HIGH TEMPERATURE

In Situ and Operando Electrochemical Techniques

huber scientific

novel measurement solutions

T. M. Huber

Join at menti.com | use code 1414 1463

Outline:

- Experiments:
  - In situ PLD **iPLD**
  - In situ XPS **EXACT-XPS**
  - In situ Auger SEM **EXACT-AEM**
  - In situ LASIS
  - In situ NAP XPS
  - In situ XPS
- How to do/start an in situ experiment
- Potential problems on the way
- Tips & tricks on how to set things up
- Electrical measurements, electrode arrangements & designs

In situ definition

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In situ (/ɪn ˈsɪtjuː, - ˈsaɪtjuː, - ˈsiː-/; often not italicized in English)[1][2][3] is a Latin phrase that translates literally to "on site"[4] or "in position."[5] It can mean "locally", "on site", "on the premises", or "in place" to describe where an event takes place and is used in many different

Experimental physics [edit]

In experimental physics *in situ* typically refers to a method of data collection or manipulation of a sample without exposure to an external environment. For example, the Si(111) 7x7 surface reconstruction is visible using a scanning tunneling microscope when it is prepared and analyzed *in situ*

Electrochemistry [edit]

In electrochemistry, the phrase *in situ* refers to performing electrochemical experiments under operating conditions of the electrochemical cell, i.e., under potential control. This is opposed to doing *ex situ* experiments that are performed under the absence of potential control. Potential control preserves the electrochemical environment essential to maintain the double layer

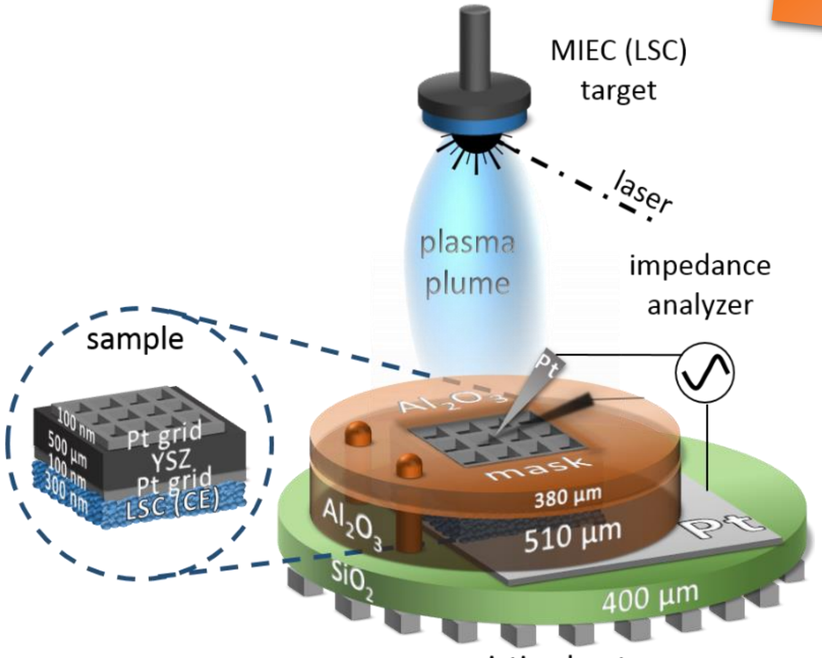
The term "*in situ*" changed to "*operando*" in the research field of catalyst spectroscopy!

Temperature

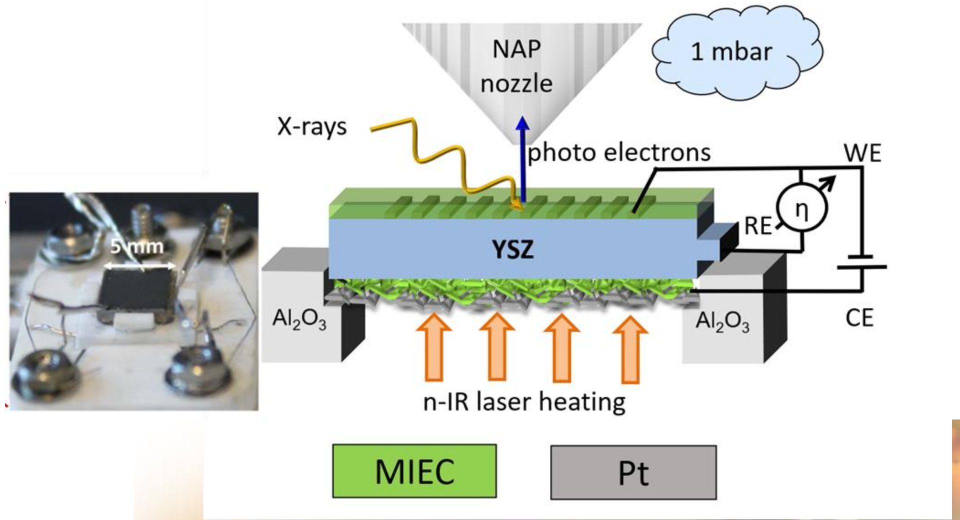
Gasses

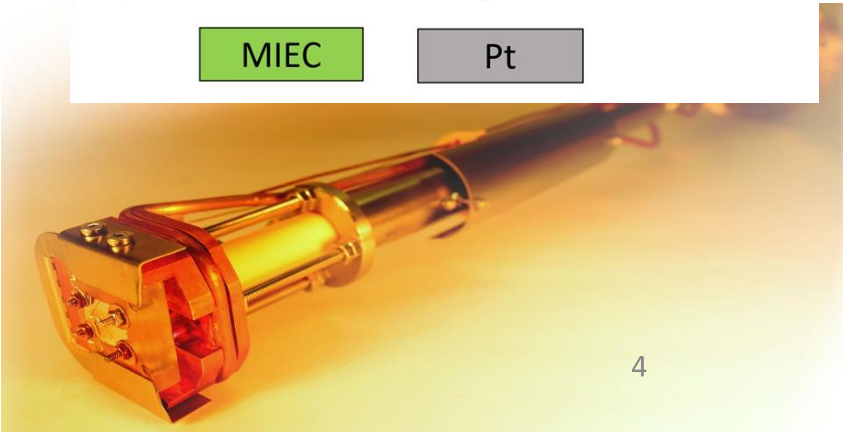
Electrical Measurements

Production/ deposition



Analytical





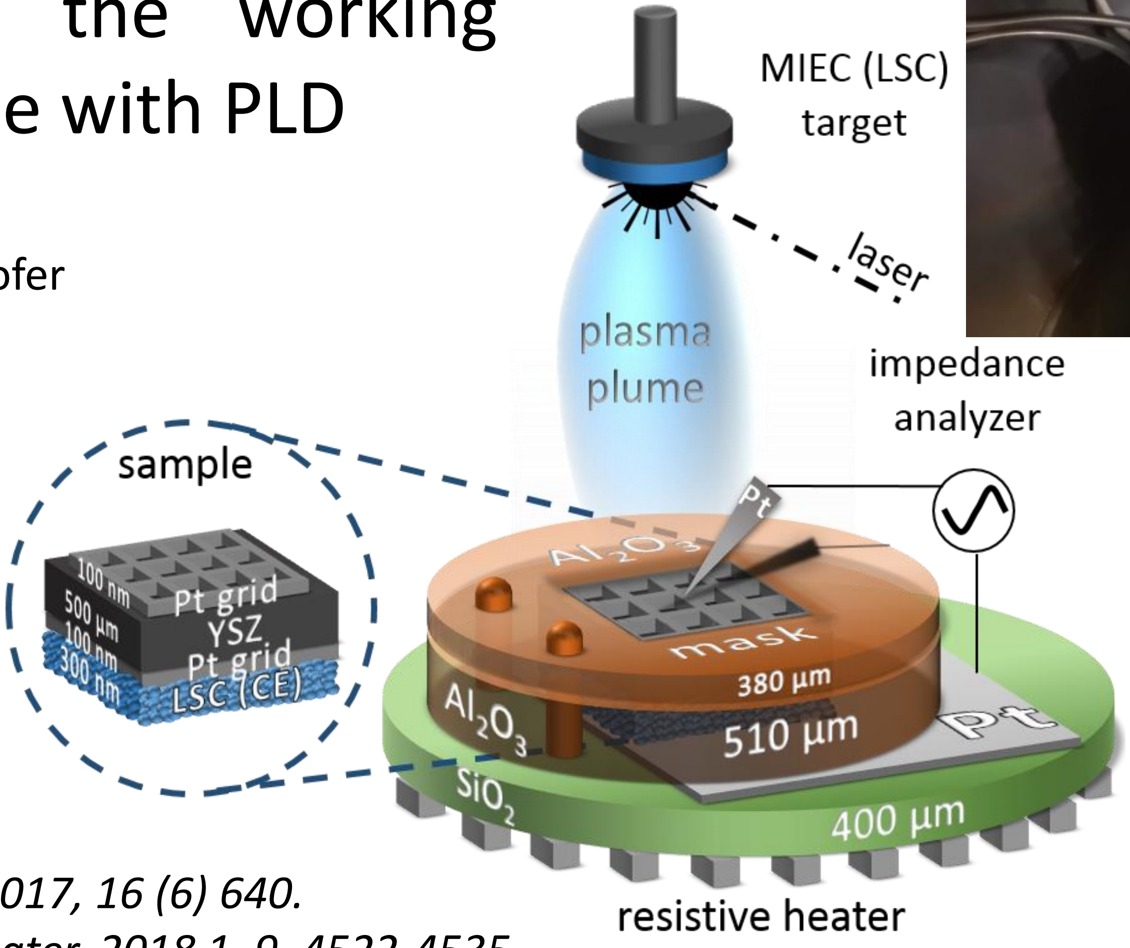
Experiments

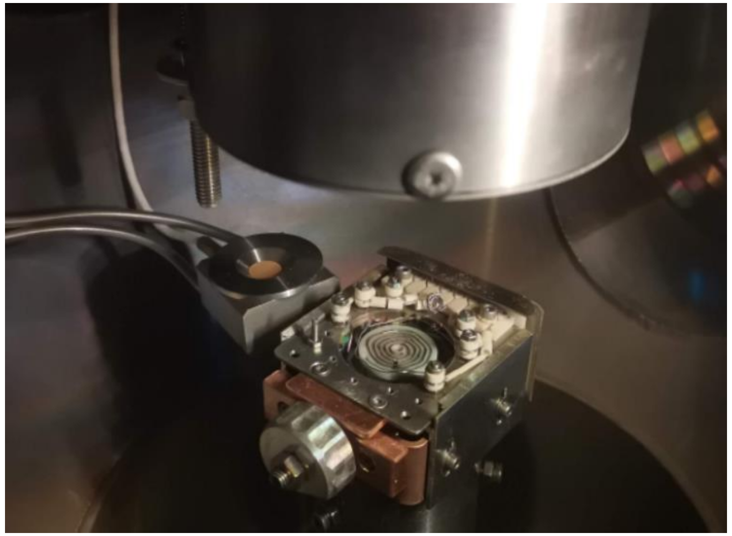
Real-time impedance monitoring in the PLD

