# Sulfur Poisoning of Ni/CGO Anodes: A Long-Term Degradation Study

Matthias Riegraf, Rémi Costa, Günter Schiller, K. Andreas Friedrich

German Aerospace Center (DLR), Stuttgart, Germany

27.07.2017

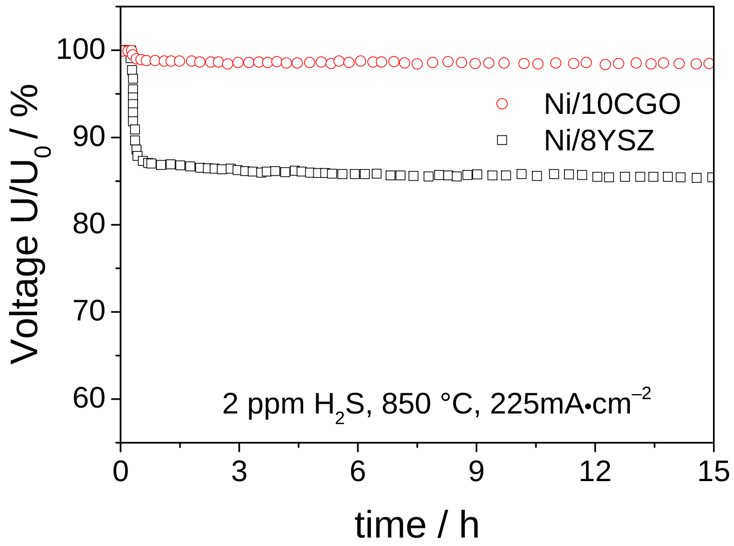
SOFC Degradation

Bundesministerium für Bildung und Forschung

DLR

# Motivation and aim of the work

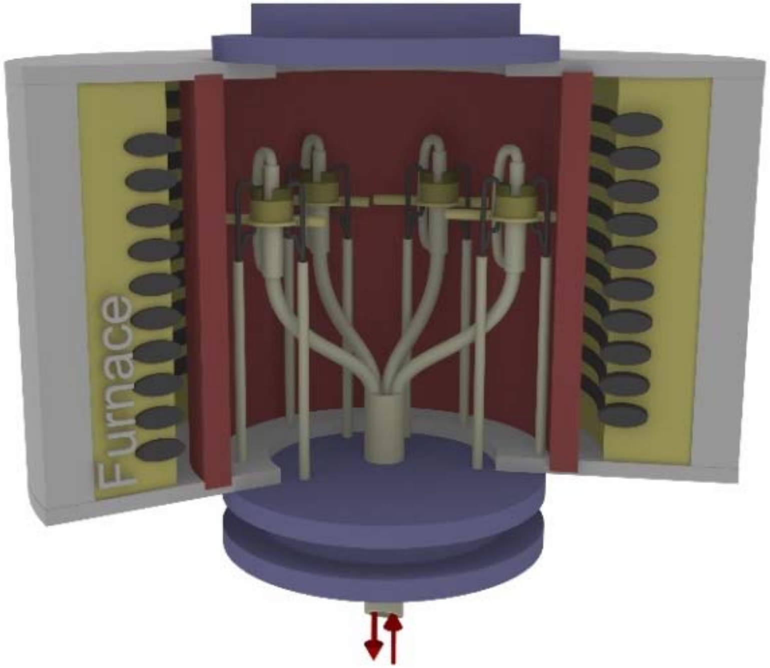
- Sulfur-containing impurities in common SOFC fuels
- Surface poisoning of Ni-based anodes with sulfur
- Higher short-term sulfur tolerance of Ni/CGO than Ni/YSZ in $H_2/H_2O$ fuels [1]
- CO conversion on Ni/CGO possible even under severe sulfur poisoning conditions
- Long-term stability?




**Goal:** Understanding of long-term degradation behavior of Ni/CGO-based cells under sulfur poisoning conditions

[1] Schubert et al., *Journal of Power Sources*, 217, (2012), 364;

