



Fuel Cell & Hydrogen Technologies JP

SP2: Catalyst and Electrodes

Borovetz, Bulgaria

June 2nd and 3rd 2014

The need for localized electrochemical measurements and the promise of Controlled Atmosphere High Temperature scanning probe microscopy

EERA FCH2-SP2 WORKSHOP in frame of EIA10

Bridging experimental and numerical research:

development and optimization of advanced characterization tools – Electrochemical Impedance Spectroscopy



Christodoulos Chatzichristodoulou

Technical University of Denmark, Department of Energy Conversion and Storage

- The Danish sustainable energy vision
- The promise and challenges of SOEC
- SOEC degradation
- Trying to understand SOEC degradation
- Limitations of modeling
- Localized in-operando probing (CAHT-SPM)
- CAHT-SPM achievements
- Future perspectives
- Conclusions

The Danish sustainable energy vision

Danish ambition

- 2020: 50% Renewable
- 2035: 100% Renewable
- 2050: 100% Renewable

Challenges

- Increasing share of fl
- Biomass resources a
- Liquid fuels from whe

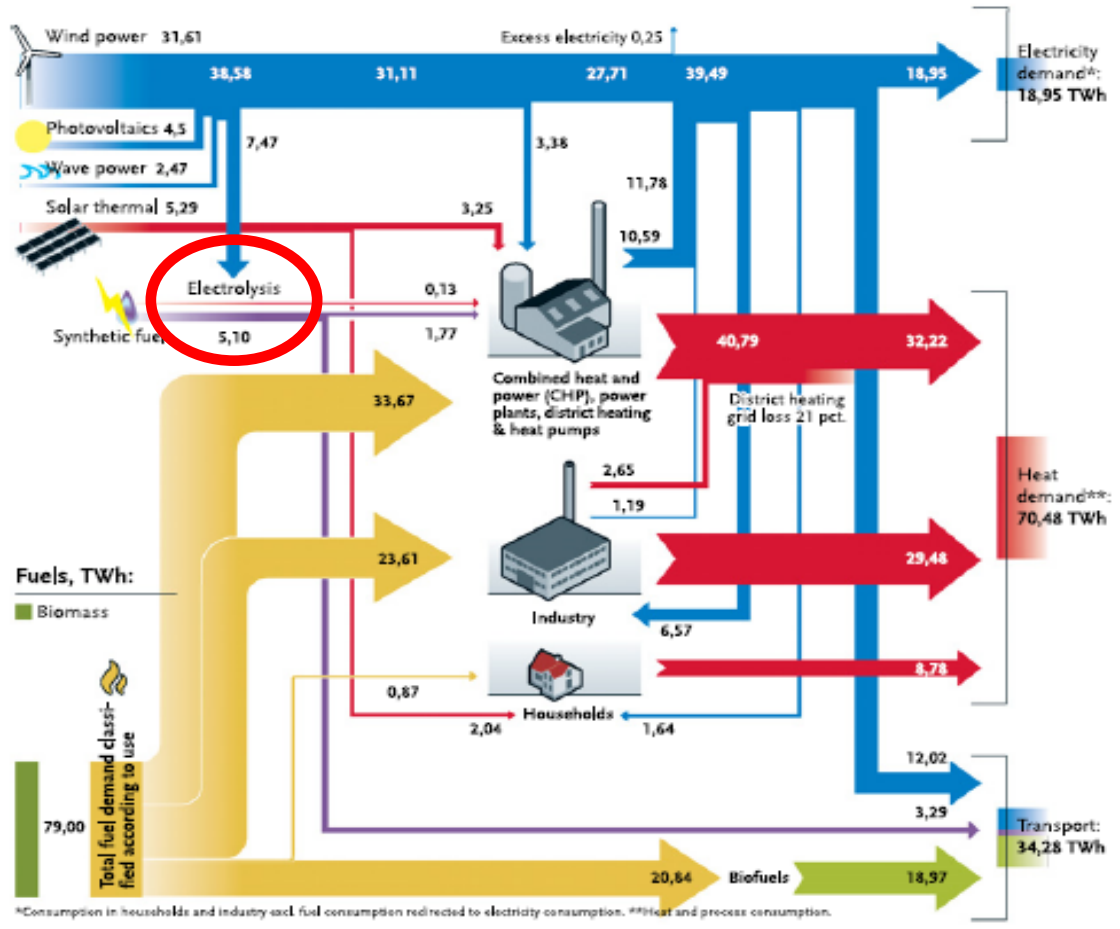
B. V. Mathiesen *et al.*, Applied Energy 88 (2011) 488–501

THE IDA CLIMATE PLAN

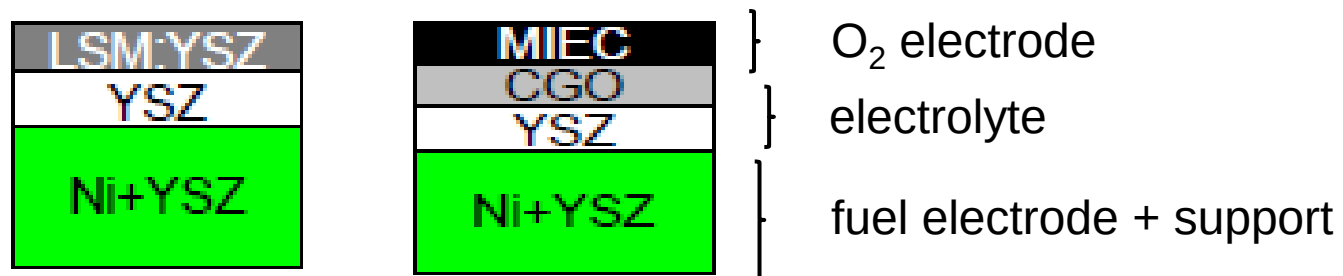
2050

100% renewable energy. Primary energy supply, total:

122,86 terawatt hour (TWh)



The promise and challenges of SOEC



Promise

- High conversion efficiency (ca. 95%)
- High production rate (ca. 1 A/cm² or 0.5 L/h·cm²)
- Low cost

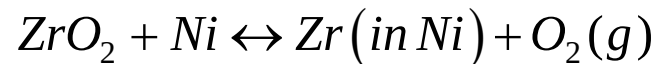
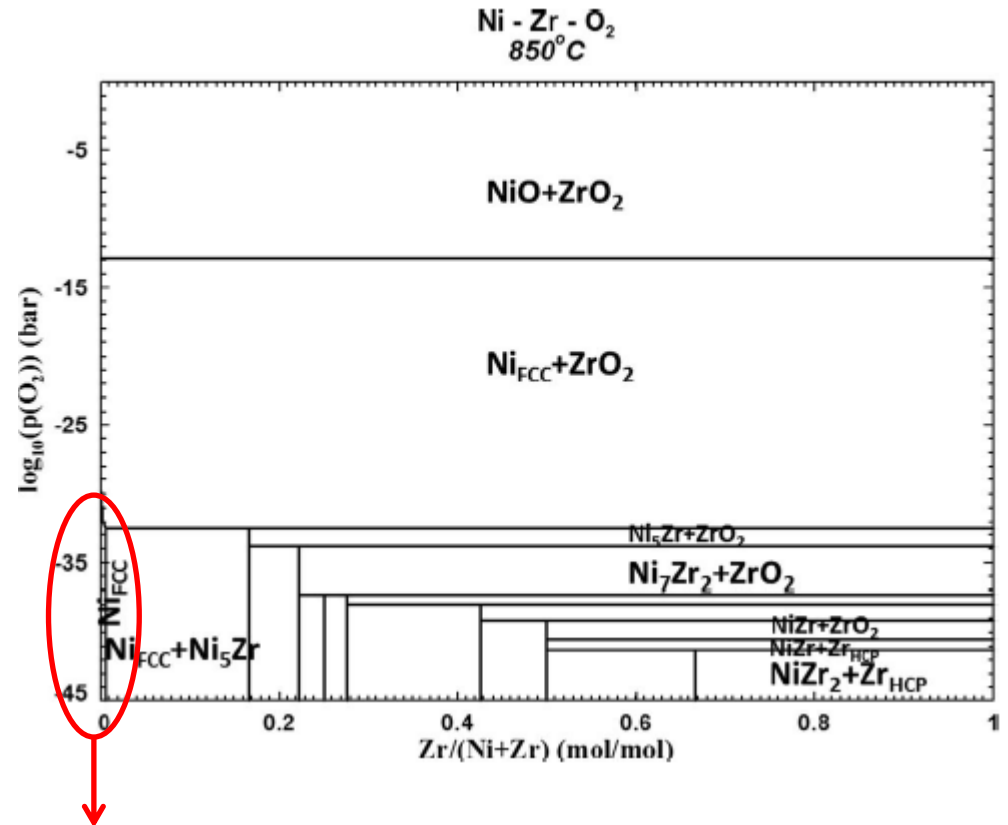
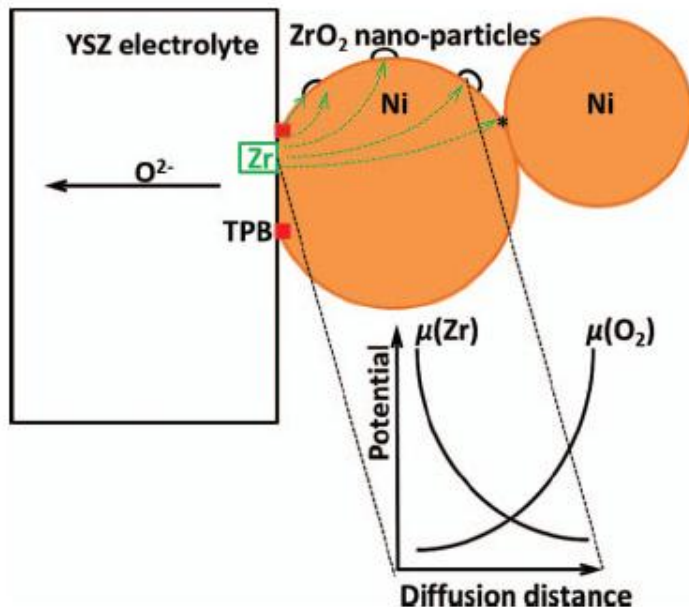
Challenges

- Durability

- Si poisoning of the fuel electrode (pH_2O)
- SiO_2 inclusions in Ni grains at the fuel electrode (pO_2)
- Formation of zirconia nanoparticles on Ni grains at the fuel electrode (pO_2)
- Evaporation of $\text{Ni}(\text{OH})_2$ and loss of electronic percolation (pH_2O)
- Formation of O_2 bubbles in the electrolyte (pO_2)
- Delamination at the electrolyte/ O_2 -electrode interface (pO_2)
- Delamination at the electrolyte/electrolyte interface (pO_2)
- Kinetic demixing and formation of Kirkendall voids (V , pO_2)
- ...

M. Chen *et al.*, *J. Electrochem. Soc.* 160 (2013) F883.
R. Knibbe *et al.*, *J. Electrochem. Soc.* 157 (2010) B1209.
F. Tietz *et al.*, *J. Power Sources* 223, (2013) 129.