Measuring a cell while growing the working electrode with PLD

Matthäus Siebenhofer
Poster on Tuesday

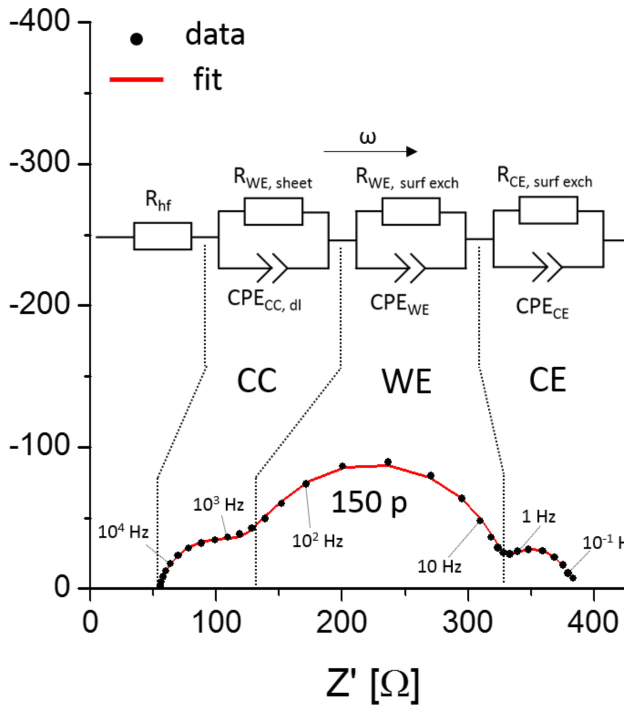
Markus Kubicek
Talk on Friday

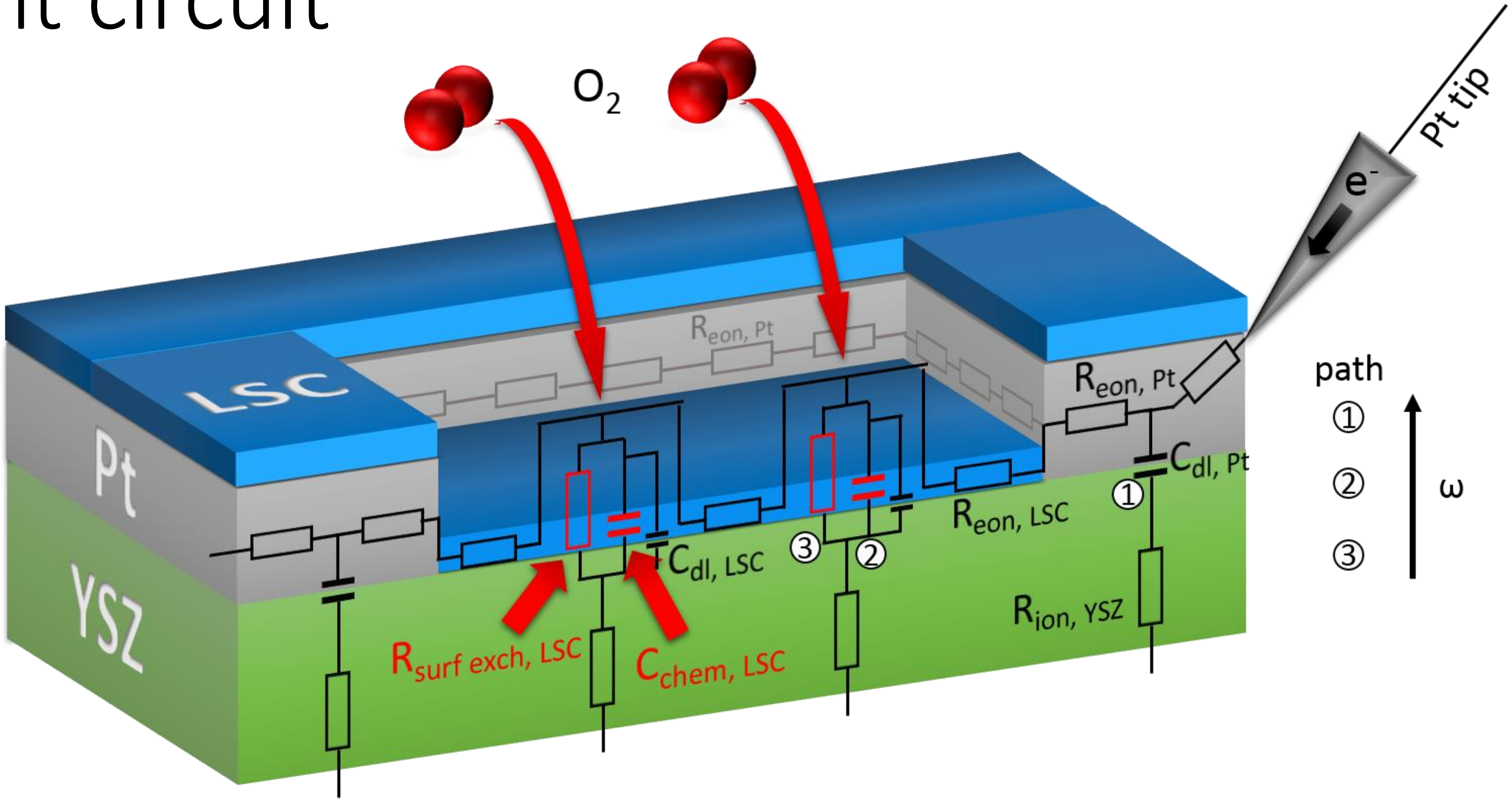




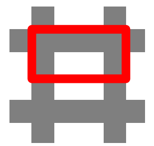
Rupp G.M. et al. Nature Materials, 2017, 16 (6) 640.
Rupp G.M. et al. ACS Appl. Energy Mater. 2018 1, 9, 4522-4535

The equivalent circuit

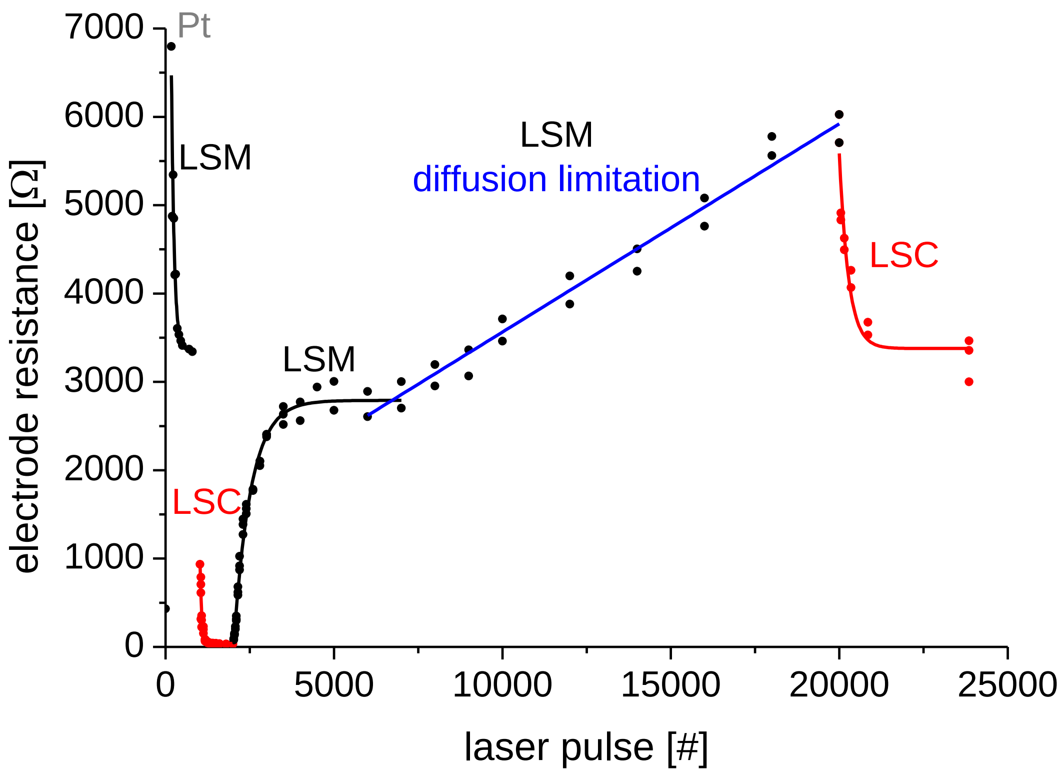




- Equivalent circuit based on Jamnik-Maier model
- Could not be used for NLLS fitting (3D, differential)
- Simplified equivalent circuit for fitting

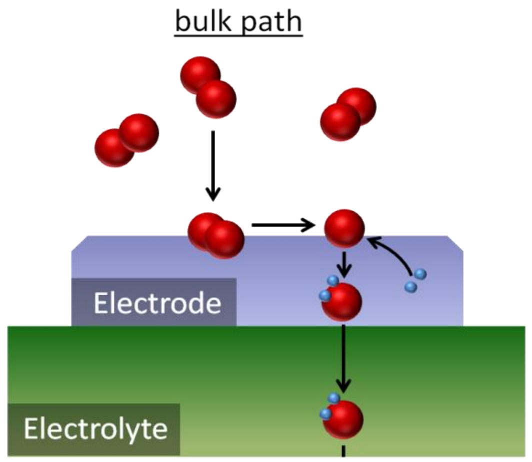


Multilayers of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$



Impedance of growing MIEC thin films

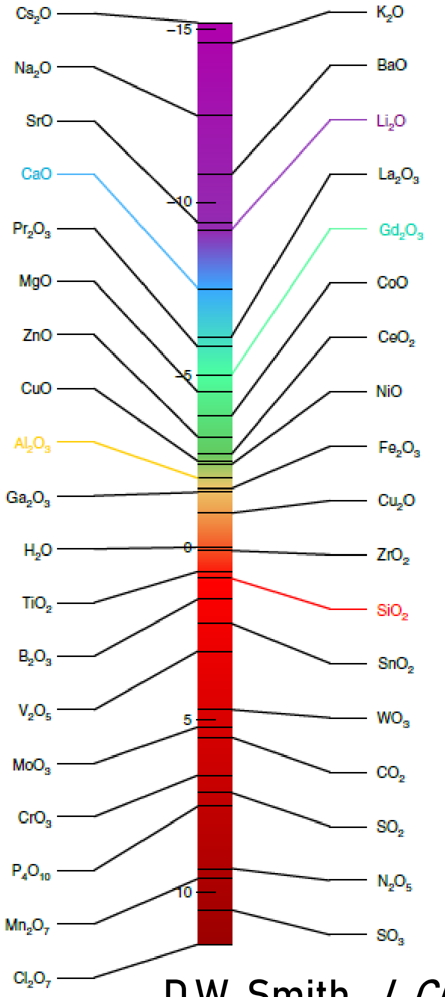
600°C, $4\cdot10^{-2}$ mbar pO_2



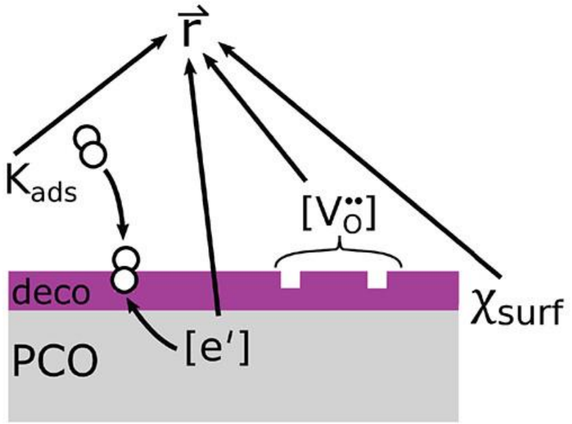
- Determine critical thickness
- Investigate co-limitations
- Customize model thin films (Rsurf vs. Rdiff)