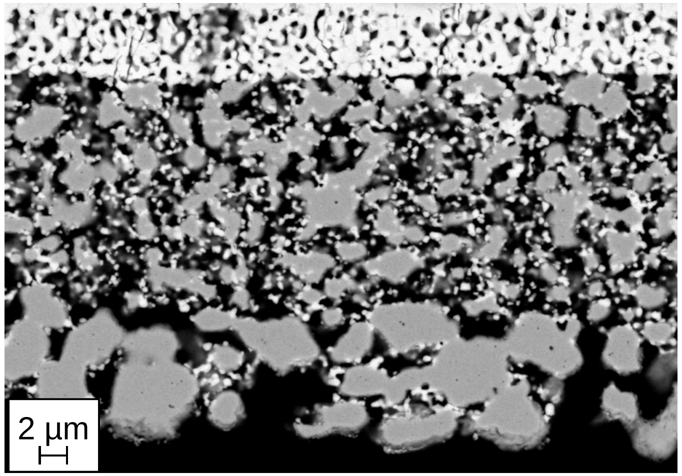
# Methodology

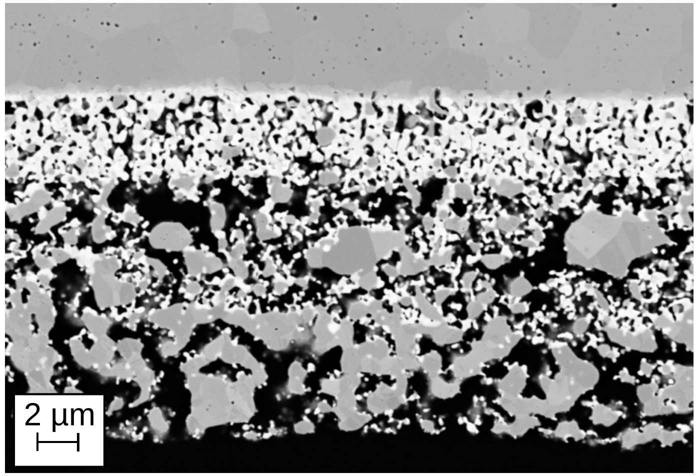



- Simultaneous measurement of up to four cells under variation of $H_2S$ concentration and current density

→ Comprehensive parameter studies

# Methodology




**<u>Cell A, Ni/CGO10 anode</u>** (25 µm)

- 90 µm 3YSZ electrolyte
- 65 µm LSM cathode
- 5 µm CGO10 barrier layer

**<u>Cell B, Ni/CGO10 anode</u>** (20 µm)

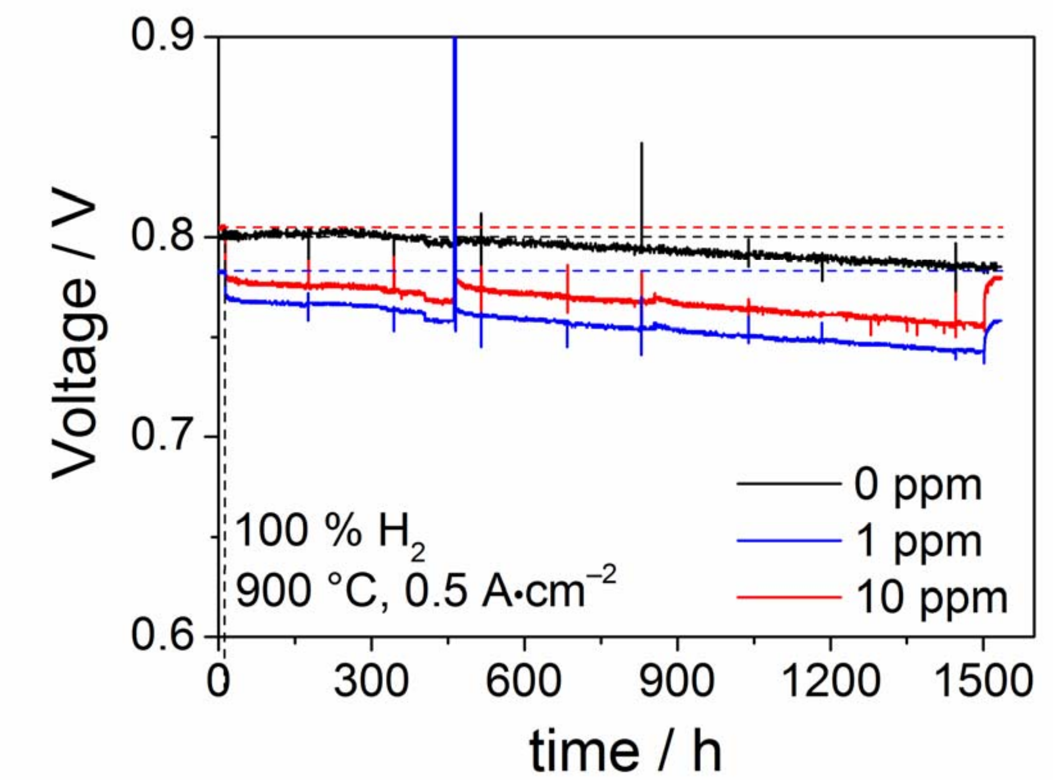
- 160 µm 10Sc1CeSZ electrolyte
- 65 µm LSMM‘ cathode
- 5 µm CGO10 barrier layer

