

Batterie- und Brennstoffzellensysteme

(Langzeit-) Stabilität von SOFC-Komponenten

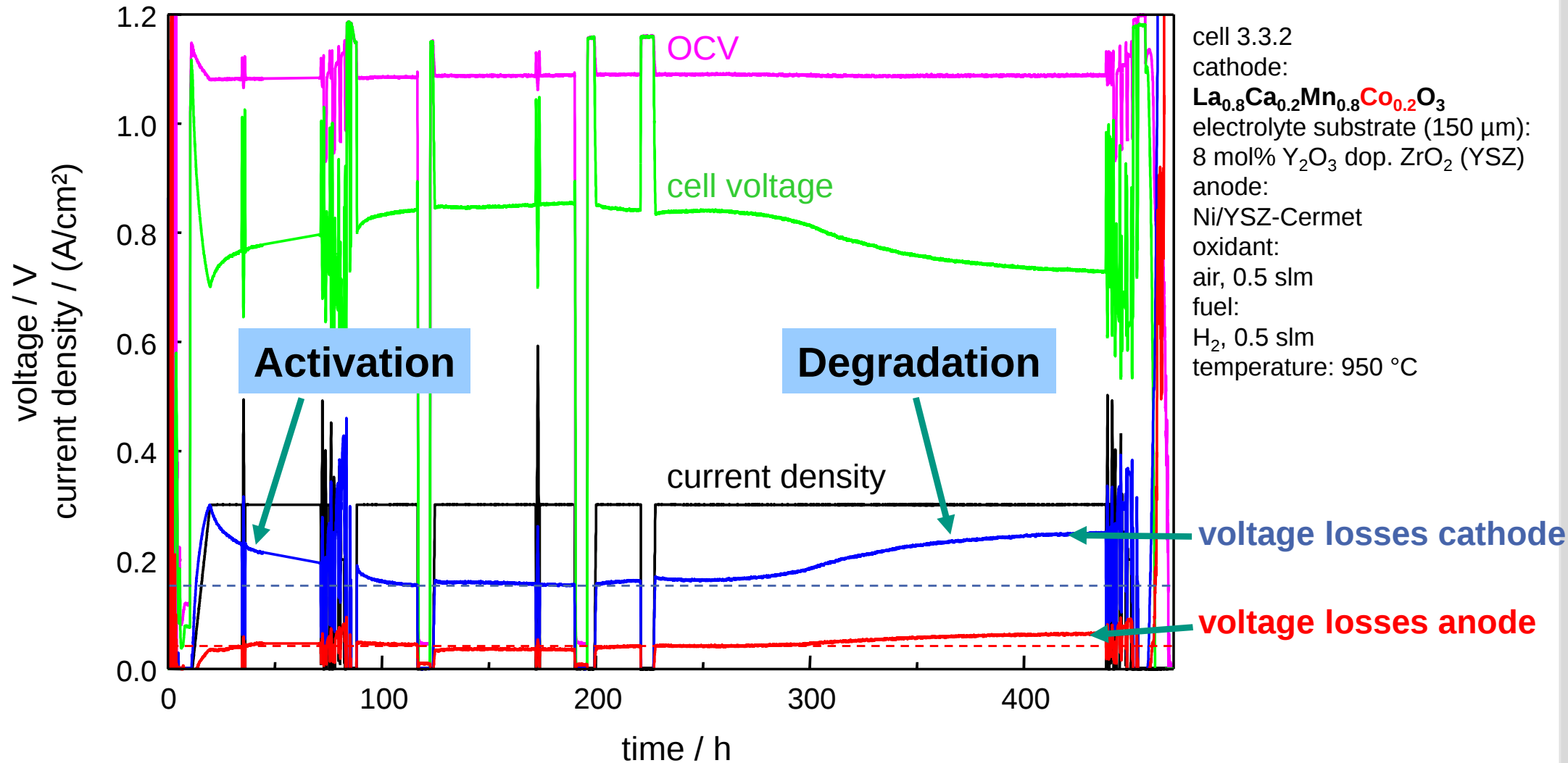
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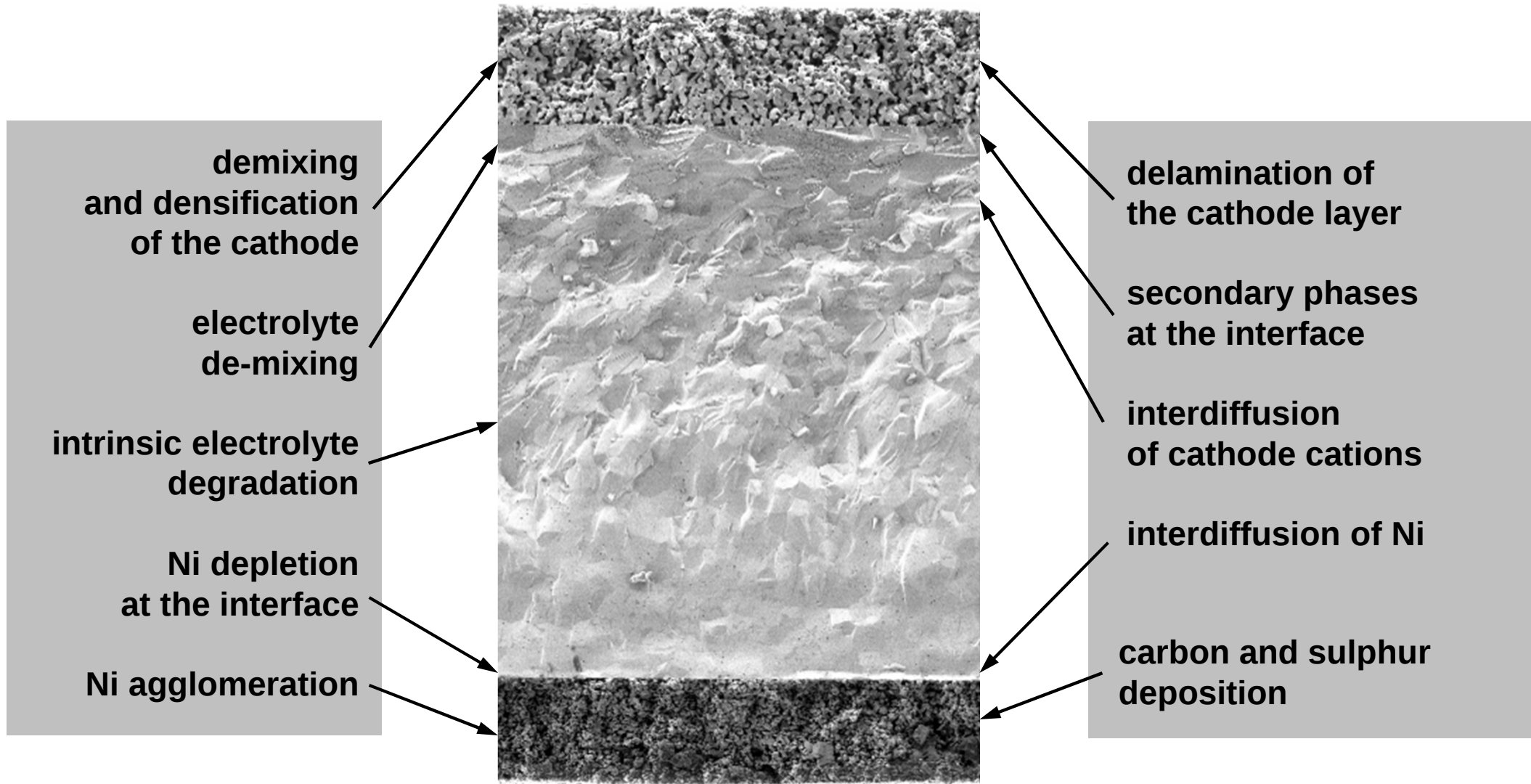
Example

Activation and Degradation of an (La,Sr)(Mn,Co)O₃-Cathode

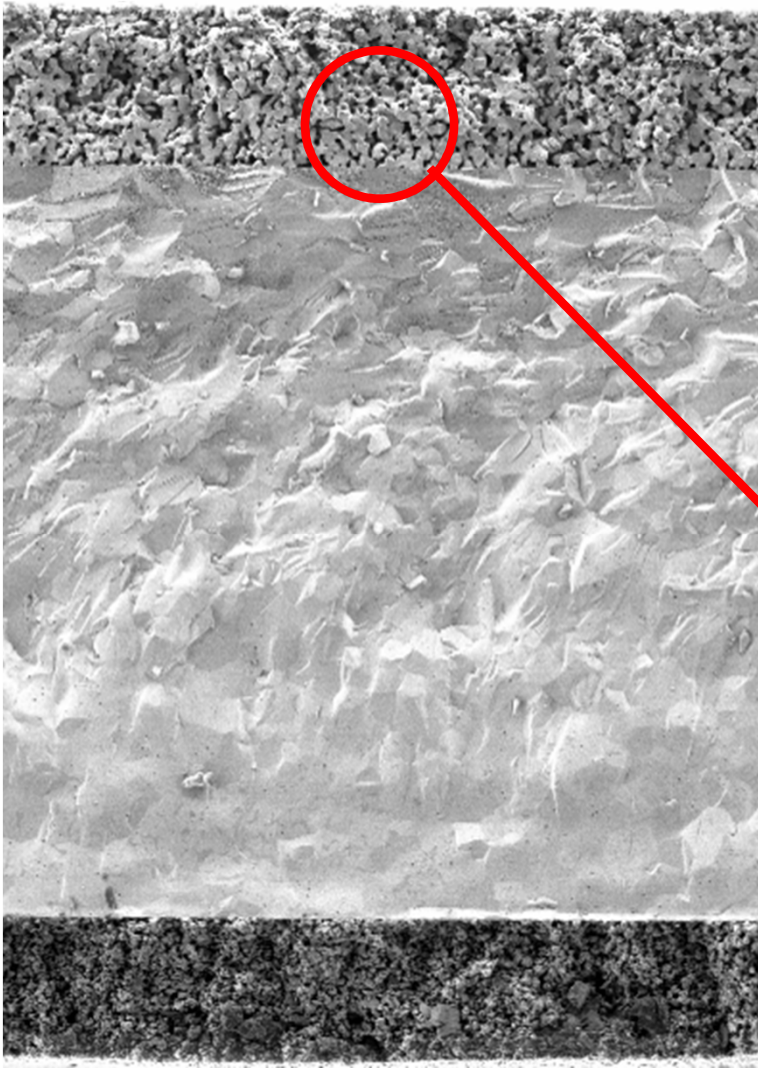


Examples

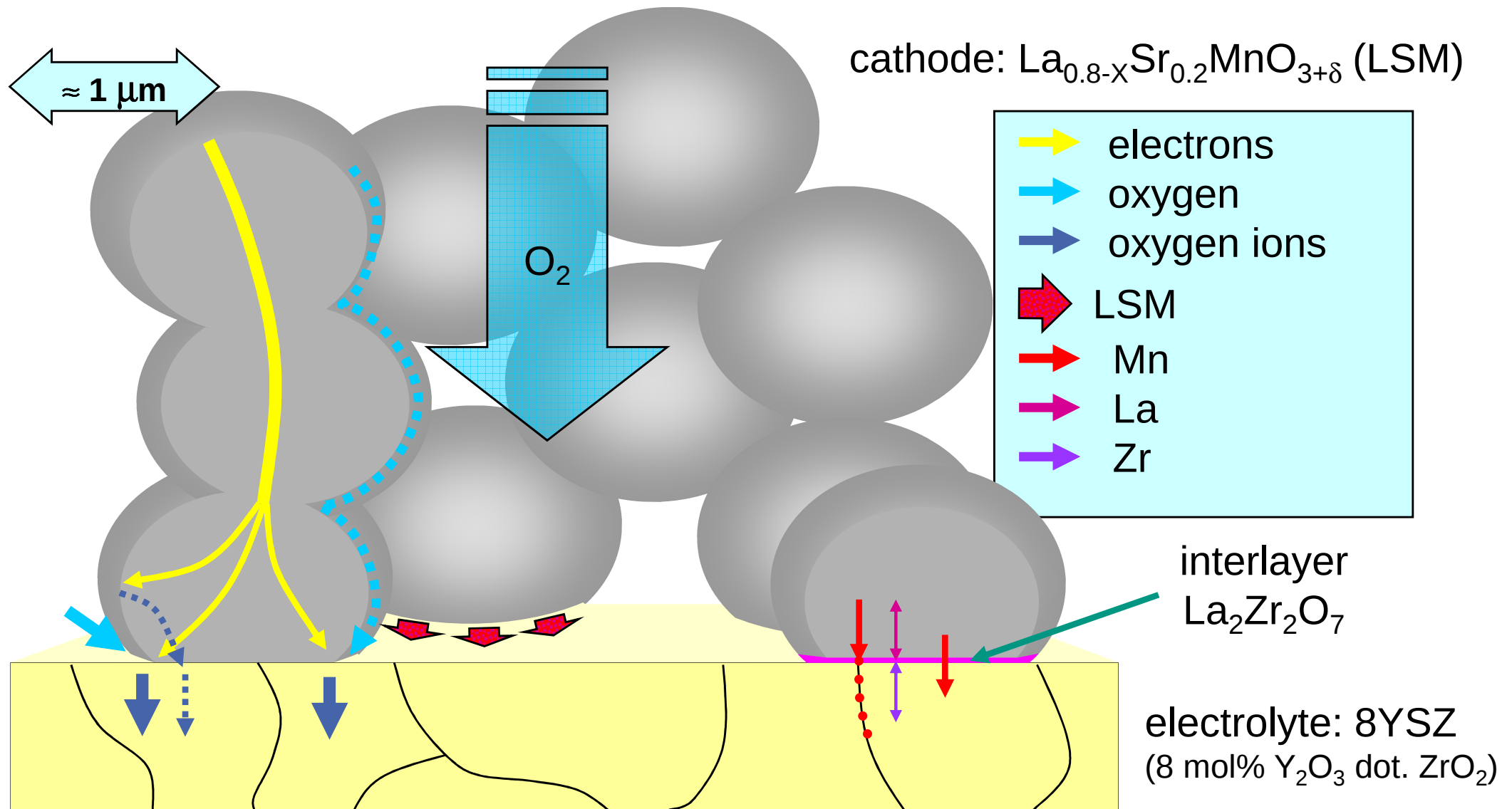
Microstructural and chemical changes during operation



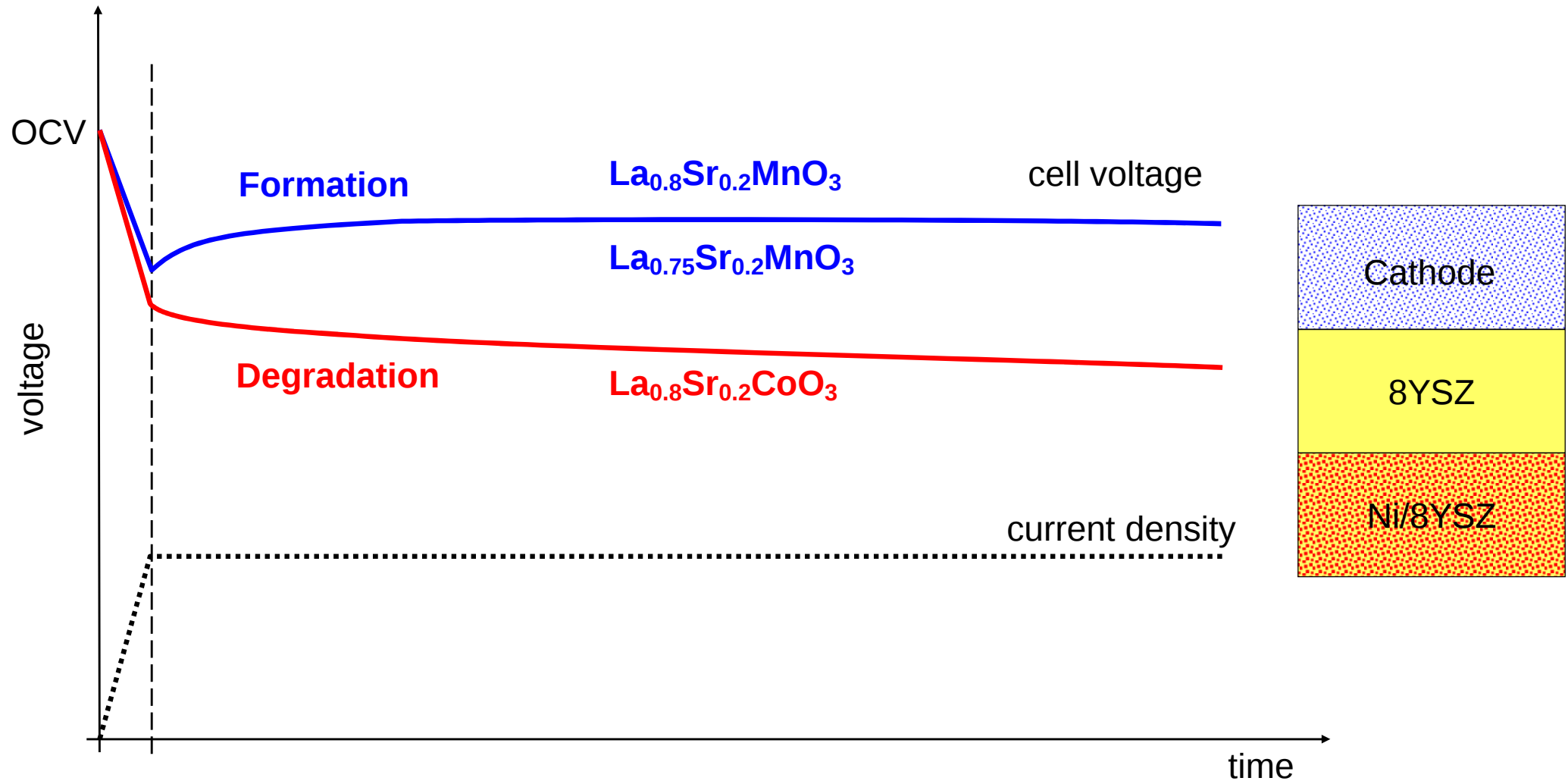
Kathode: Formierung



Cathode Degradation Transport Processes



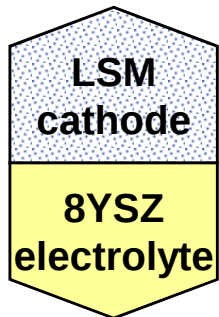
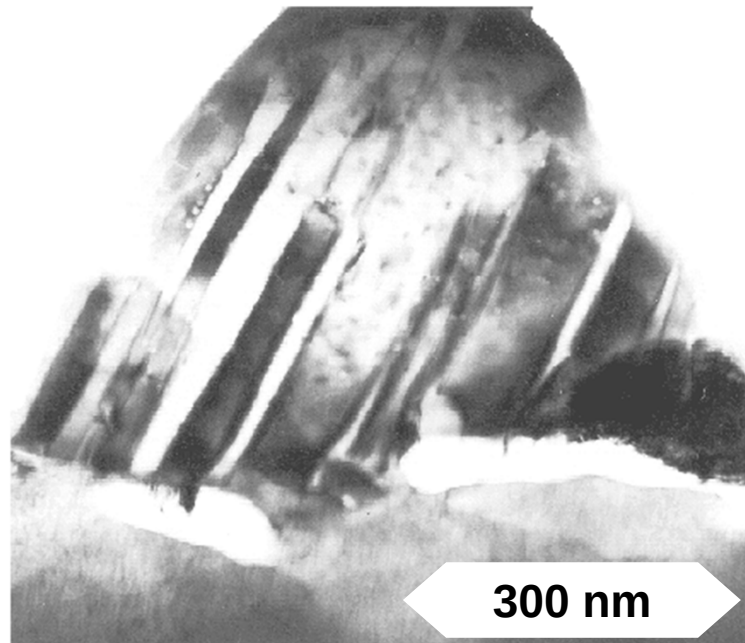
Startup Behavior of SOFC Single Cells and Stacks Formation and Degradation



Cathode Degradation

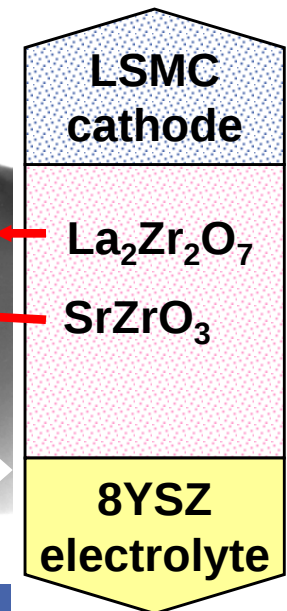
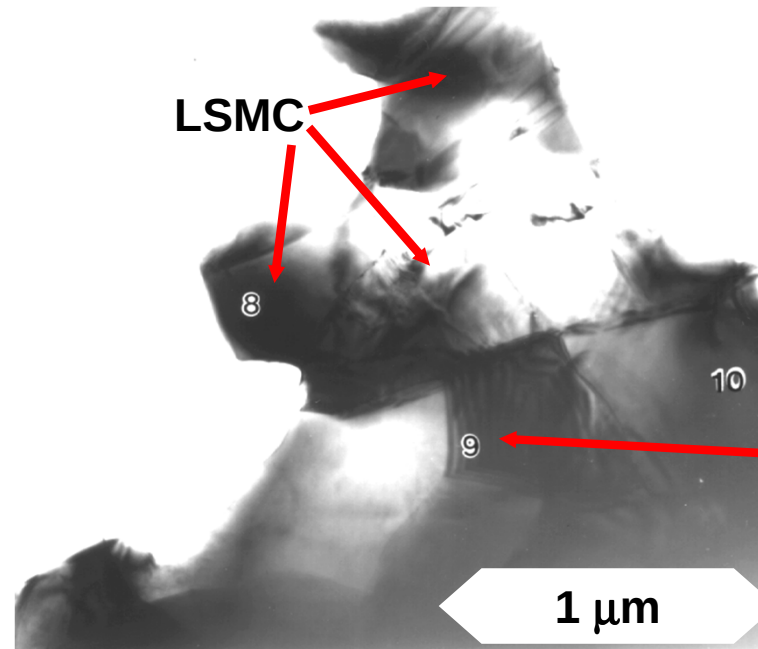
Growth of Secondary Phases at the Cathode/Electrolyte-Interface

Interface LSM/8YSZ
(LSM: $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$)



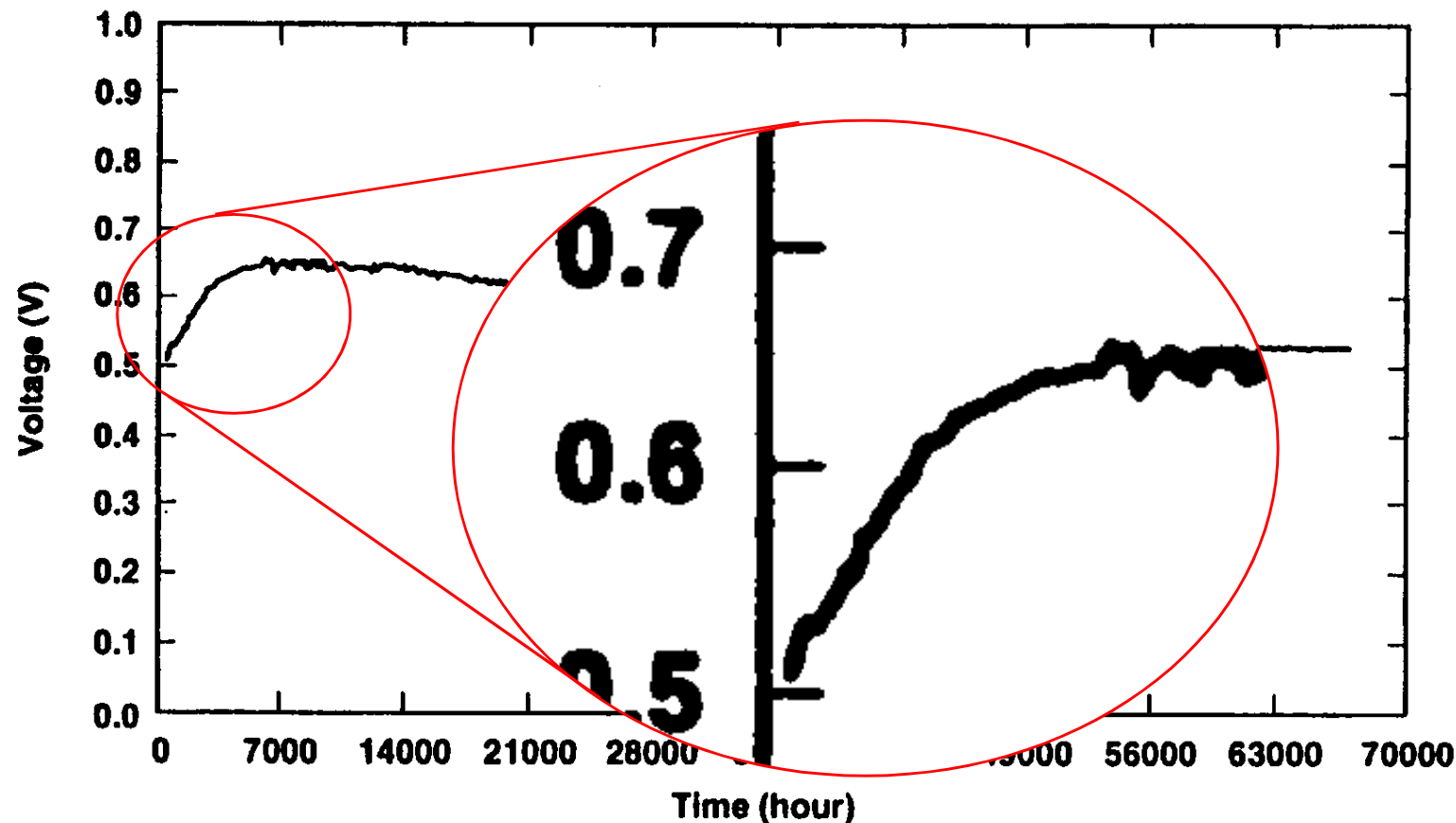
**Decreased Cathode Resistance
due to Formation**

Interface LSMC/8YSZ
(LSMC: $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}_{3+\delta}$)



**High Cathode Resistance
due to Secondary Phases**

SOFC: Formation and Long Term Test of a tubular Cell Siemens-Westinghouse SWPC (1997)



$V_{\text{start}} : 0.50 \text{ V}$

$V_{\text{max}} : 0.65 \text{ V}$

► V_{max} : Point of
max. performance

► time to V_{max} :
 $\approx 5.000 \text{ hours}$

Fig. 1. Long term test of an early-technology PST cell.