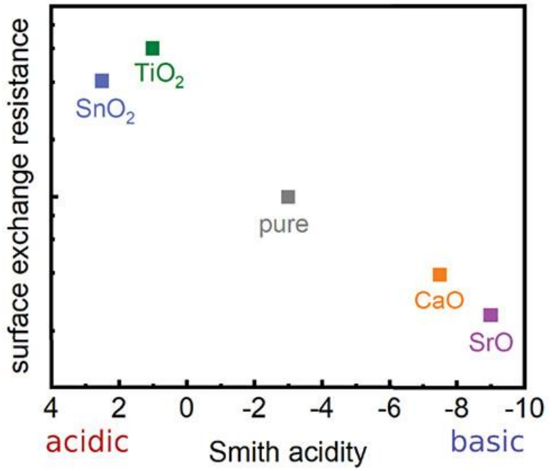
Surface manipulaion

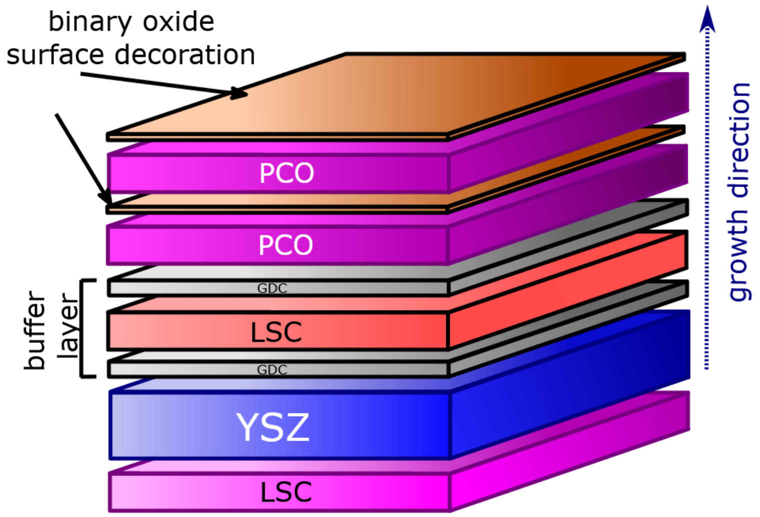
Acidity scale for oxides:
Transfer of O^{2-}



D.W. Smith, *J. Chem. Educ.*, (1987), 64, 6, 480.







surface charge – work function – catalytic activity

C. Riedl, … M Kubicek et al.
J. Mater. Chem. A, (2022) ,10, 2973-2986

M Siebenhofer, …, M Kubicek
J. Electrochem. Soc. (2023) 170 014501

F Fahrnberger, … M Kubicek
Appl. Surf. Sci., (2023), 640, 158312

M Siebenhofer, … M Kubicek
J. of Mater. Chem. A, (2023), 11(24), pp. 12827–12836

M Siebenhofer, …, M Kubicek
Nature Comm., (2024), 15, 1, 1730

In situ thin film growth in atmosphere

Methods

Challenges	Optical (UV/VIS/IR) Characterization	X-Ray Based Spectroscopy	X-Ray and Neutron Diffraction	Electron & Ion Beam Methods	Electrical AC & DC Measurements
Temperature Incompatibility	✓ *IR background*	✓ *desorption of surface species*	✓	✓ *limited resolution*	✓
Pressure Gap	✓	✓	✓ *Neutrons dependence on atmosphere*	✓	✓
Set up/Mechanical Incompatibility	✓	✓ *Needs custom made solution*			✓

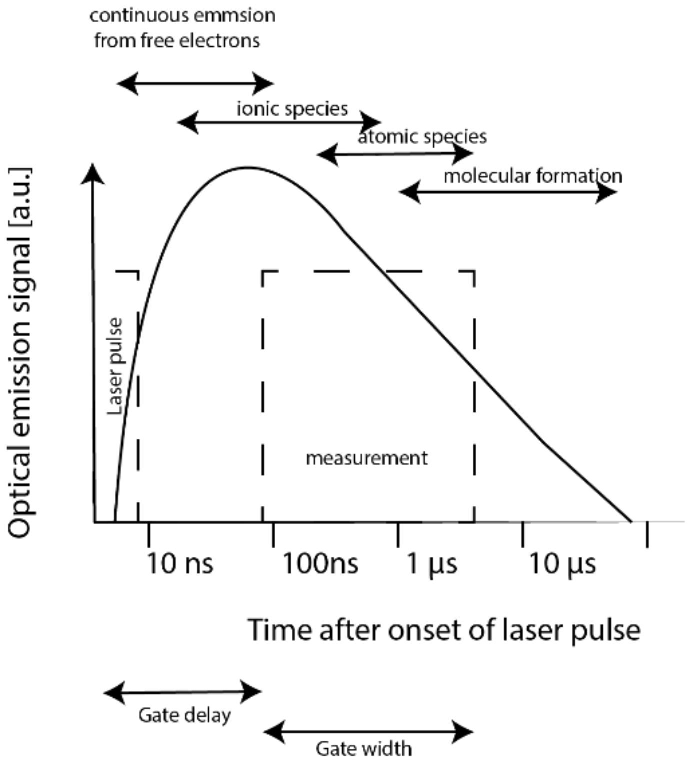
Markus Kubicek et al. J. Phys. Energy 2024 roadmap on "Advanced/operando characterisation of solid state materials and devices for energy applications"

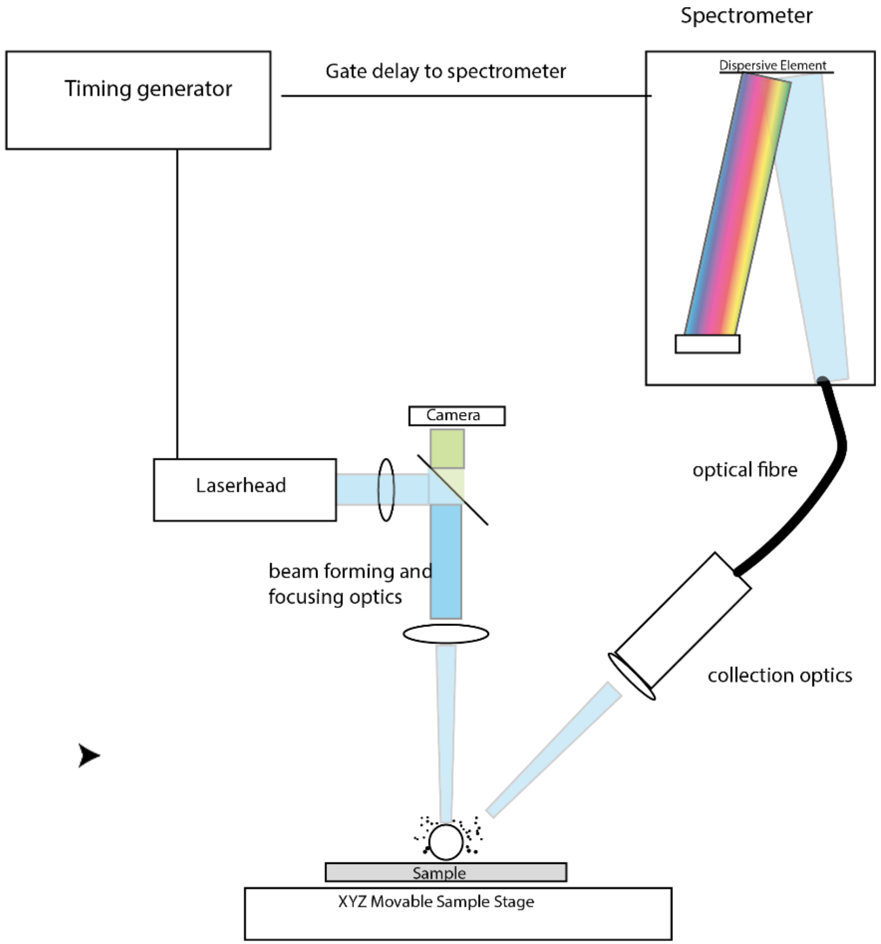
Laser induced breakdown spectroscopy

- **Laser pulse evaporates sample**
  - **(same mechanism as PLD)**
- **Plasma emits characteristic elemental emission → detected and quantified**

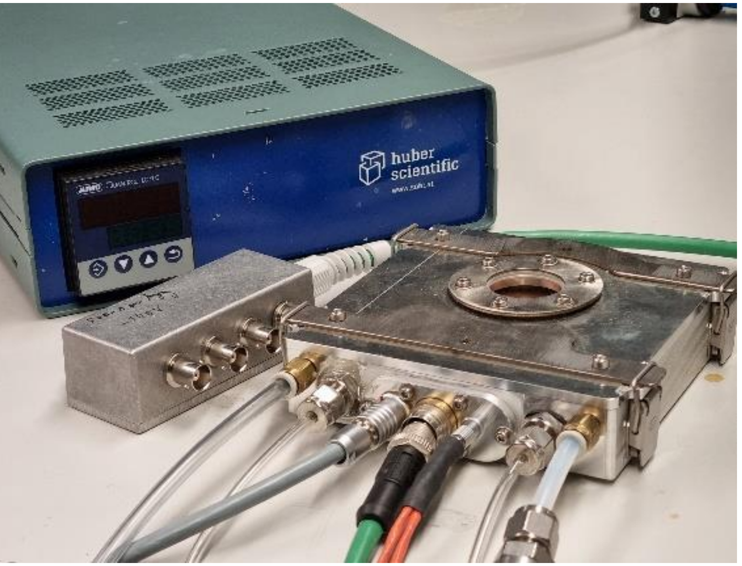
Melanie Anstiss
Tuesday 2A3 St. James
10.30
& Poster on Tuesday