➢ 4 long-term tests (up to 4 cells) between 200-1500 h

➢ 900 °C, to allow operation with high current densities

# Long-term test 1

Cell A, 0.5 A•cm$^{-2}$ , **100 % $H_2$**

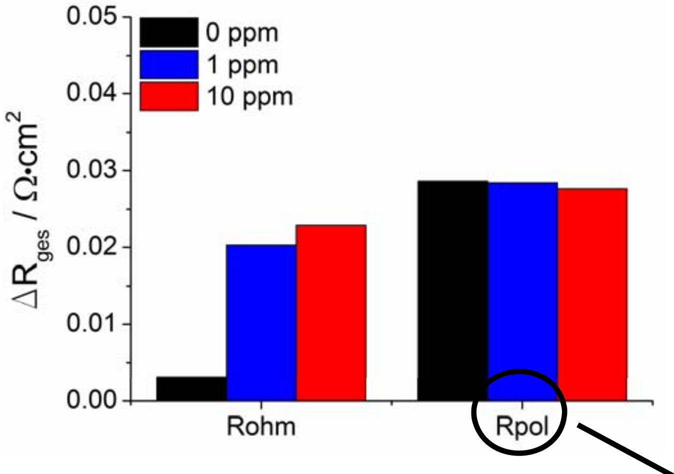


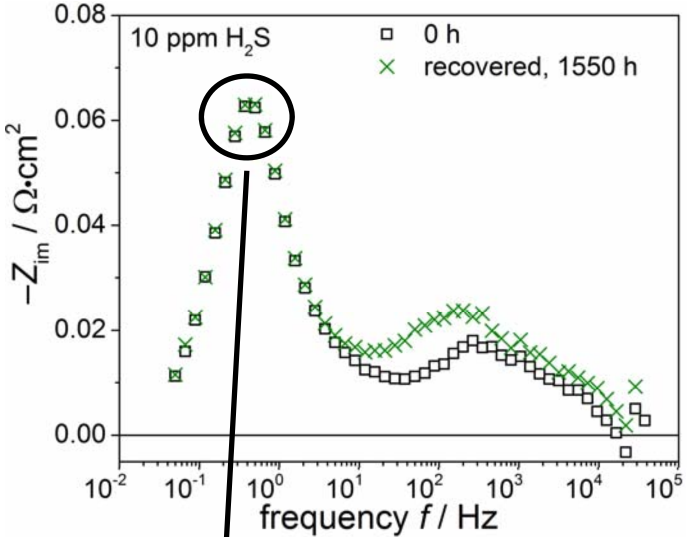

| Sulfur content | ΔV [mV] |
|---|---|
| 0 ppm | 14 |
| 1 ppm | 25 |
| 10 ppm | 23 |

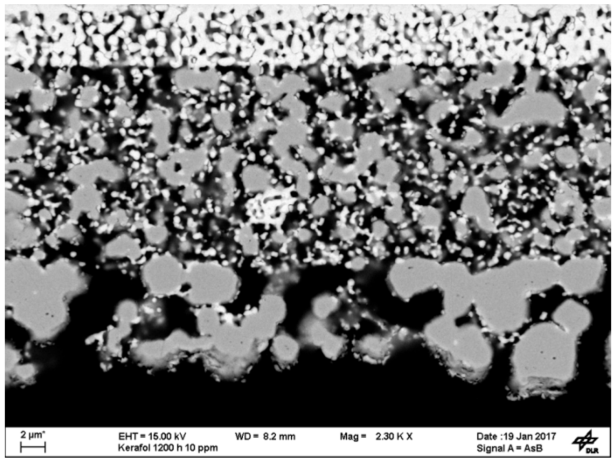
Only little sulfur-induced degradation!