S. C. Singhal, Recent Progress in Tubular Solid Oxide Fuel Cell Technology, Proc. 5th Int. Symposium on SOFC, Ed. U. Stimming, S. C. Singhal, H. Tagawa, W. Lehnert, The Electrochemical Society, PV 97-40, 37-50, (1997)

SOFC: Formation and Long Term Test of a 5-cell Stack Sulzer Hexis (1999)

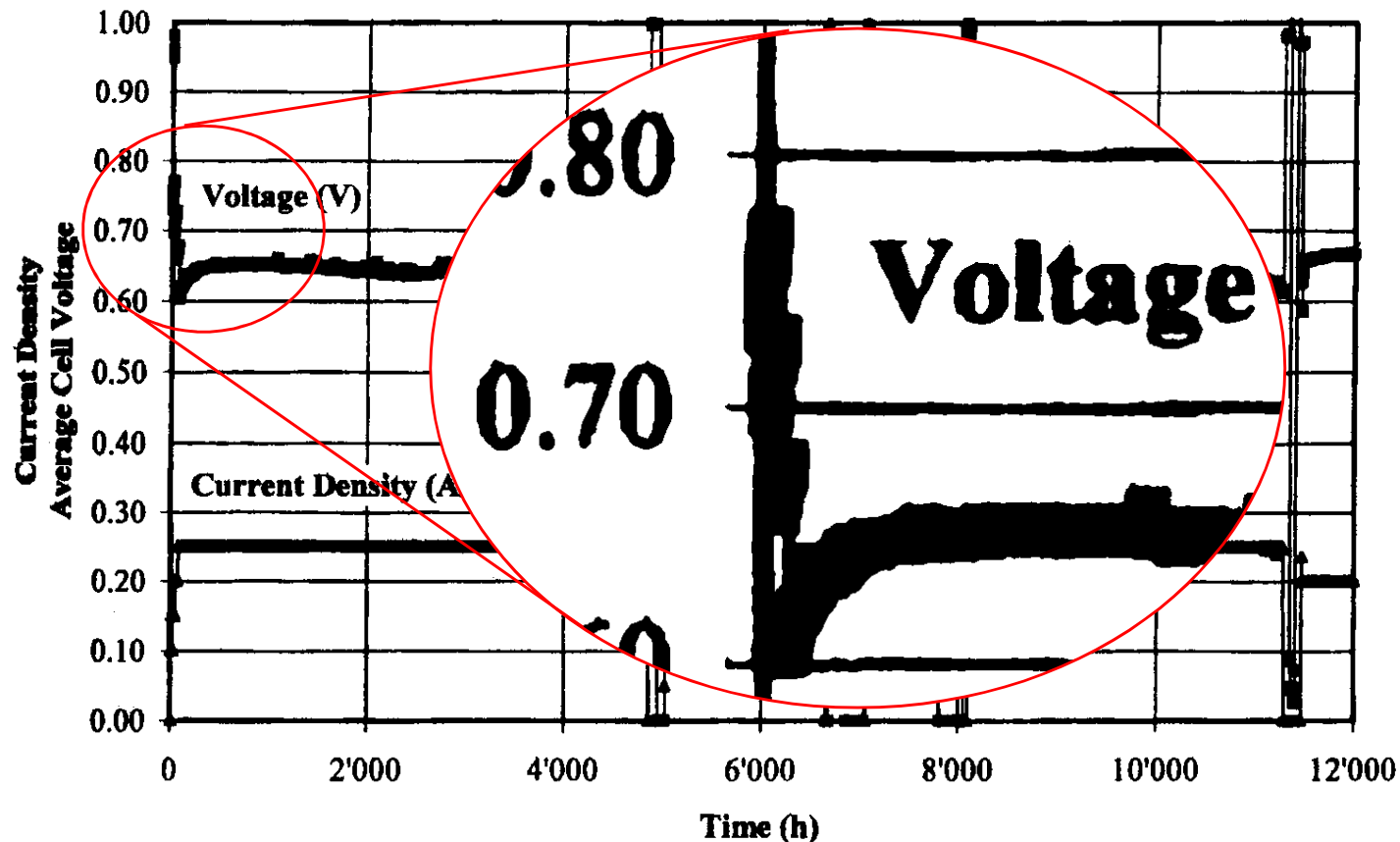


Figure 2: Negligible degradation of a five cell stack

$V_{\text{start}} : 0.60 \text{ V}$

$V_{\text{max}} : 0.65 \text{ V}$

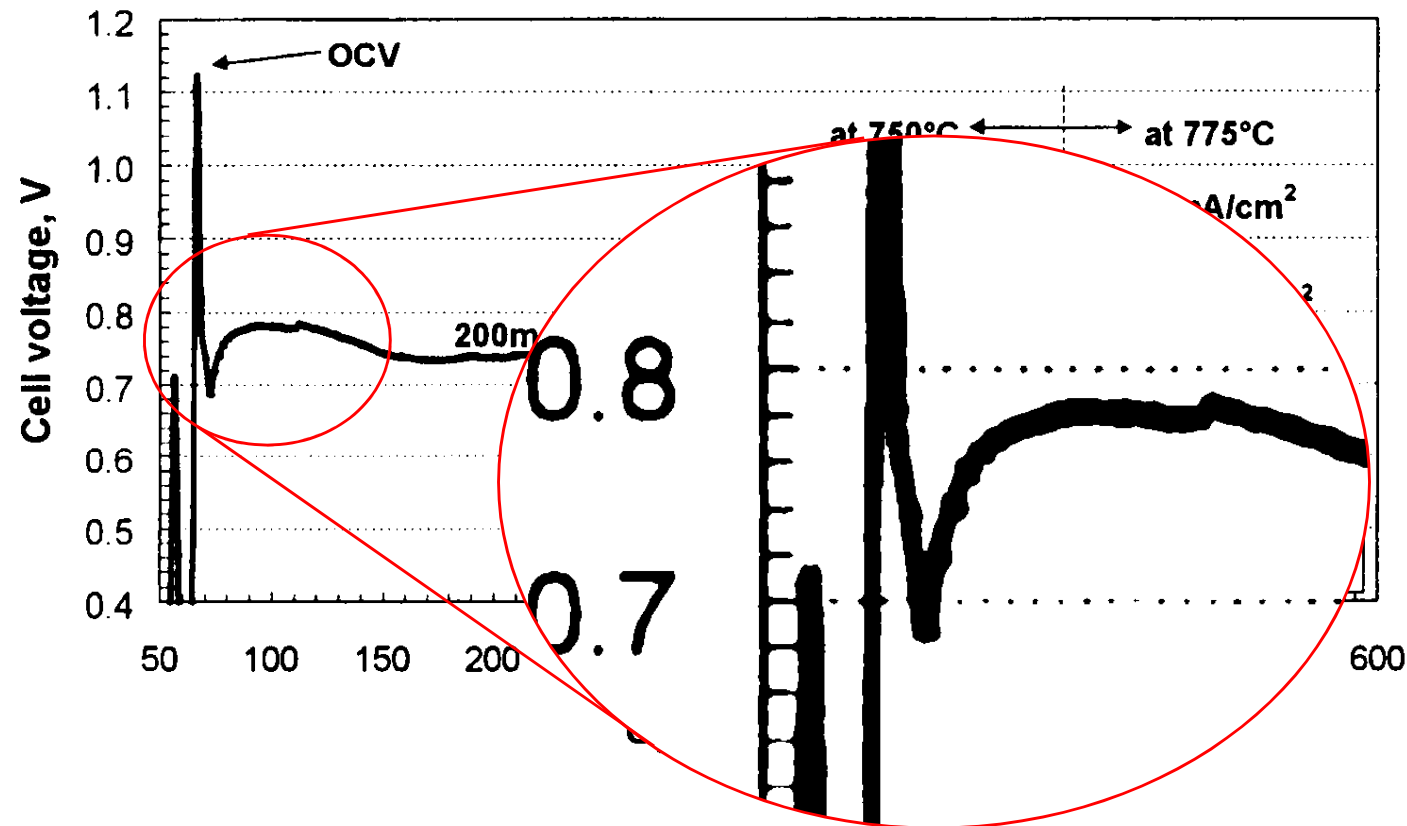
► V_{max} : Point of max. performance

► time to V_{max} :

$\approx 200 \text{ hours}$

R. Diethelm, M. Schmidt, Status of the Sulzer Hexis Product Development, Proc. 6th Int. Symp. on SOFC, Ed. S. Singhal und M. Dokiya, The Electrochemical Society, PV 99-19, 60-67, (1999)

SOFC: Formation and Long Term Test of a planar Cell Ceramic Fuel Cells Ltd. CFCL (1999)



$V_{\text{start}} : 0.68 \text{ V}$

$V_{\text{max}} : 0.78 \text{ V}$

► V_{max} : Point of
max. performance

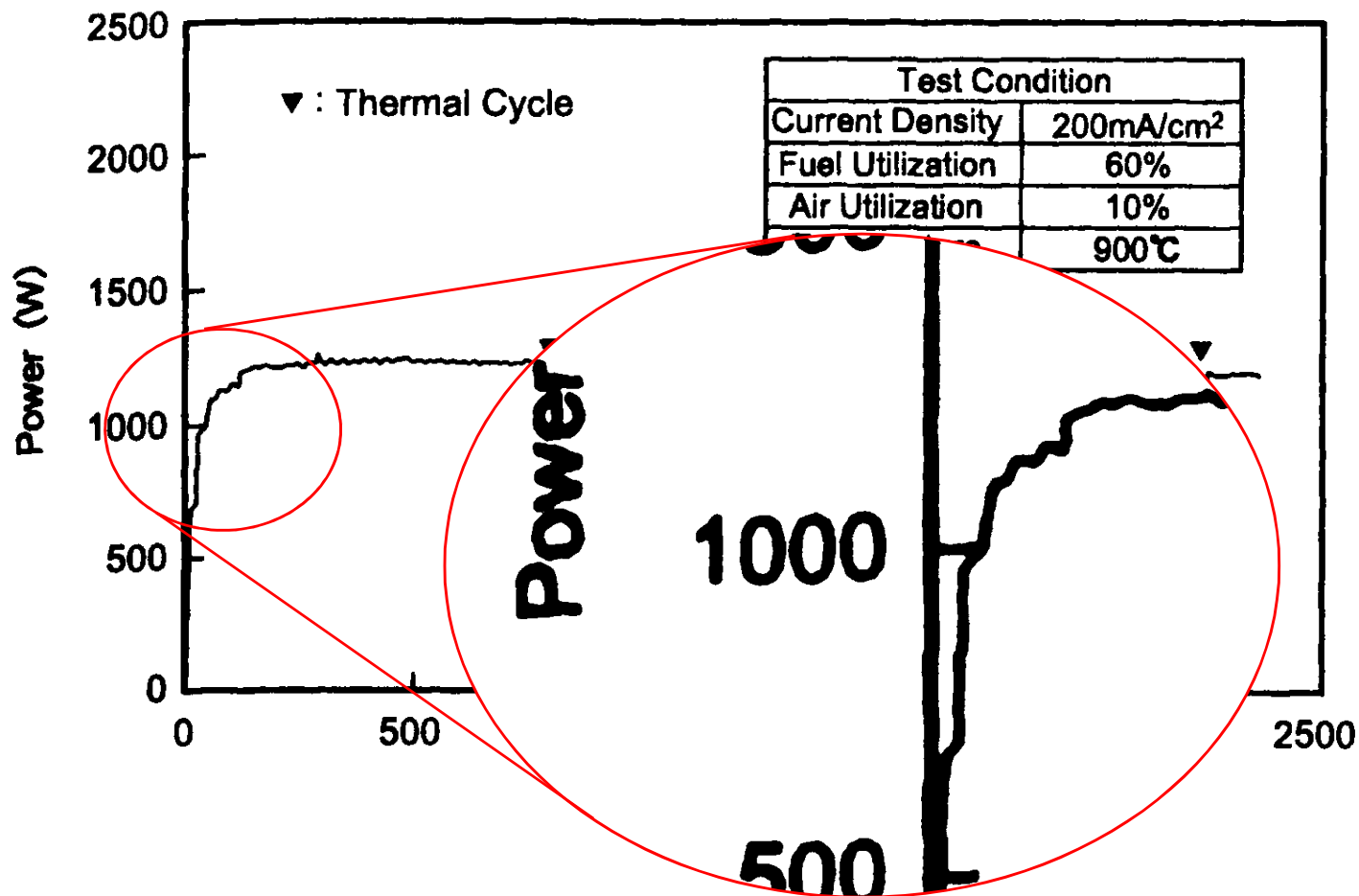
► time to V_{max} :
 $\approx 50 \text{ hours}$

Figure 2. Cell performance at 750 and 775°C tested in alumina assembly

K. Föger et al., Demonstration of Anode Supported Cell Technology in kW Class Stack, Proc. 6th Int. Symp. on SOFC, Ed. S. Singhal und M. Dokiya, The Electrochemical Society, 95-100, PV 99-19, (1999)

SOFC: Formation and Long Term Test of a 1 kW Stack

Mitsubishi Heavy Industries MHI (1999)



P_{start} : 700 W

P_{max} : 1250 W

► P_{max} : Point of max. performance

► time to P_{max} :
≈ 300 hours

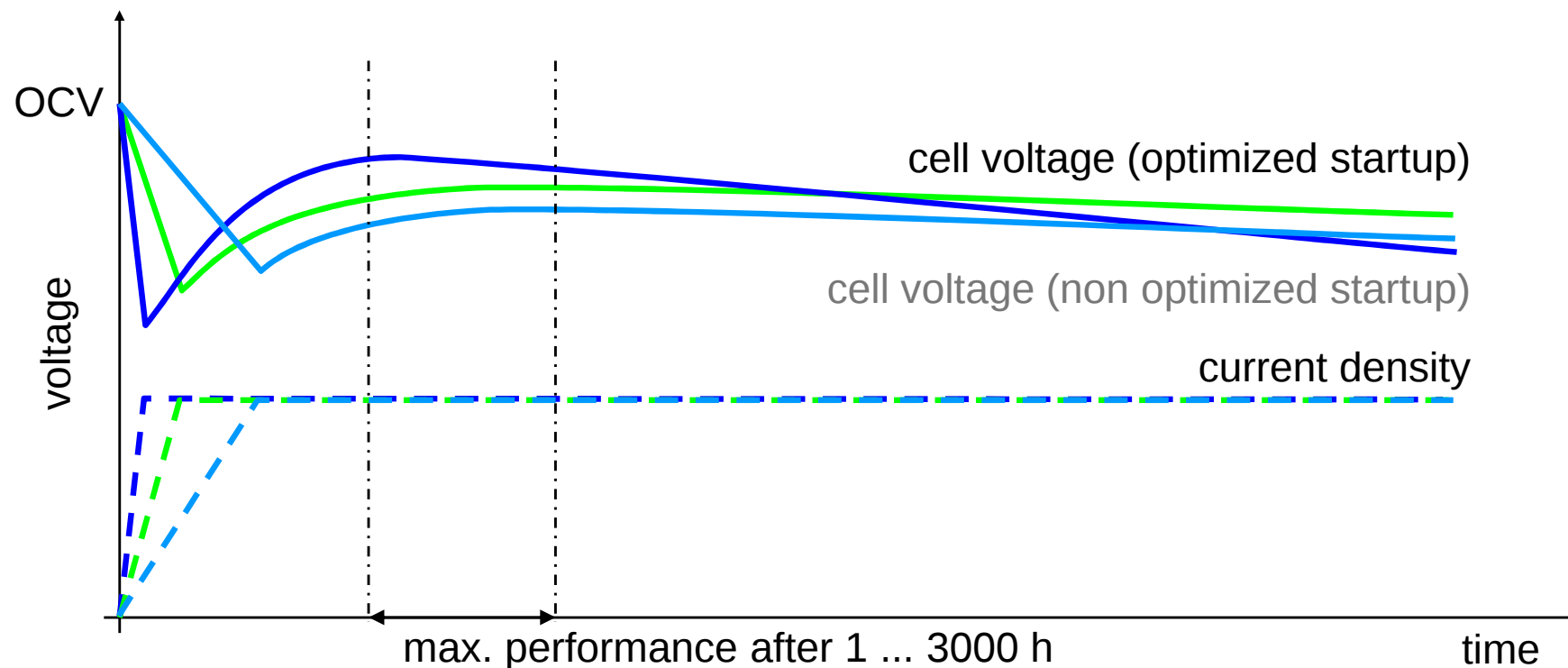
Fig. 12 Endurance Test of 1kW Module with Co-Sintered Cell Stack

H. Mori et al., Pressurized 10 kW Class Module of SOFC, Proc. 6th Int. Symp. on SOFC, Ed. S. Singhal und M. Dokiya, - The Electrochemical Society, PV 99-19, 52-59, (1999)

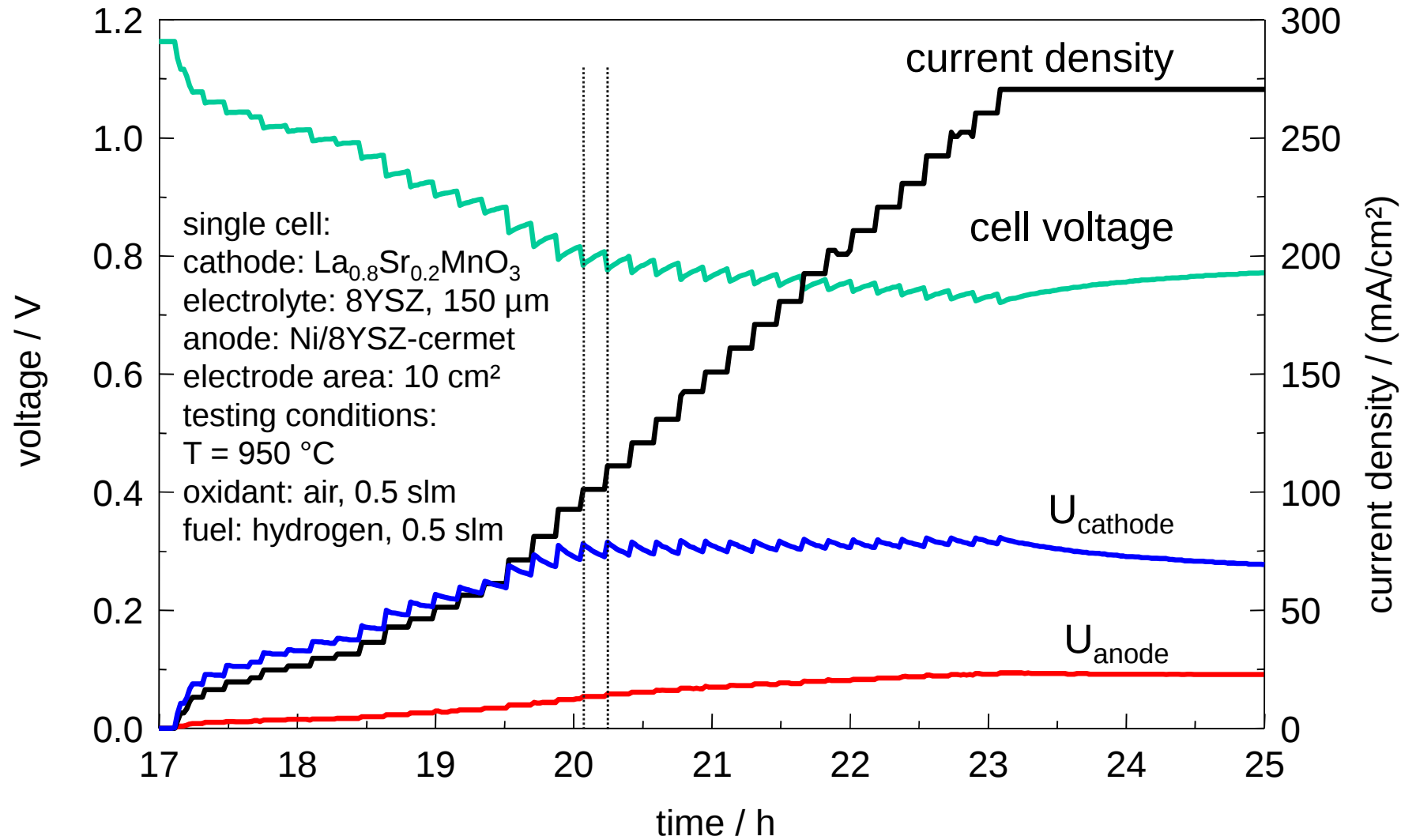
Startup Behavior of SOFC Single Cells and Stacks

Formation and Degradation

max. performance	degradation
++	-
+	+
-	+

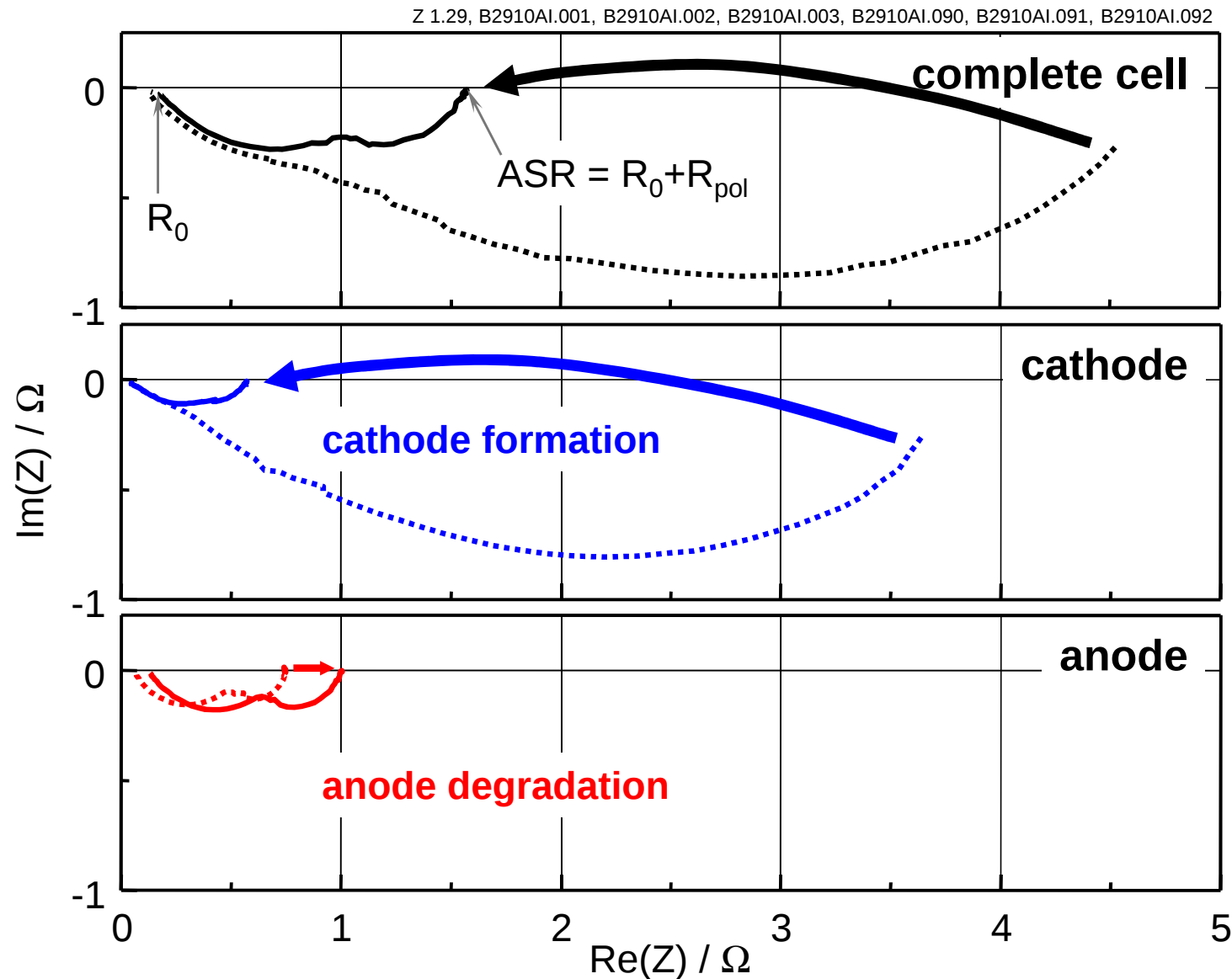


Cell Dynamics during Formation



Cell Dynamics during Formation

Impedance Spectra of a single cell (Cathode: $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$)