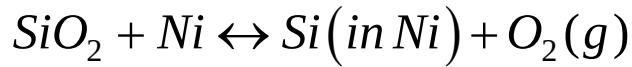
SOEC degradation - Formation of zirconia nanoparticles on Ni grains at the fuel electrode



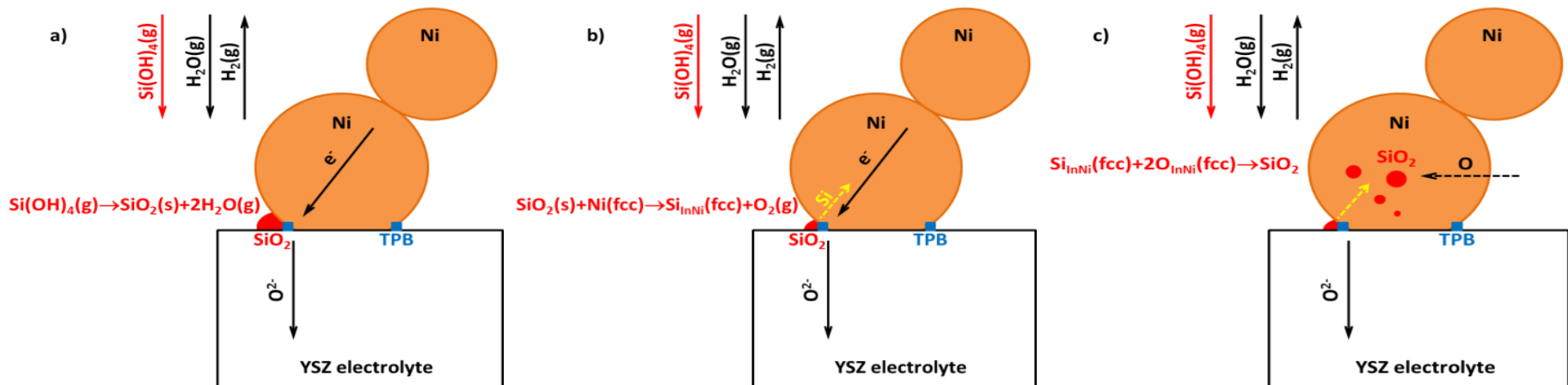
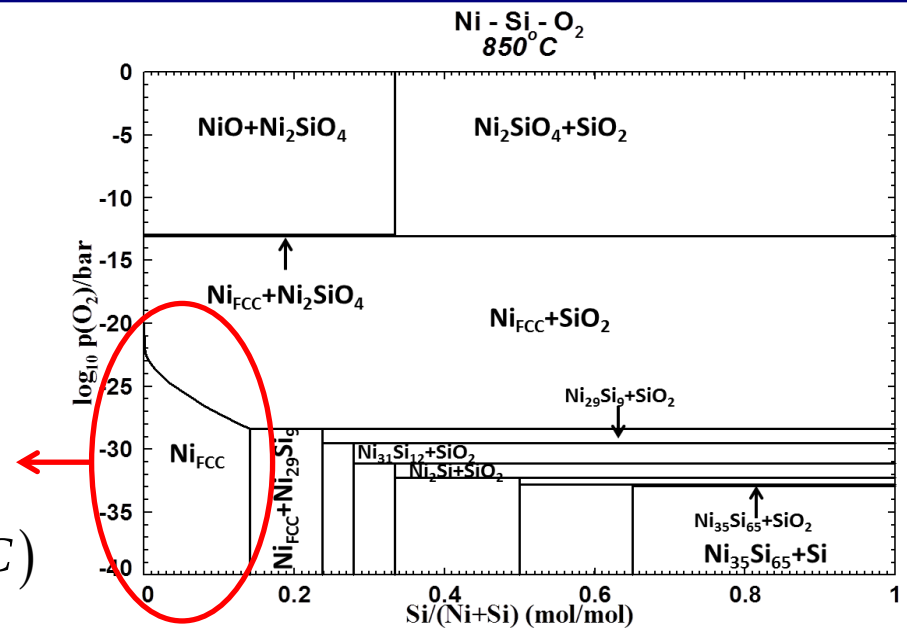
$$1 \text{ ppm Zr}(\text{in Ni}) \rightarrow p_{\text{O}_2} \approx 1 \cdot 10^{-29 \pm 3} \text{ atm} (@ 850^\circ \text{C})$$

M. Chen et al., *J. Electrochem. Soc.* 160 (2013) F883.

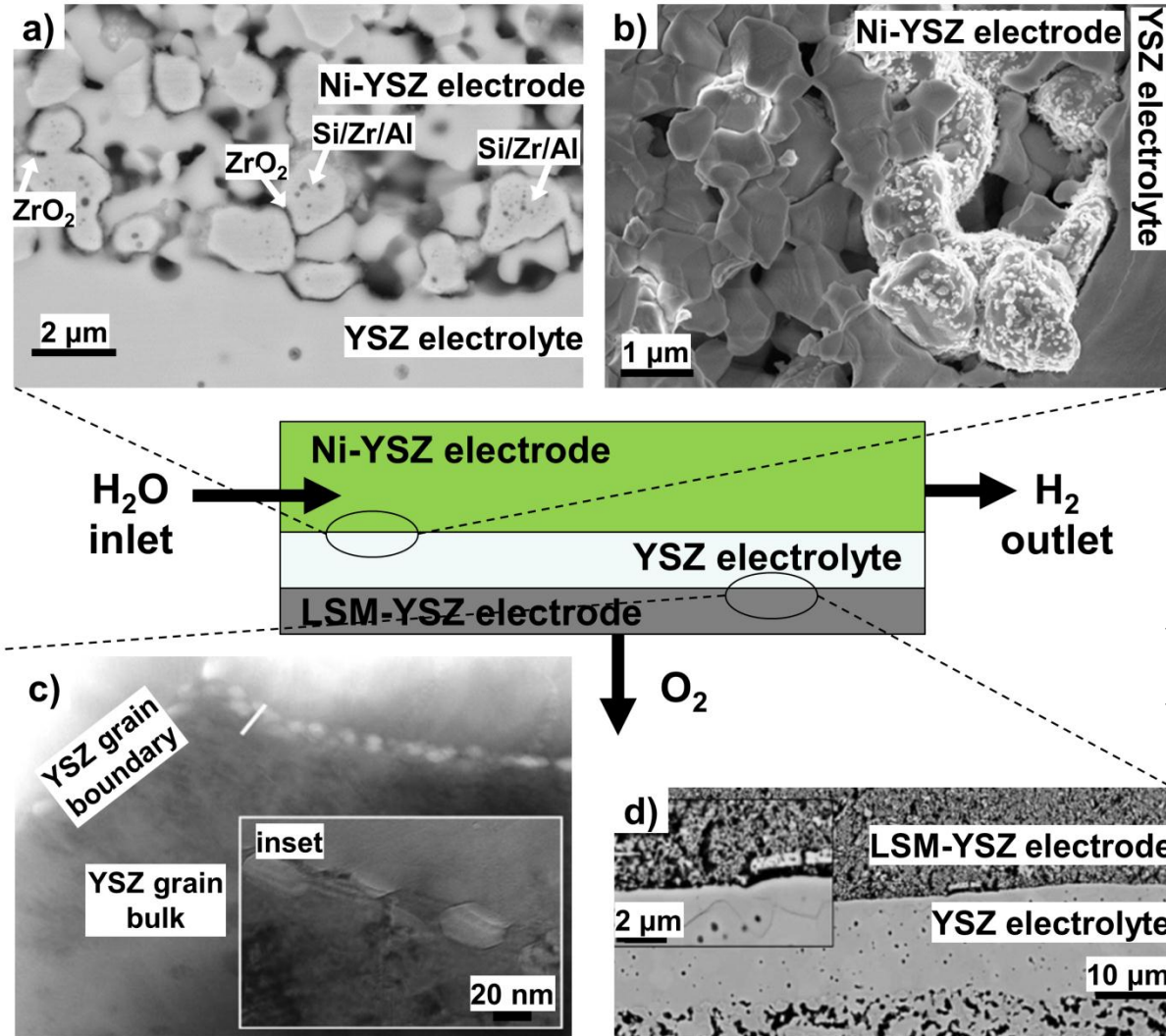
SOEC degradation -SiO₂ inclusions in Ni grains at the fuel electrode



$$1 \text{ ppm Si}(\text{in Ni}) \rightarrow p_{\text{O}_2} \approx 1 \cdot 10^{-19} \text{ atm} (@850^\circ\text{C})$$

