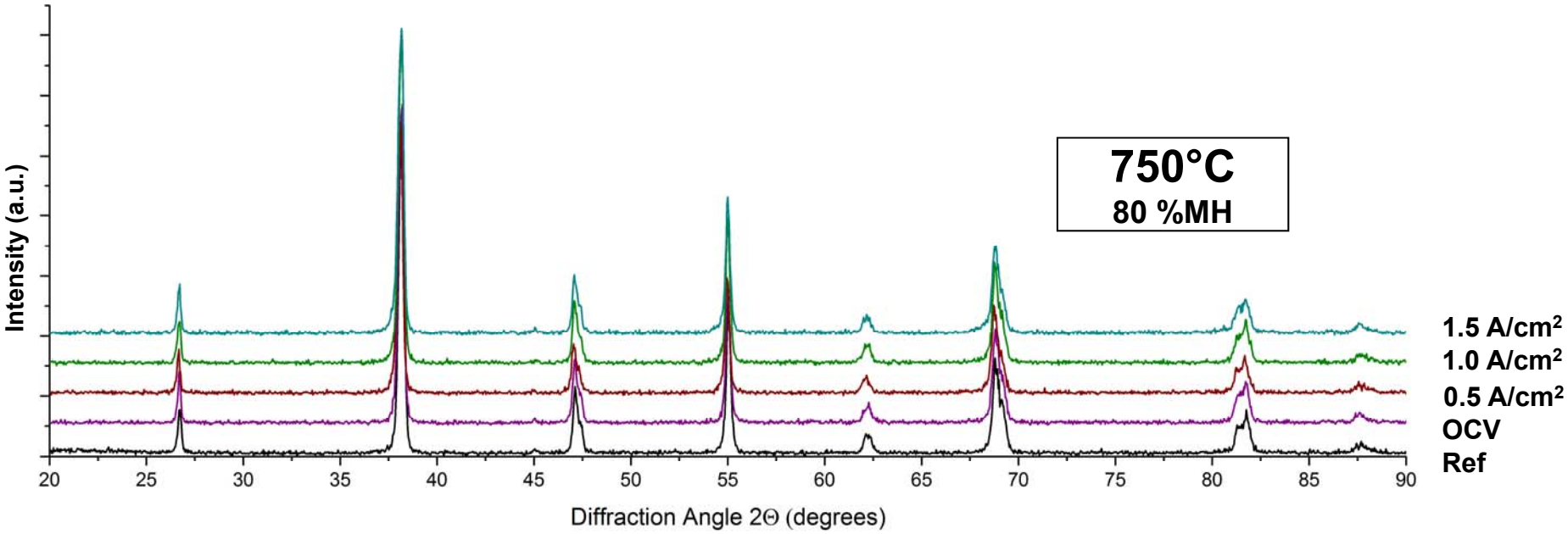
- Change in phase composition observable in BSE-SEM
- Correlates with new peaks on XRD pattern
- Correlates with degradation of electrochemical activity