..... **Start of formation**
 — **End of formation**

cell 1.29

cathode: $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$

electrolyte: 8YSZ

anode: Ni/8YSZ - cermet

electrode area: 1 cm^2

oxidant: air, 0.25 slm

fuel: hydrogen, 0.25 slm

temperature: 950°C

impedance spectroscopy:

amplitude: 6 mA/cm^2

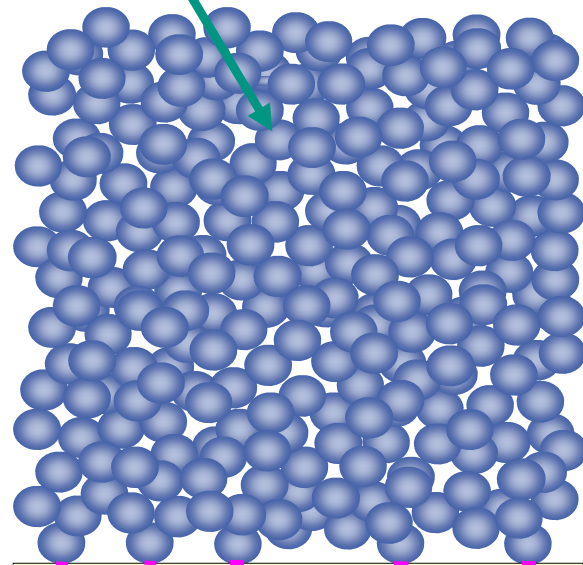
bias: 6 mA/cm^2

frequency: 0.1 Hz ... 300 kHz

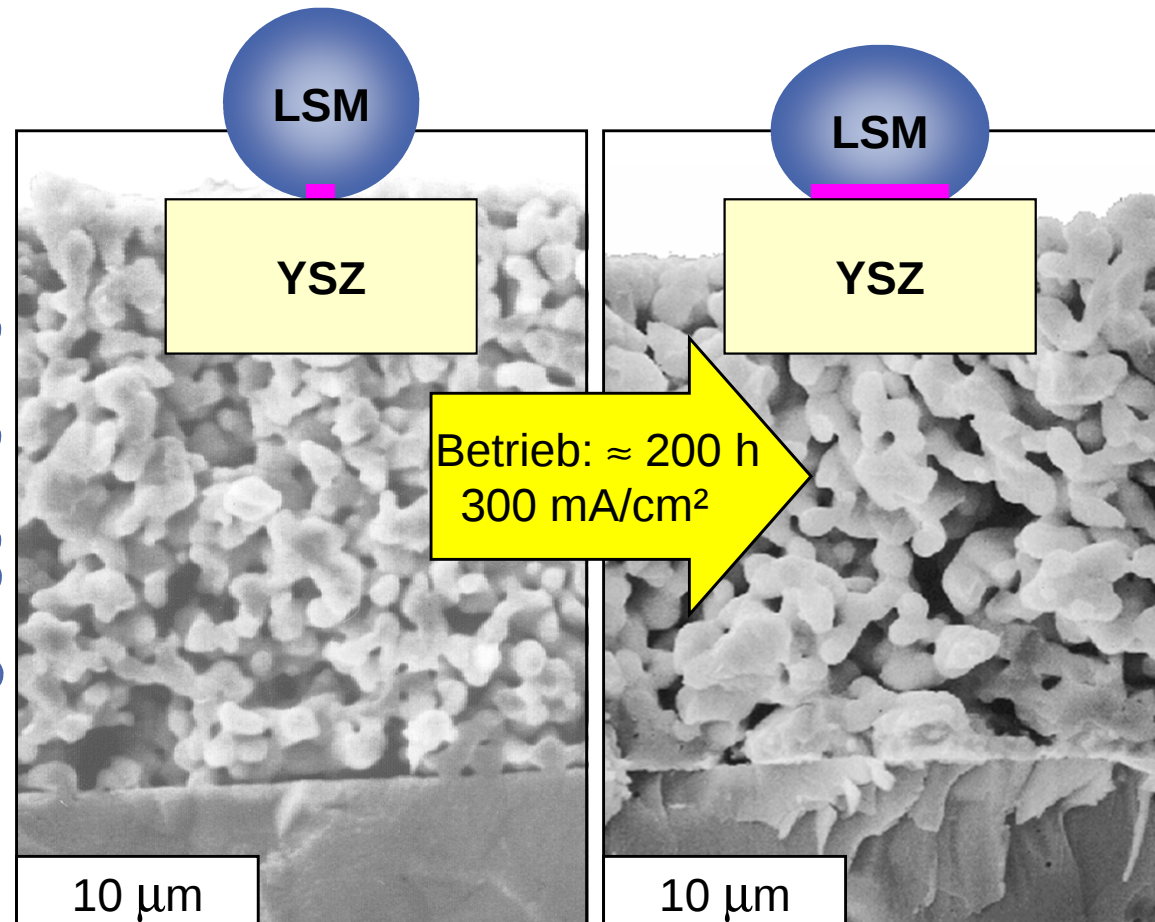
Formierung von SOFC-Kathoden

Veränderung der Mikrostruktur der LSM-Kathode

siebgedruckte
LSM-Kathodenschicht

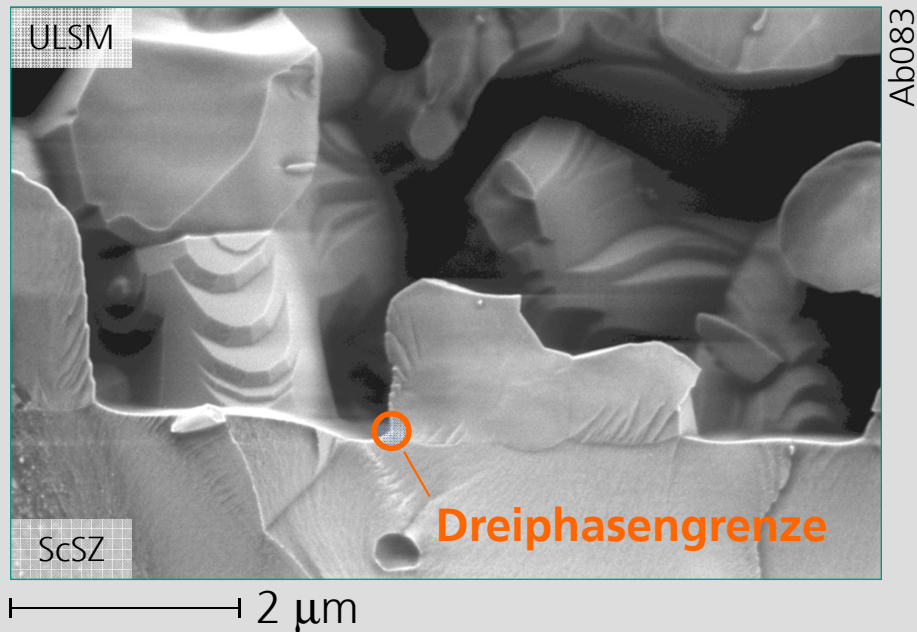


YSZ-Elektrolyt

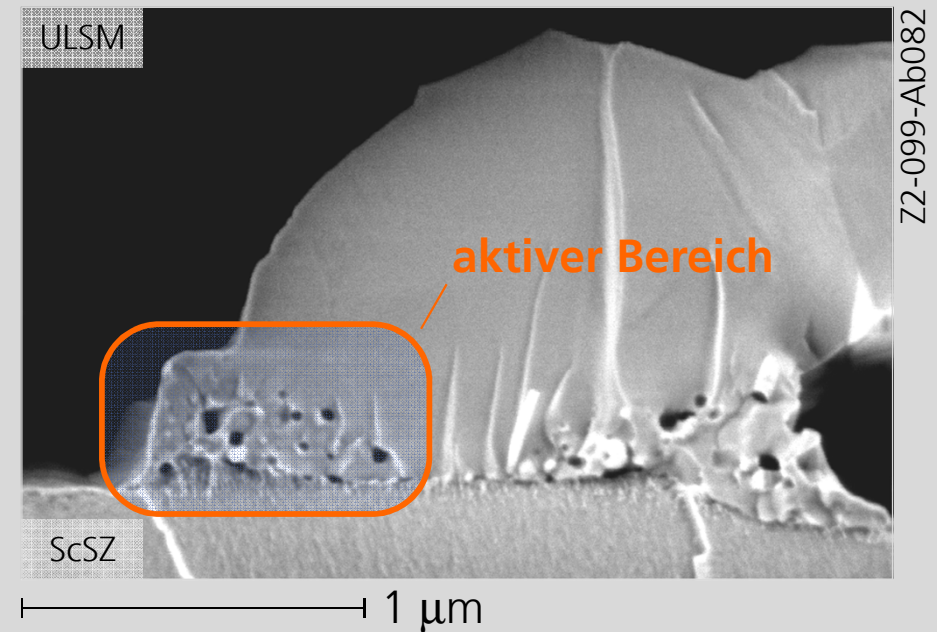


- Veränderung der Grenzfläche Kathode/Elektrolyt
- Zunahme der Dreiphasengrenze

unbelastete MEA



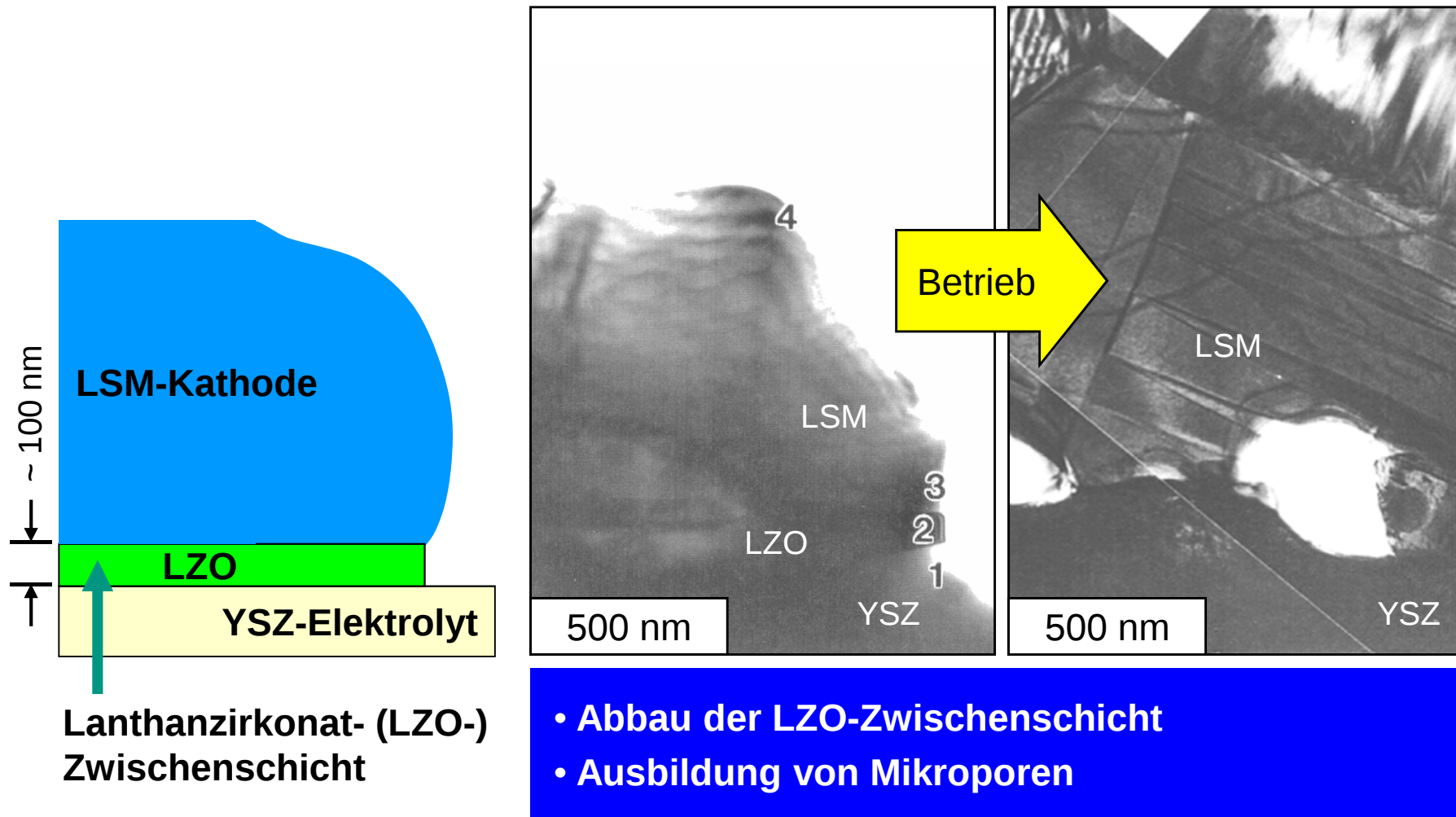
nach Aktivierung



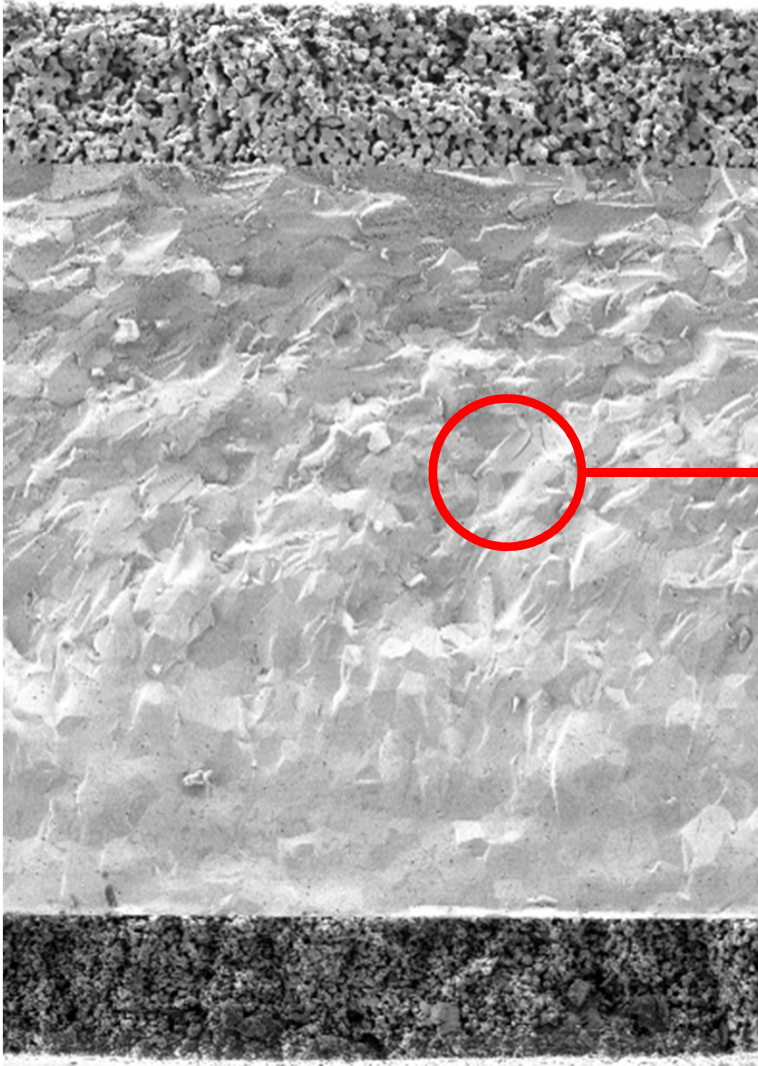
- Bildung eines porösen Bereichs im ULSM-Korn nahe der Grenzfläche unter Belastung
- Reaktionsraum vergrößert $\Rightarrow$ höhere elektrochemische Leistungsfähigkeit der Kathode

Formierung von SOFC-Kathoden

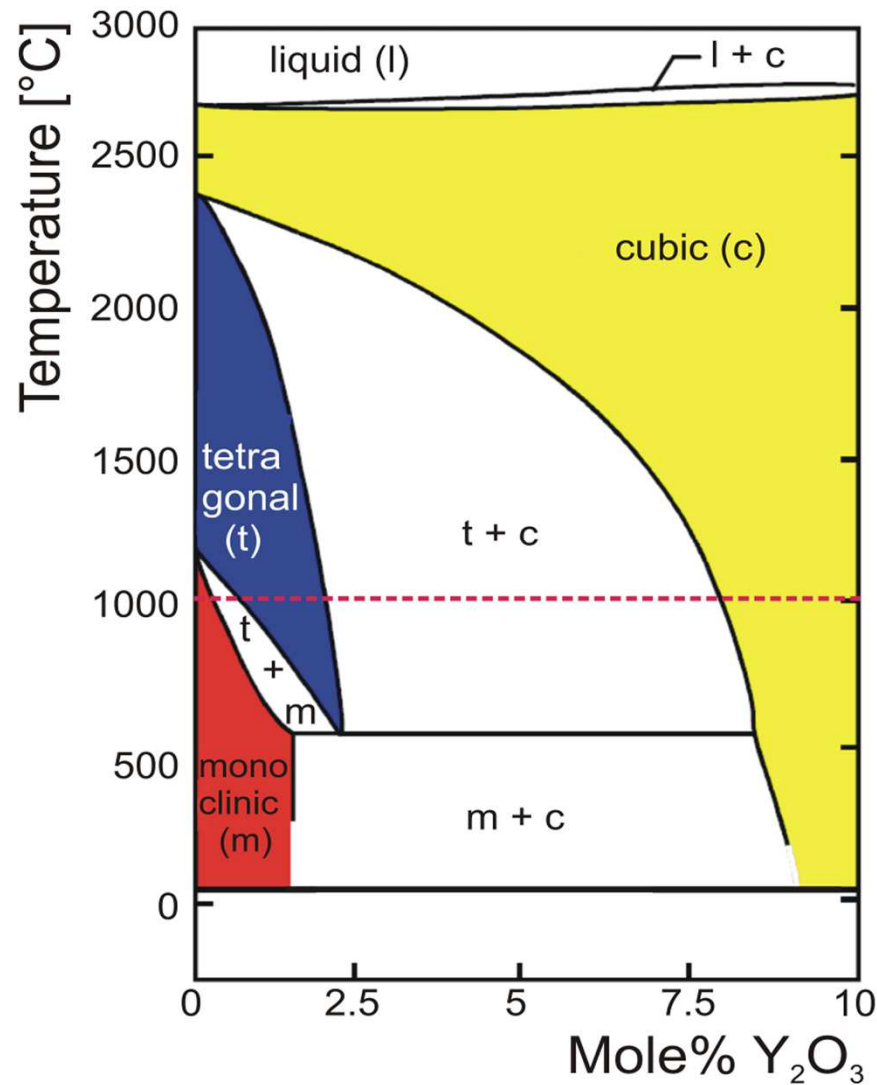
Veränderung der Grenzfläche Kathode/Elektrolyt



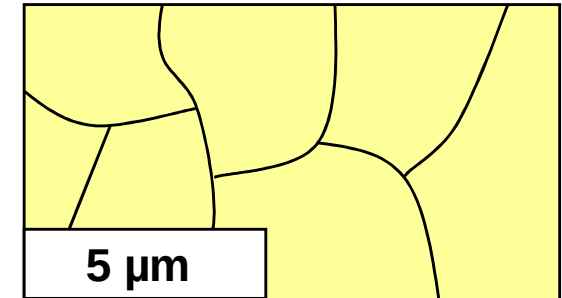
Elektrolyt: Verlust ionischer Leitfähigkeit



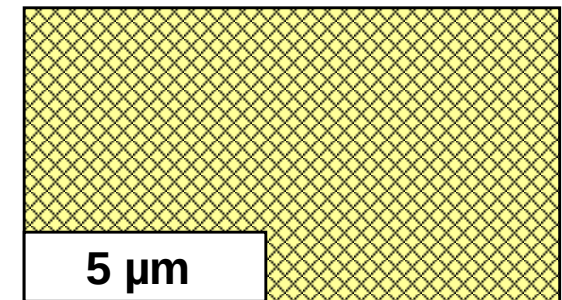
Yttria doped Zirconia (YSZ) Phase Diagram



FSZ
Fully Stabilized
Zirconia
cubic
 $\geq 8 \text{ mol\% } Y_2O_3$

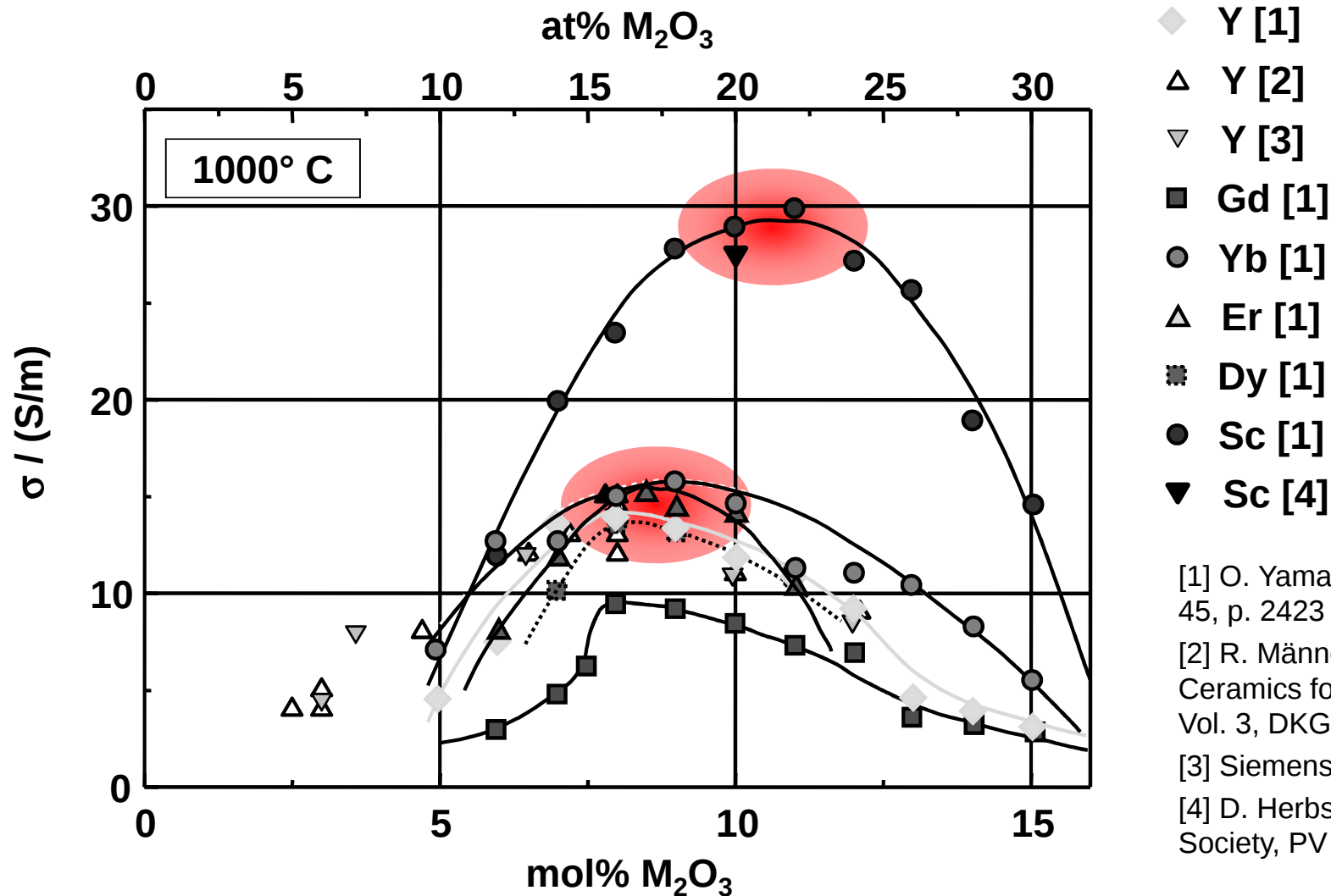


TZP
Tetragonal
Zirconia
Polycrystal
tetragonal
 $\leq 3 \text{ mol\% } Y_2O_3$



Electrical Conductivity of Fluorites $\text{ZrO}_2 - \text{Me}_2\text{O}_3$

Impact of various dopants on the conductivity of ZrO_2



[1] O. Yamamoto, *Electrochimica Acta* 45, p. 2423 (2000)

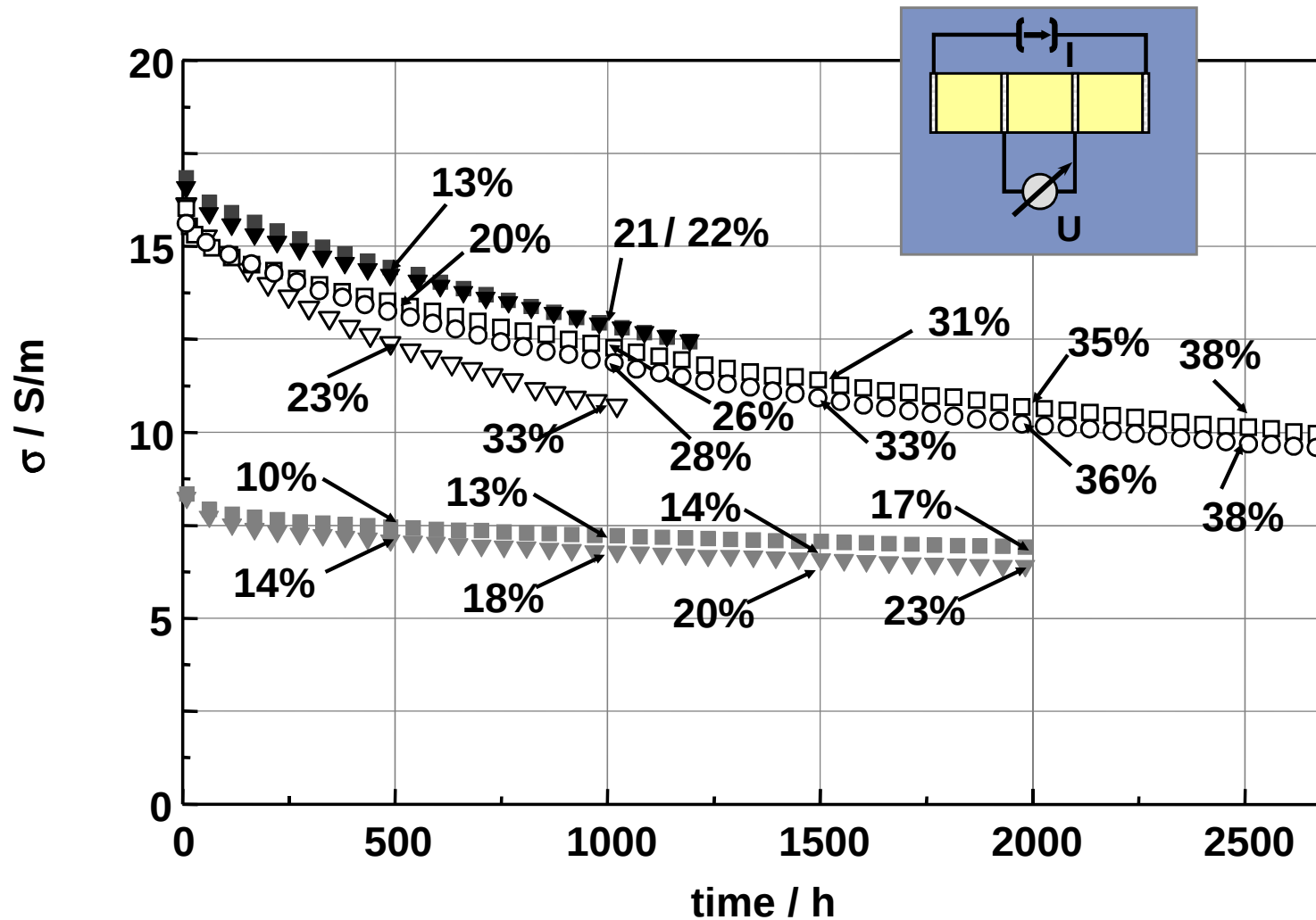
[2] R. Männer, *Electroceramics and Ceramics for Special Applications*, Vol. 3, DKG (1992)

[3] Siemens, unpublished data

[4] D. Herbstritt, *The Electrochemical Society*, PV 2001-16, p. 349, (2001)

Long term stability of $\text{ZrO}_2 - \text{Me}_2\text{O}_3$ Oxide Ion Conductors