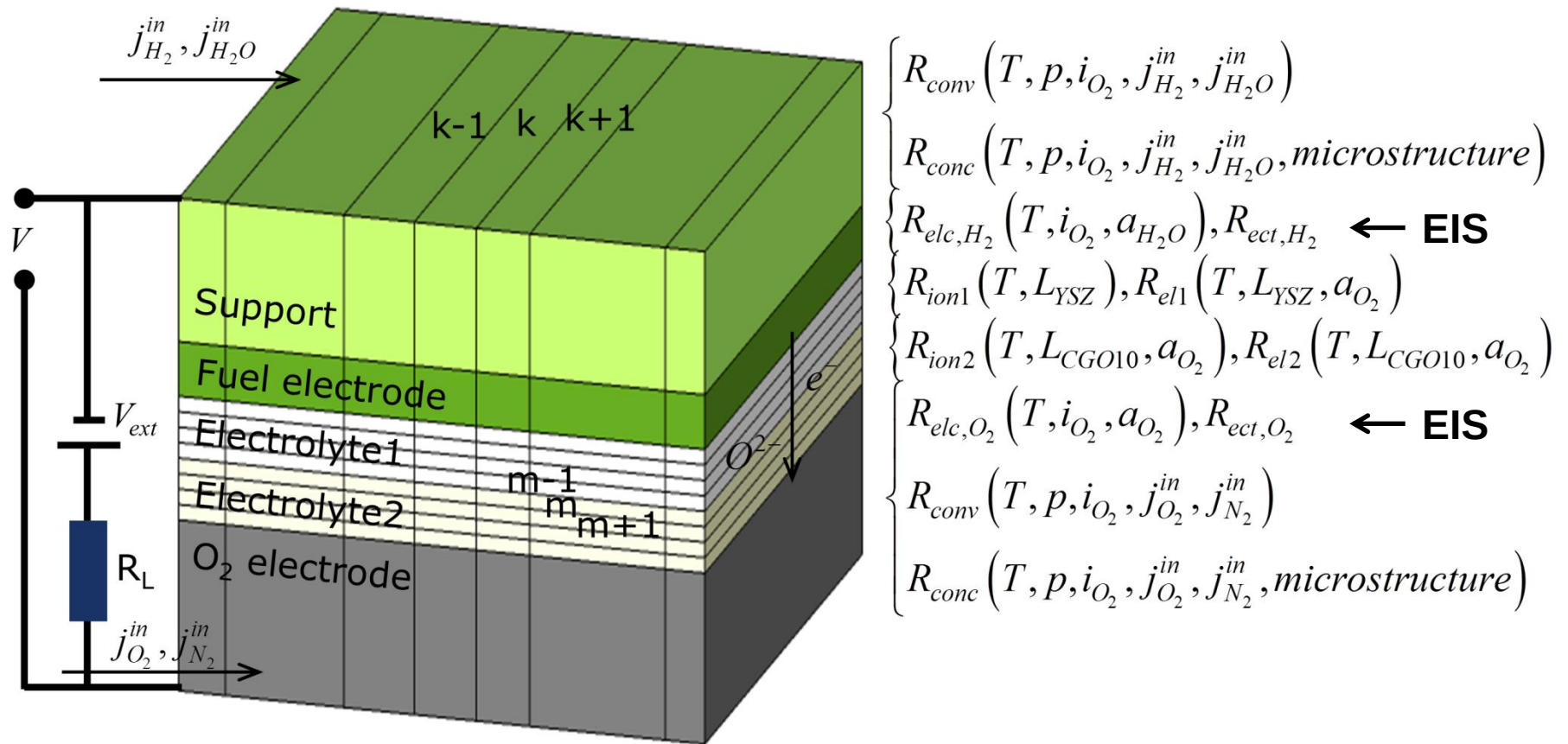


SOEC degradation is location specific



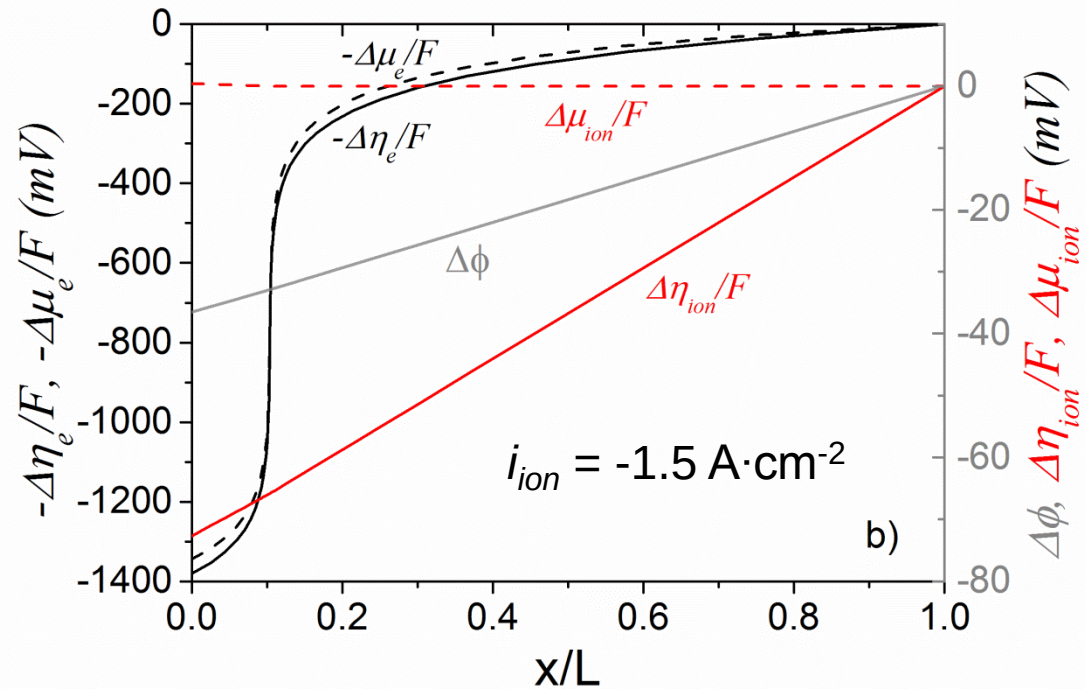
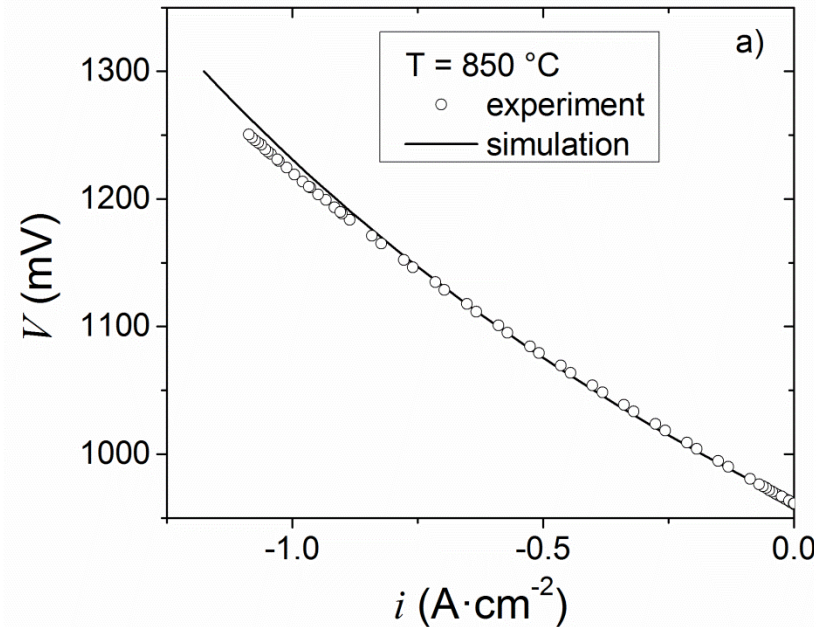
M. Chen *et al.*, *J. Electrochem. Soc.* 160 (2013) F883.
R. Knibbe *et al.*, *J. Electrochem. Soc.* 157 (2010) B1209.

Trying to understand SOEC degradation



C. Chatzichristodoulou et al., to be submitted

Trying to understand SOEC degradation – model validation



Ni-YSZ/YSZ(10 μm)/LSM-YSZ

$T = 850\text{ }^{\circ}\text{C}$

$p = 1\text{ atm}$

$j_{H_2}^{in} = 200\text{ Nml}\cdot\text{min}^{-1}, j_{H_2O}^{in} = 200\text{ Nml}\cdot\text{min}^{-1}$

$j_{O_2}^{in} = 400\text{ Nml}\cdot\text{min}^{-1}$

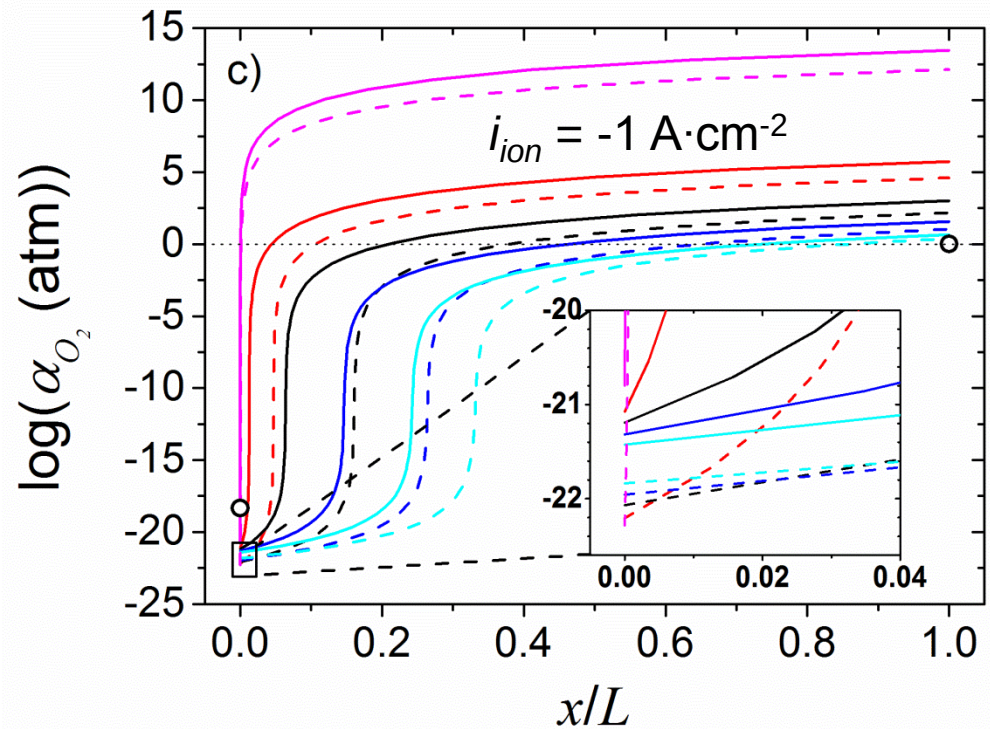
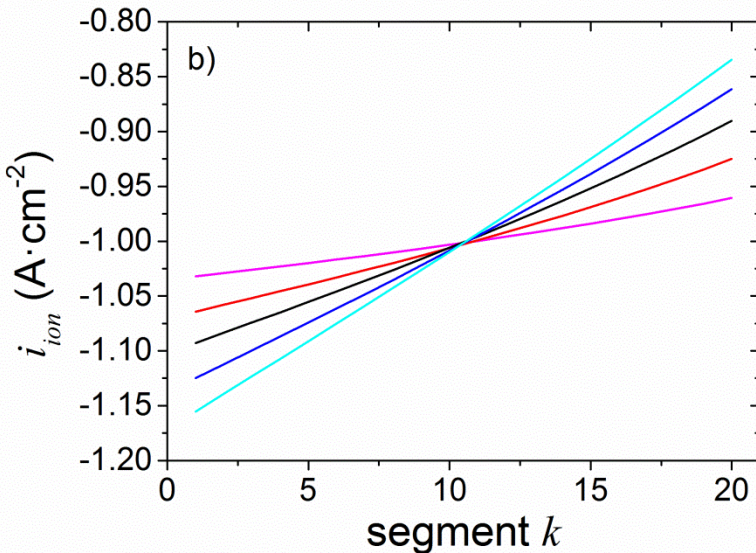
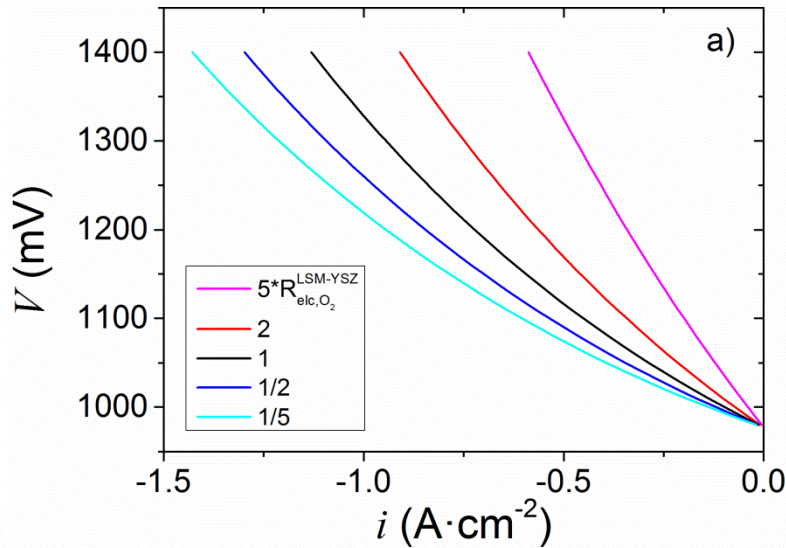
Trying to understand SOEC degradation – polarization resistance of the O₂ electrode

Ni-YSZ/YSZ(10μm)/LSM-YSZ

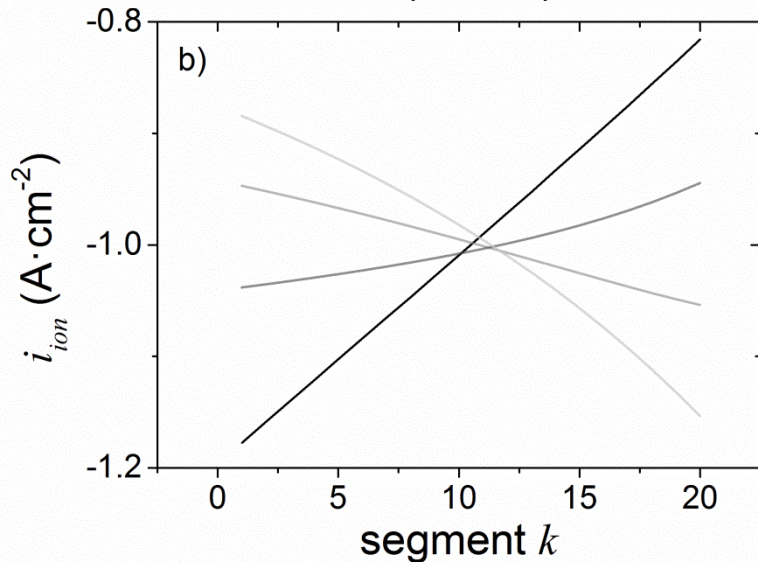
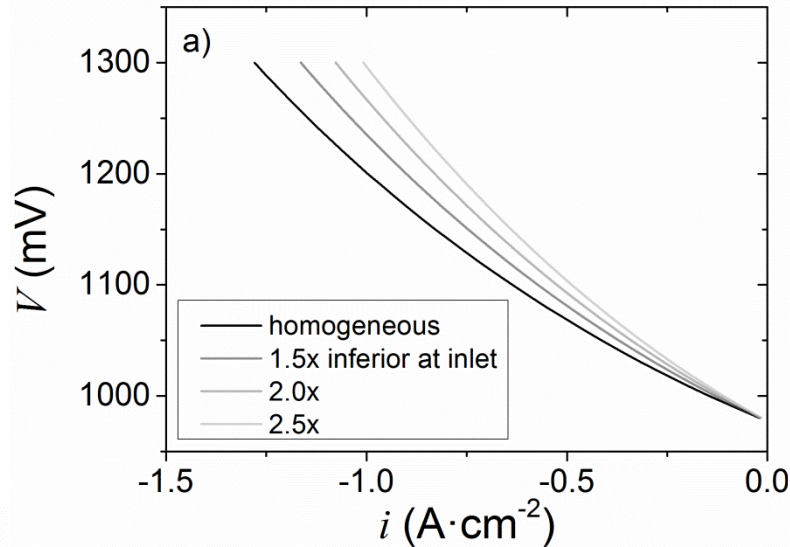
$T = 800\text{ }^{\circ}\text{C}$

$p = 1\text{ atm}$

$j_{H_2}^{in} = 200\text{ Nml} \cdot \text{min}^{-1}, j_{H_2O}^{in} = 200\text{ Nml} \cdot \text{min}^{-1}$