# Long-term test 1

$T$ = 0.5 A•cm$^{-2}$ , 100 % $H_2$



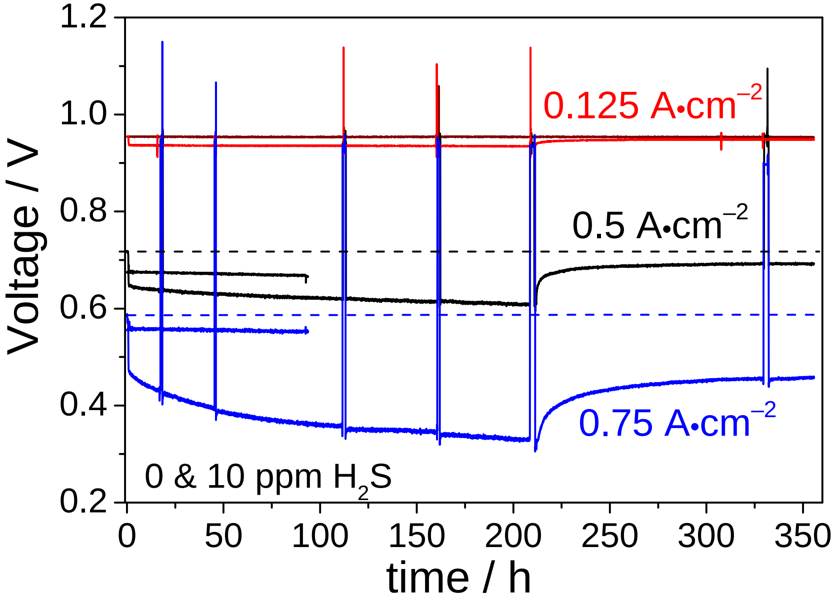



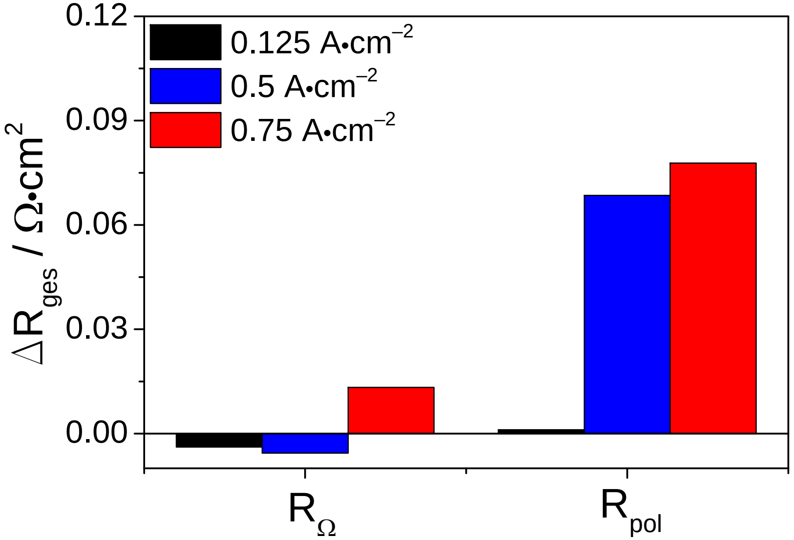

- No resistance increase of anode charge transfer process
- No microstructural changes visible
- Increase of ohmic resistance due to electronic conductivity decrease of CGO?

⇨ Tests under more critical conditions

# Long-term test 2

Cell A, 0.125, 0.5 & 0.75 A•cm$^{-2}$ , 0 & 10 ppm, **25 % $H_2$ ,75 % $N_2$**



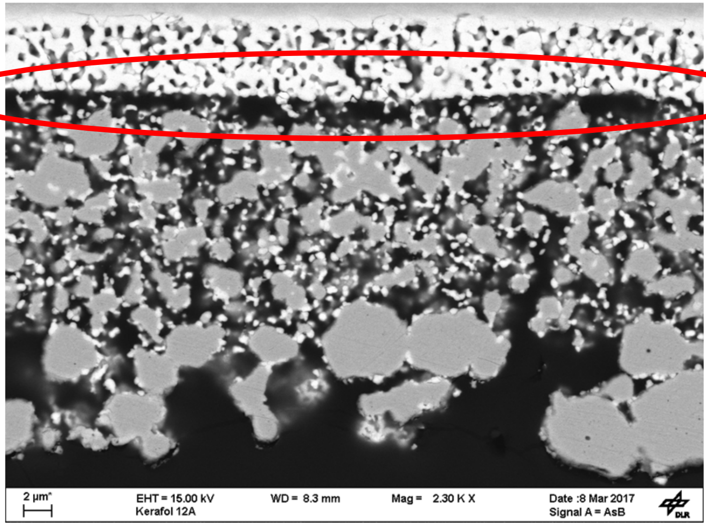




- Higher fuel utilization (47 % for 0.75 A cm$^{-2}$) and $pH_2S/pH_2$ (= 40 ppm)
- Degradation of anode charge transfer resistance at 0.5 & 0.75 A cm$^{-2}$
- $pH_2S/pH_2$ = 40 ppm is not the only determining parameter
- Reason: Large anode overpotential (smaller anode potential step) + $H_2S$ exposure?

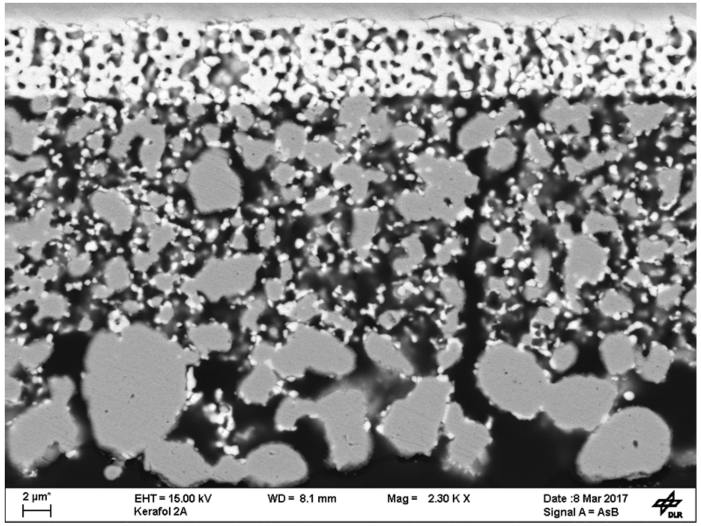
DLR

# Long-term test 2

0.75 A•cm$^{-2}$ ,10 ppm




0 ppm




- Ni depletion at electrode/electrolyte interface
- Has been reported in SOFC mode before [1,2]
- Similar to degradation in electrolysis mode [3,4] → However, operation at completely different potential

[1] Holzer et al, *J. Power Sources*, **196**, 1279 (2011). [2] Zekri et al., *Fuel Cells*, **17**, 359 (2017).
[3] Hoerlein et al., *ECS Trans.*, **68**, 3553–3561 (2015). [4] Chen et al., *J. Electrochem. Soc.*, **160**, F883 (2013)