FSZ: 8YSZ



$T_{op}=956^\circ\text{C}$, $170\text{mA}/\text{cm}^2$

○ 8YSZ, $T_{sint}=1550^\circ\text{C}$

□ 8YSZ, RCS @ 1500°C

▽ 8YSZ, RCS @ 1350°C

$T_{op}=956^\circ\text{C}$, $600\text{mA}/\text{cm}^2$

■ 8YSZ, RCS @ 1500°C

▼ 8YSZ, RCS @ 1350°C

$T_{op}=861^\circ\text{C}$, $120\text{mA}/\text{cm}^2$

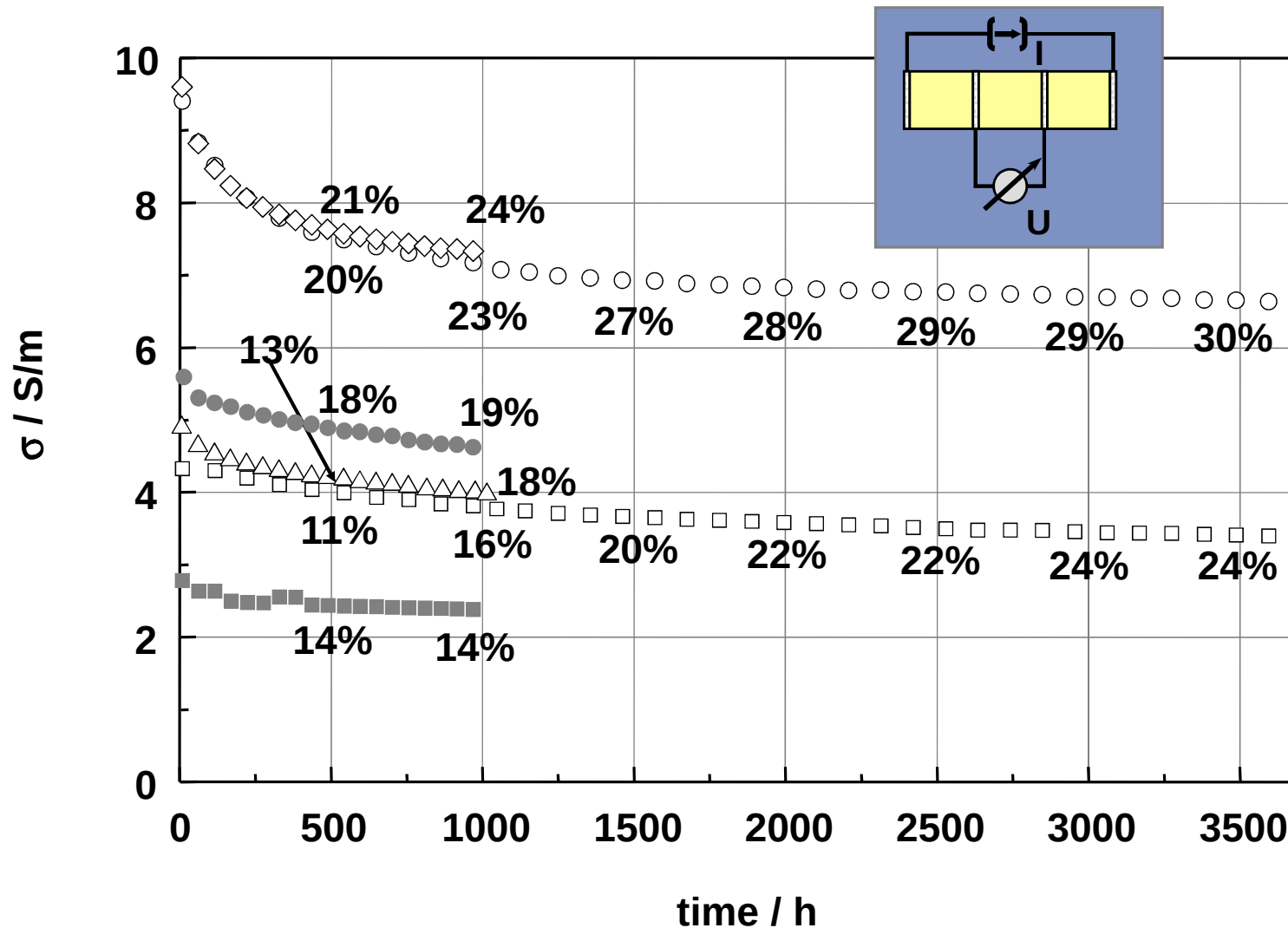
■ 8YSZ, RCS @ 1500°C

▼ 8YSZ, RCS @ 1350°C

RCS:
rate controlled sintering
constant shrinkage

Long term stability of of $\text{ZrO}_2 - \text{Me}_2\text{O}_3$ Oxide Ion Conductors

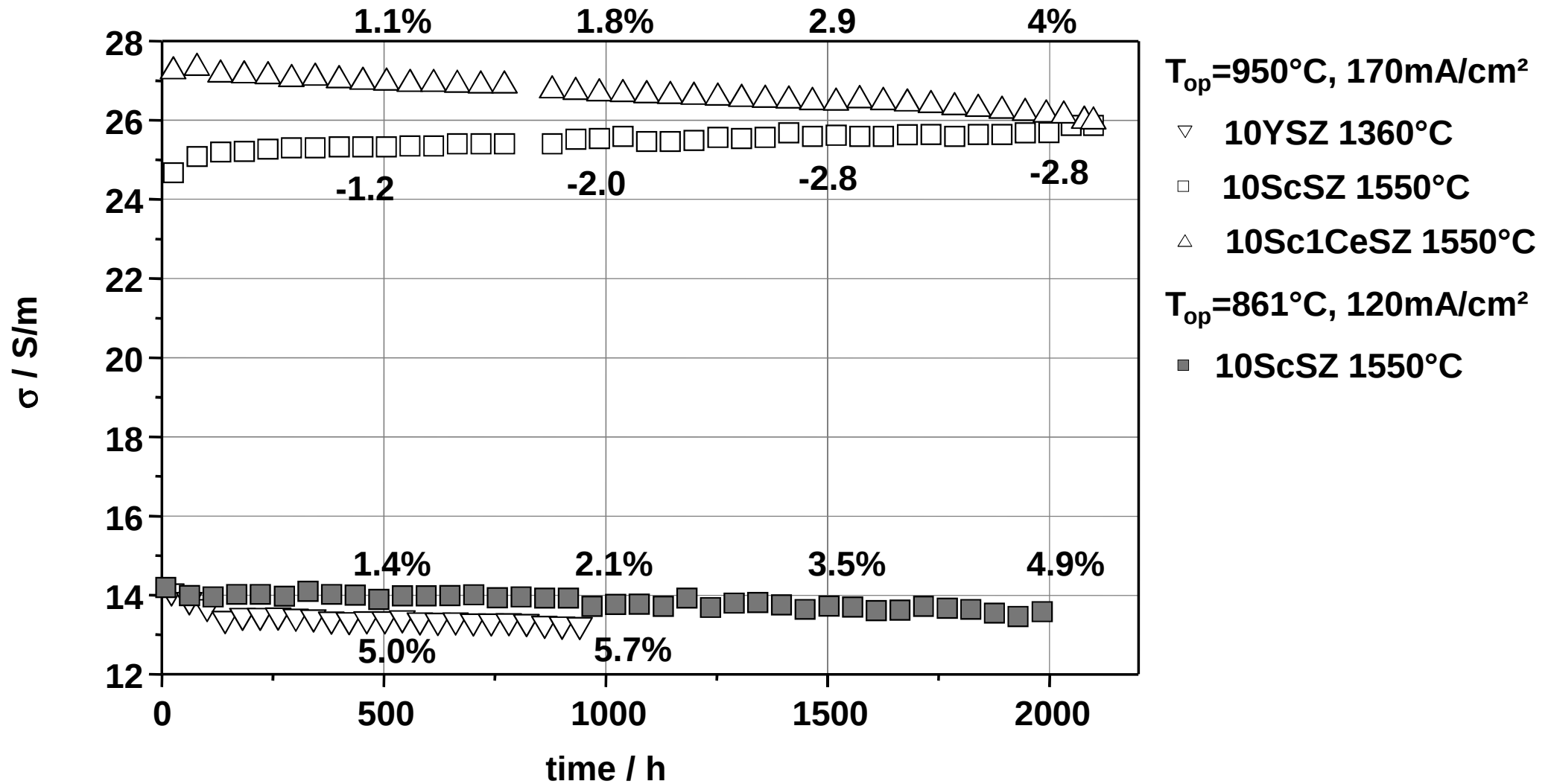
TZP: 3YSZ and 4ScSZ



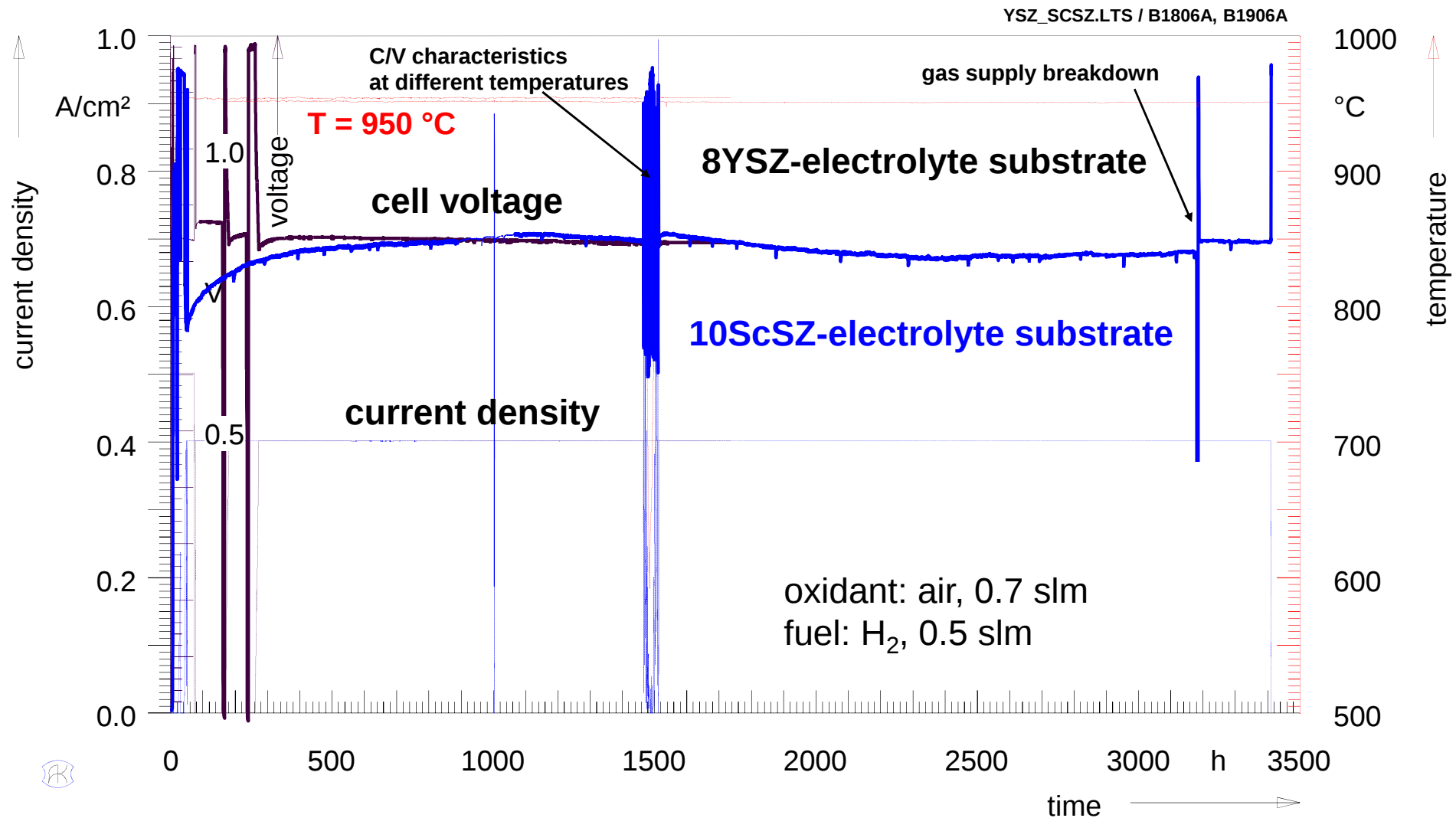
- $T_{op}=956^\circ\text{C}$, $170\text{mA}/\text{cm}^2$
- 3YSZ, $T_{sint}=1430^\circ\text{C}$
 - △ 3YSZ, $T_{sint}=1300^\circ\text{C}$
 - 4ScSZ, $T_{sint}=1350^\circ\text{C}$
 - ◇ 4ScSZ, $T_{sint}=1300^\circ\text{C}$
- $T_{op}=861^\circ\text{C}$, $120\text{mA}/\text{cm}^2$
- 3YSZ, $T_{sint}=1430^\circ\text{C}$
 - 4ScSZ, $T_{sint}=1350^\circ\text{C}$

Long term stability of $\text{ZrO}_2 - \text{Me}_2\text{O}_3$ Oxide Ion Conductors

FSZ: 10YSZ and 10ScSZ

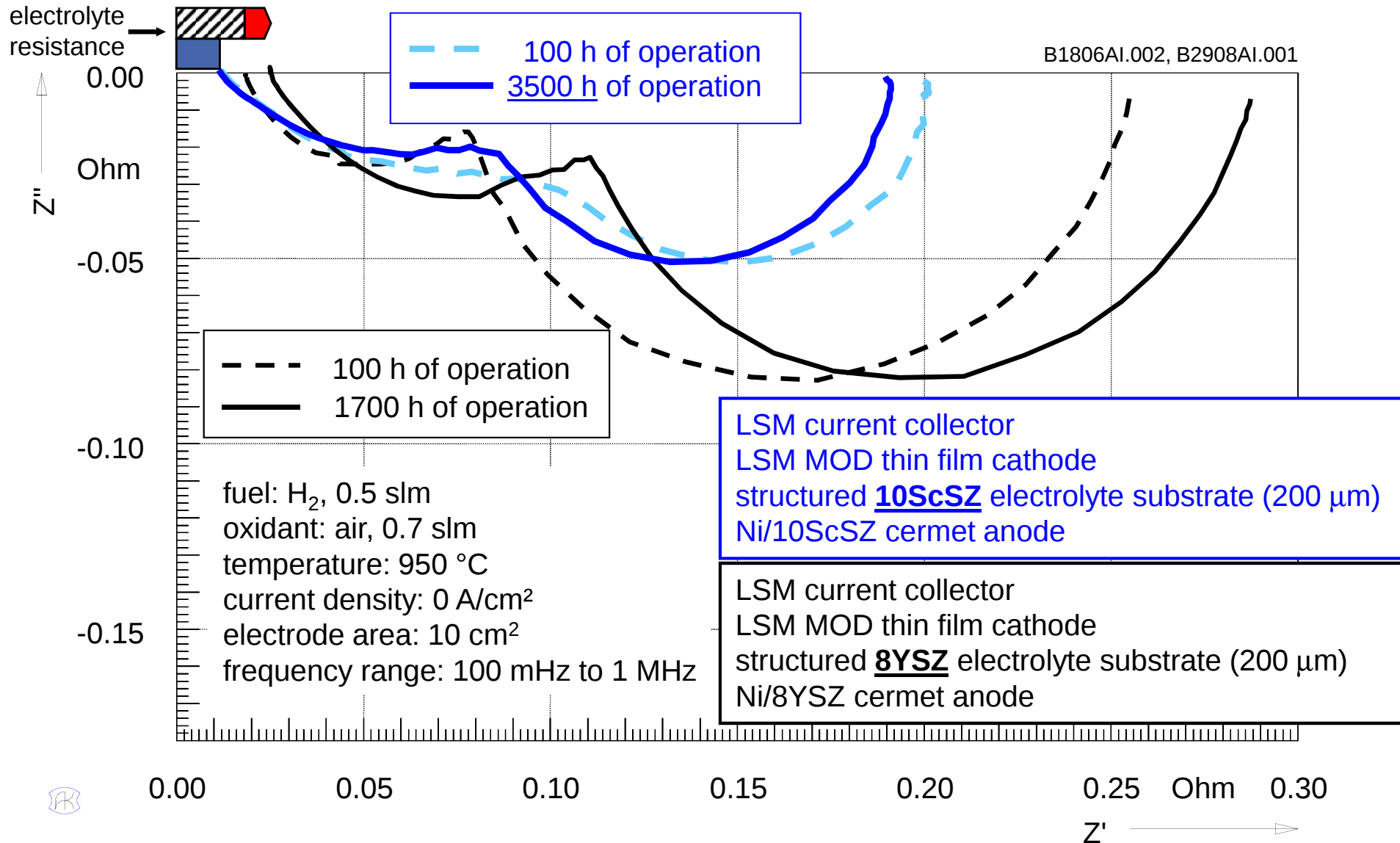


Long Term Stability of Electrolyte supported Single Cells with 8YSZ and 10ScSZ Electrolyte Substrate



Electrolyte Degradation ()

Long term stability: 10ScSZ () vs. 8YSZ () at 950°C

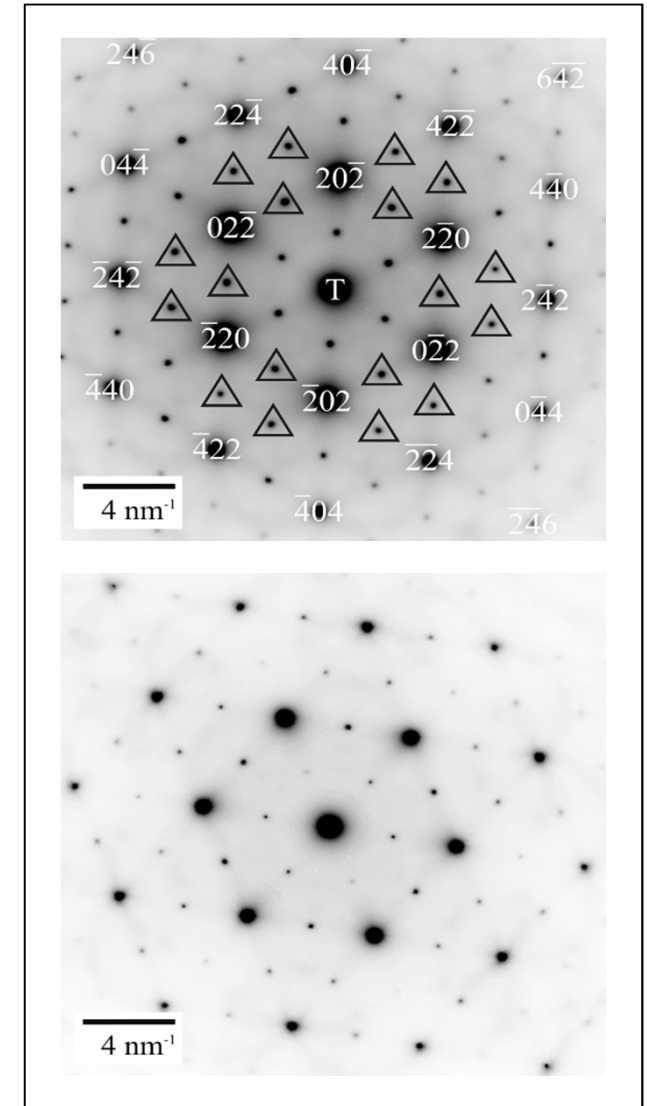


Electron diffraction: Tetragonal Phase

$[110]$, $[111]$, $[112]$, $[013]$, $[123]$

- Three variants of tetragonal phase:
c-axis along all cubic $\langle 100 \rangle$ -axes
- Double diffraction in thicker sample regions

→ Clear identification of tetragonal phase
(no superstructures!)



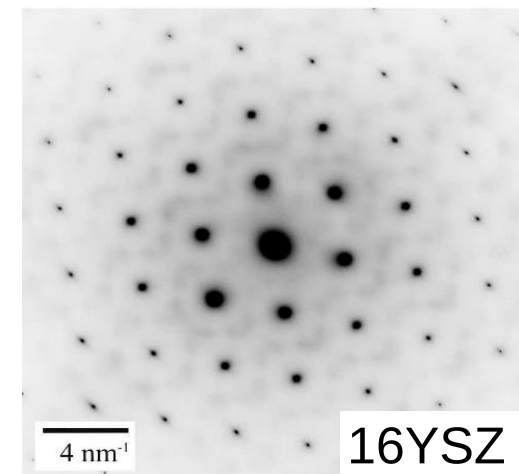
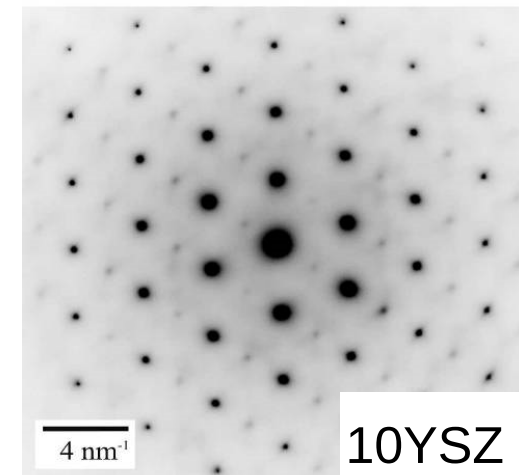
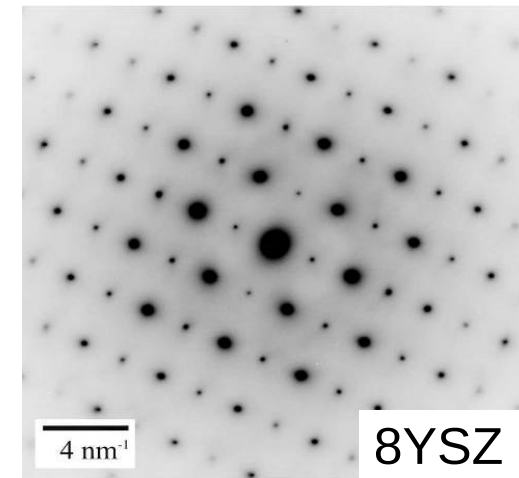
$[111]$ 8YSZ

www.iam.kit.edu/wet

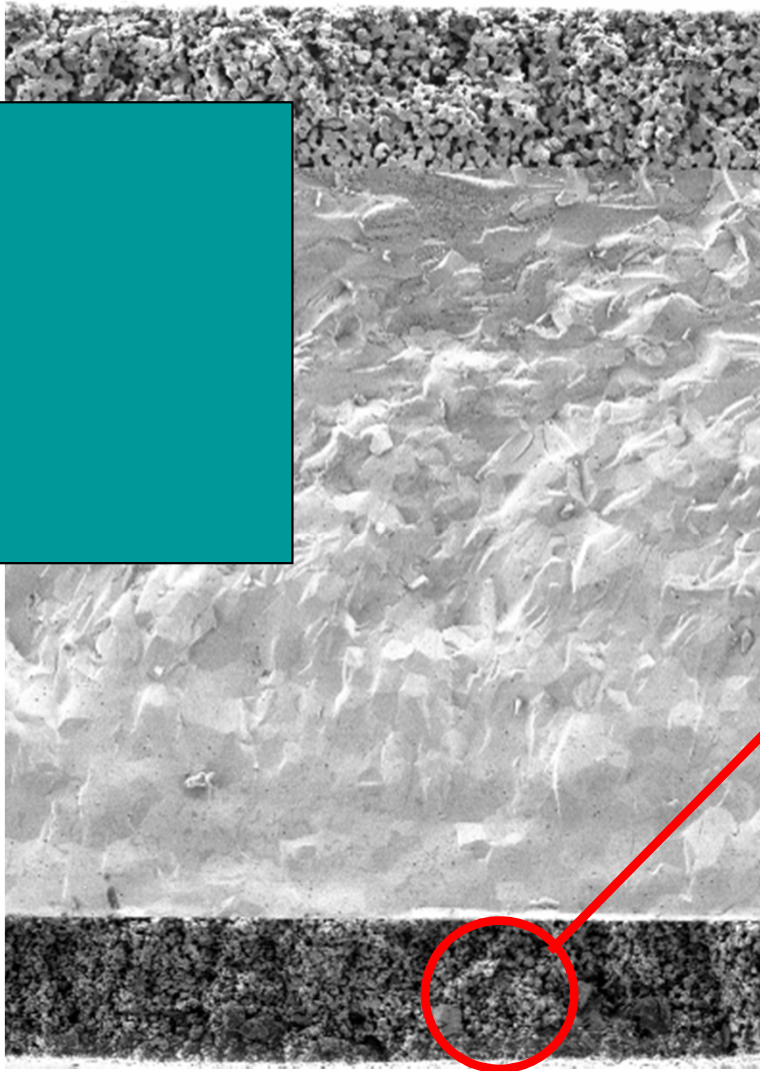
Electron diffraction

- Exists in 8YSZ and 10YSZ, not in 16YSZ
- Decreasing volume fraction with increasing doping concentration