Trying to understand SOEC degradation – inhomogeneous fuel electrode response

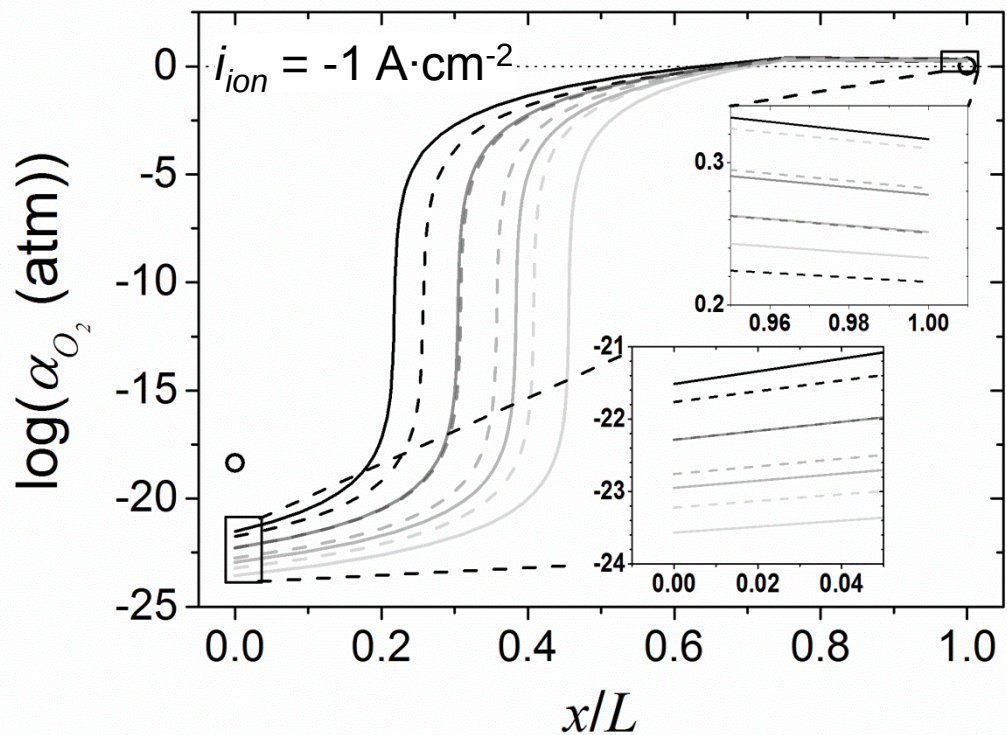


Ni-YSZ/YSZ(7.5 μm)/CGO10(2.5 μm)/LSC-CGO10

$T = 800\text{ }^{\circ}\text{C}$

$p = 1\text{ atm}$

$j_{H_2}^{in} = 200\text{ Nml}\cdot\text{min}^{-1}$, $j_{H_2O}^{in} = 200\text{ Nml}\cdot\text{min}^{-1}$

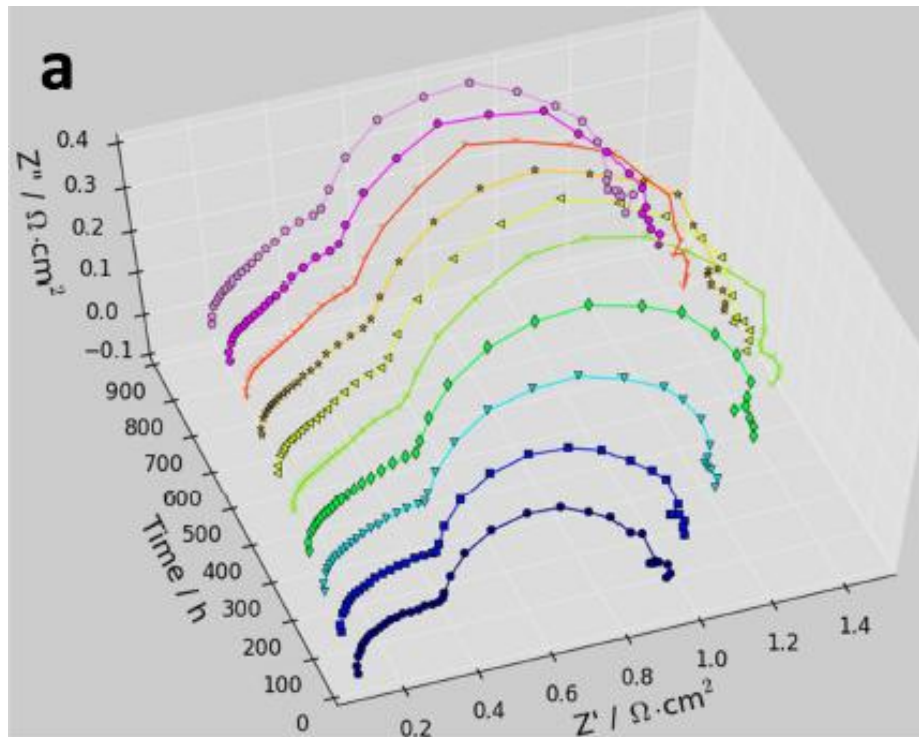


Trying to understand SOEC degradation

Ni-YSZ/YSZ(10 μ m)/LSM-YSZ: (0 $\rightarrow$ 900 h)

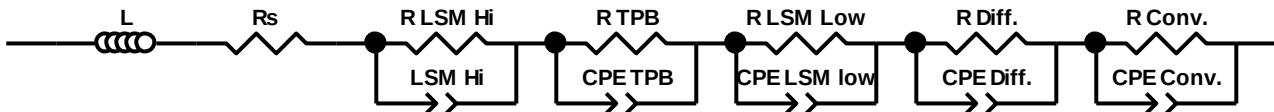
$T = 850\text{ }^{\circ}\text{C}$

$p = 1\text{ atm}$ $j_{H_2}^{in} = 200\text{ Nml} \cdot \text{min}^{-1}$, $j_{H_2O}^{in} = 200\text{ Nml} \cdot \text{min}^{-1}$, $j_{O_2}^{in} = 400\text{ Nml} \cdot \text{min}^{-1}$

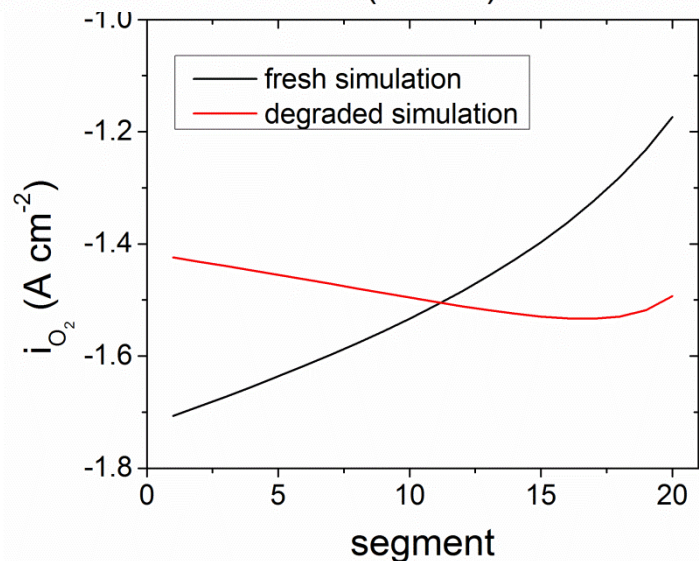
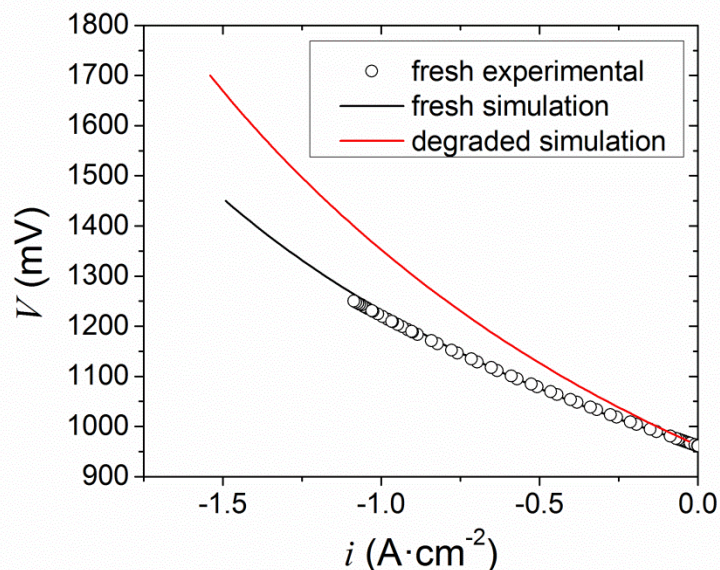


$i = -1.5\text{ A} \cdot \text{cm}^{-2}$

$\rightarrow$ $R_{elc}(t)$
 $R_s(t)$



Trying to understand SOEC degradation



Ni-YSZ/YSZ(10 μm)/LSM-YSZ

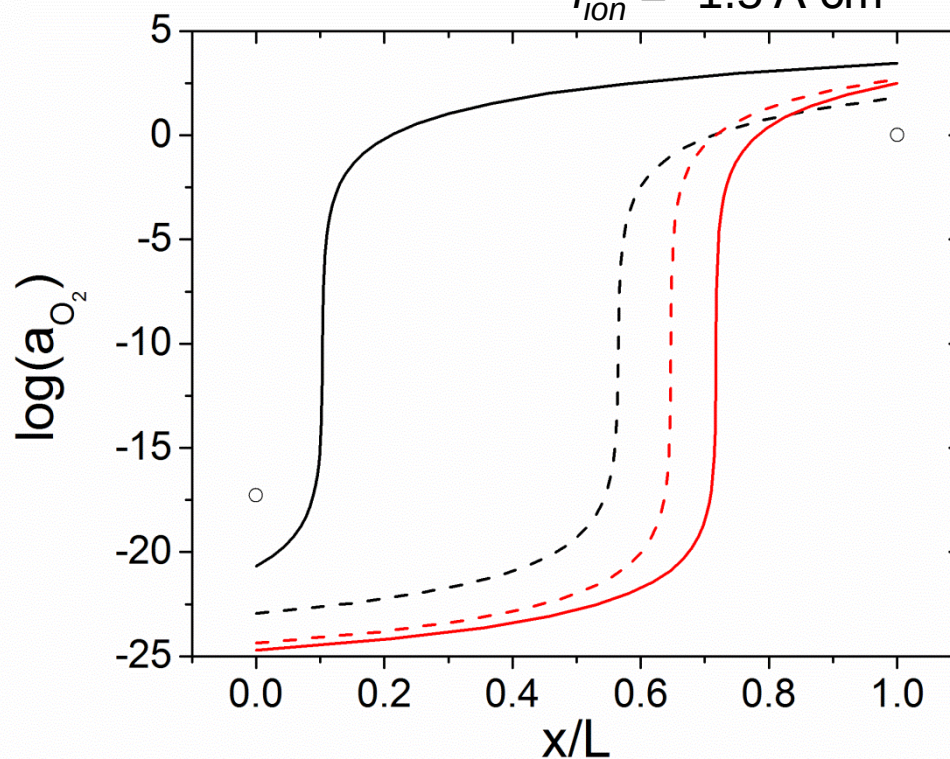
$T = 850^\circ\text{C}$

$p = 1 \text{ atm}$

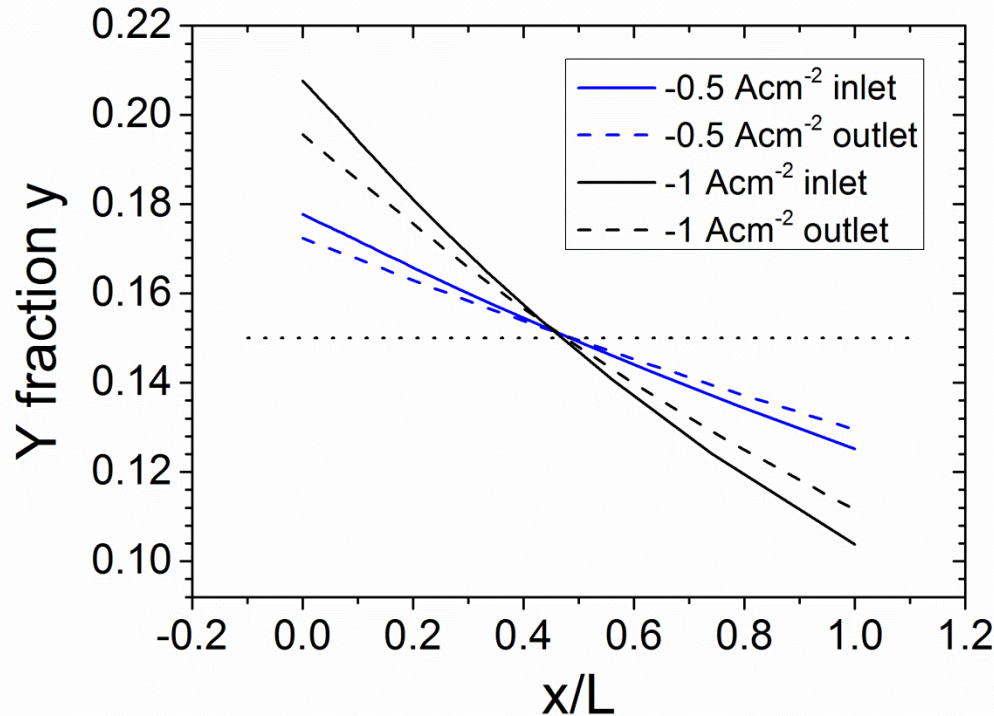
$j_{\text{H}_2}^{\text{in}} = 200 \text{ Nml} \cdot \text{min}^{-1}$, $j_{\text{H}_2\text{O}}^{\text{in}} = 200 \text{ Nml} \cdot \text{min}^{-1}$