# Long-term test 2: 3D reconstruction via FIB/SEM [1]

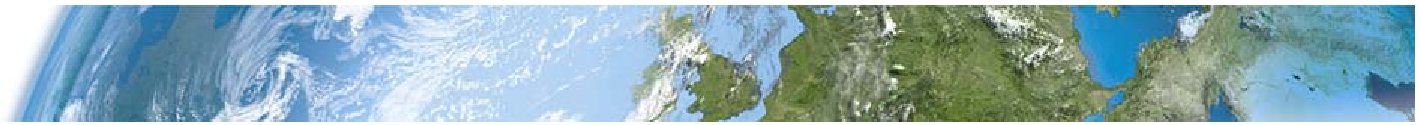
Reduced reference cell, 0.125 (with 10 ppm) & 0.75 A•cm$^{-2}$ (with 10 ppm)
12.2 x 12.73 x 12.75 µm$^3$ (=1980 µm$^3$)

| | Test | Ni content | CGO content | Pore content | Percolation Ni | TPB density [µm•µm$^{-3}$] |
|---|---|---|---|---|---|---|
| | **Reference** | 28.5 | 15.3 | 56.2 | 92.7 | 4.59 |
| Not degraded | **0.125-10ppm** | 28.5 | 14.8 | 56.7 | 93.4 | 3.14 |
| Degraded | **0.75-10ppm** | **24.4** | 14.8 | **60.8** | **90.9** | **2.79** |

- Degraded sample: Ni depletion correlates with increased porosity
- Also loss in Ni percolation and decreased TPB length

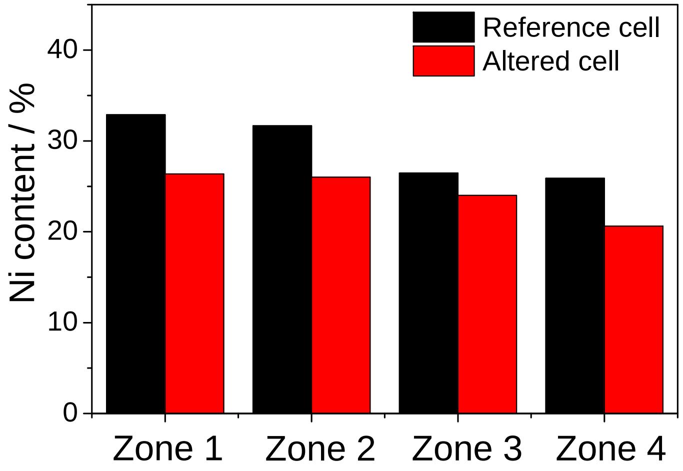
⇨ Microstructural changes related to Ni → Where does the Ni go?

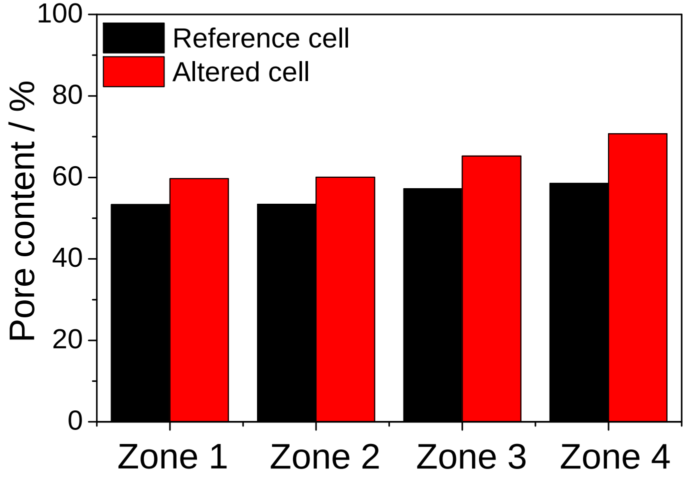
[1] Measurements carried out by Atef Zekri at University of Oldenburg

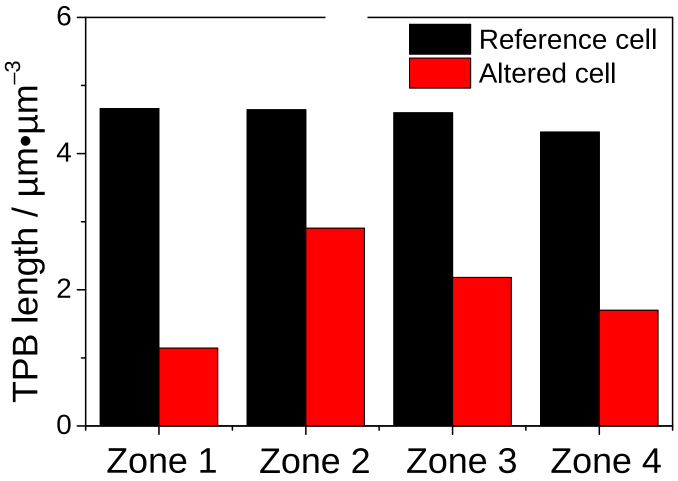


# Long-term test 2: 3D reconstruction via FIB/SEM [1]

Four segments in the anode functional layer
1: at electrolyte,…,4: at contact layer (3.0 x 12.73 x 12.75 µm³)