→ Dark field images with tetragonal intensity

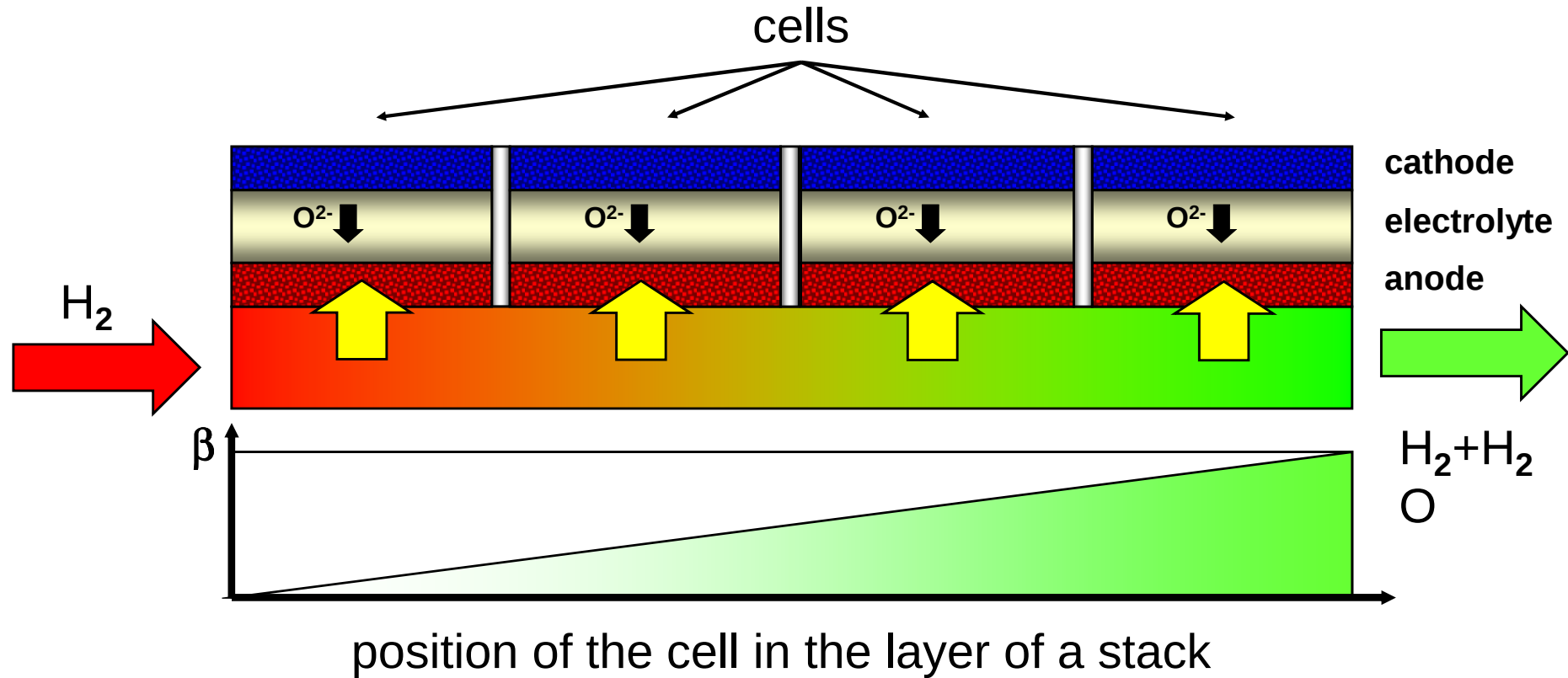


Anode: Agglomeration der Nickel-Partikel



Anode Degradation

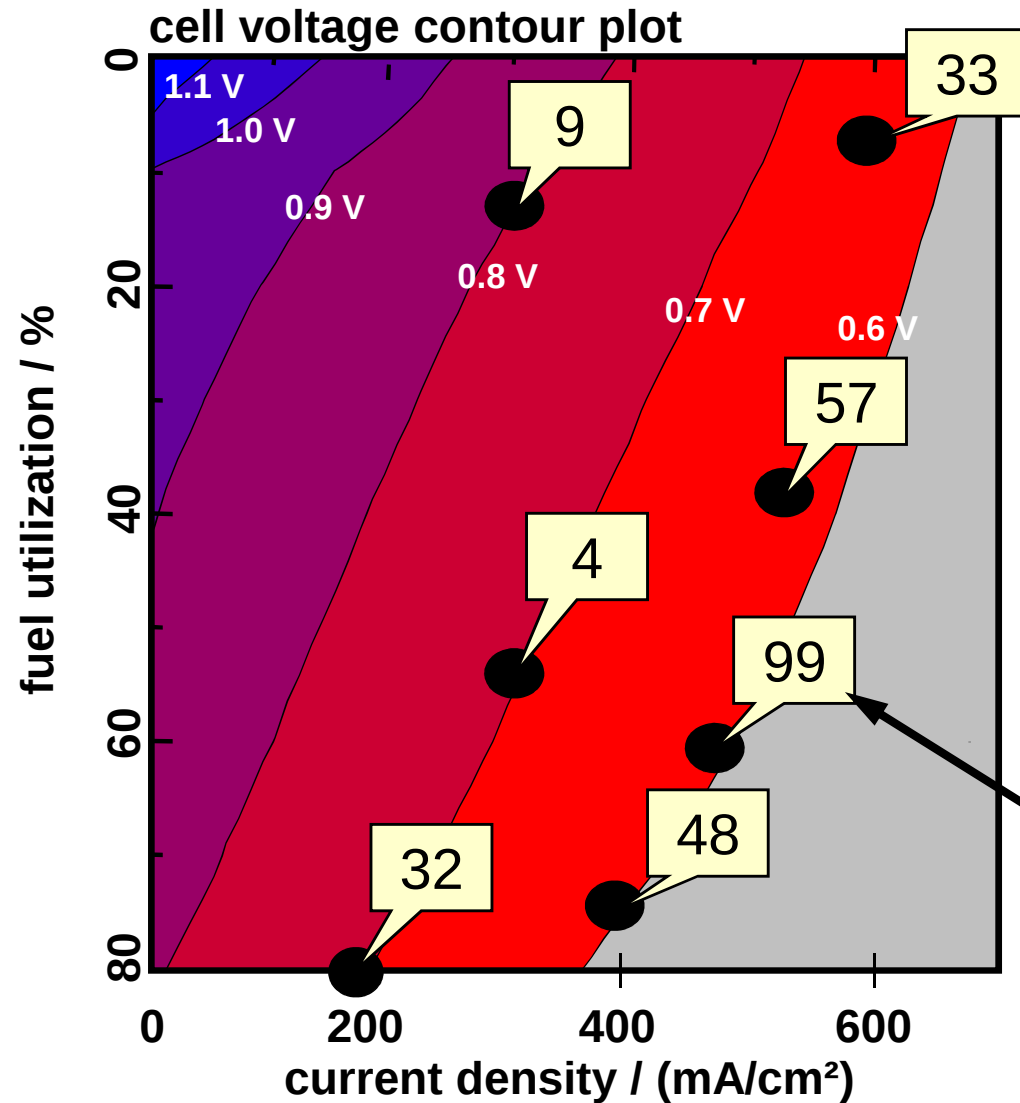
Stack position and fuel utilization



fuel utilization:
$$\beta = \frac{p(H_2O)}{p(H_2O) + p(H_2)}$$

Anode Degradation

Influence of current density and fuel utilization



Performance plot

Long term measurements

Operation time: 700 ... 1000 h

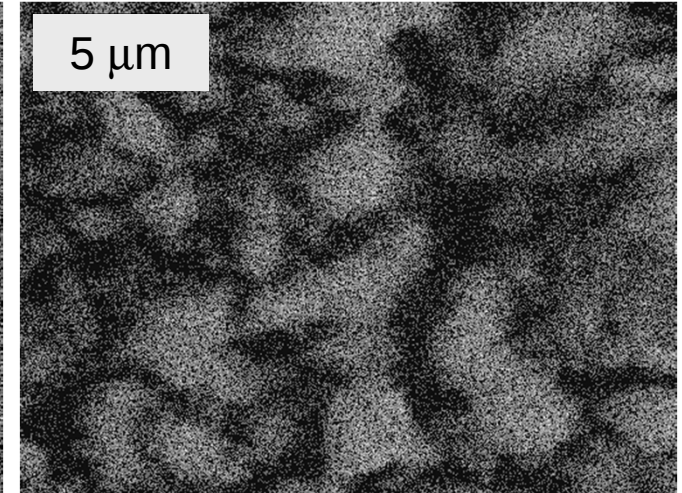
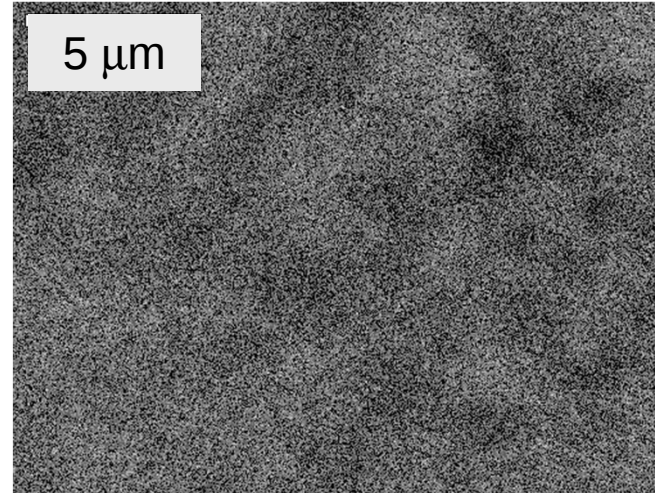
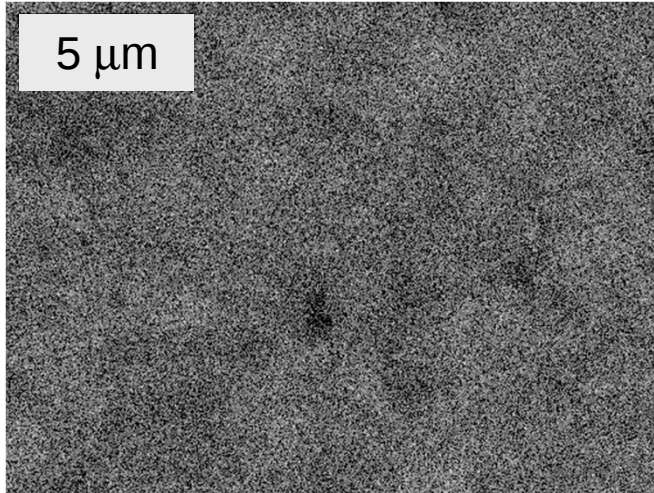
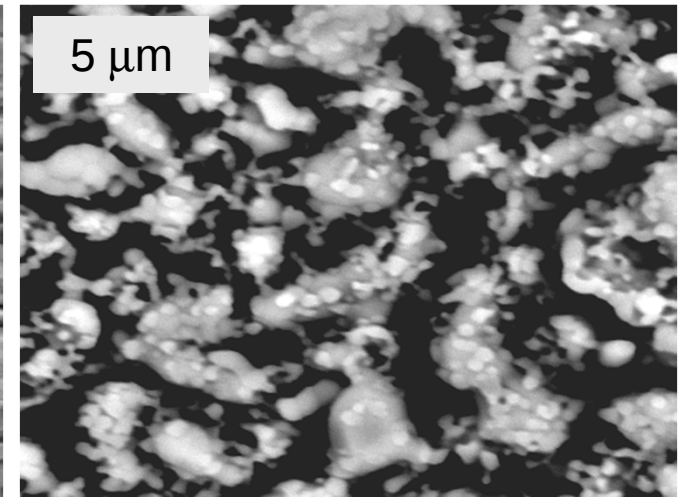
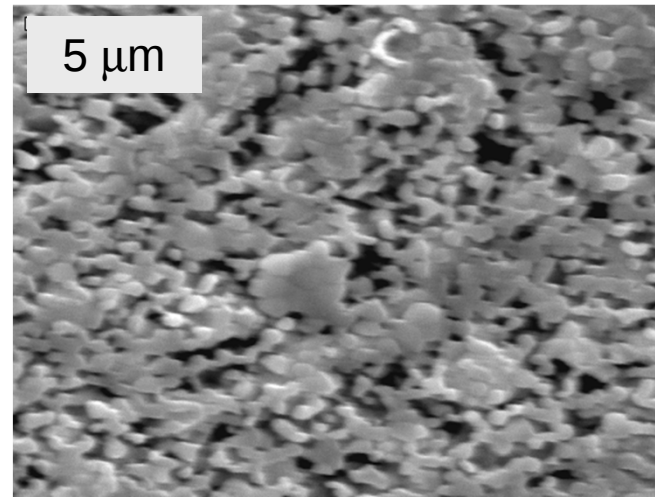
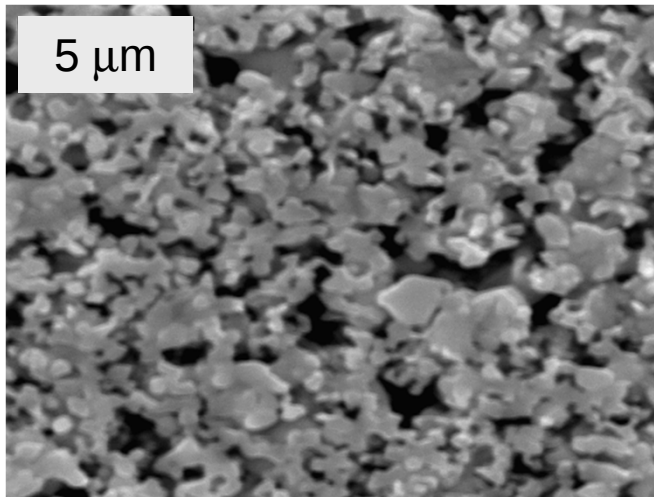
Temperature : 950 °C

Oxidant : air

Aim: <1 mV/1000h

Degradation rates in mV/1000h

Anode Degradation Ni-Agglomeration

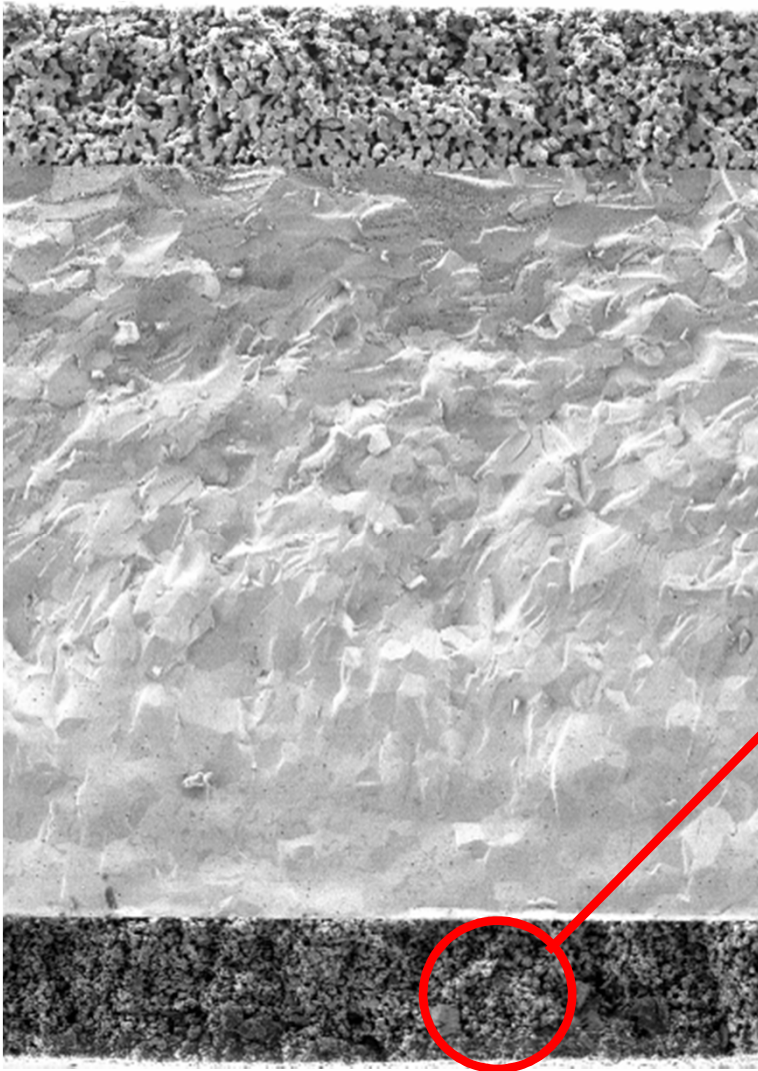


before operation

after operation 1000 h, 950 °C
80 % fuel utilization, 0 A/cm²

after operation 1000 h, 950 °C
80 % fuel utilization, 0.2 A/cm²

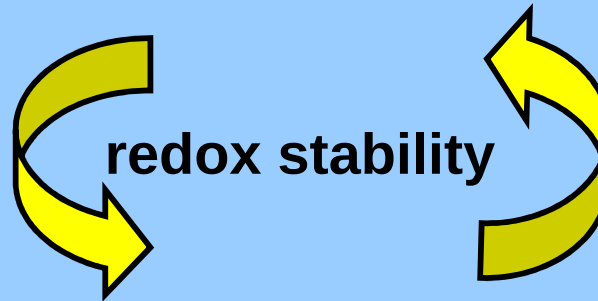
Anode: Alterung unter Redox-Zyklen



Anode Redox-Stability

Oxidation of anode metal phase
→ Volume increase ($\text{Ni} \rightarrow \text{NiO}$)

Reducing atmosphere (H_2)
during operation

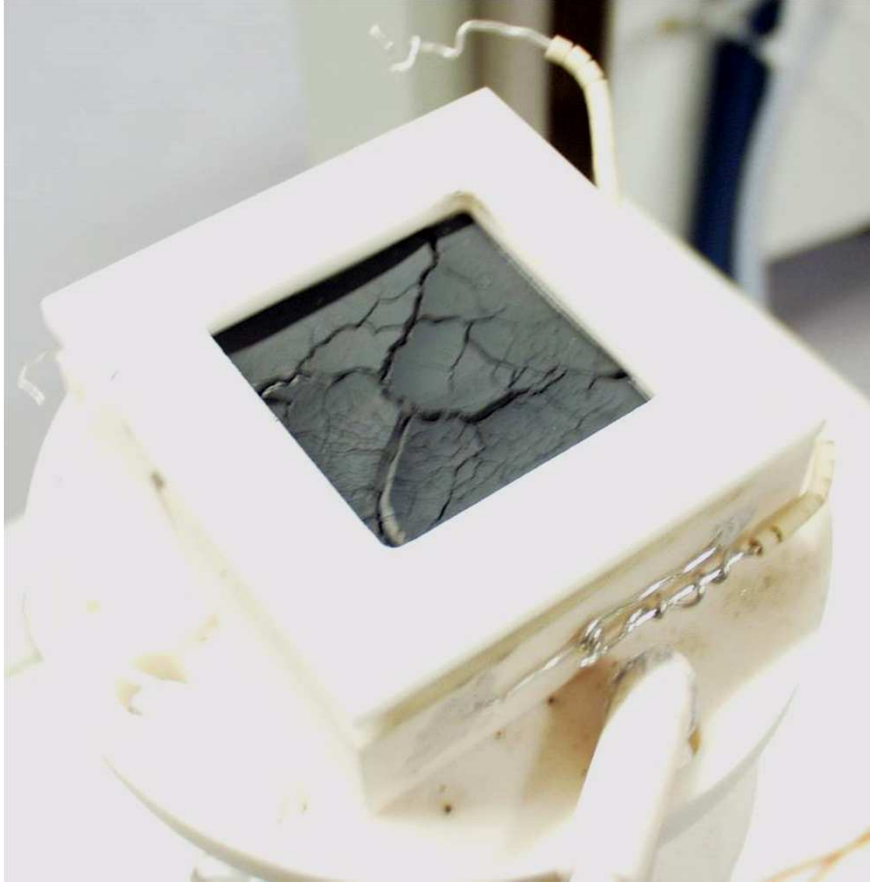


Oxidizing atmosphere (Air)
during operation interrupt

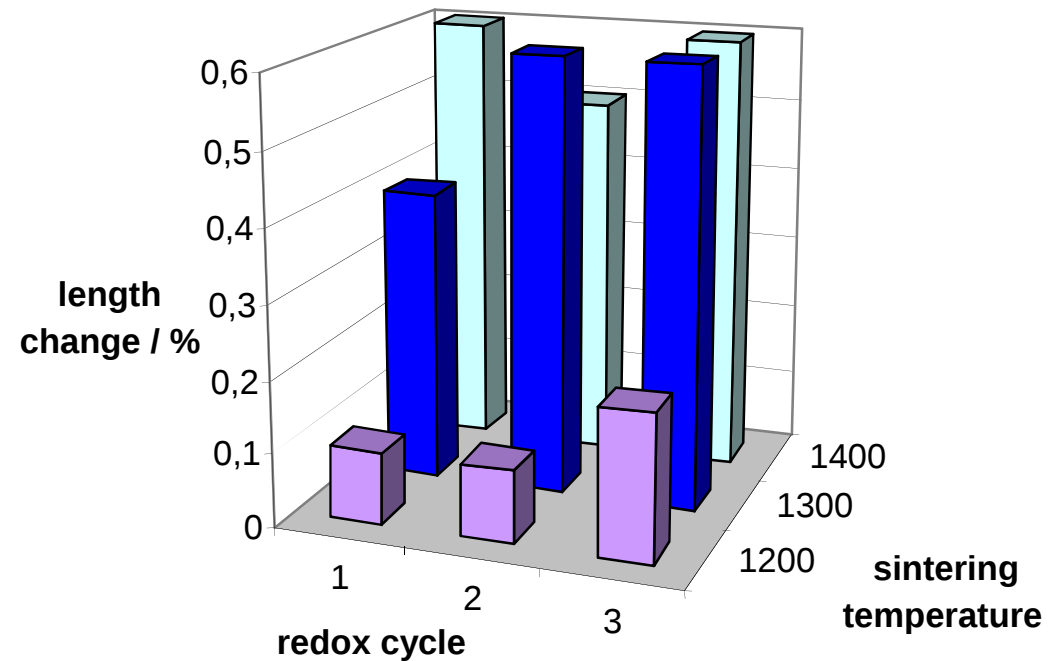
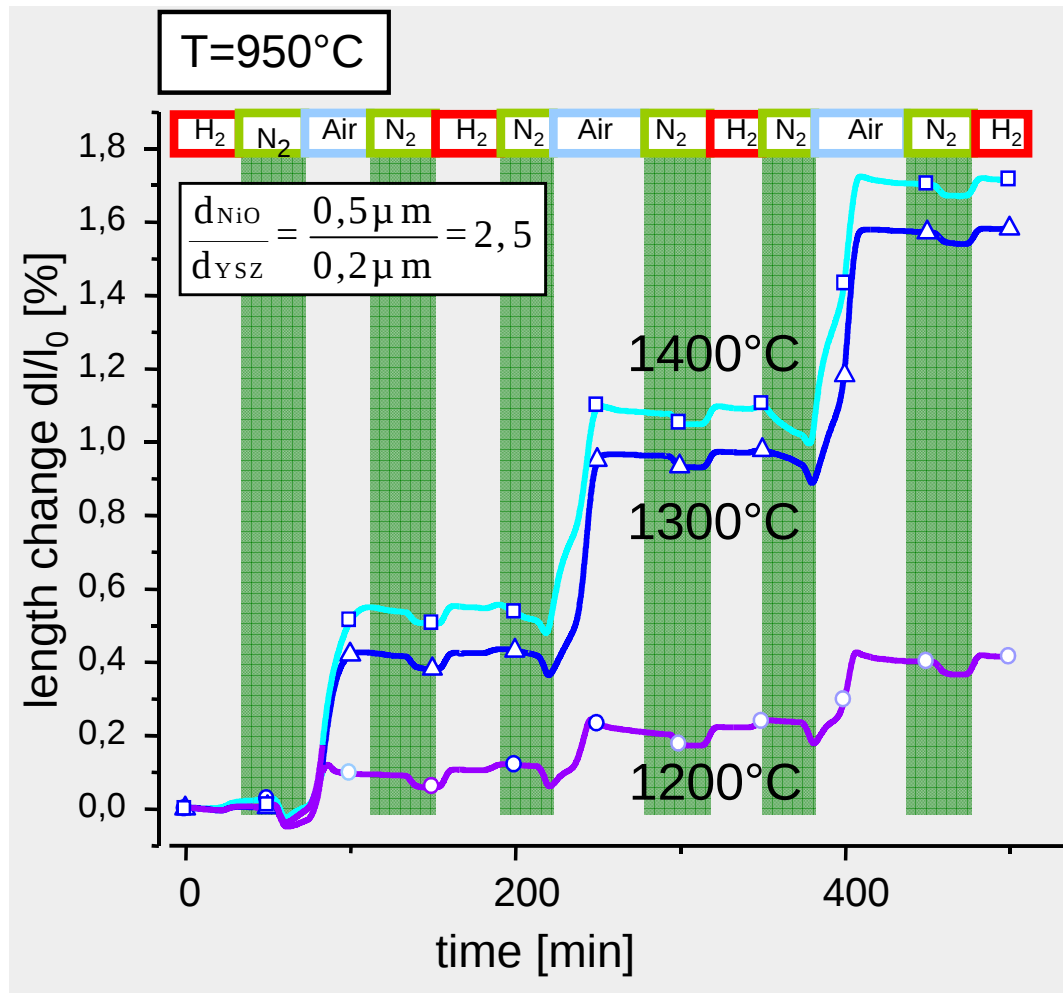
Reduction of anode metal phase
→ Volume decrease ($\text{NiO} \rightarrow \text{Ni}$)

Extrinsic Degradation

Cracking of an Anode Supported Electrolyte after Redox-Cycling



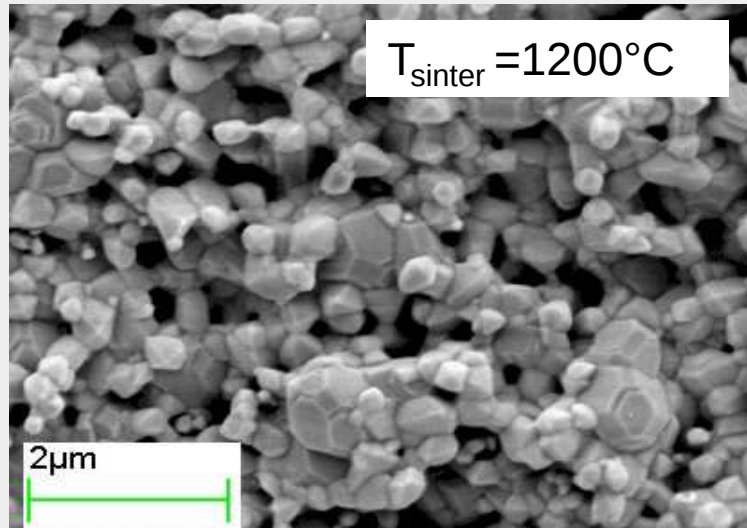
Impact of Redox Cycle on Length Change of Ni/YSZ Bulks: Different Sintering Temperatures



➤ minimum length change at lowest sintering temperature of 1200 °C

Impact of Redox Cycles on Microstructure of Ni/YSZ Bulks

Different Sintering Temperatures

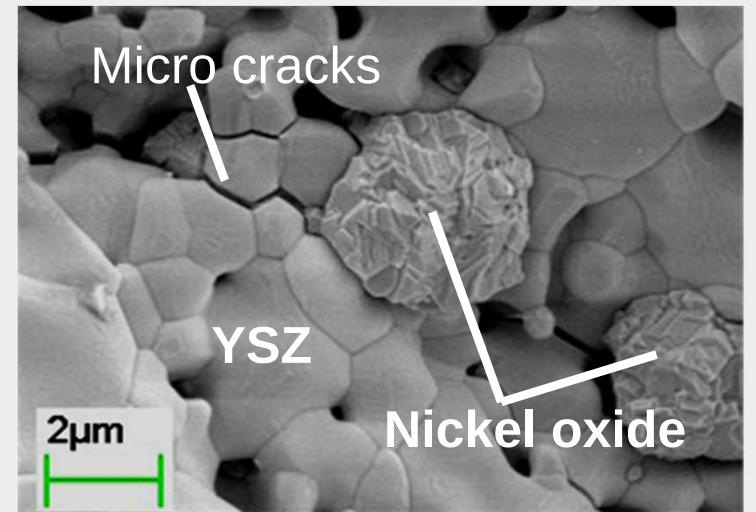
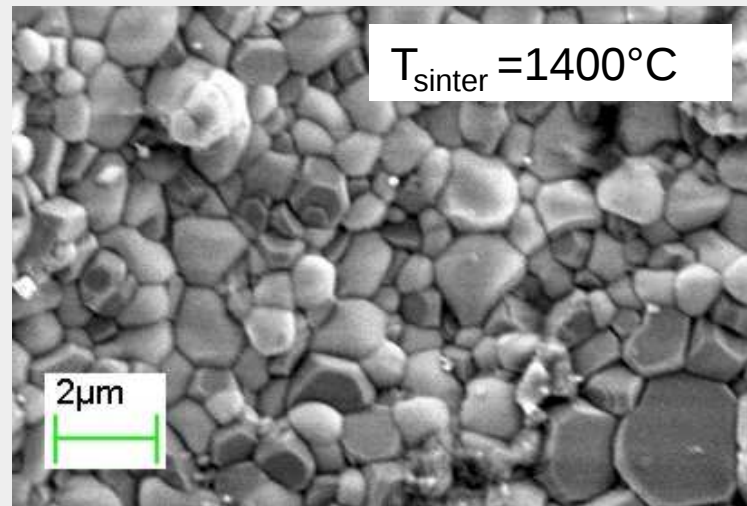
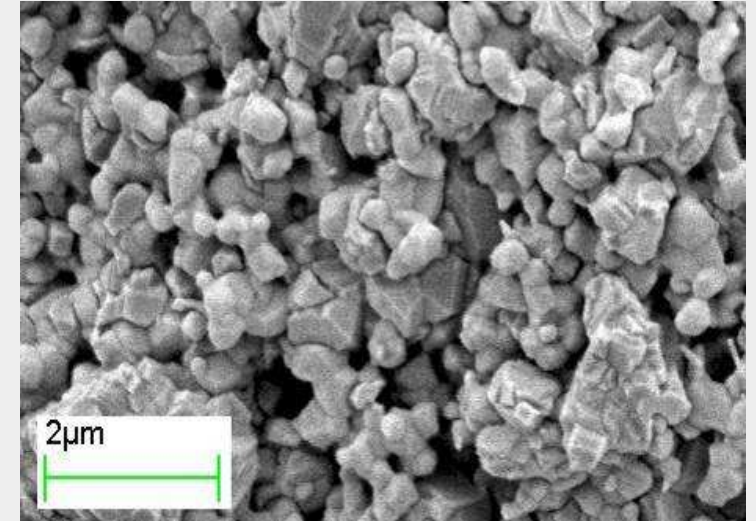