Degradation Results: Oxygen Electrode



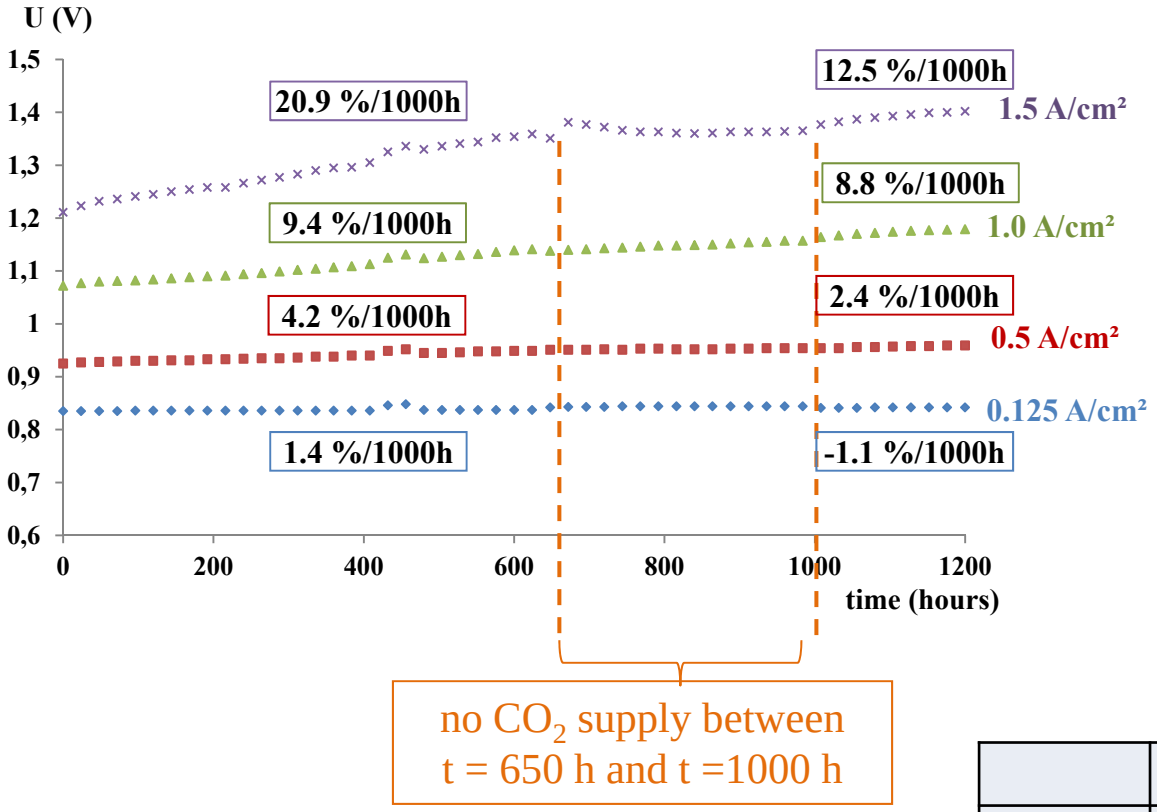
- New peaks in XRD patterns → suggest formation of new crystalline phase
- Observable at all current densities, but no clear trend
- Similar at 800 °C and 850 °C

Degradation Results: Oxygen Electrode



- New peaks in XRD patterns → suggest formation of new crystalline phase
- Observable at all current densities, but no clear trend
- Similar at 850 °C and 800 °C
- Not detectable at 750 °C

Long-term Operation (1200 h) in Co-Electrolysis Mode



Operating conditions:

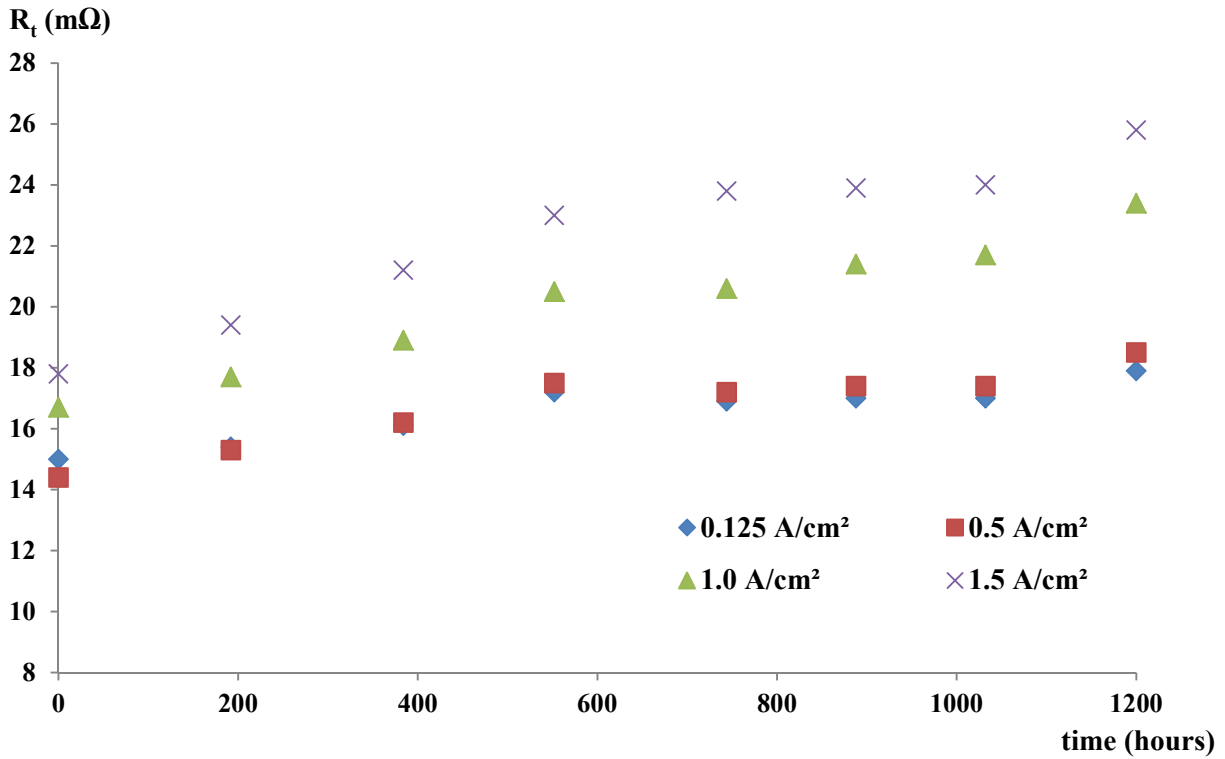
T = 800°C

Oxygen electrode: O_2

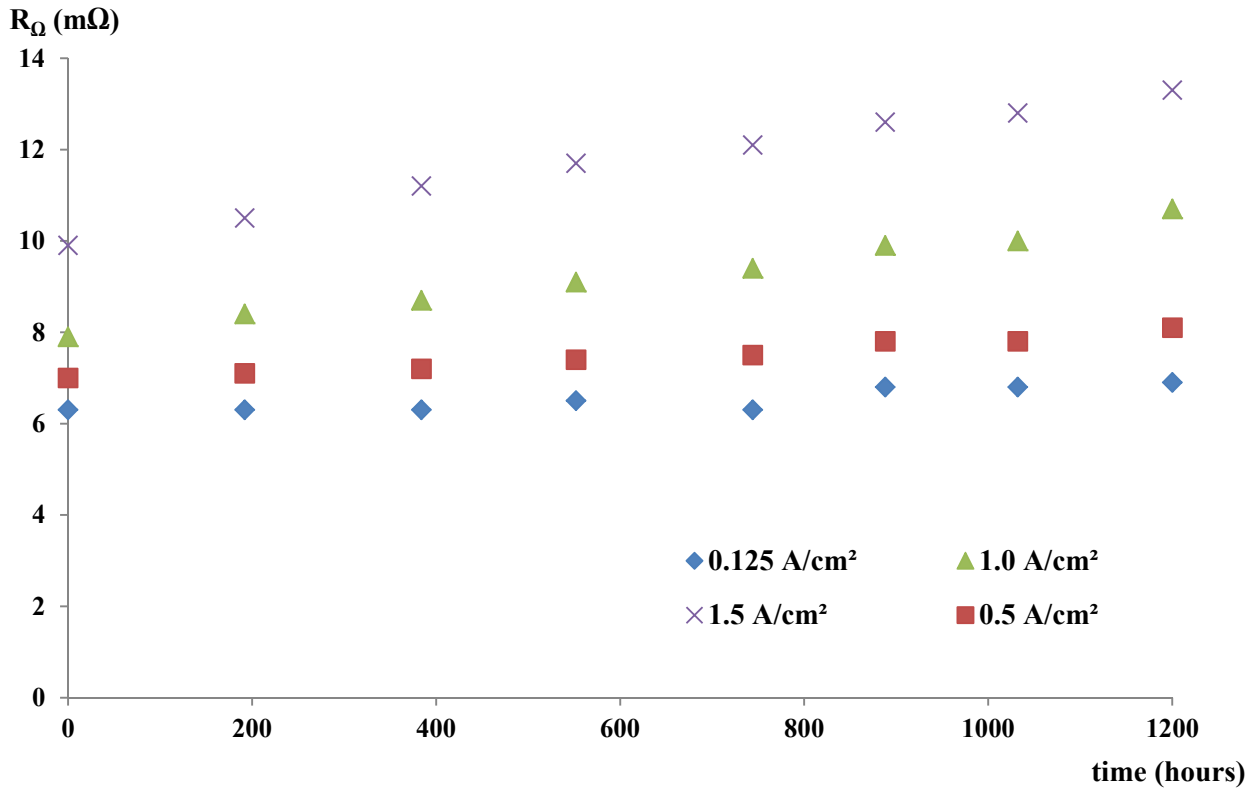
Fuel electrode: 75% H_20 + 20% CO_2 + 5% H_2