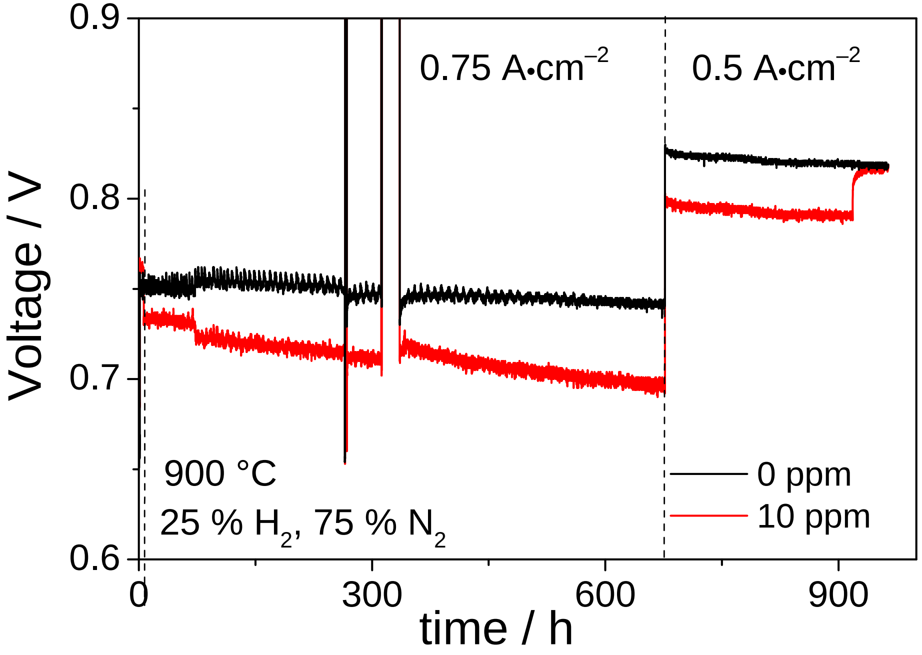

- Spatial resolution
- General trends: Ni depletion, increased porosity, decreased TPB length

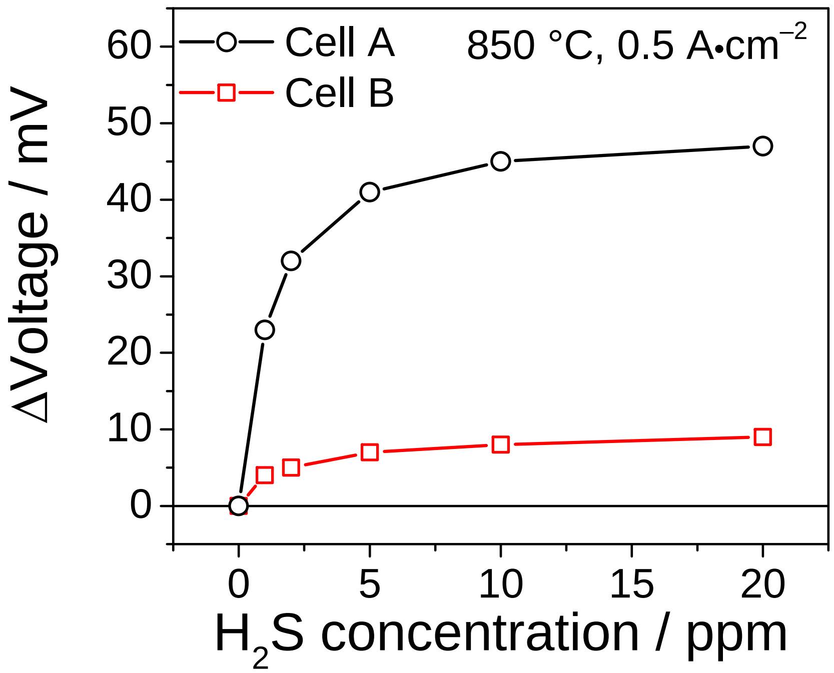
→ Ni migrates away from anode functional layer

[1] Measurements carried out by Atef Zekri at University of Oldenburg

# Long-term test 3

**Cell B,** 0.5 & 0.75 A•cm$^{-2}$ , 25 % $H_2$ ,75 % $N_2$




- Same conditions as for cell A → No visible degradation
- Confirms effect of anode overpotential on onset of degradation

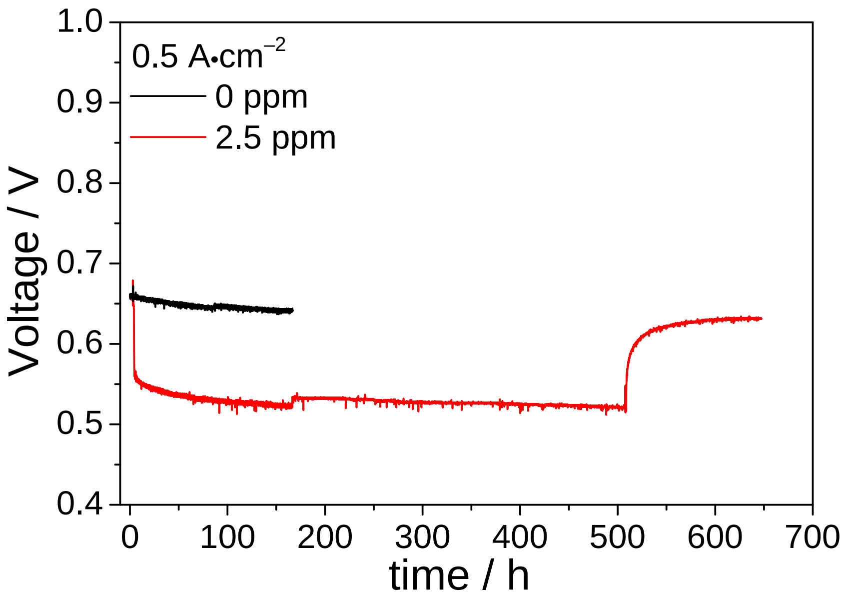
→ Extent of short-term poisoning indicates long-term stability