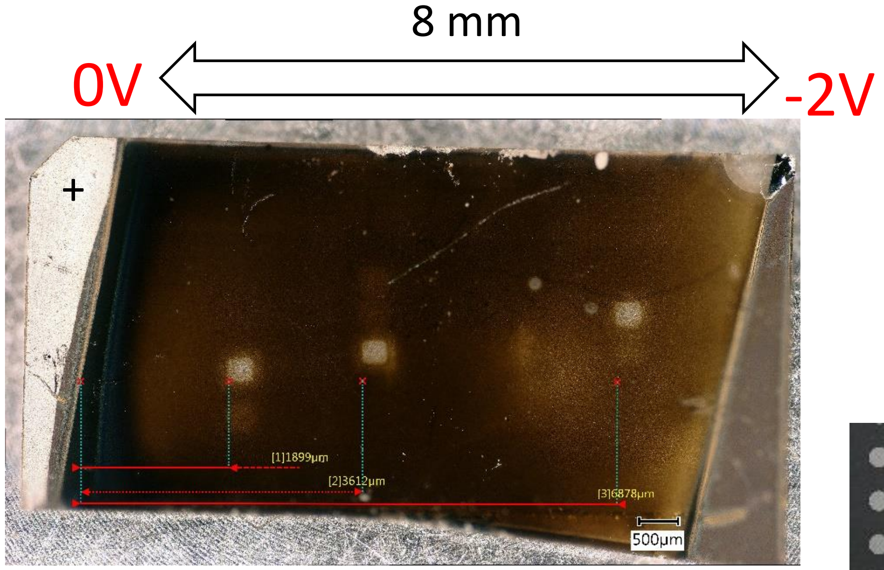
Maximilian Weiss
Poster on Tuesday

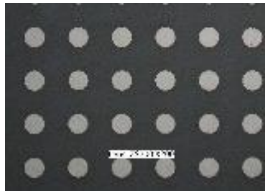




In situ LIBS measurements





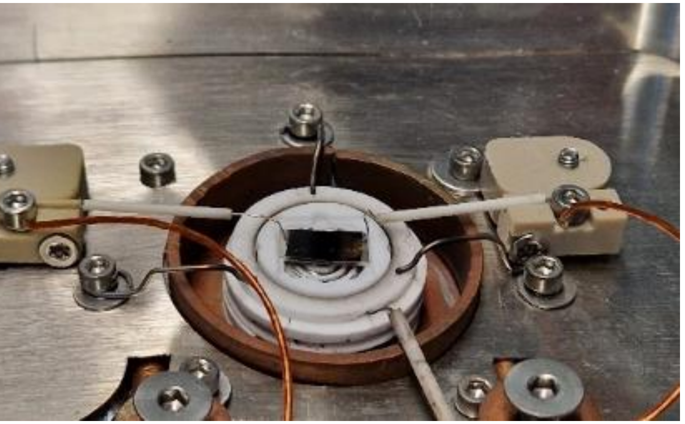


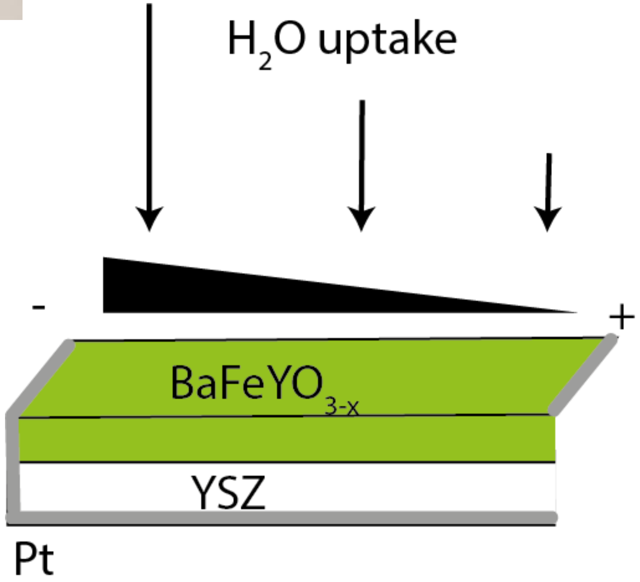
0V -0.19V -0.62V -1.2V -2V

Voltage drop (measured by microelectrodes)

0.2 2E-06 2E-17 1E-32 1E-53 bar

Effective p(O2)





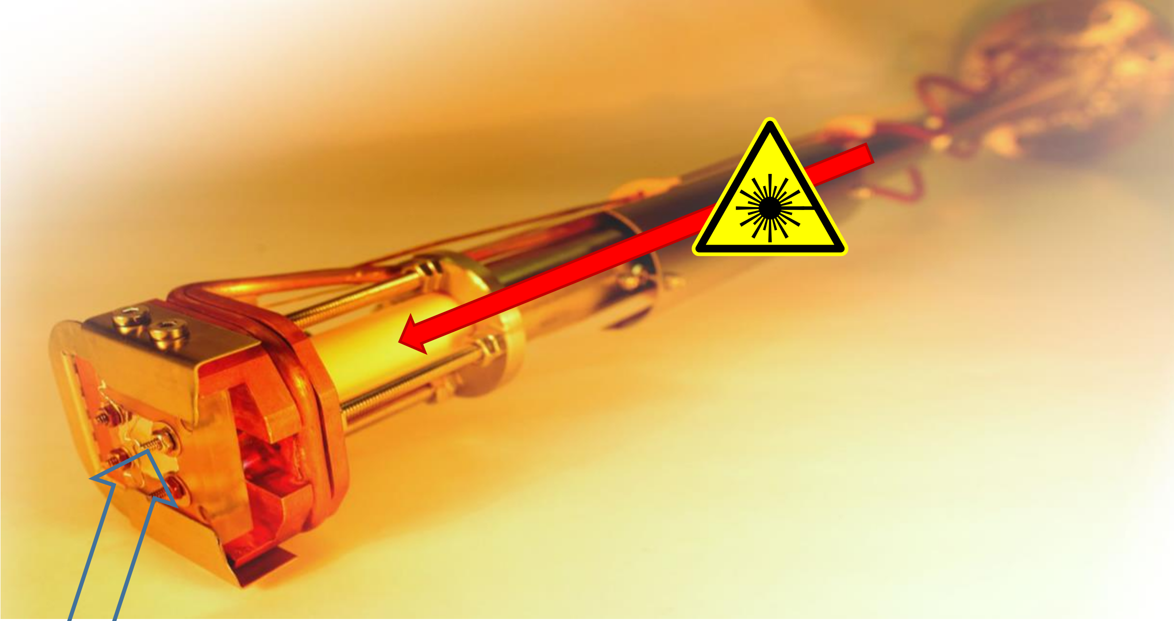
→Voltage / p(O_2) drop across sample

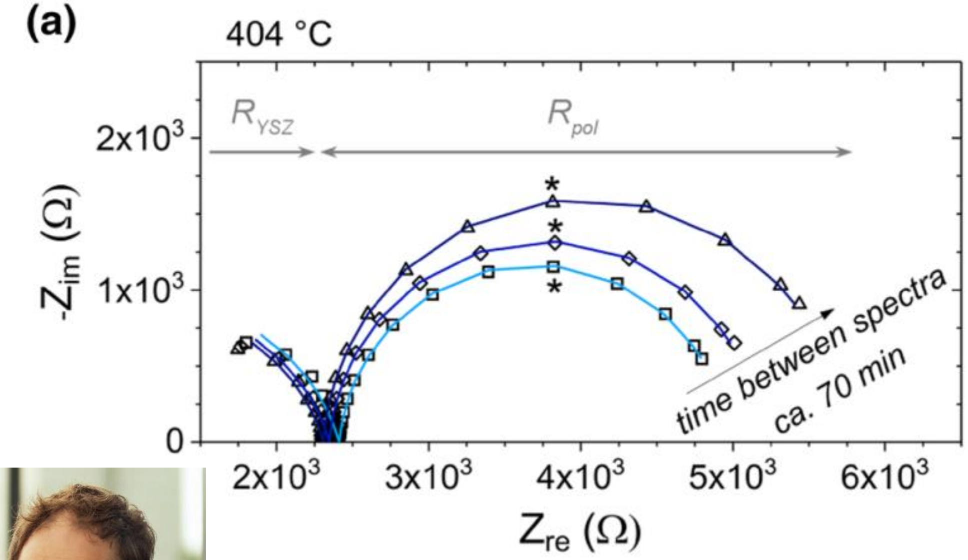
→Large p(O_2) range on just one sample

→Measure OH uptake laterally

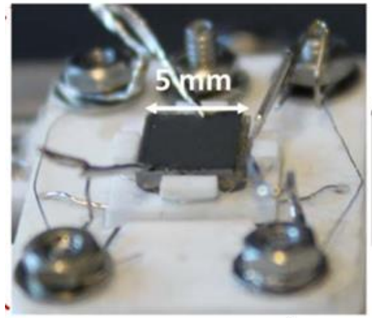
NAP-XPS + EIS measurements

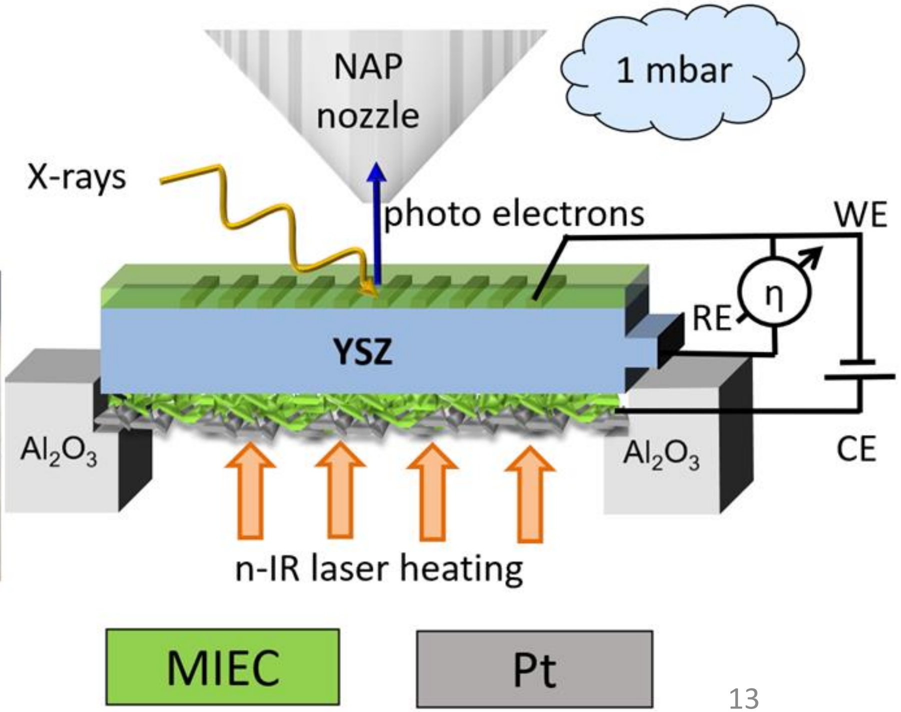
- Direct correlation of surface chemistry and activity
- Example: Sr segregation on $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) electrodes