$d_{50}: \text{NiO} = 0,5\mu\text{m}$
 $d_{50}: \text{YSZ} = 0,2\mu\text{m}$

length change
 $dl/l_0 = 0,4\%$

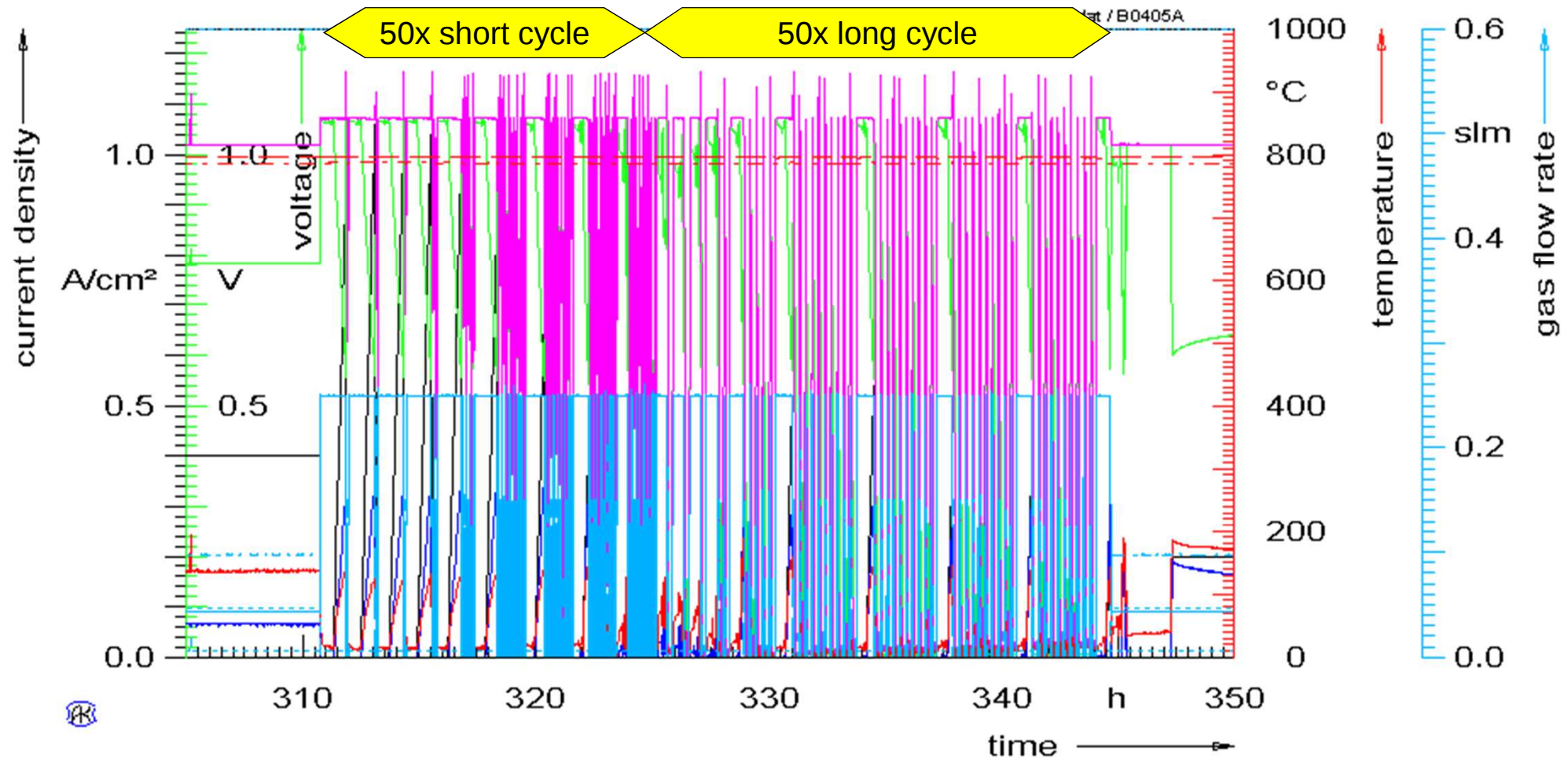
3 redox cycles

length change
 $dl/l_0 = 1,7\%$

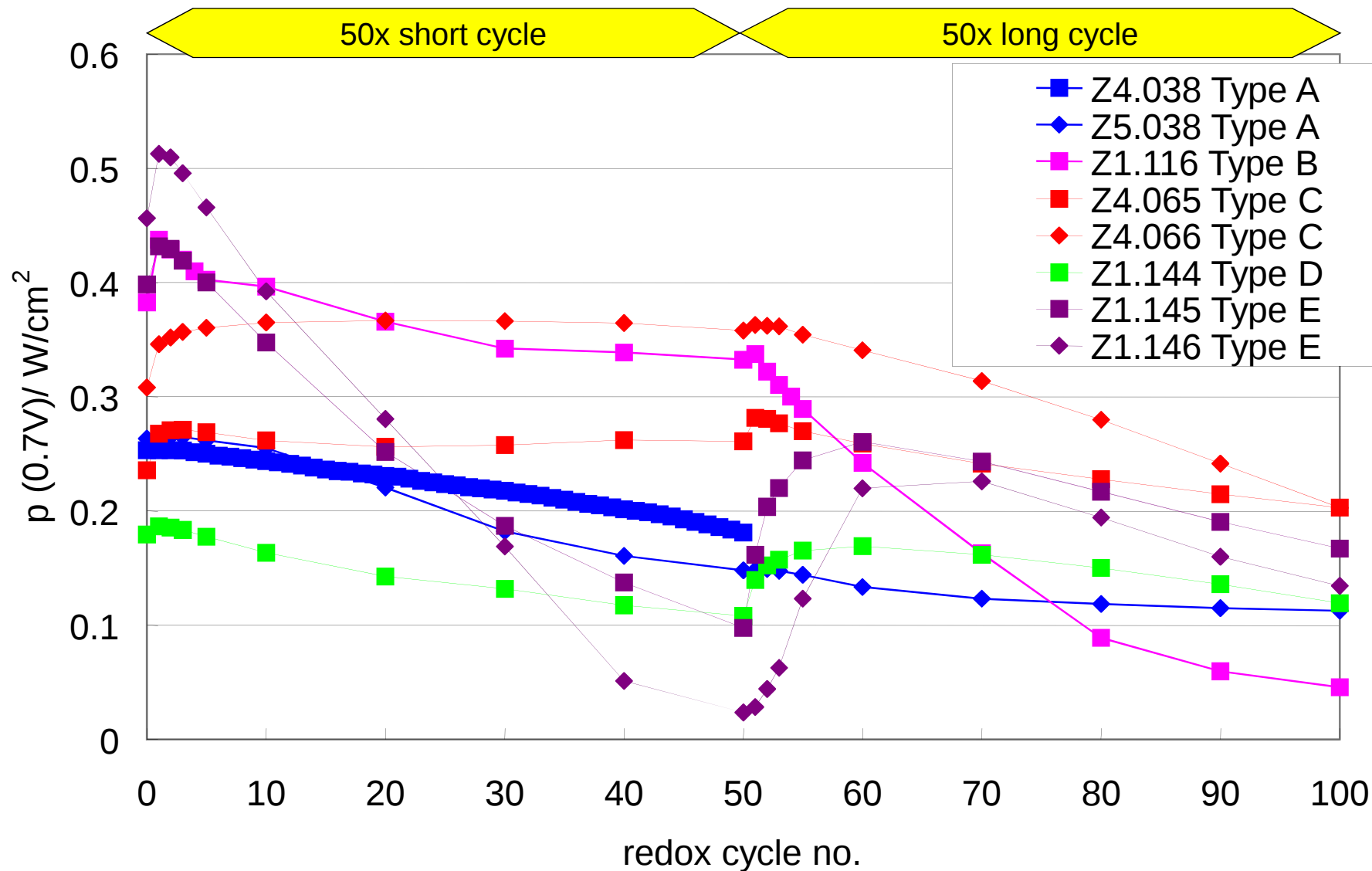


Degradation Tests for SOFC

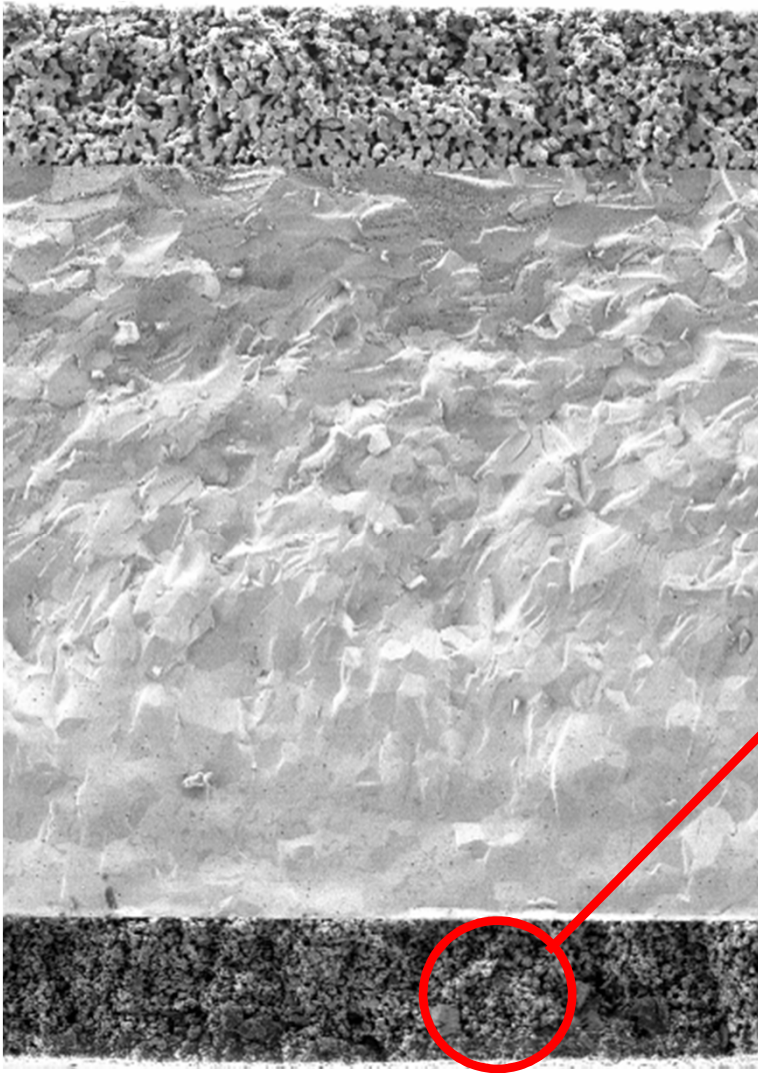
Redox Stability (100 Redox-Cycles in 35 h)



Redox Stability of Electrolyte Supported SOFC

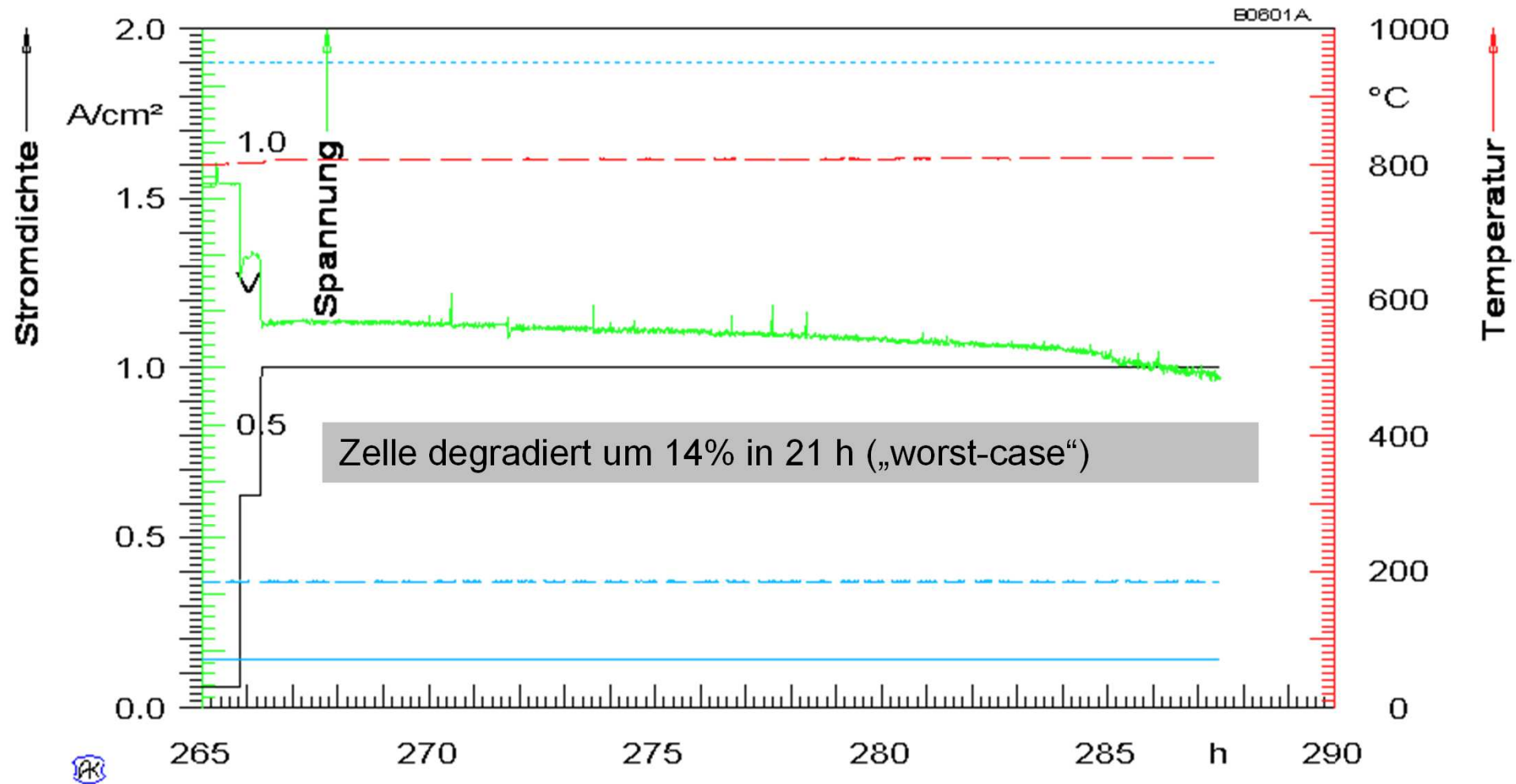


Anode: Aufkohlung im Betrieb mit C_nH_m



Operation on Hydrocarbons

Severe Degradation with higher Hydrocarbons C_nH_m



Gasgemisch: H_2 , CO , H_2O , CO_2 , N_2 , C_2H_2 (Ethin), C_7H_8 (Toluol), Methylnaphtalin ($C_{11}H_{10}$)

Operation on Hydrocarbons

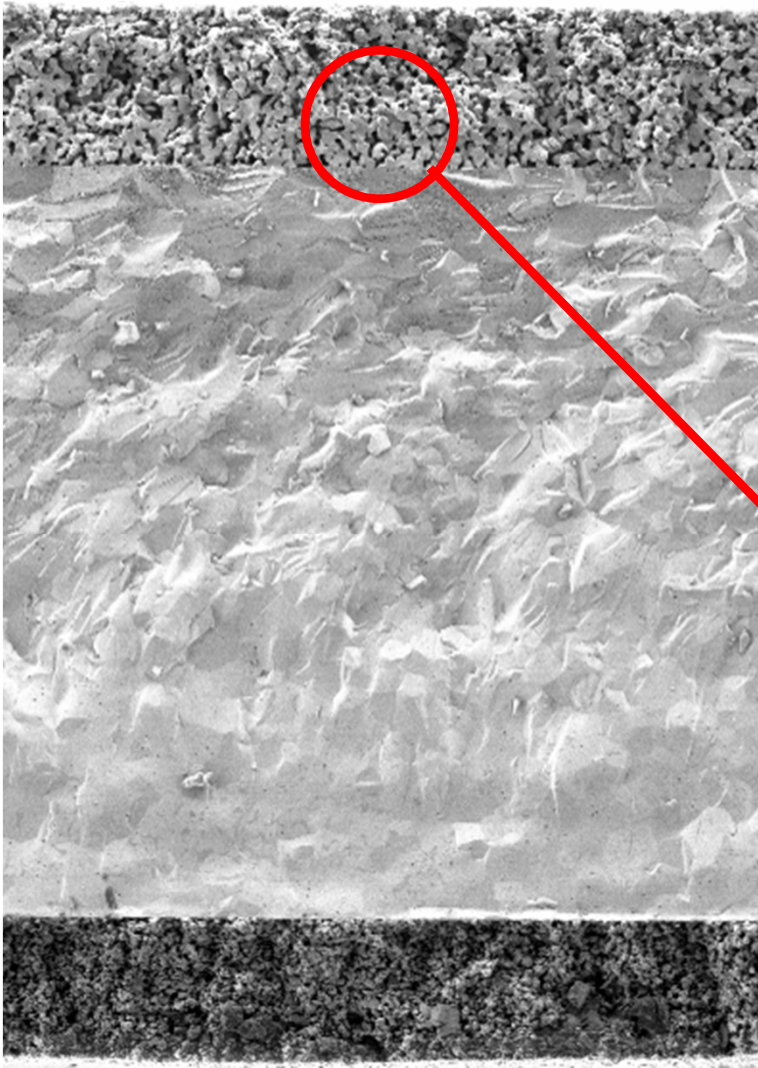
Severe Degradation with higher Hydrocarbons C_nH_m



→
Flussrichtung

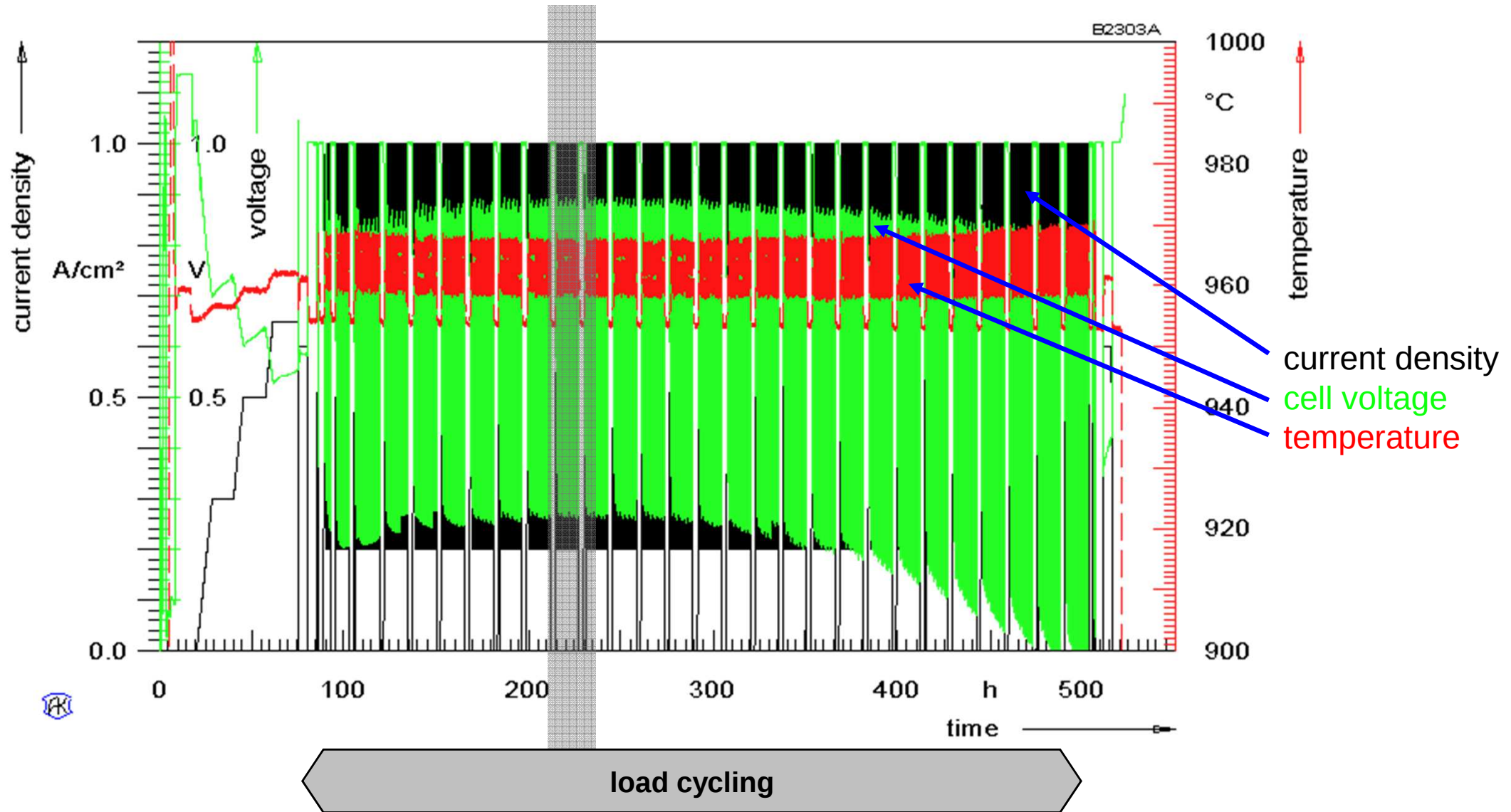
Aufgekohlte Zelle nach Betrieb mit einem Gasgemisch bestehend aus H_2 , CO , H_2O , CO_2 , N_2 , C_2H_2 (Ethin), C_7H_8 (Toluol) und Methylnaphtalin ($C_{11}H_{10}$)

Kathode: Alterung im Betrieb mit Lastzyklen



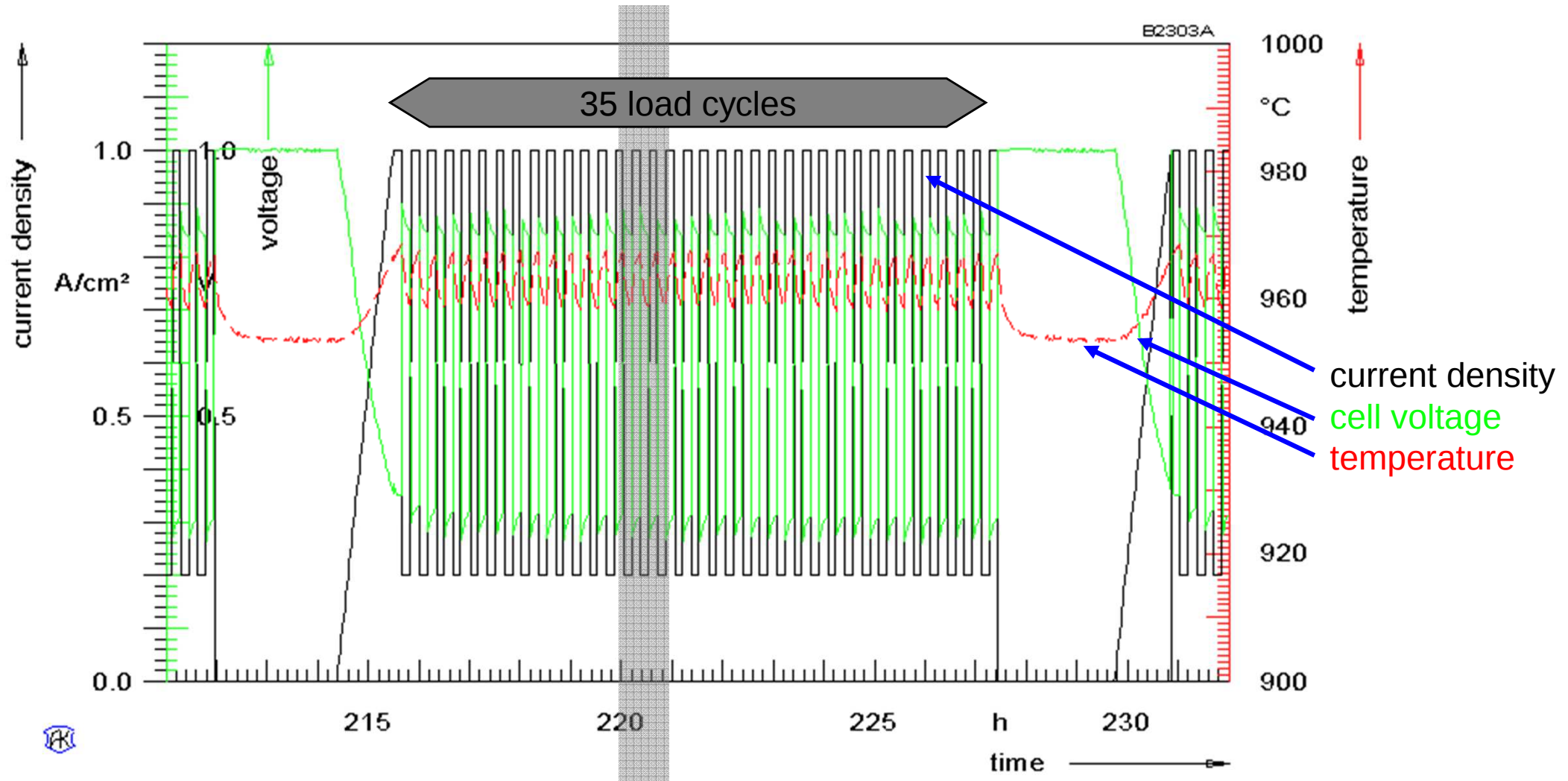
Electrochemical Characterization of Degradation Phenomena