	Cell 1	Cell 2	Cell 3	Cell 4
I (A)	2	8	16	24
i (A/cm^2)	**0.125**	**0.5**	**1.0**	**1.5**

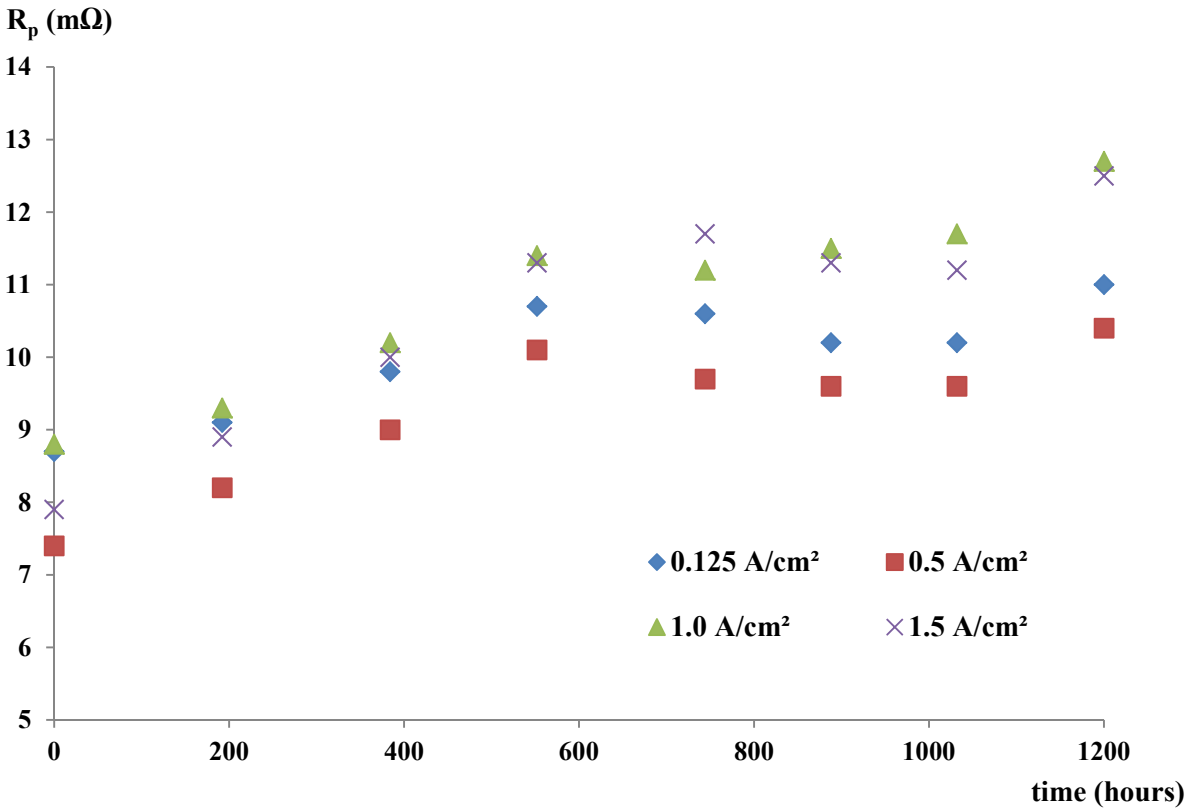
Degradation Results: Total Resistance R_t over Time



Degradation Results: Ohmic Resistance R_Ω over Time



Degradation Results: Polarization Resistance R_p over Time



Summary

Steam electrolysis: Correlation between degradation and operating conditions such as current density, temperature and humidity has been investigated

- Ohmic degradation dominates overall degradation and increases with current density
- Two major ohmic degradation processes:
  - Ni depletion: f(i) above T and humidity threshold
  - "Underlying" degradation: lower at higher temperatures, ~~f(humidity)~~
- Changes in the oxygen electrode:
  - Oxygen electrode contributes to degradation and is independent of current density
  - XRD and BSE-SEM images show change of phase composition
  - Correlates with degradation of electrochemical activity
- Fuel electrode degradation:
  - Stronger at higher current densities
  - Ni agglomeration at high T

Co-electrolysis: Degradation study similar to steam electrolysis mode has been started and will be continued to elucidate detailed degradation mechanisms

Acknowledgment

I‘d like to thank my PhD student Michael Hörlein for his scientific work and strong effort as well as Dr. Aziz Nechache for continuing this work.

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Thank you for your attention