Andreas Nenning
Talk and poster on Tuesday



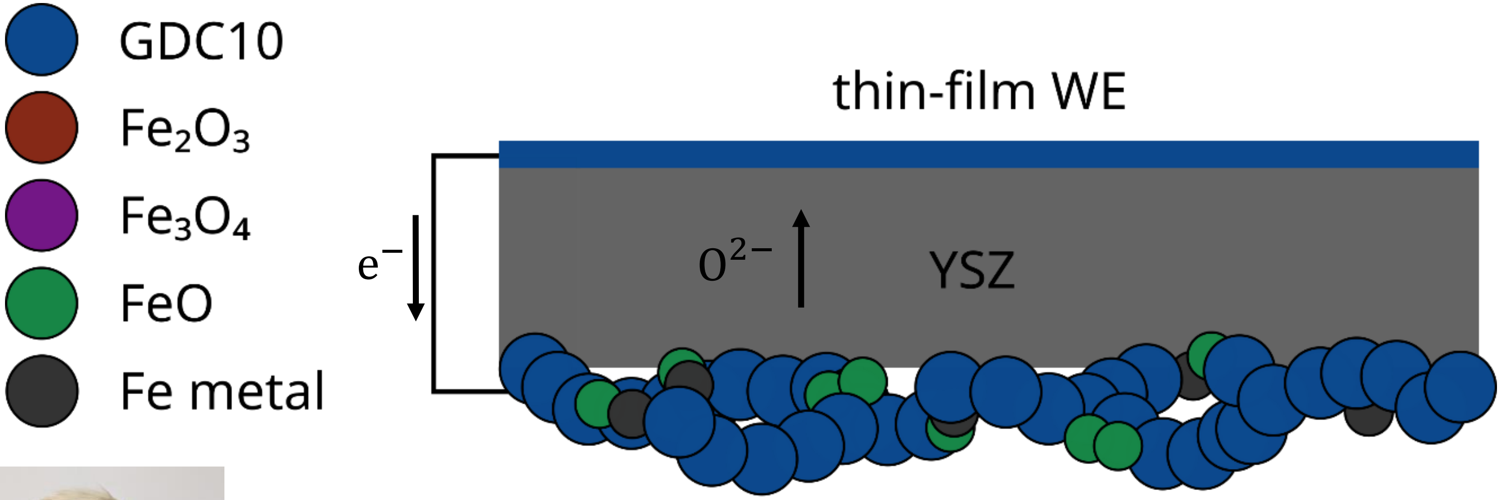


ELECTROCHEMICAL OXYGEN ACTIVITY CONTROL (EXACT) AEM IN UHV

CE conditioning

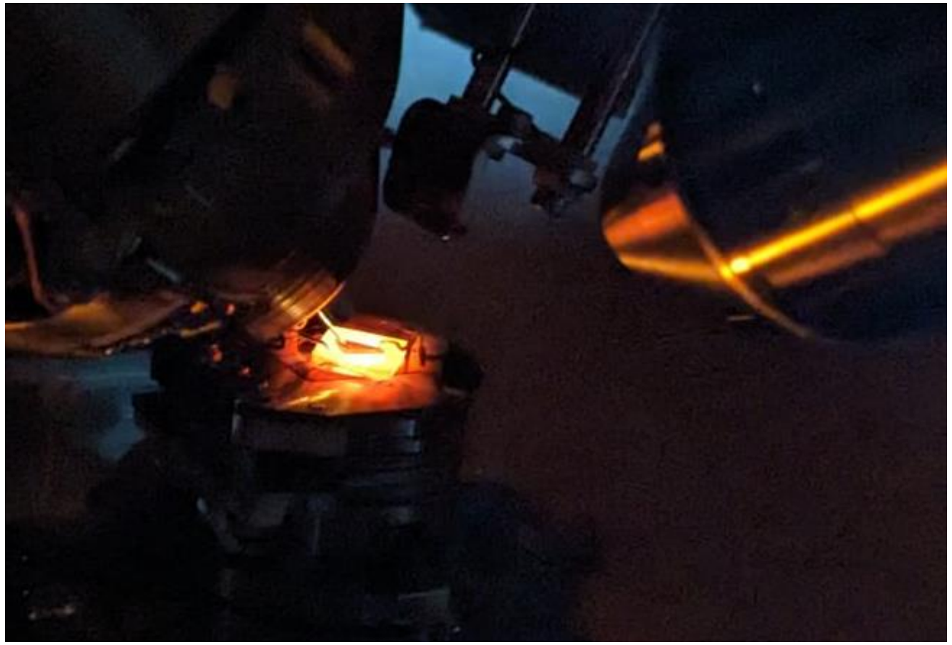
goal: constant μ(O) in CE
high CE capacity

$Fe_2O_3 \rightleftharpoons Fe_3O_4$	1/3 e^- per Fe atom	-500 mV vs. air
$Fe_3O_4 \rightleftharpoons FeO$	2/3 e^- per Fe atom	-890 mV vs. air
$FeO \rightleftharpoons Fe$	2 e^- per Fe atom	-1050 mV vs. air