# Long-term test 4

0.5 A•cm$^{-2}$ , 25 % $H_2$ ,75 % $N_2$, **500 ml/min**

Experiments at more realistic fuel utilization (FU = 60 %)

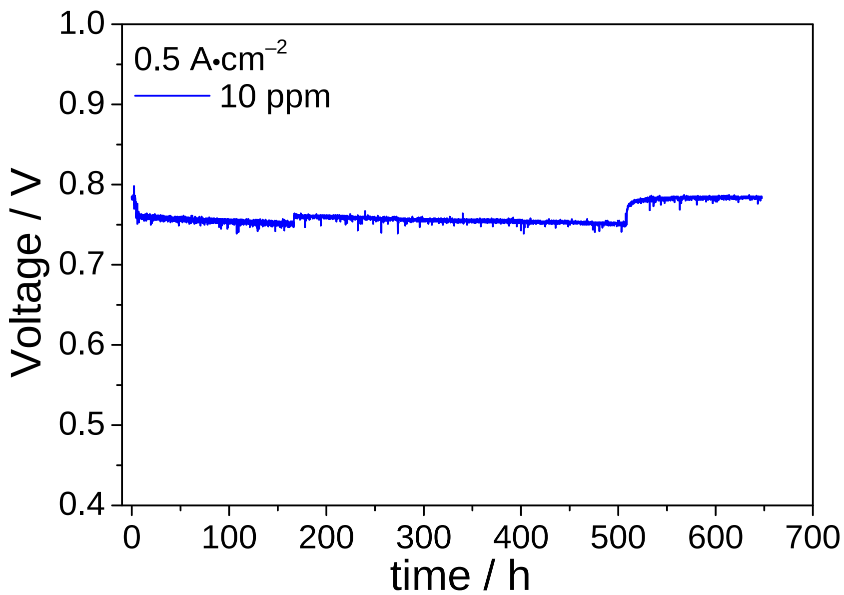
Cell A (Low sulfur tolerance)




- Degradation at 10 ppm $H_2S$
- No degradation at 2.5 ppm $H_2S$

⇨ Influence of sulfur coverage on Ni

Cell B (High sulfur tolerance)




- Voltage degradation similar to previous experiment

⇨ Stable operation with 10 ppm $H_2S$ at 60 % FU

# Discussion of mechanisms

Identification of 2 degradation effects:

1) Increased ohmic resistance
   - Only visible after ~ 1000 hours
   - No significant phase transformation detected via XRD
   - Decreased electronic conductivity of CGO?

2) Increased anode charge transfer resistance (consistent with Ni/YSZ [1])
   - Triggered by small anodic potential step and large sulfur coverage on Ni
   - Ni depletion at electrolyte/electrode interface
   - Mechanism unclear

[1] Hauch, et al., *J. Electrochem. Soc.*, **161**, F734–F743 (2014)

# Discussion of mechanism

- Dissolution of sulfur into Ni bulk phase at high chemical oxygen potential → Ni surface reconstruction, enhanced Ni diffusion [1]
- Changes could lead to loss in Ni percolation
- Purely chemical mechanism not sufficient → Influence of electrochemical oxygen potential on sulfur dissolution?
- Transport mechanism either Ni evaporation or Ni diffusion
- Ni migrates away from electrolyte → Ni evaporation likely
- Possibly via $Ni(OH)_x$ formation? $pH_2O$ as driving force?
- Loss in Ni percolation precursor for Ni evaporation, similar to electrolysis mode? [2]

[1] Kishimoto et al., *J. Electrochem. Soc.*, **157**, B802 (2010); [2] Mogensen et al., *Fuel Cells*, 1 (2017).

# Summary and conclusions

- Promising long-term stability of Ni/CGO anodes
- Degradation is induced by combined influence of sulfur coverage on Ni and large anode overpotential
- Identifikation of two degradation effects: Increase of ohmic and anode charge transfer resistance
- Ni depletion at electrolyte/electrode interface
- Short-term sulfur poisoning as indicator for long-term stability

→ Operation of SOFC without desulfurization unit possible?