$j_{\text{O}_2}^{\text{in}} = 400 \text{ Nml} \cdot \text{min}^{-1}$

$i_{\text{ion}} = -1.5 \text{ A} \cdot \text{cm}^{-2}$



Trying to understand SOEC degradation - demixing



Ni-YSZ/YSZ(10 μm)/LSM-YSZ

$T = 800 \text{ }^{\circ}\text{C}$

$p = 1 \text{ atm}$

$j_{\text{H}_2}^{\text{in}} = 200 \text{ Nm} \cdot \text{min}^{-1}$, $j_{\text{H}_2\text{O}}^{\text{in}} = 200 \text{ Nm} \cdot \text{min}^{-1}$

bulk diffusion: $\tau_{\text{st.st.}} \sim 160.000.000 \text{ years}$

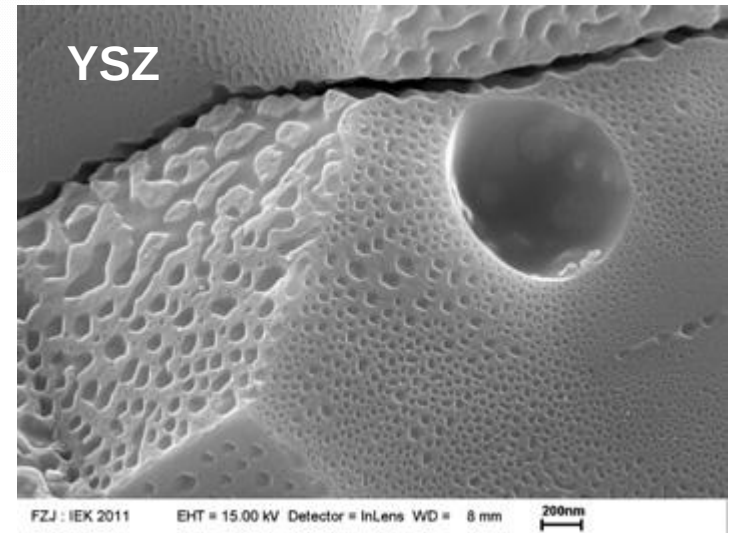
grain boundary diffusion: $\tau_{\text{st.st.}} \sim 1,6 \text{ years}$

Ni-YSZ/YSZ(10 μm)/CGO(5 μm)/LSCF

$T = 780 \pm 6 \text{ }^{\circ}\text{C}$

$p = 1 \text{ atm}$

$t = 1 \text{ year}$



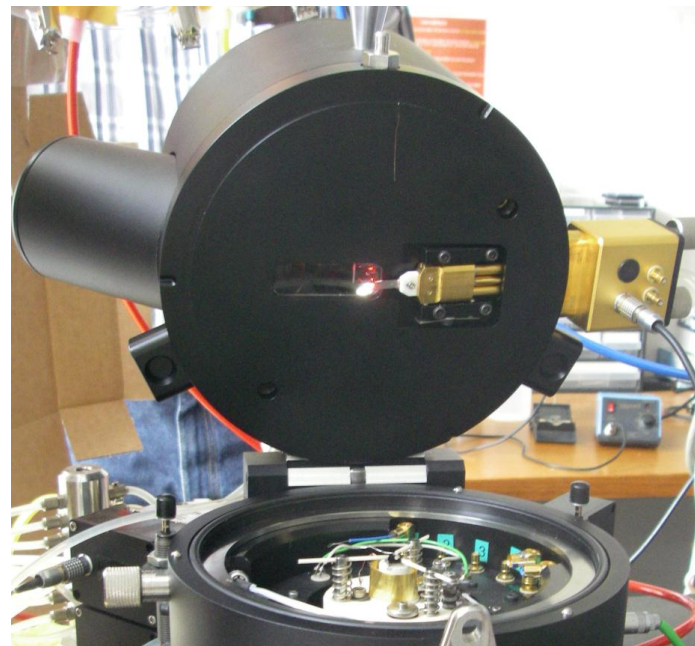
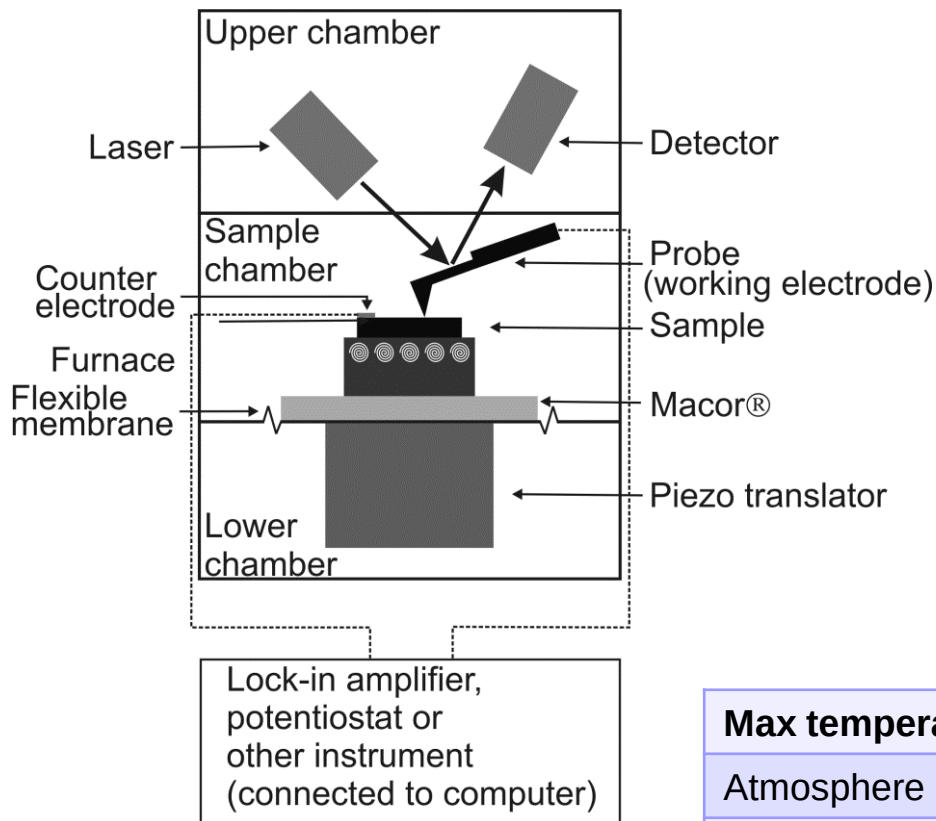
F. Tietz, D. Sebold, A. Brisse, J. Schefold, J. Power Sources 223 (2013) 129-135

A lot of complexity is ignored/simplified:

- grain boundaries/interfaces
- segregation/deposition of impurities
- microstructural heterogeneities
- microstructural changes
- compositional changes
- mechanical strain

Localized in-operando probing is needed

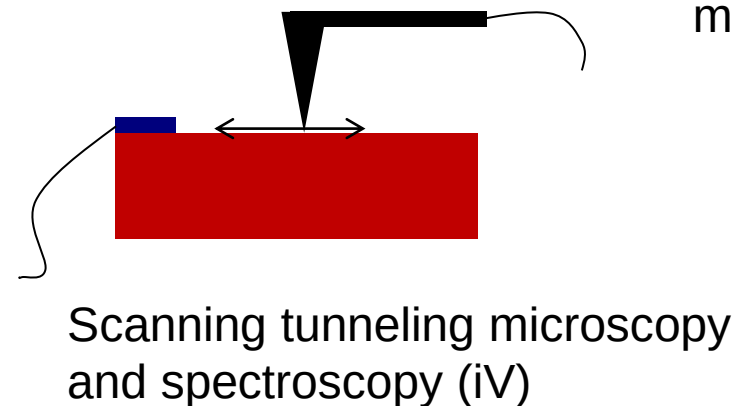
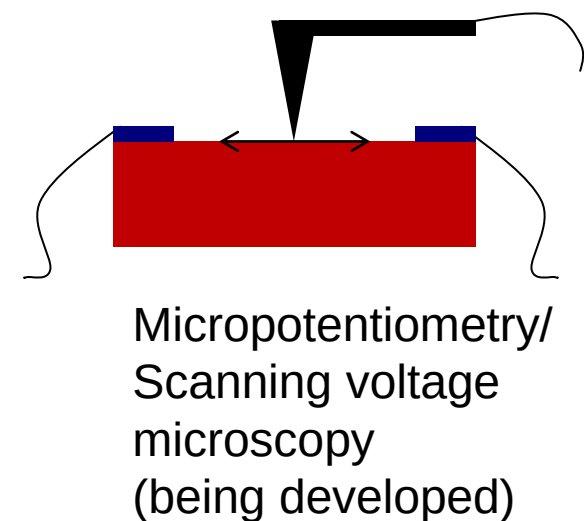
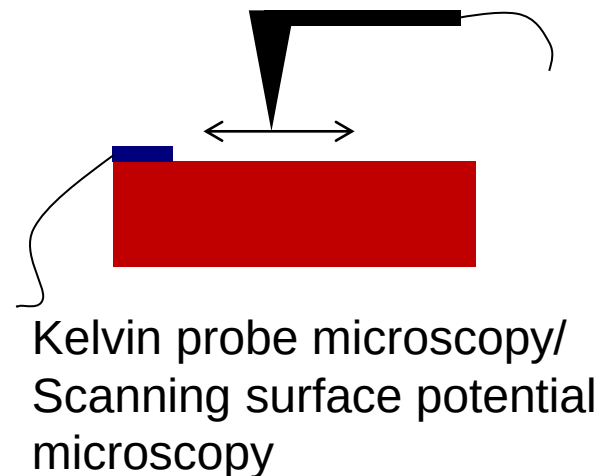
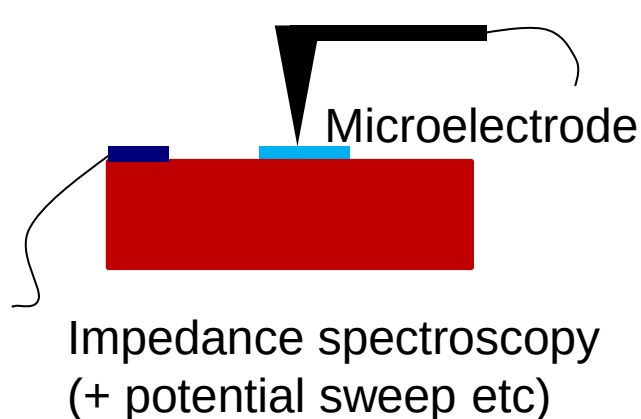
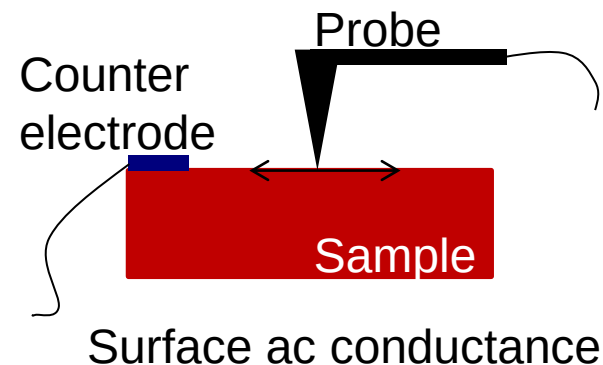
Localized in-operando probing (CAHT-SPM)