porous CE

$$a(O_2)_{CE} = e^{\left(\frac{2\Delta G_f(\mathrm{FeO})}{RT}\right)}$$

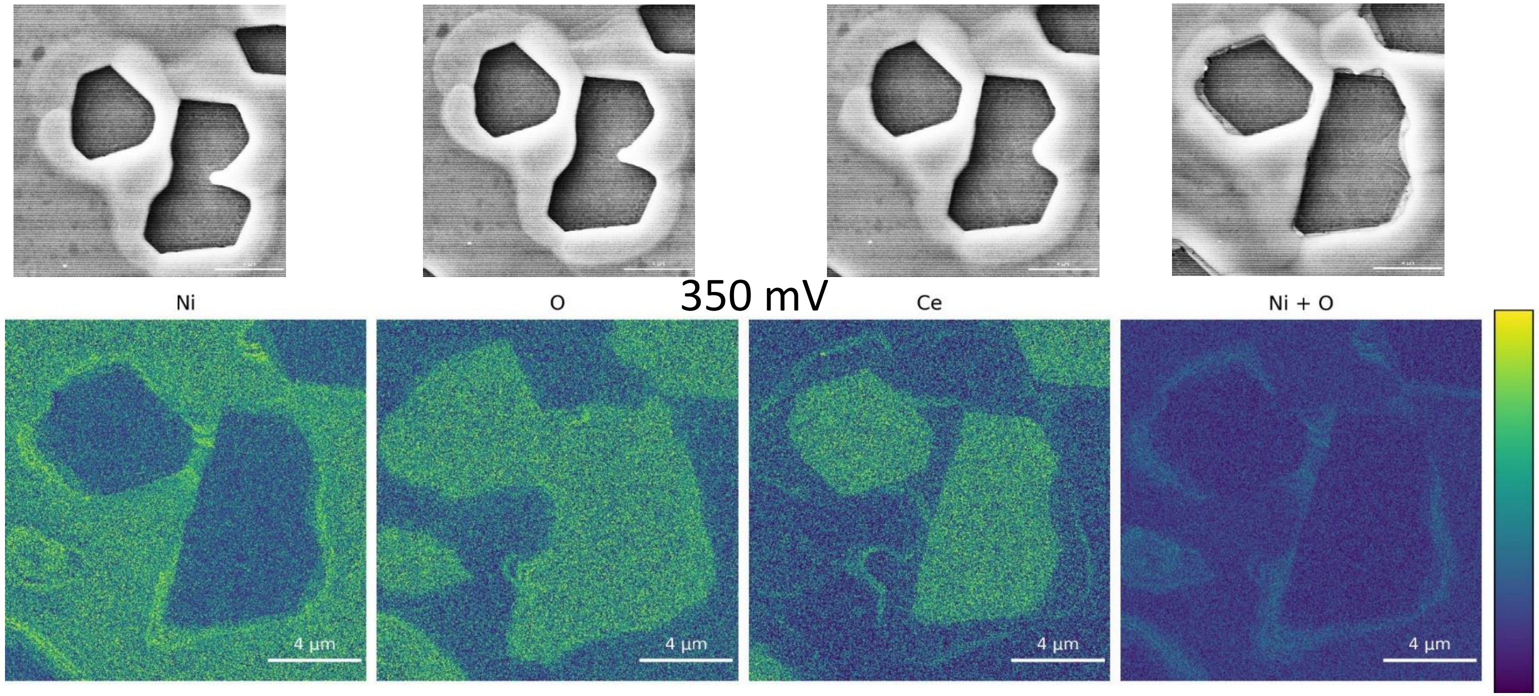


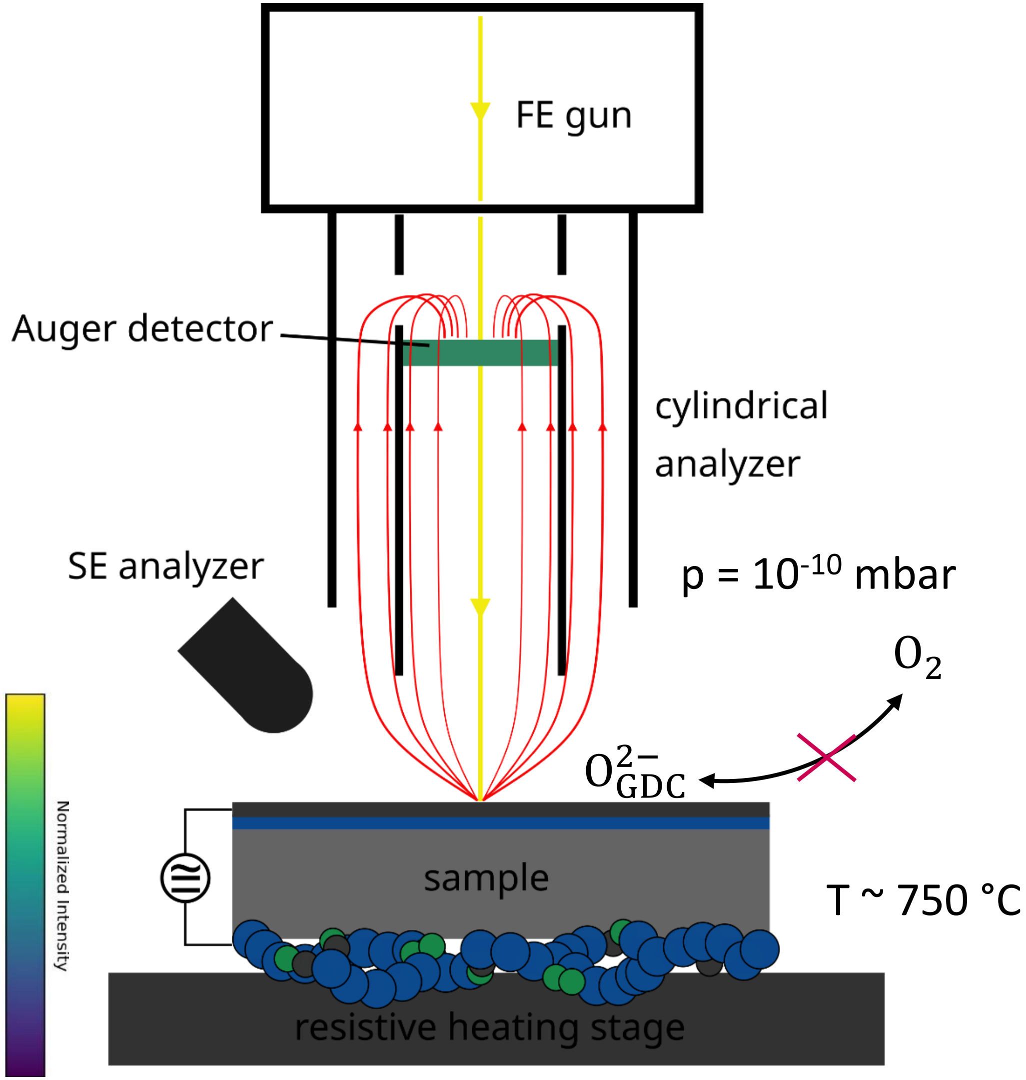
T = 750 °C

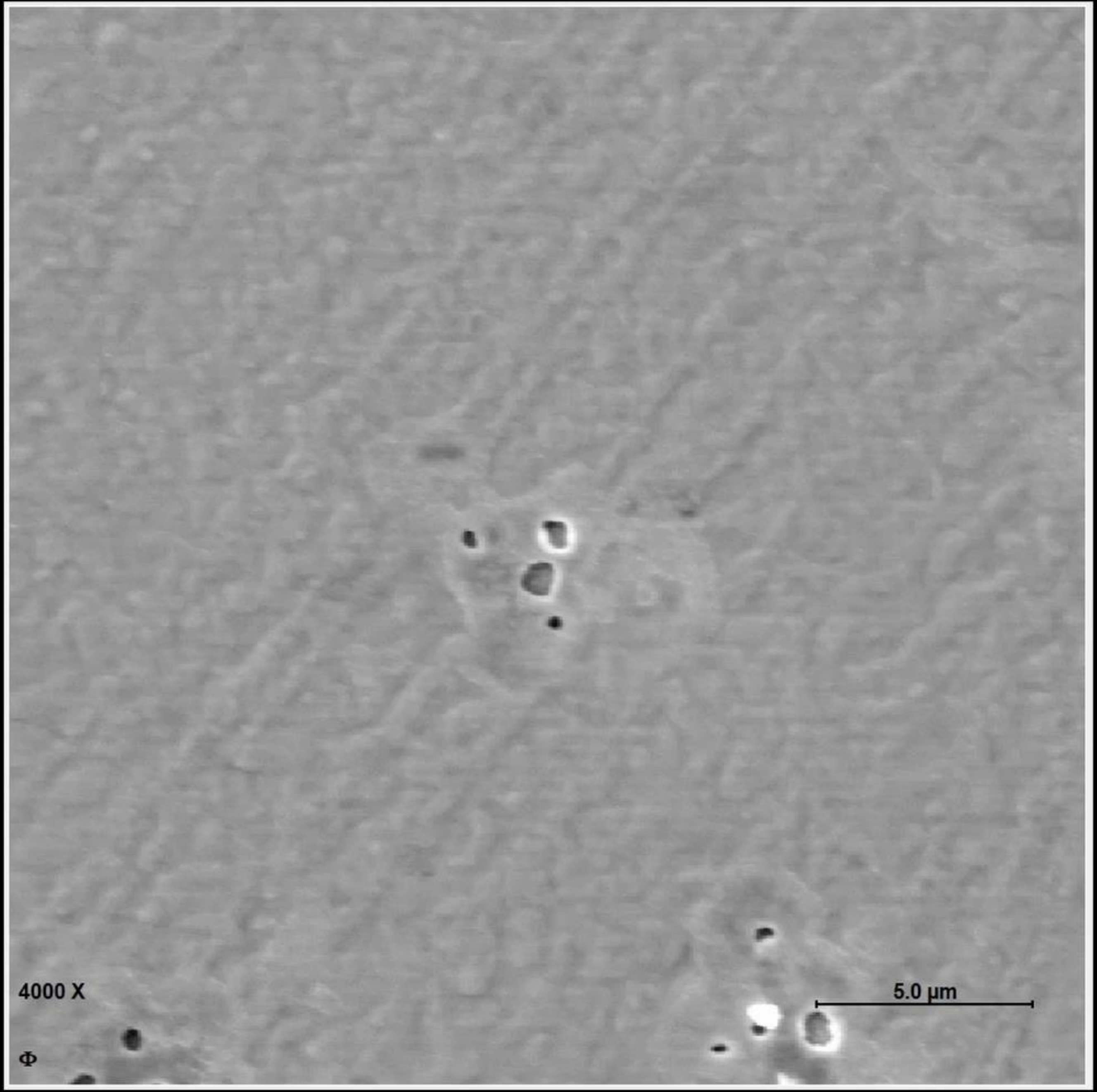
Christian Melcher
Monday 16:35, 5A4 Room: Moore

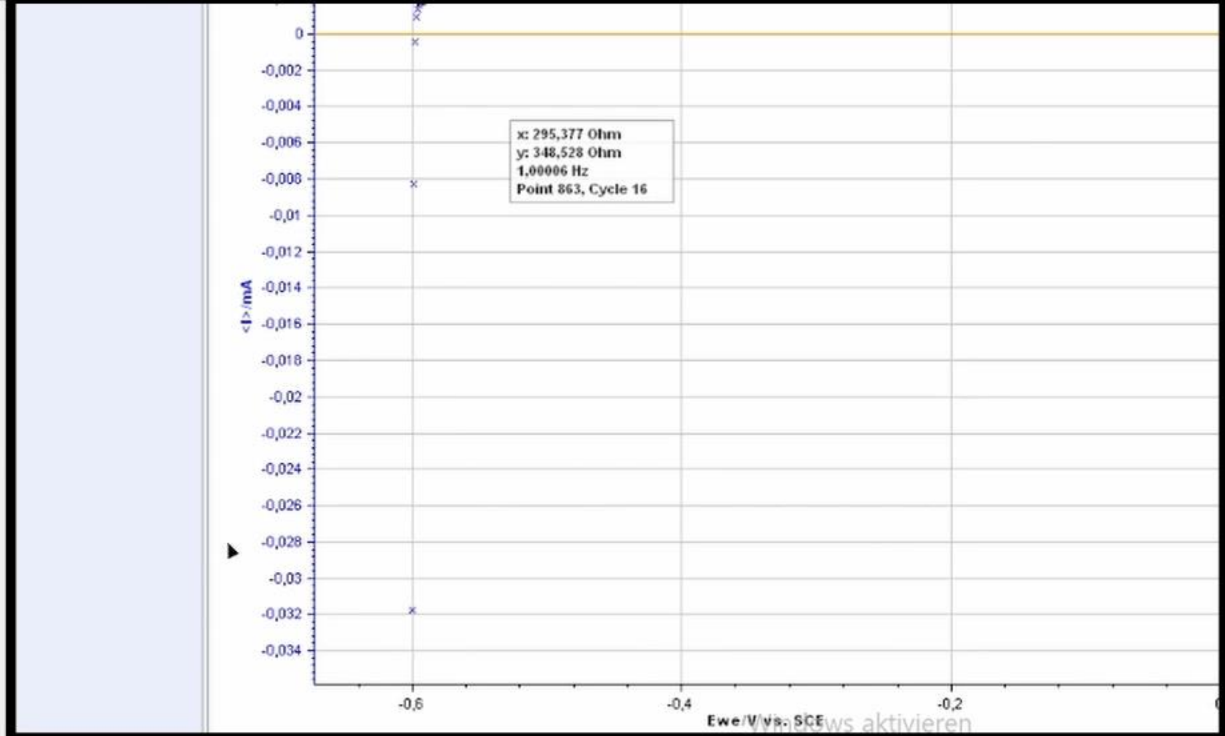
In situ Auger electron microscopy (AEM)
Ni thin film on GDC

- SEM imaging
- spatially resolved surface spectroscopy
- elemental mapping
- UHV conditions required





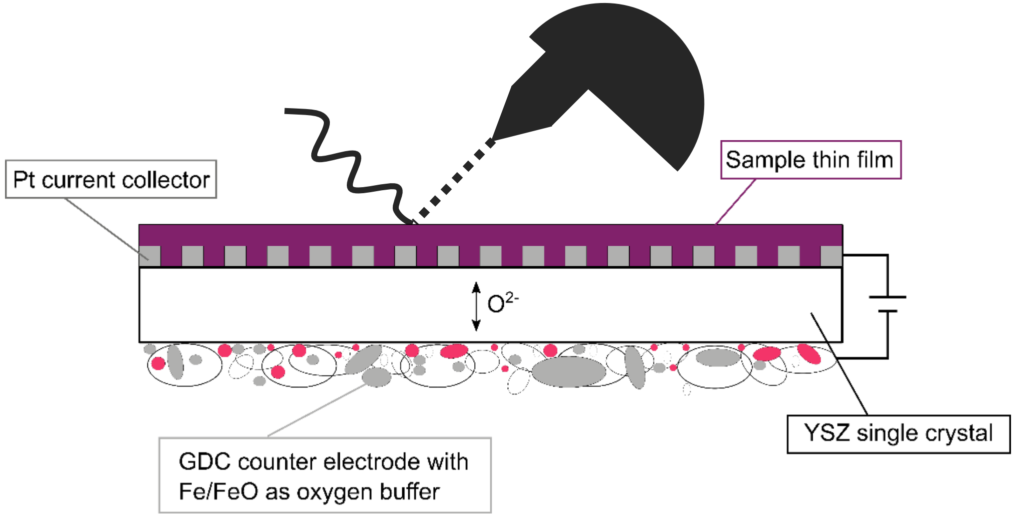

4000 X
5.0 µm


x: 295,377 Ohm
y: 348,528 Ohm
1,00006 Hz
Point 863, Cycle 16
<I>/mA
Ewe/V vs. SCE