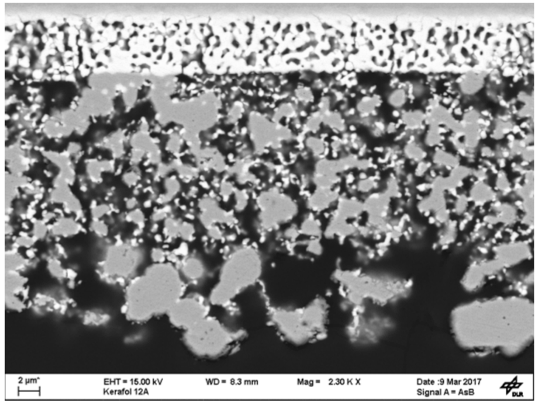
→ Especially ESC with 3YSZ electrolyte

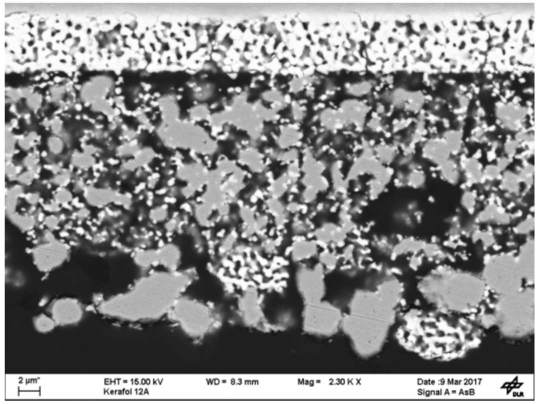
# Acknowledgments

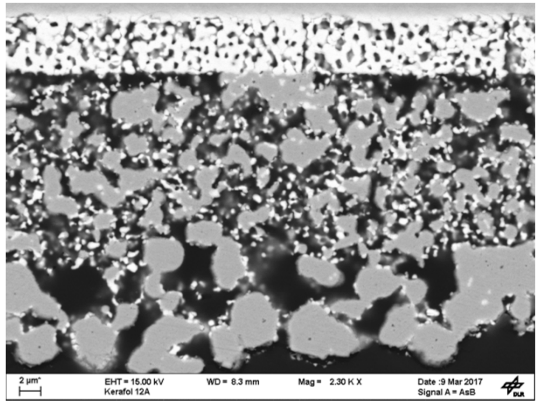

- Financial support from the German Ministry of Education and Research (BMBF) in the framework of the **“SOFC Degradation”** (Verbundvorhaben SOFC Degradation: Analyse der Ursachen und Entwicklung von Gegenmaßnahmen) project.


**Thank you for your attention!**

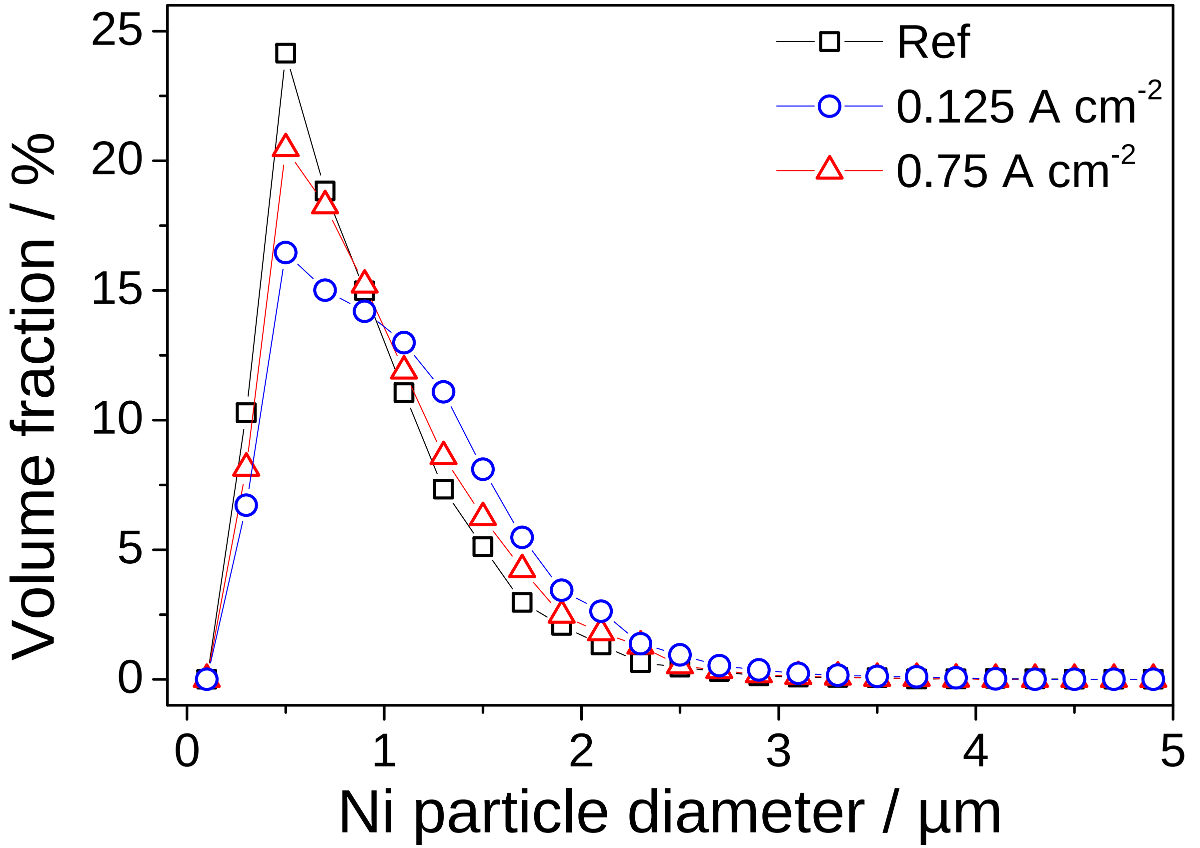
# Supplementary Information




# Particle size distribuion



# FIB/SEM