K. V. Hansen *et al.*, *Rev. Sci. Instrum.* 84 (2013) 073701.

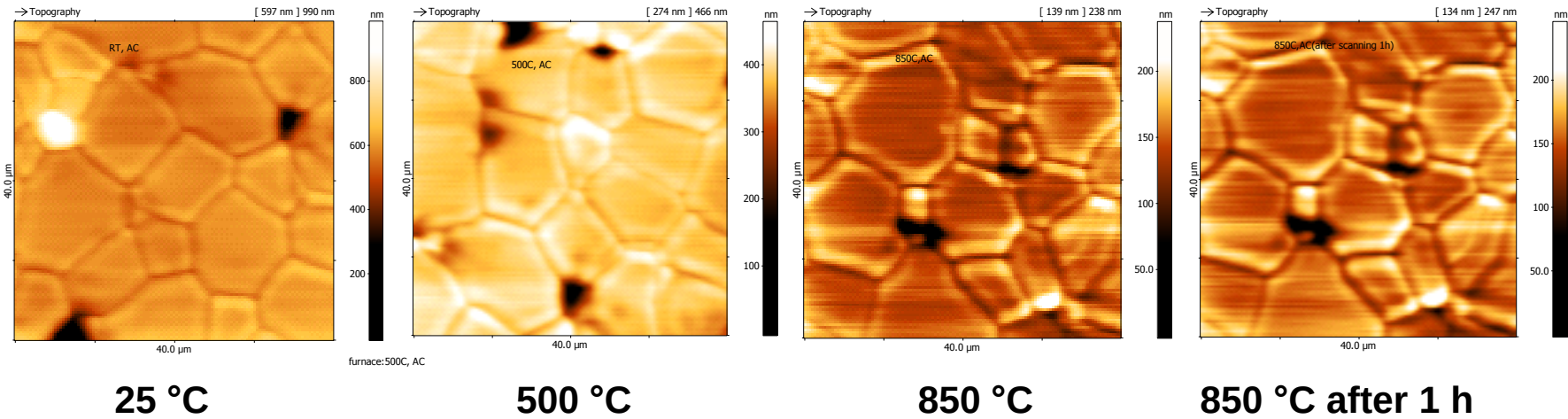
Max temperature	850 °C
Atmosphere	N ₂ -O ₂ , 9% H ₂ , CO ₂ , ... from bottle
Humidity	0.8 - 8 %
pO ₂ measurement	Risø pO ₂ monitor
Probes	Commercial AFM probes for RT/LT Home made Pt-Ir or ceramic probes for HT

Possible electrical/electrochemical techniques

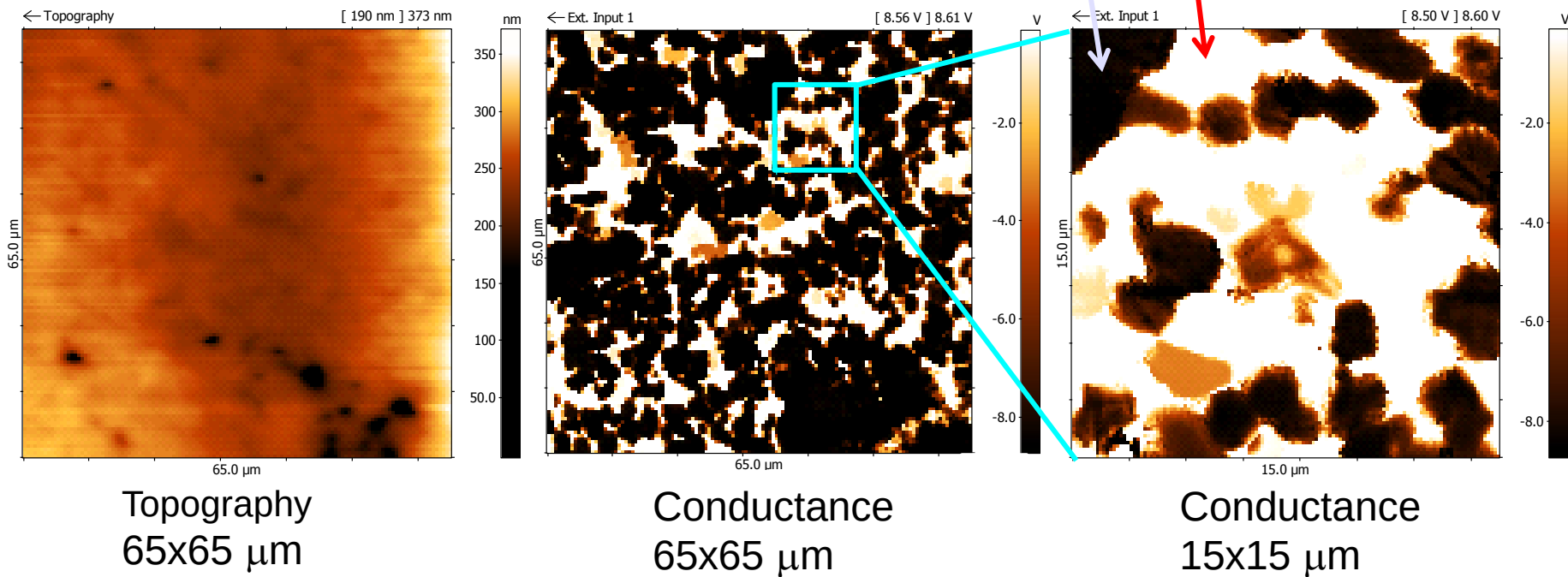


Area 40x40 μm , polished and heat treated YSZ

Tapping mode

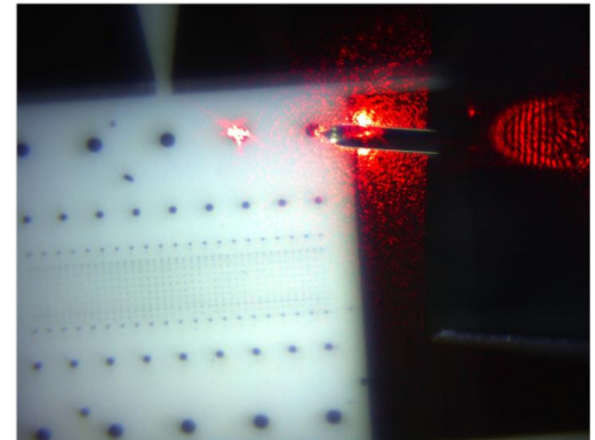
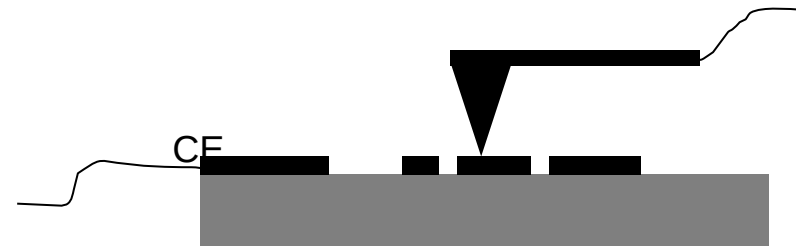


(La,Sr)MnO₃-YSZ at 800 °C



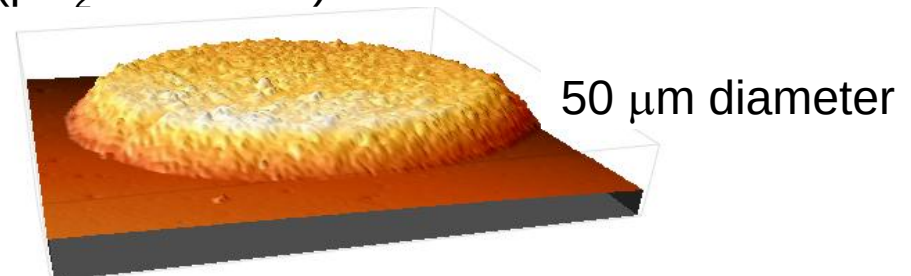
Microelectrodes

- Can be dense
- Have a well defined area
- Have a favourable geometry for TPB calculations
- Many electrodes in a small area
- Easy to vary thickness and size (and composition?)
- Produced by photo-lithography



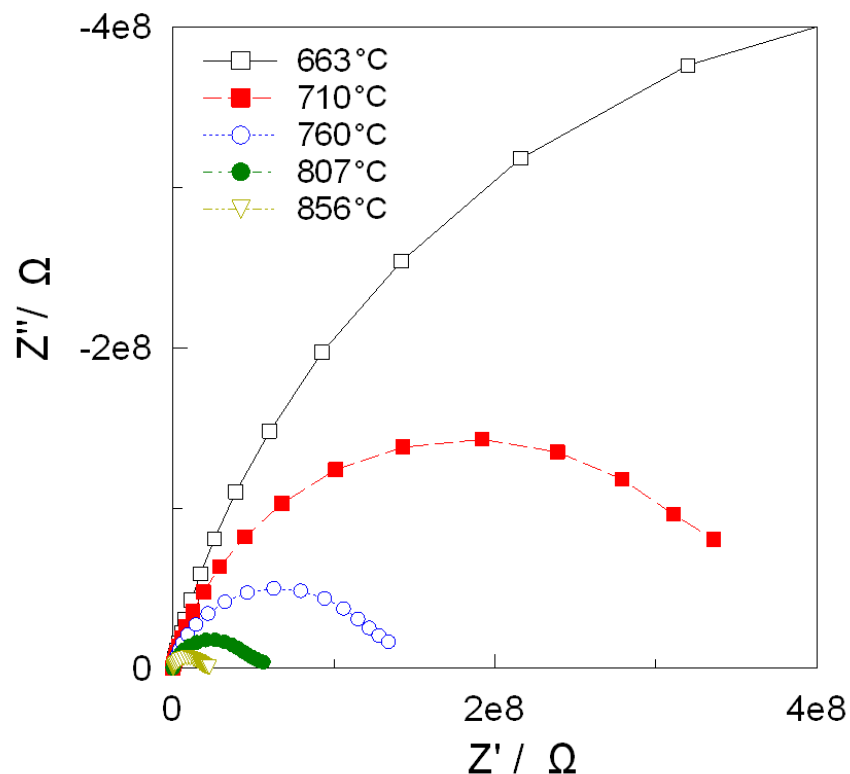
Impedance spectroscopy

- 20, 50 and 100 μm electrodes
- Performed in oxygen, air, and nitrogen ($p\text{O}_2 = 10^{-4}$ atm)
- 663-856 $^{\circ}\text{C}$
- Cathodic and anodic polarisation
- Gamry potentiostat "femtostat"

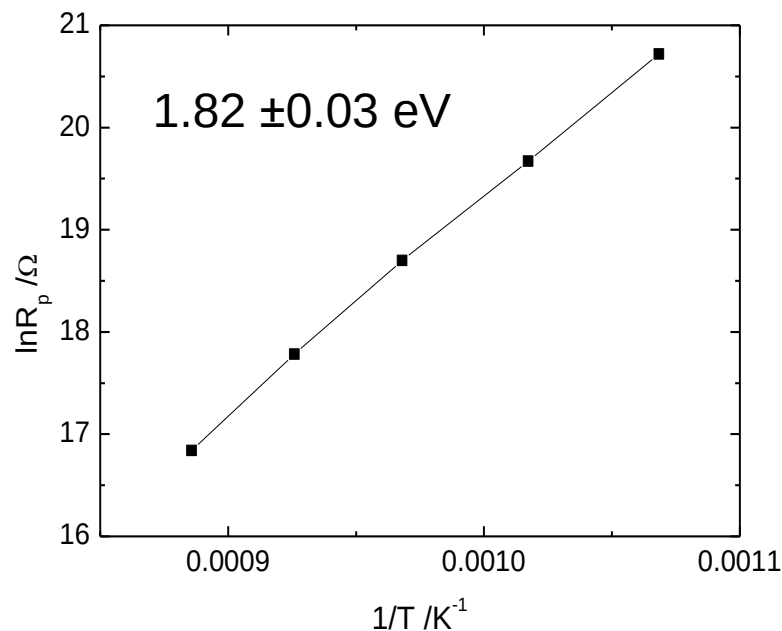


Y. Wu et al., *ECS Trans.* 57 (2013) 1673-1682

Temperature dependence in air:



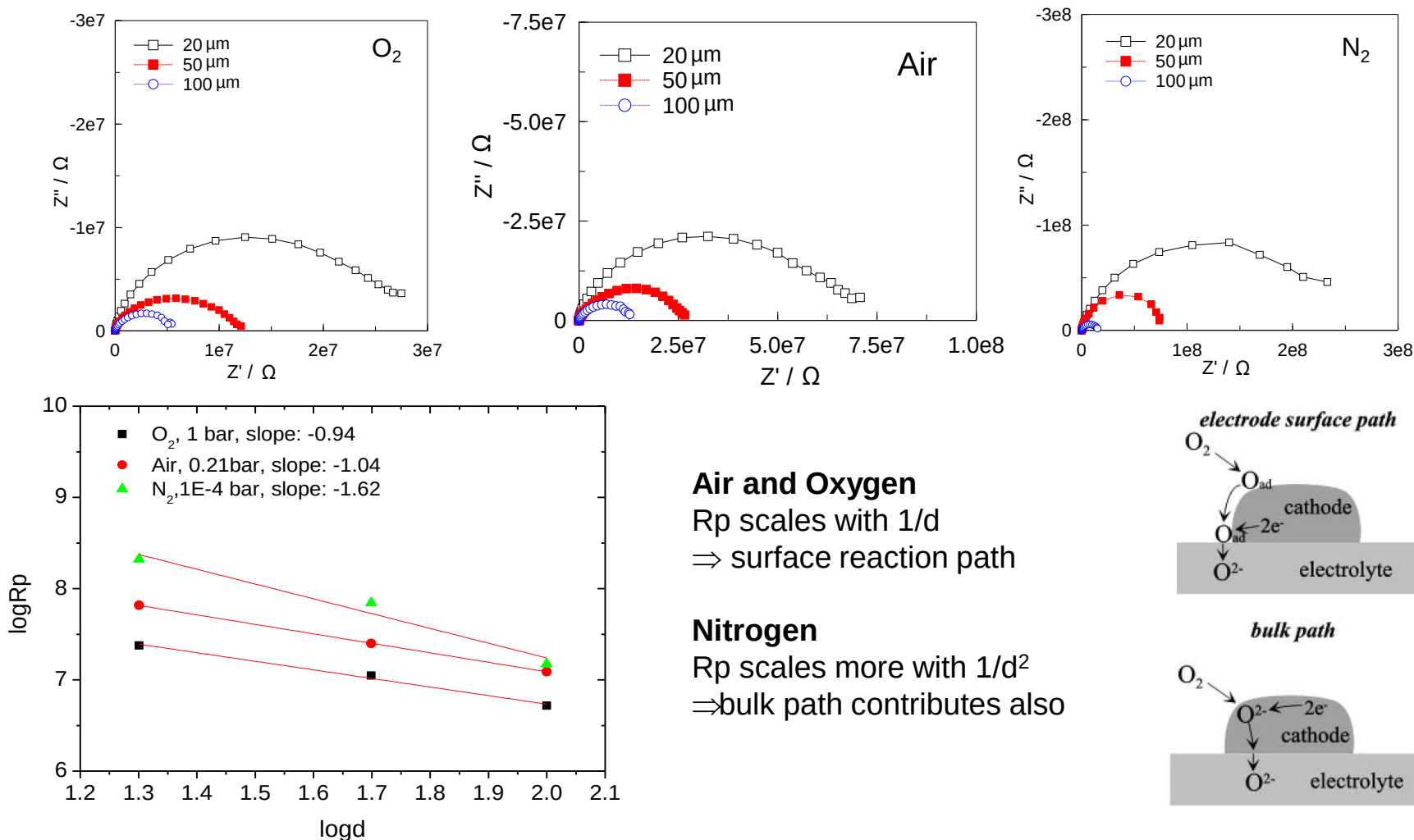
Impedance spectra of a 50 μm diameter LSM microelectrode in air.



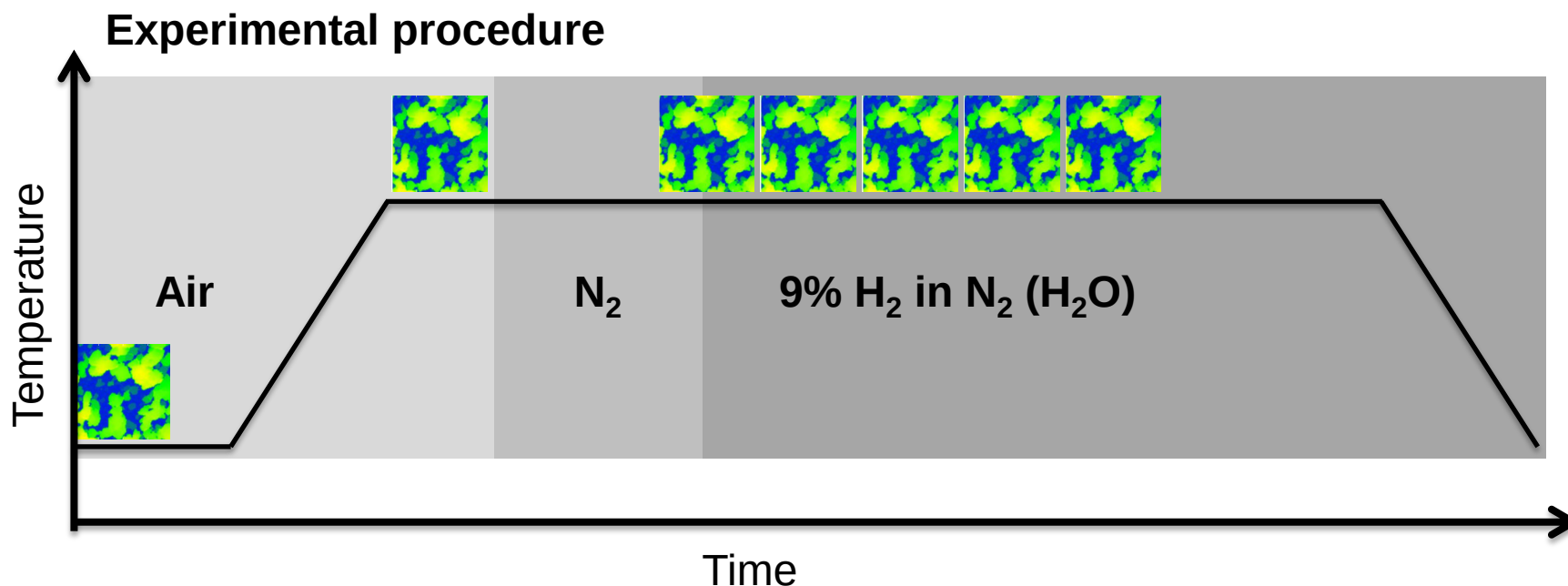
Arrhenius plot of the polarisation resistance in air.

E_a is in good agreement with literature

Atmosphere dependence at 856 °C

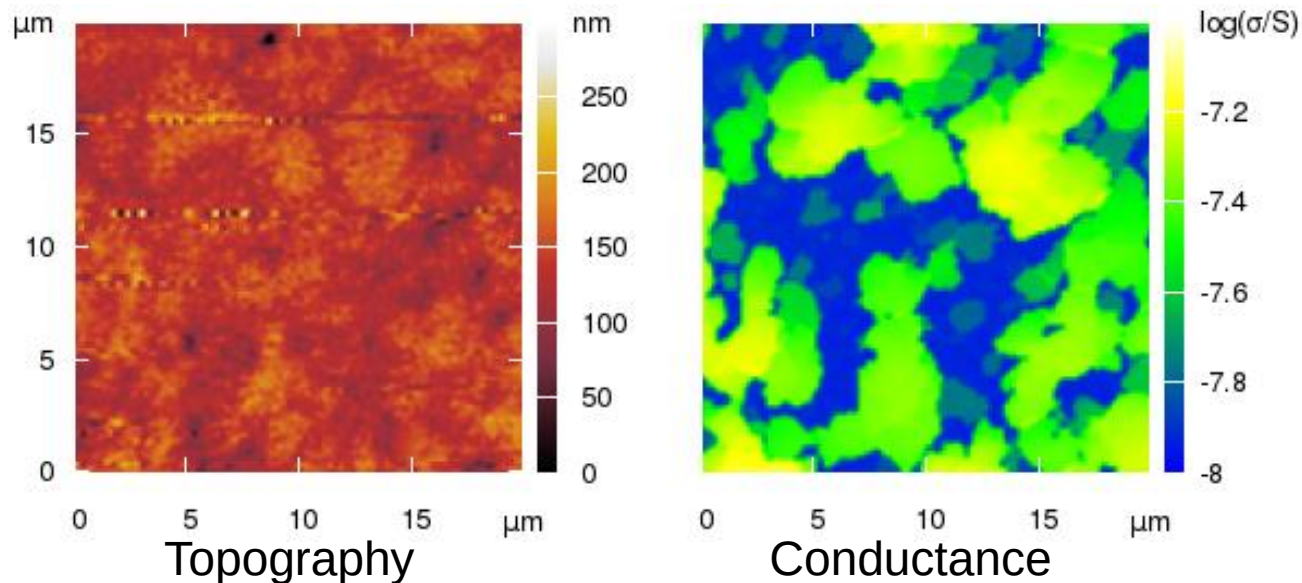


- Samples: polished anode support of symmetrical cells (NiO/YSZ/alumina)
- 13 reduction experiments were carried out
- 312 – 525 °C (the possible window due to reduction time)



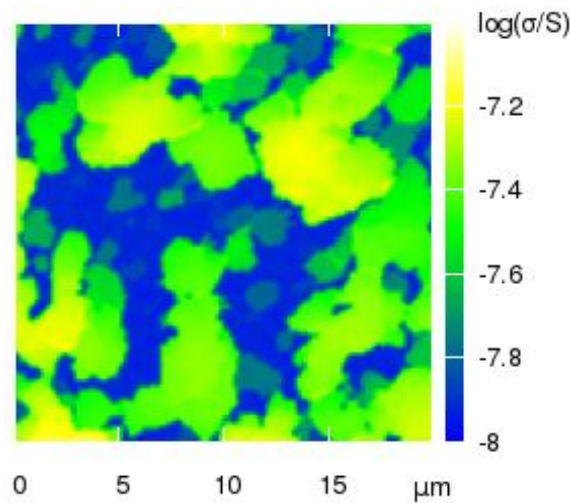
K. V. Hansen *et al.*, *J. Solid State Electrochem.* (2014) DOI 10.1007/s10008-014-2428-9

Unreduced $\text{NiO-YSZ-Al}_2\text{O}_3$ at 500 °C:

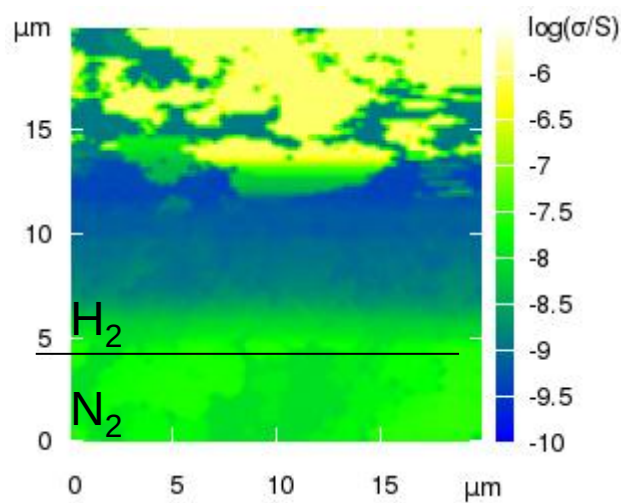


- Conductivity of NiO is due to Ni^{3+}
- Conductance depends on the size of the NiO particles and nature of contact

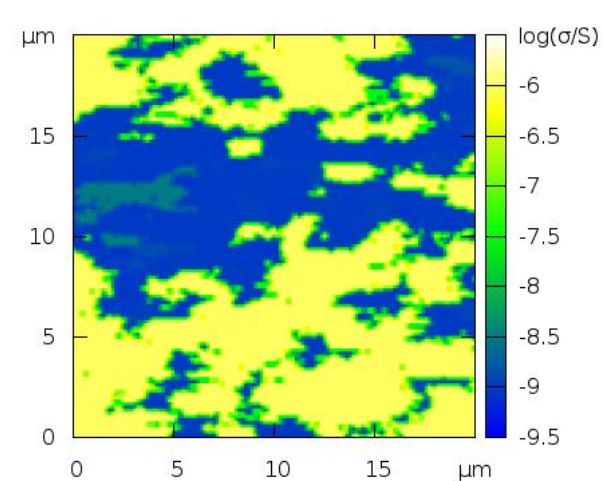
Reduction at 500 °C in 9% H_2 and 3 % H_2O :