Load Cycling Test (966 cycles within ~ 400 hours)



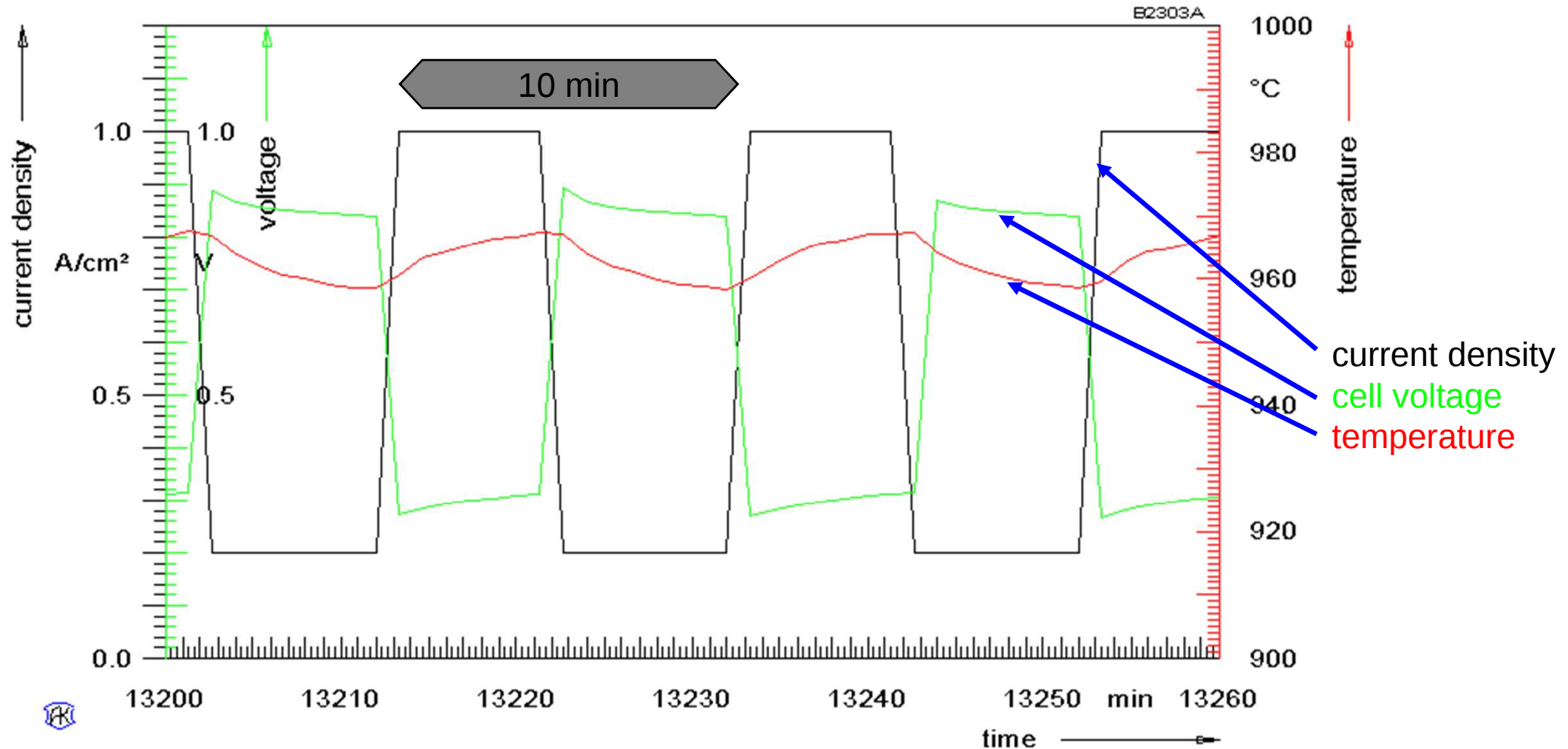
Electrochemical Characterization of Degradation Phenomena

Load Cycling Test



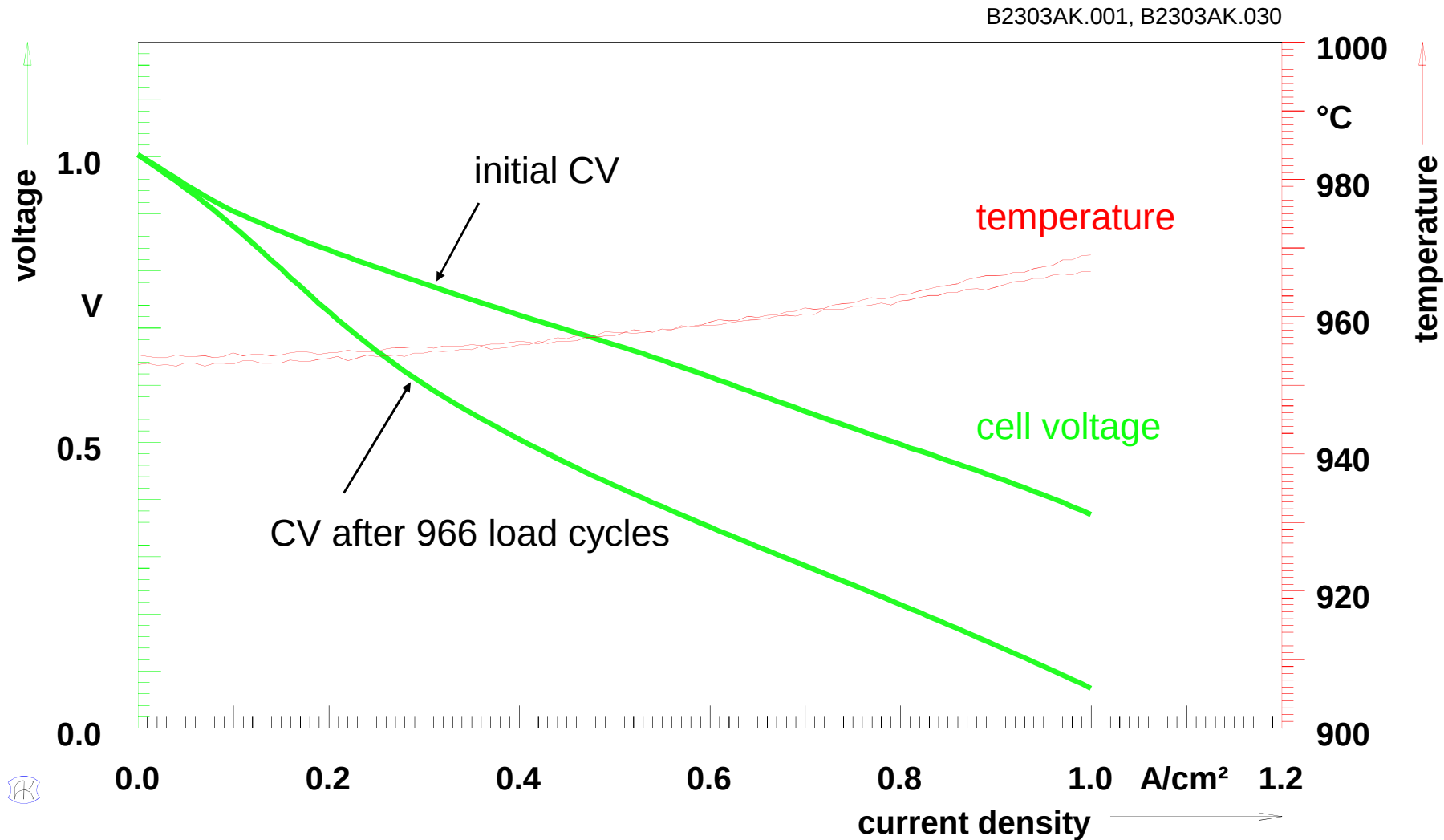
Electrochemical Characterization of Degradation Phenomena

Load Cycling Test



Electrochemical Characterization of Degradation Phenomena

CV-characteristic before and after Load Cycling Test



CV: current voltage characteristic



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Modeling of Degradation Phenomena

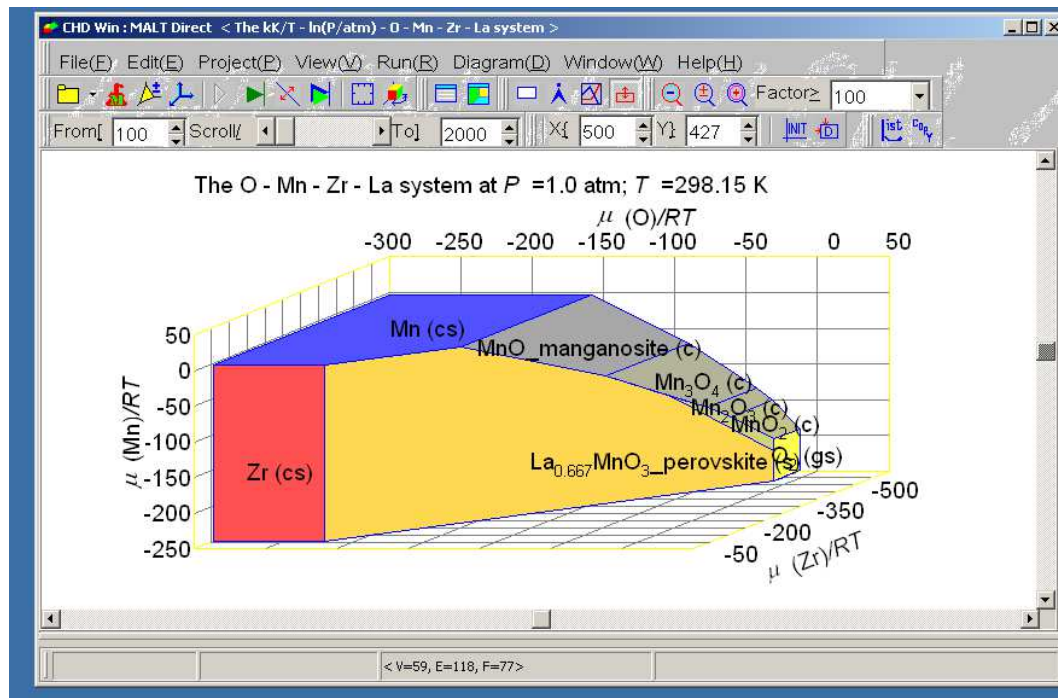
Chemical Potential Diagrams and Thermodynamic Equilibrium Calculations

MALT (MAterials oriented Little Thermodynamic database*)

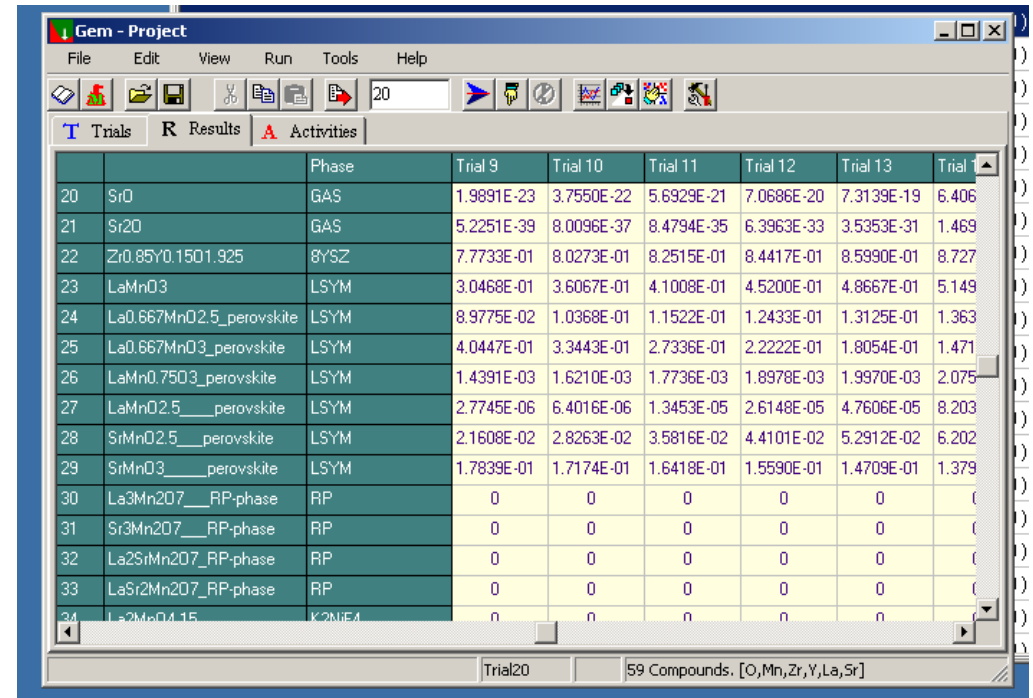
$\Delta_f G^\circ$, $\Delta_f H^\circ$, S° , C_p° at 298.15 K

temperature coefficients of heat capacities, transition temperatures, transition enthalpies

Calculation of Chemical Potential Diagrams (CHD)



Thermodynamic Equilibrium Calculations (GEM: Gibbs Energy Minimizer)



	Phase	Trial 9	Trial 10	Trial 11	Trial 12	Trial 13	Trial 14
20	SrO	GAS	1.9891E-23	3.7550E-22	5.6929E-21	7.0686E-20	7.3139E-19
21	Sr2O	GAS	5.2251E-39	8.0096E-37	8.4794E-35	6.3963E-33	3.5353E-31
22	Zr0.85Y0.1501.925	8YSZ	7.7733E-01	8.0273E-01	8.2515E-01	8.4417E-01	8.5990E-01
23	LaMnO3	LSYM	3.0468E-01	3.6067E-01	4.1008E-01	4.5200E-01	4.8667E-01
24	La0.667MnO2.5_perovskite	LSYM	8.9775E-02	1.0368E-01	1.1522E-01	1.2433E-01	1.3125E-01
25	La0.667MnO3_perovskite	LSYM	4.0447E-01	3.3443E-01	2.7336E-01	2.2222E-01	1.8054E-01
26	LaMn0.75O3_perovskite	LSYM	1.4391E-03	1.6210E-03	1.7736E-03	1.8978E-03	1.9970E-03
27	LaMnO2.5_perovskite	LSYM	2.7745E-06	6.4016E-06	1.3453E-05	2.6148E-05	4.7606E-05
28	SrMnO2.5_perovskite	LSYM	2.1608E-02	2.8263E-02	3.5816E-02	4.4101E-02	5.2912E-02
29	SrMnO3_perovskite	LSYM	1.7839E-01	1.7174E-01	1.6418E-01	1.5590E-01	1.4709E-01
30	La3Mn2O7_RP-phase	RP	0	0	0	0	0
31	Sr3Mn2O7_RP-phase	RP	0	0	0	0	0
32	La2SrMn2O7_RP-phase	RP	0	0	0	0	0
33	LaSr2Mn2O7_RP-phase	RP	0	0	0	0	0
34	La2MnO4.15	K2NHE4	0	0	0	0	0

Trial20 | 59 Compounds. [O,Mn,Zr,Y,La,Sr]

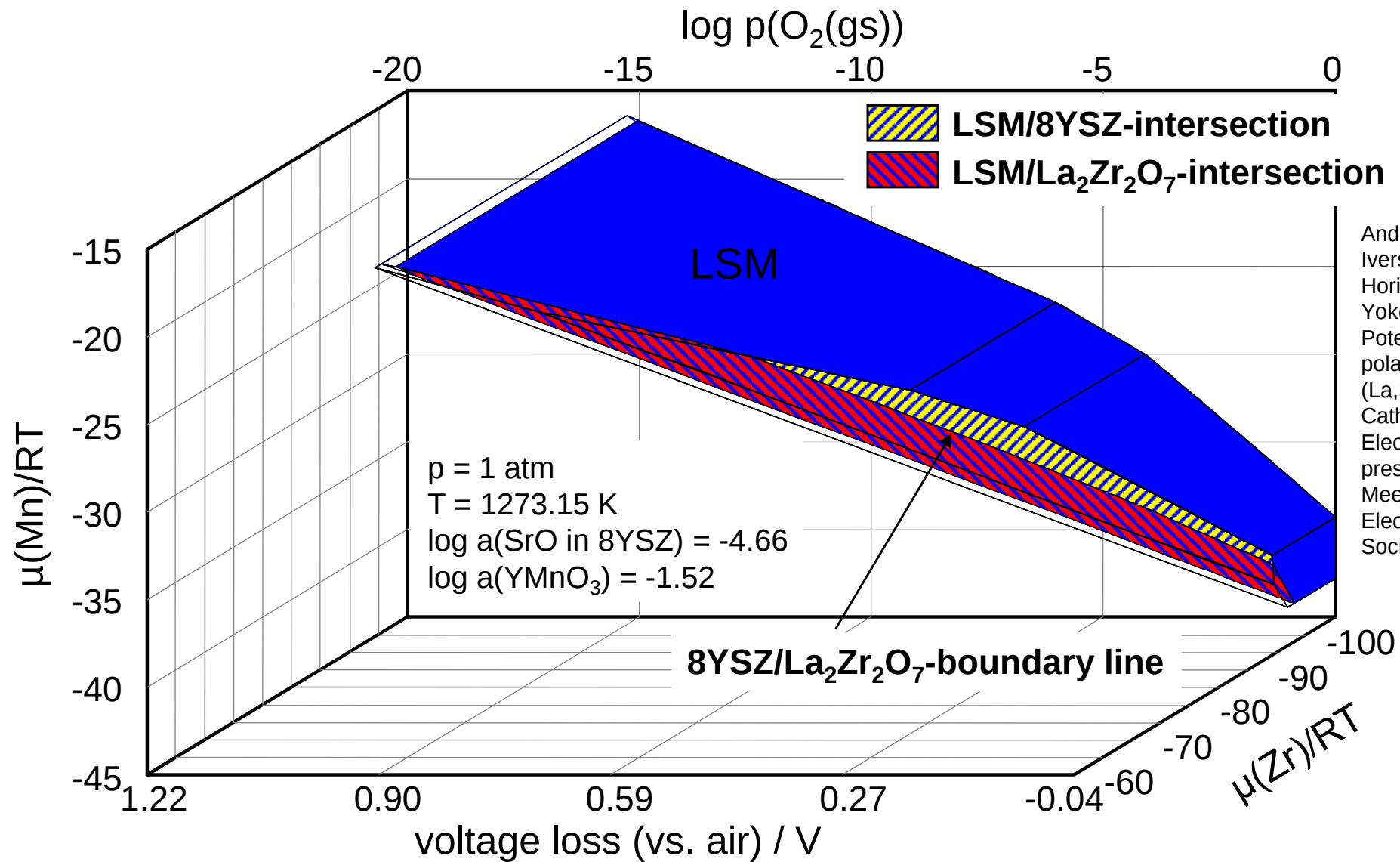
* H. Yokokawa et al., Thermochimica Acta 245, 45-55 (1994)
MALT for Windows, see <http://www.kagaku.com/malt/index.html>



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Modeling of Degradation Phenomena

Chemical Potential Diagram for the polarized LSM / 8YSZ - Interface

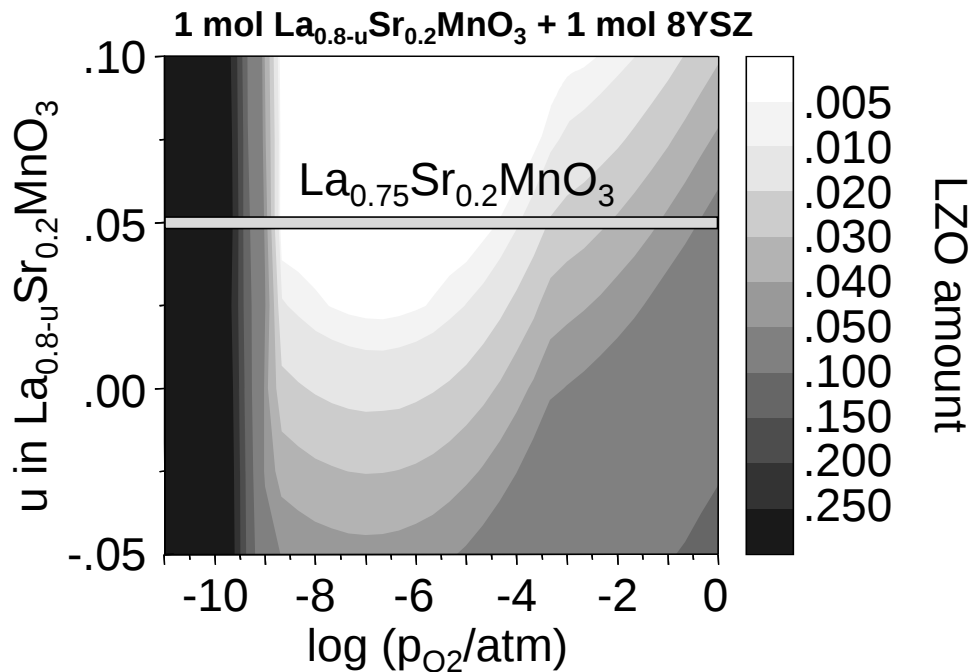


André Weber, Ellen Ivers-Tiffée, Teruhisa Horita, Harumi Yokokawa, Chemical Potential Diagrams for polarized (La,Sr)MnO_{3+d}-Cathode/8YSZ-Electrolyte-Interfaces", presented at the 206th Meeting of The Electrochemical Society, 2004

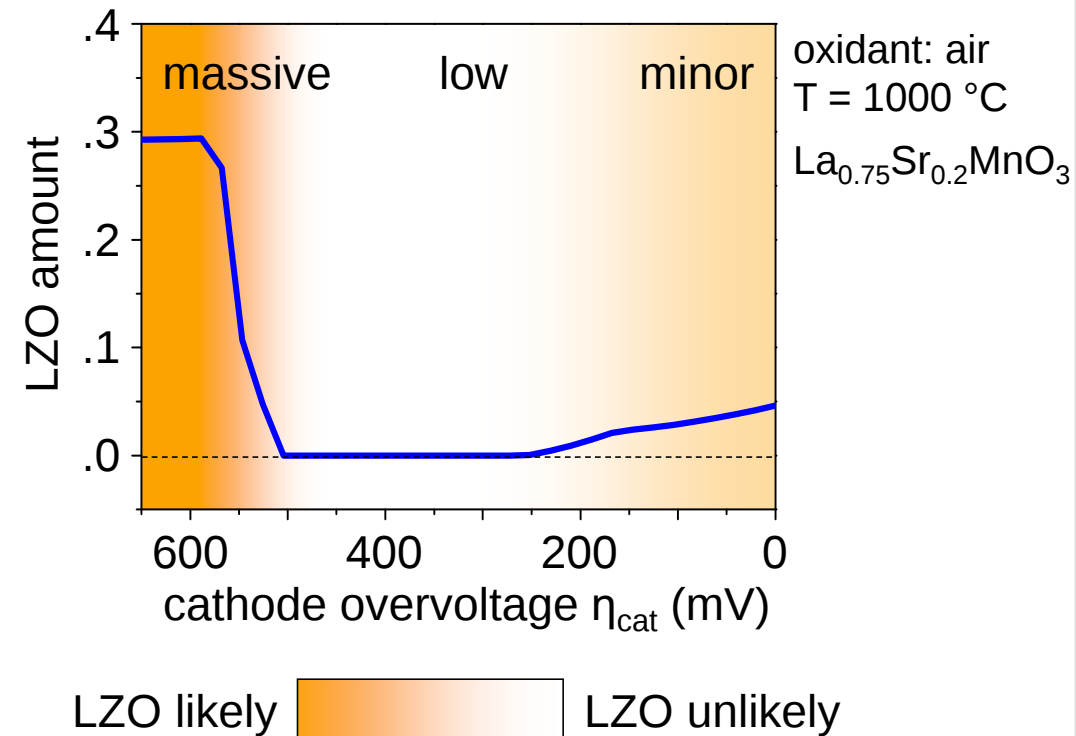
Modeling of Degradation Phenomena

Formation of insulating LZO-layers at the LSM/8YSZ Interface

calculated amount of LZO



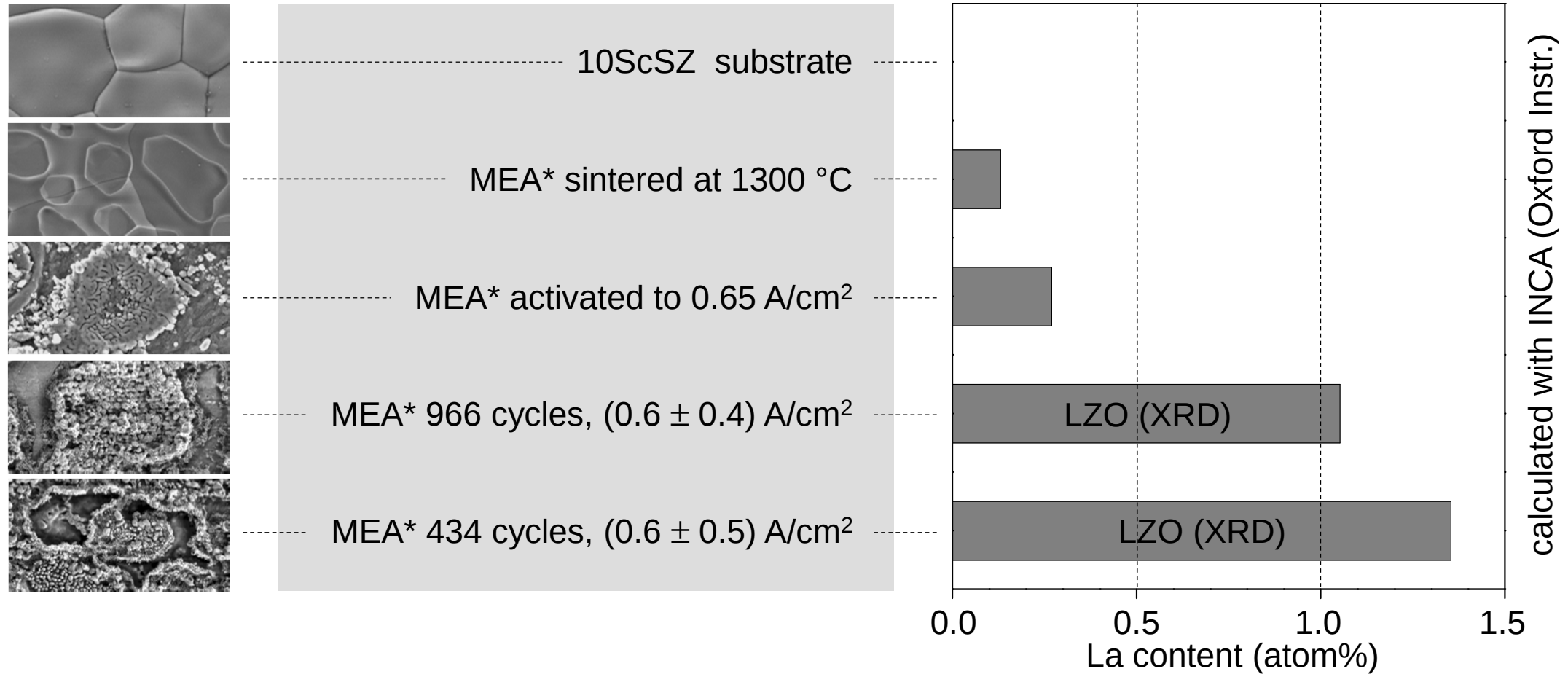
impact of cathode overvoltage η_{cat}



M. J. Heneka, E. Ivers-Tiffée: Degradation of SOFC Single Cells Under Severe Current Cycles. In: S. C. Singhal, J. Mizusaki (Hrsg.), Proc. 9th Int. Symp. on SOFC, PV 2005-07, The Electrochemical Society, 534-543 (2005)