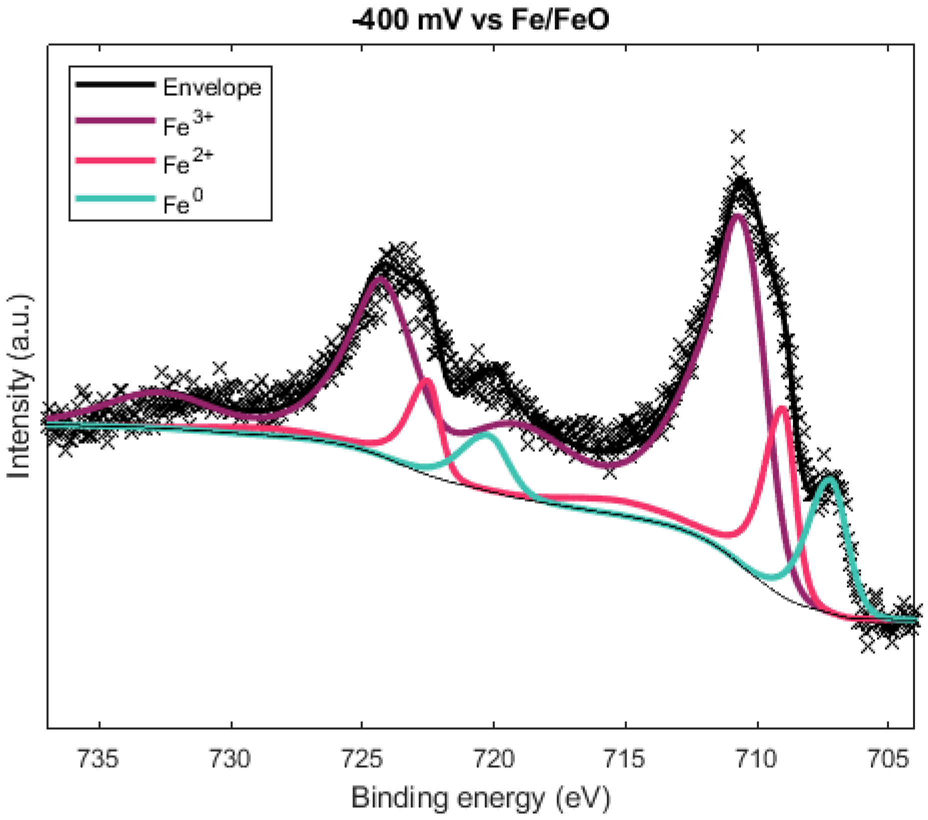
00:00:00:00

Electrochemical oXygen ACTivity control

(EXACT) XPS



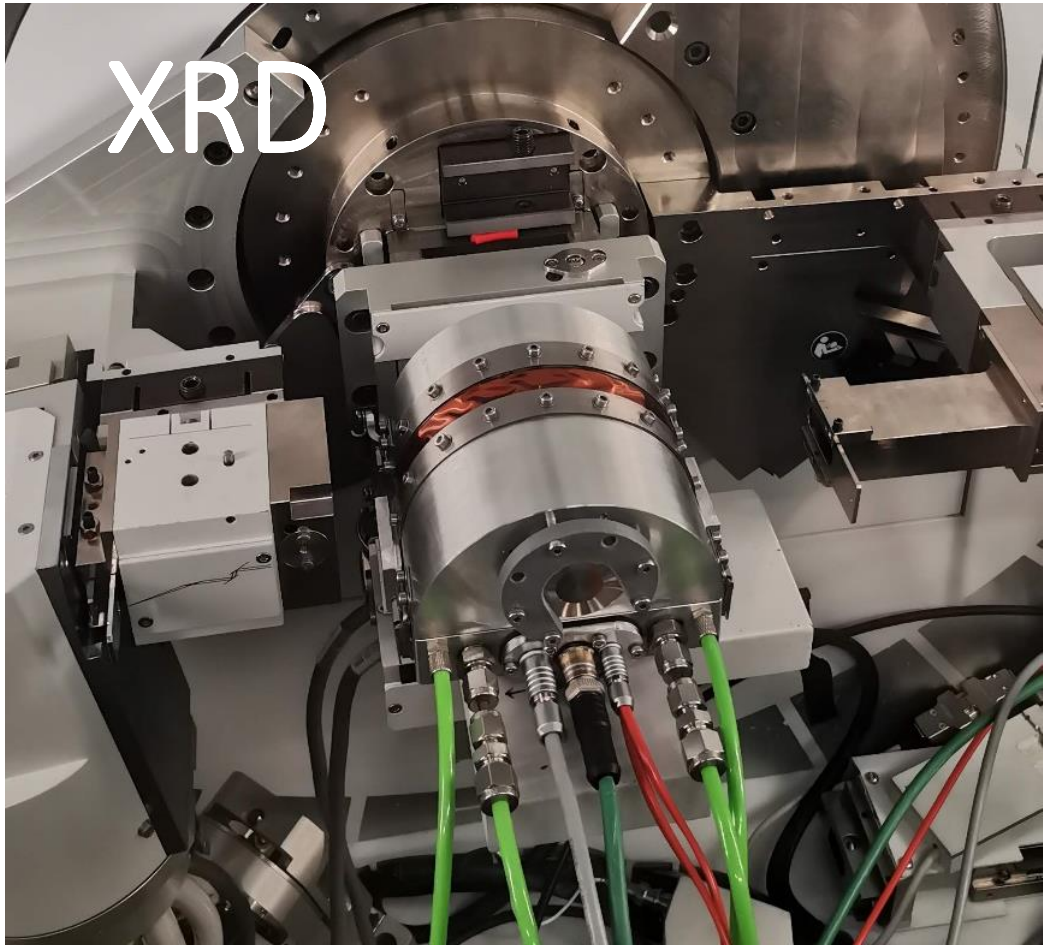
$$a(O_2)_{WE} = e^{\left(\frac{4F \cdot U + 2\Delta_f G^0(FeO)}{RT}\right)}$$