**Conductance
in air**

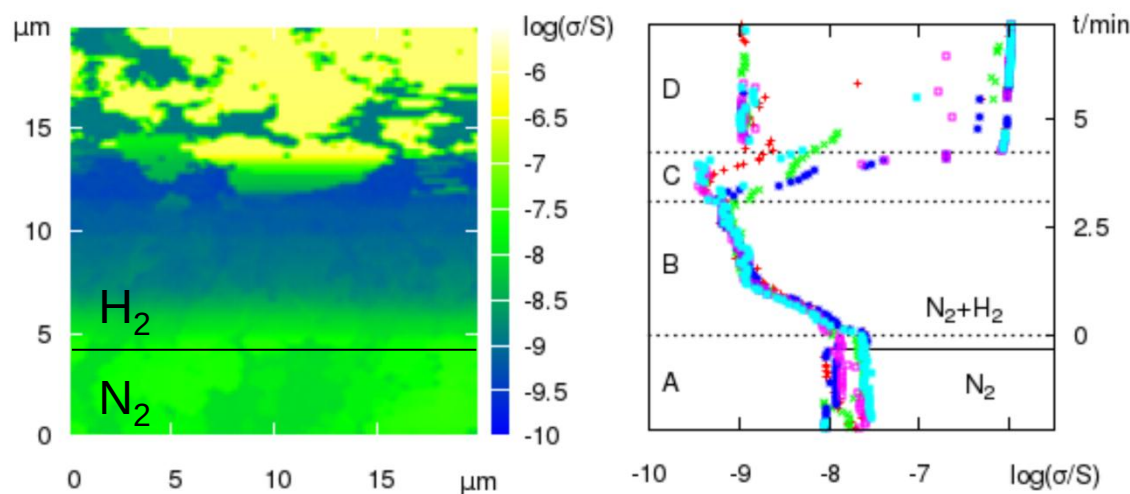


**Conductance
during reduction**



**Conductance
after reduction**

Reduction at 500 °C in 9% H_2 and 3 % H_2O :



Conductance cross sections at 0, 5, 10, 15, and 20 μm

Section B

Introduction of hydrogen
Conductance decrease.
"Incubation period"

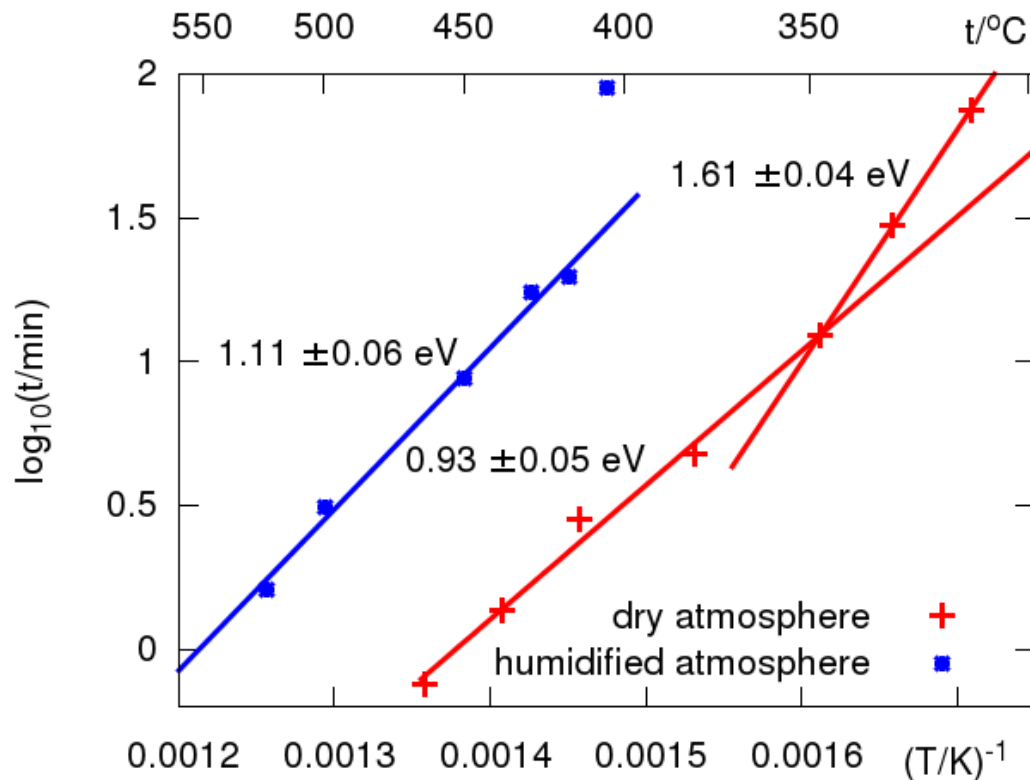
Section C

Growth of Ni areas.
Connectivity increases.

Section D

Maximum conductance reached. All surface Ni is connected.

Arrhenius plot of incubation period length:



Retarding effect of water
(longer incubation time)

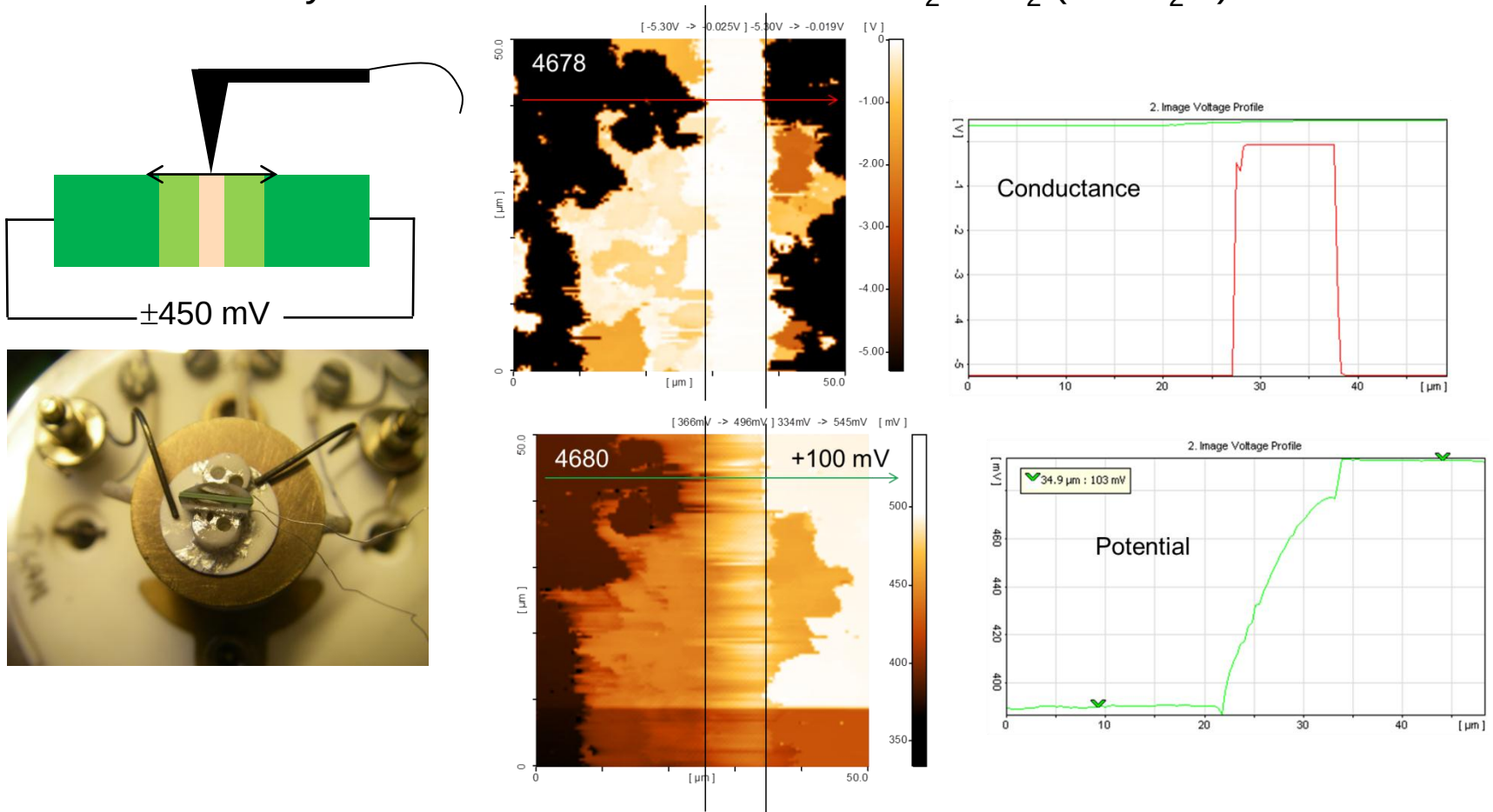
Low T and high T regions
for dry reductions

Two activation energies –
two different rate limiting steps

Two different microstructures

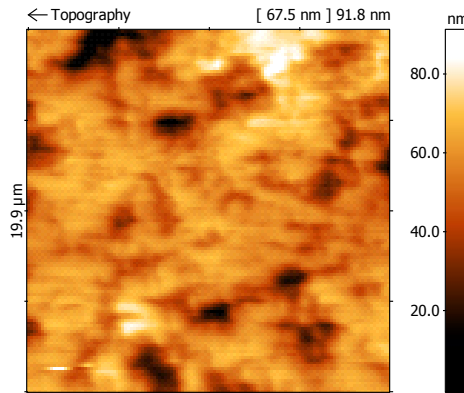
Micropotentiometry:

Initial tests on a symmetrical cell at 650 °C in 9% H₂ in N₂ (3% H₂O)

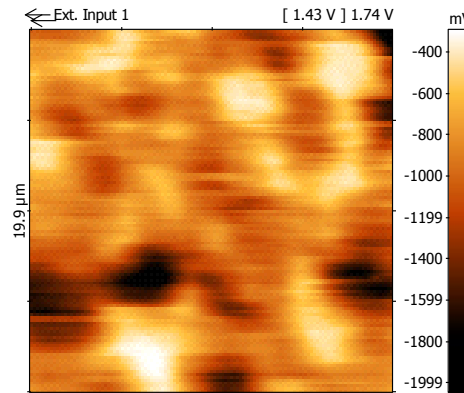


Surface potential by Kelvin Probe Microscopy:

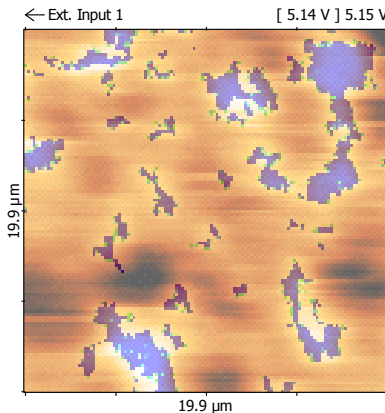
Ni-YSZ at RT



Topography (20x20 μm)

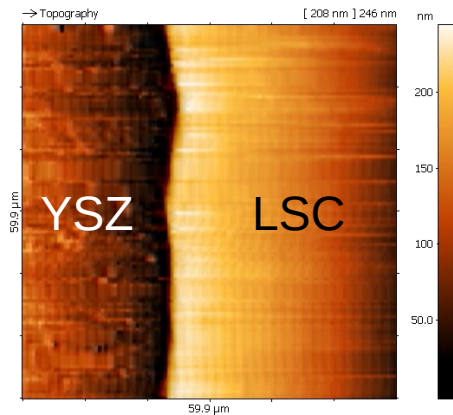


Surface potential

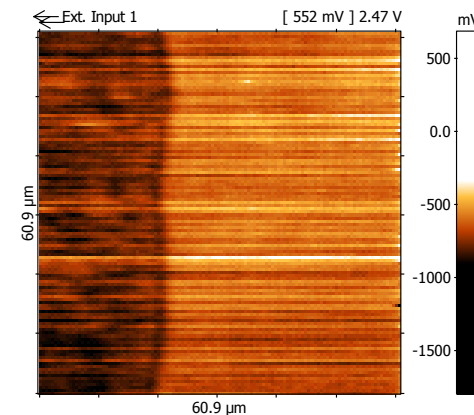


Surface potential and conductance

LSC on YSZ at 500 °C



Topography (60x60 μm)



Surface potential

- SOEC degradation is location specific
- 2D modeling + EIS + post-mortem EM can yield valuable insight into SOEC degradation
- Important aspects of real SOEC are ignored/simplified in numerical models
- In-operando local probes of the electrochemistry, chemistry, microstructure, ... are needed
- CAHT-SPM can yield local electrical, electrochemical and microstructural information in-operando with sub- μm resolution
- Ongoing developments will provide even more versatility and higher spatial resolution in the future

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- The Programme Commission on Sustainable Energy and Environment, The Danish Council for Strategic Research, via the Strategic Electrochemistry Research Center (SERC) (www.serc.dk), contract no. 2104-06-0011. (2006-2012)
- The Catalysis for Sustainable Energy (CASE) initiative funded by the Danish Ministry of Science, Technology and Innovation.
- Energinet.dk through the projects ForskEL 2010-1-10432 “planSOEC-R&D and commercialization roadmap for SOEC electrolysis” and ForskEL 2011-1-10609 “Development of SOEC cells and stacks”