Analysis of Degradation Phenomena

Impact of Load Cycles on LZO-layer at the LSM/8YSZ Interface

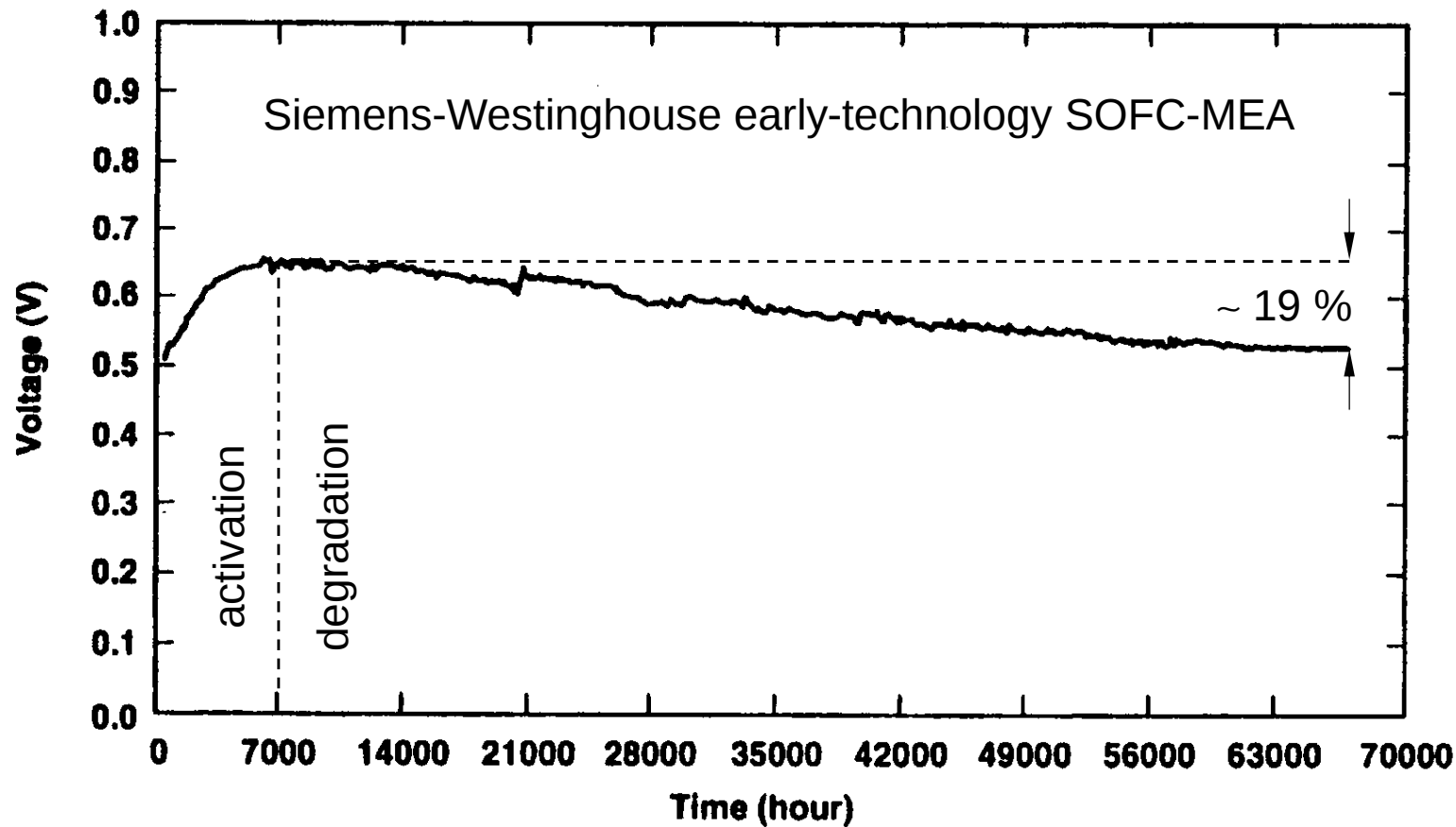


the more intensive the current treatment (amplitude/ cycles), the more the LZO-content increases.

M. J. Heneka, E. Ivers-Tiffée: Degradation of SOFC Single Cells Under Severe Current Cycles. In: S. C. Singhal, J. Mizusaki (Hrsg.), Proc. 9th Int. Symp. on SOFC, PV 2005-07, The Electrochemical Society, 534-543 (2005)

Analysis of Fuel Cell Long-Term Stability

Can we Afford Long-Term Measurements?



[S.C. Singhal, SOFC V, PV97-40, 1997]

duration

69,000 h
8 years
1989 – 1997

assume

\$ 100 per day

cost

\$ 300,000 total

degradation

19 % total
0.3 % / 1,000 h

results

available after
5...10 years

MEA: membrane-electrode assembly



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Quelle: IWE

www.iam.kit.edu/wet

Vorlesung BBS 07 - Langzeitstabilität.pptx, Folie: 51, 22.07.2017

Analysis of Fuel Cell Long-Term Stability

Motivation for Accelerated Lifetime Testing

lifetime

lifetime is a critical issue for the success of fuel cells at market.

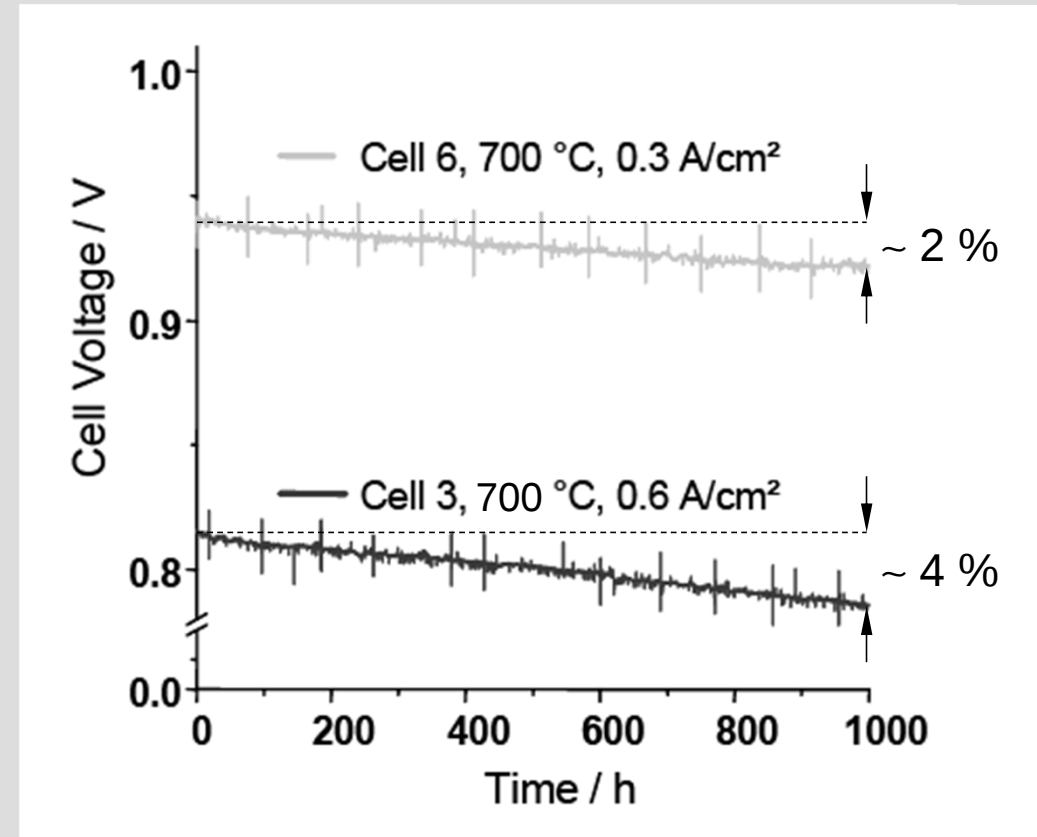
challenges

- long-term measurements are time consuming and thus expensive.
- if the total damage obtained during long-term test is low, the physical degradation mechanisms are difficult to identify.

possible solution

accelerated life testing (ALT) for fuel cell components and single cells

example: damage during long-term test may be low.



(M. Becker et al., SOFC IX, PV2005-07, 2005)

Basic Concepts in Reliability Engineering

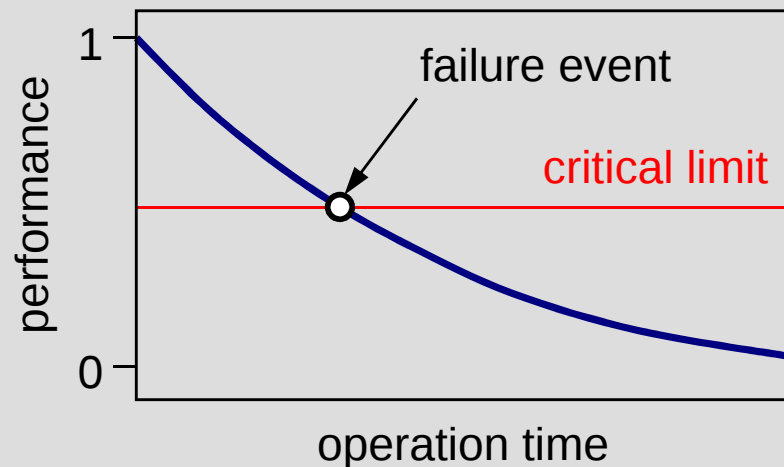
Definition of Failure Event and Time-To-Failure

soft failure

gradual performance loss until (pre-defined) critical level is reached.

example

- voltage/ power degradation in fuel cells



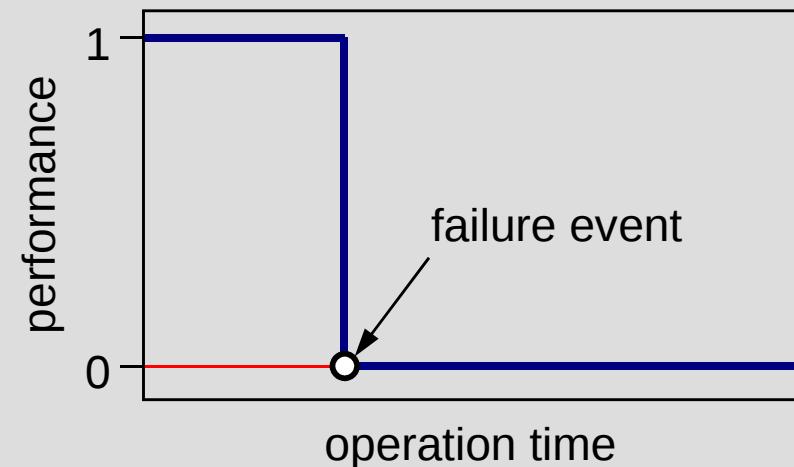
(Meeker et al., Technometrics, 40, 1998)

hard failure

sudden loss of functionality – the device stops working.

example

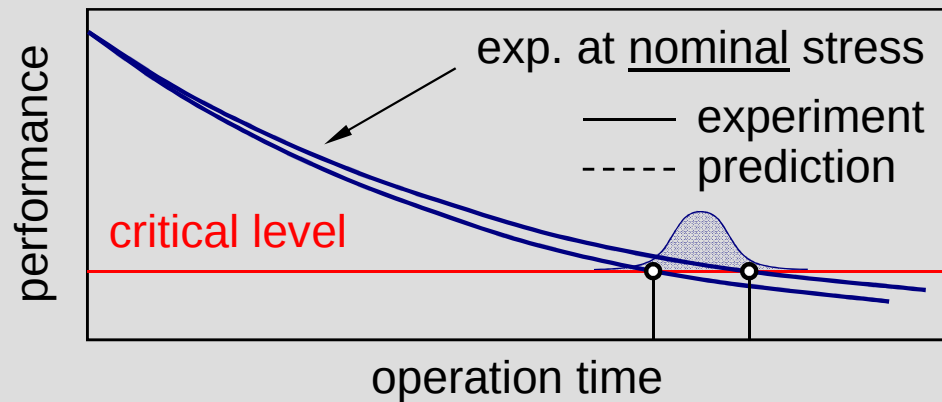
- light bulb burns out



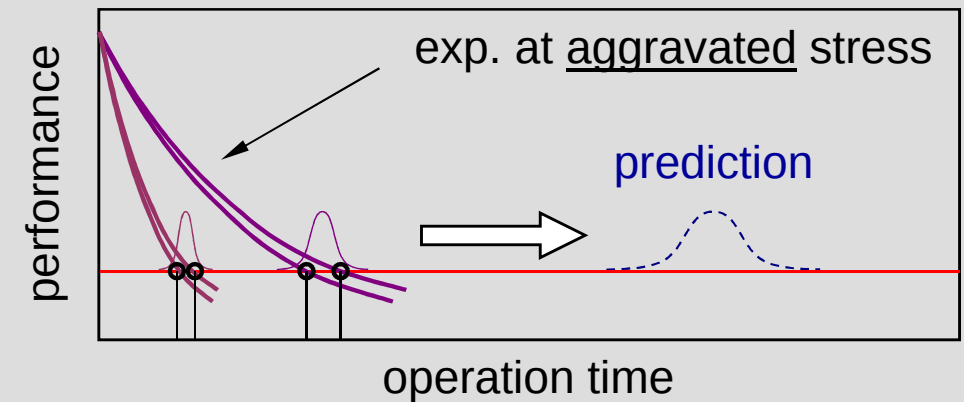
Lifetime and Degradation Assessment

Overview of Life Testing Methods

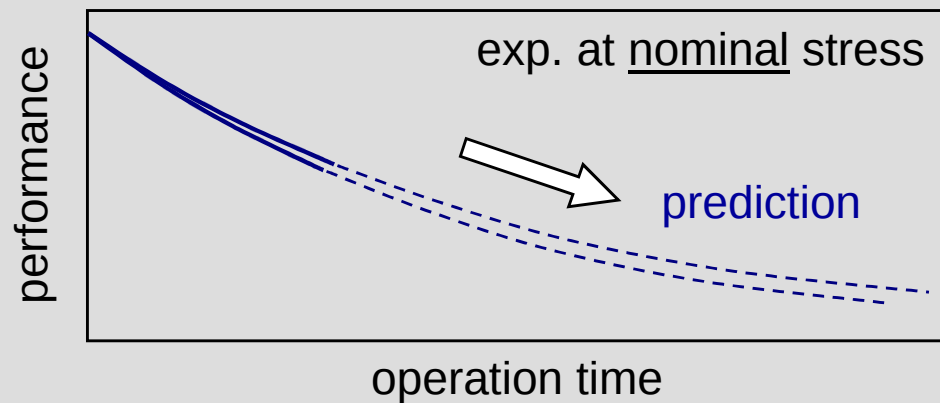
"conventional" life testing



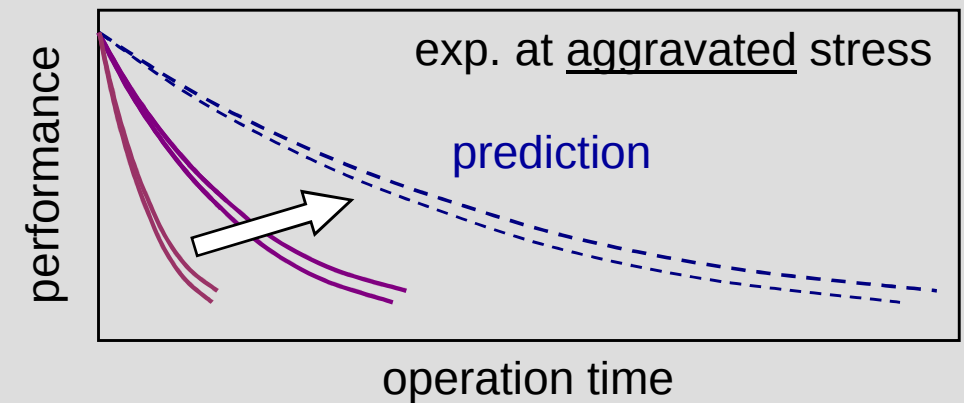
accelerated life testing



degradation testing



accelerated degradation testing



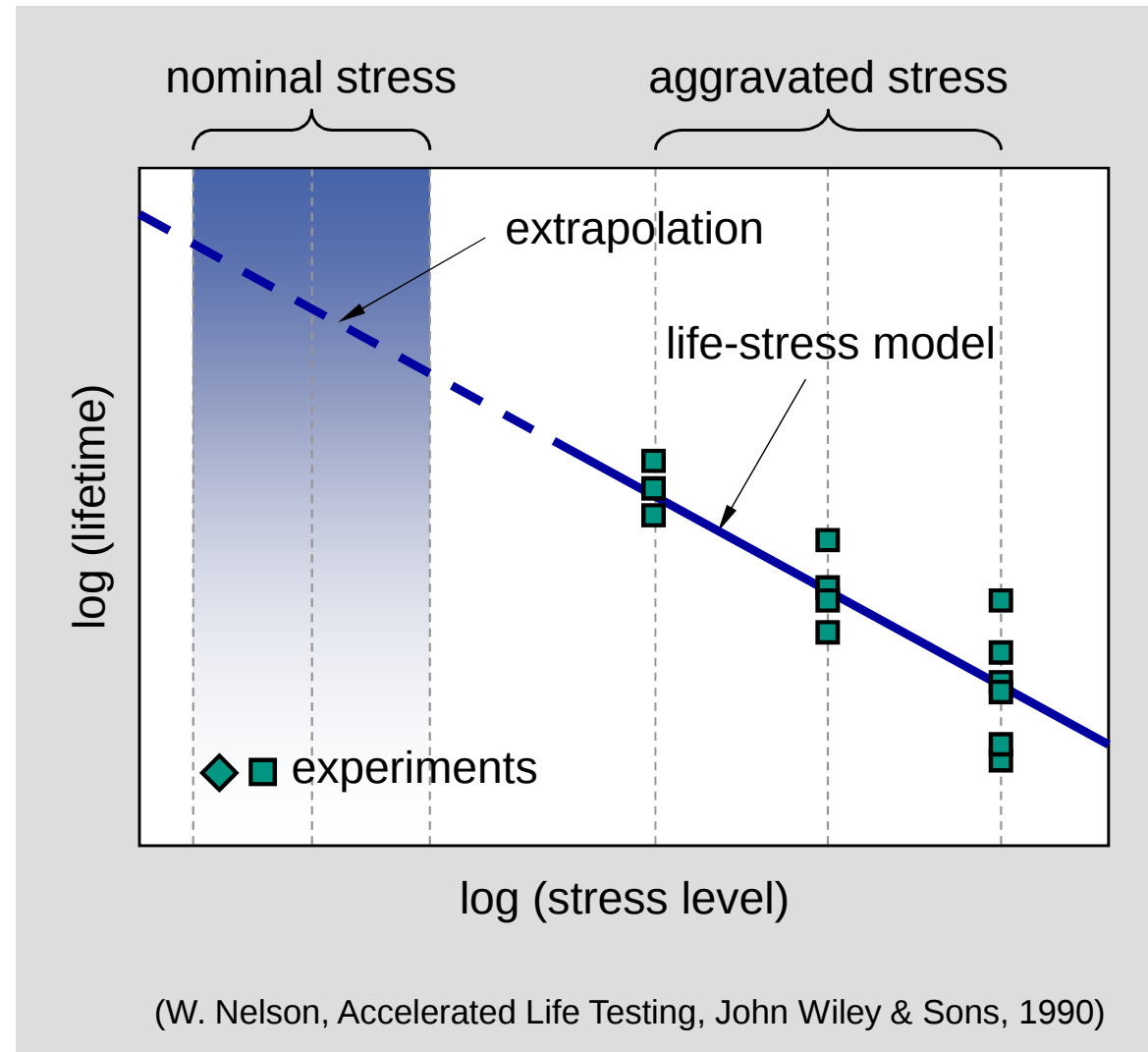
Accelerated Life Testing Approach and Advantages

approach

- degradation is accelerated by means of aggravated stress (current load, temperature, etc.).
- life-stress relationship is modelled by the use of failure data.
- extrapolation of life-stress model gives a prediction for service life at nominal stress.

advantages

- physical consequences of degradation appear more clearly, mechanisms are identified more easily.
- precious measurement time is saved, lifetime is evaluated rapidly.



Accelerated Life Testing

Competing Failure Modes in Accelerated Testing

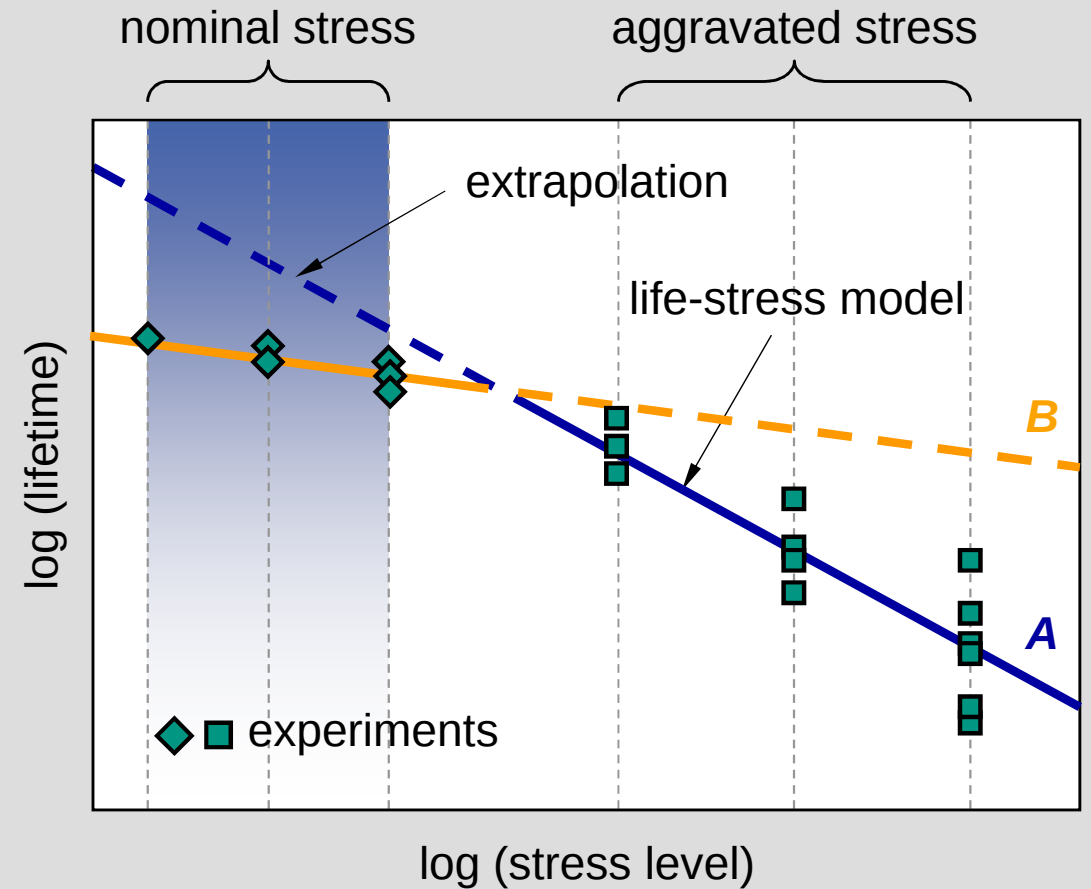
difficulty

- if there are competing failure modes, accelerated life testing may lead to incorrect statements.

example

- two degradation processes *A*, *B*.
- degradation mechanism *B* is masked by failure mode *A* at aggravated stress levels.
- extrapolation of life-stress model to nominal stress levels will be wrong.

failure mechanisms *A*, *B* need to be separated for correct life modelling!



(W.Q. Meeker et al., IEEE Transactions on Reliability, 47, 1998)

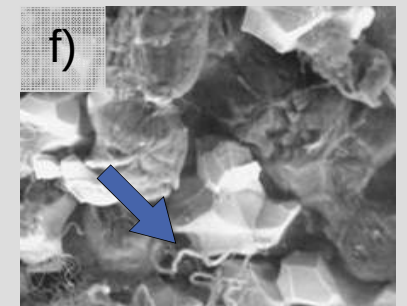
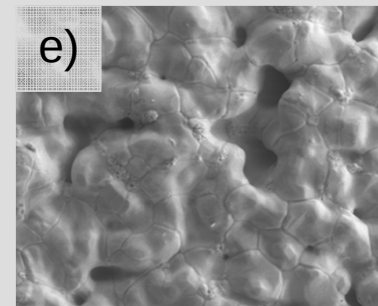
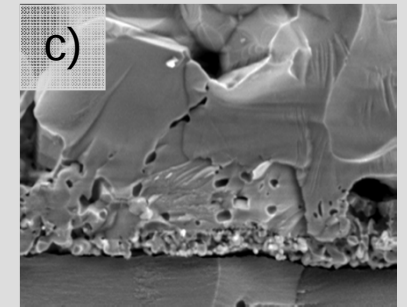
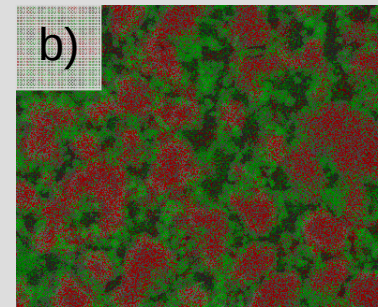
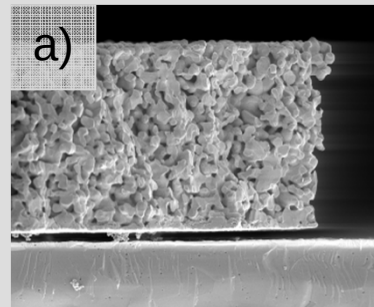
Accelerated Life Testing

Competing Degradation Processes in Solid Oxide Fuel Cells

in SOFC

many potentially competing degradation mechanisms are known:

- a) delamination of layers
- b) agglomeration of catalyst particles
- c) formation of secondary phases
- d) interdiffusion and demixing
- e) densification of porous electrodes
- f) carbon deposition in anode
- g) electrolyte conductivity loss
- h) corrosion of interconnects
- i) etc.



⇒ in addition, activation processes that improve the performance are known (from cathodes).