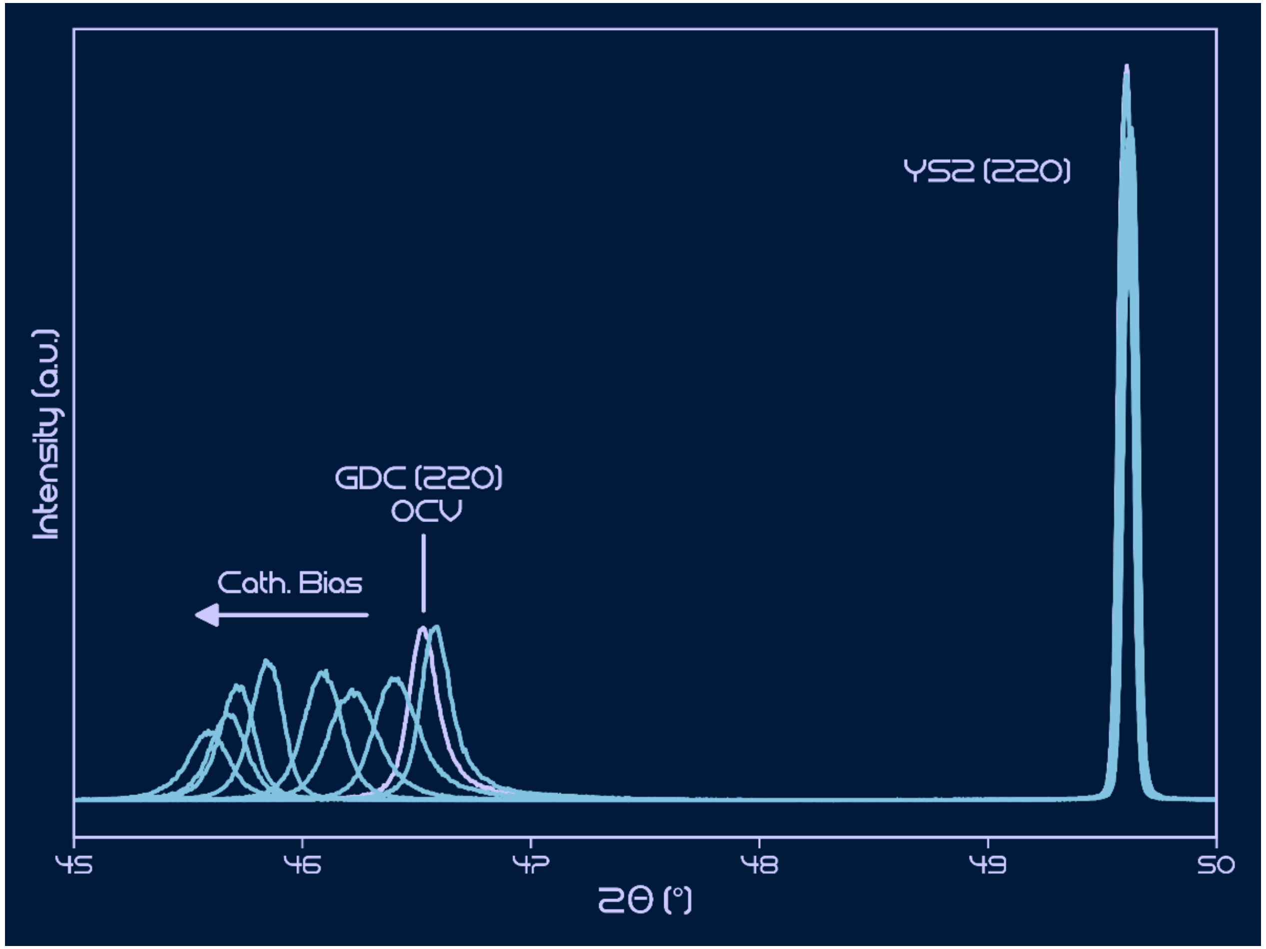


Stanislaus Breitwieser
Talk on Monday

Andreas Nenning
Talk and poster on
Tuesday

600 °C, UHV





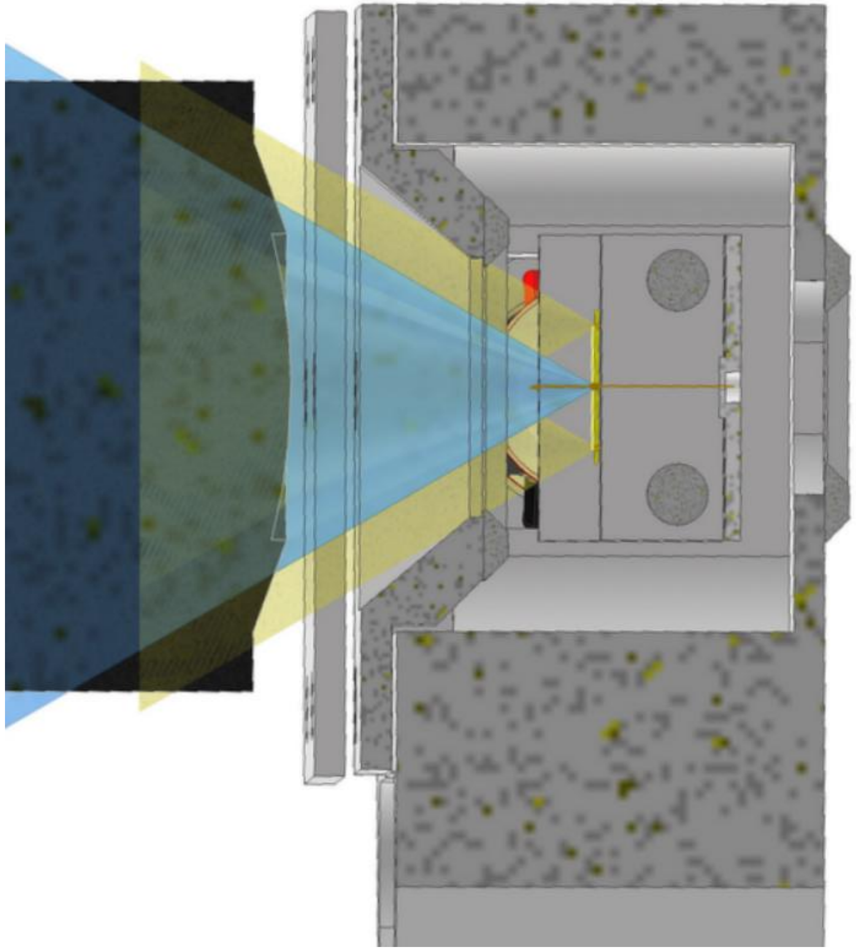
GDC thin film on YSZ

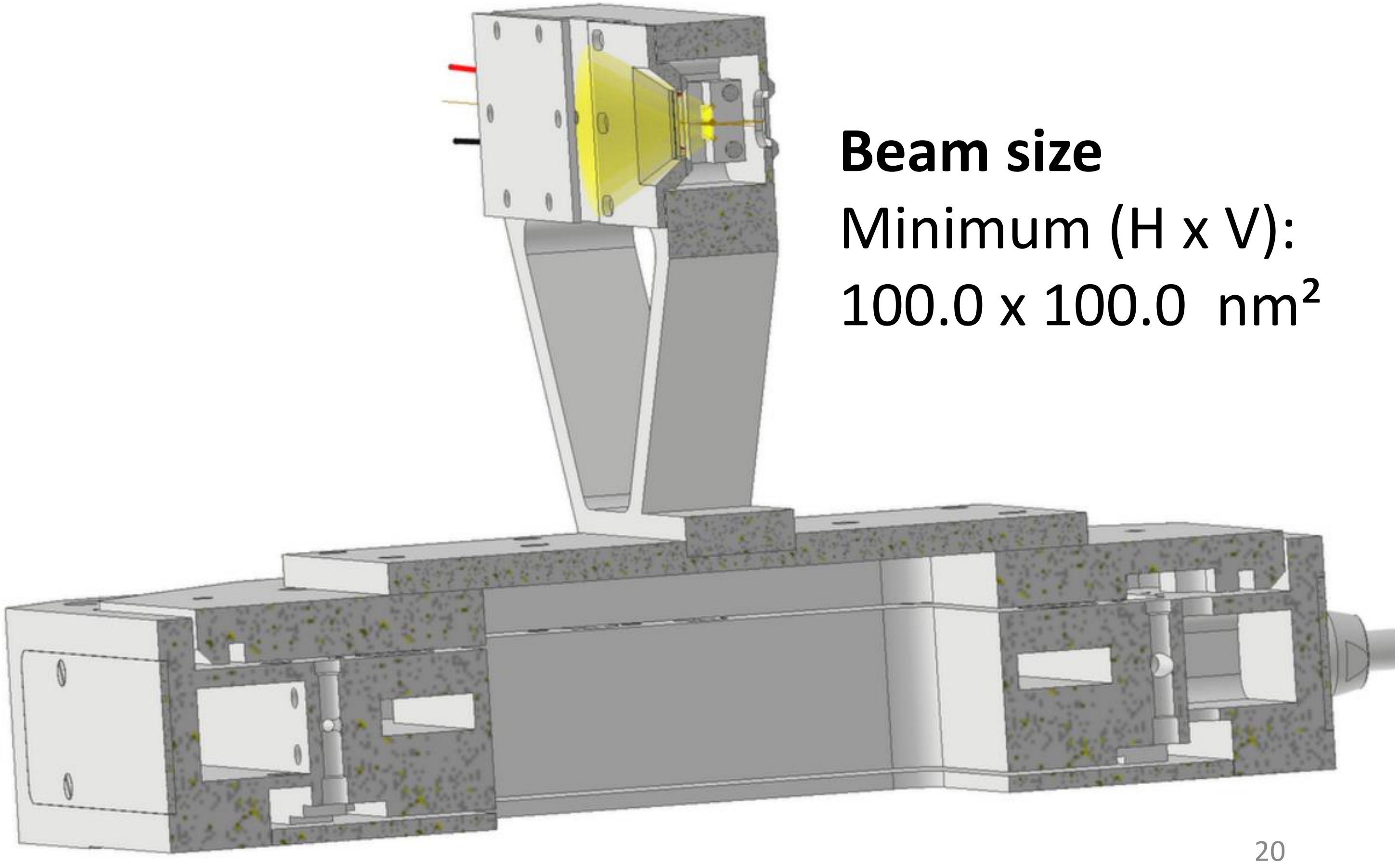
Kirsten Rath
Talk on Monday 3A4 Moore 12:05

- Compression with anodic bias
- Expansion with cathodic bias

YSZ reflex does not shift!

Solid-State Lithium-Ion battery ESRF ID13 Microfocus BL





Beam size

Minimum (H x V):

100.0 x 100.0 nm^2

How to start an in situ project

a) heating

f) sample transfer

b) electrical measurements

e) gasses

g) sensor at the sample

d) polarization

c) cooling

Material incomparability

UHV chambers → in situ chambers

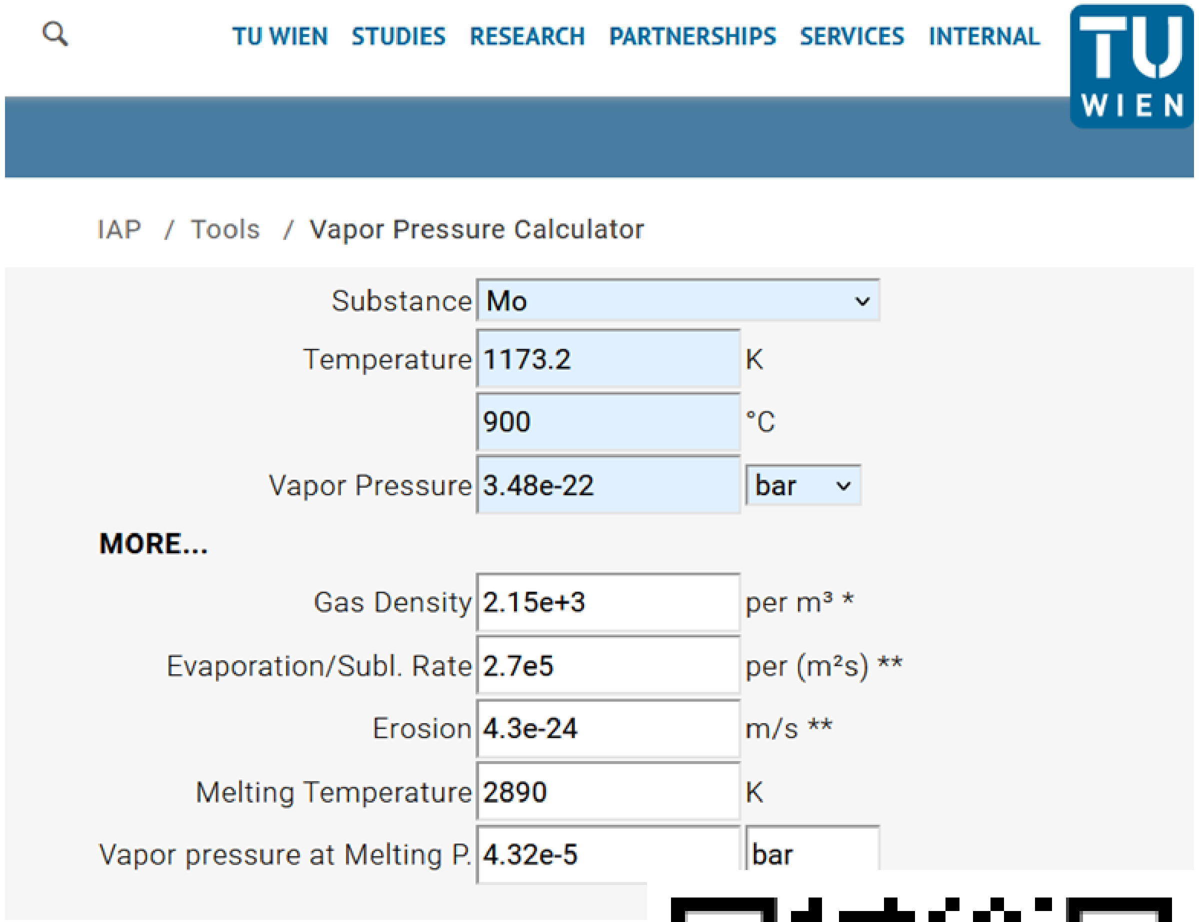
UHV heaters contain molybdenum

Formula	Melting point [°C]
Mo	2623[1]
MoO_2	1100 (decom-position) [1]
MoO_3	801[1]

high vapor pressure!

sublimates noticeably at 700 °C

(1)www.webelements.com/compounds/molybdenum/molybdenum_dioxide.html



From: Michael Schmid, www.tuwien.at/en/phy/iap/tools/vapor-pressure-calculator

Structural materials for in situ heater

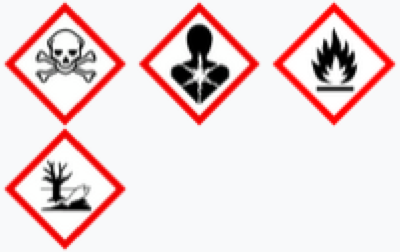
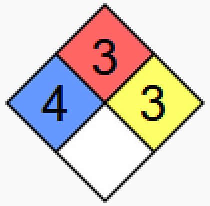
- Preferable: high temperature oxides
  - e.g. Alumina, Zirconia, Sapphire, Quartz glass,…
- Metals, Ni-based alloys

- Water cooled parts
  - Non high temperature materials possible
  - BUT anticipate a cooling failure!

Nickel tetracarbonyl & Iron pentacarbonyl

- CO & Ni
- CO & Fe

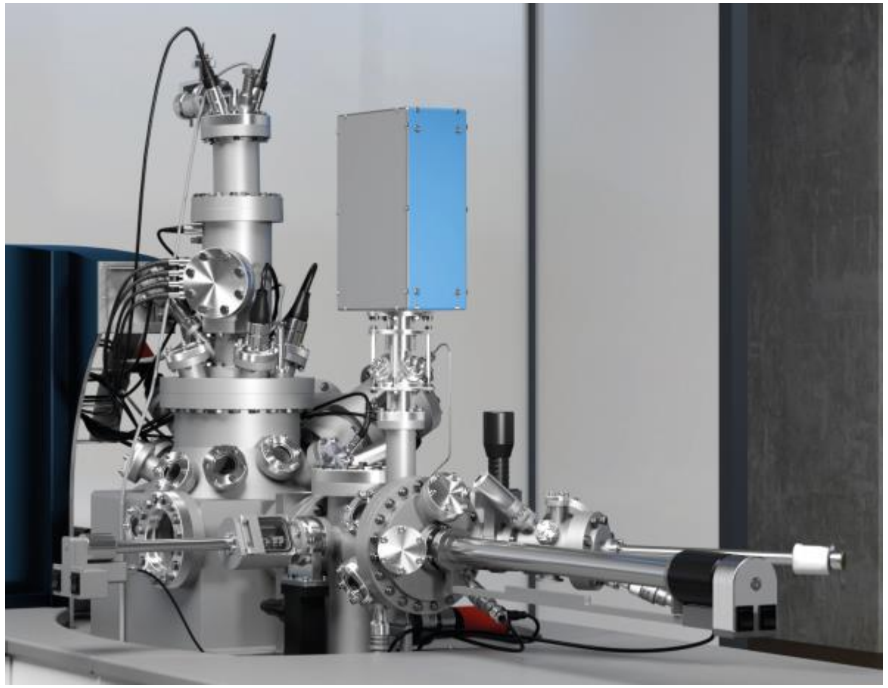
(e.g. stainless steel)

GHS labelling:	
Pictograms	
Hazard statements	H225, H300, H301, H304, H310, H330, H351, H360D, H410
Precautionary statements	P201, P202, P210, P233, P240, P241, P242, P243, P260, P271, P273, P280, P281, P284, P303+P361+P353, P304+P340, P308+P313, P310, P320, P370+P378, P391, P403+P233, P403+P235, P405, P501
NFPA 704 (fire diamond)	

Flash point	4 °C (39 °F; 277 K)
Autoignition temperature	60 °C (140 °F; 333 K)
Explosive limits	2–34%
Lethal dose or concentration (LD, LC):	
LC_{50} (median concentration)	266 ppm (cat, 30 min) 35 ppm (rabbit, 30 min) 94 ppm (mouse, 30 min) 10 ppm (mouse, 10 min)[3]
LC_{Lo} (lowest published)	360 ppm (dog, 90 min) 30 ppm (human, 30 min) 42 ppm (rabbit, 30 min) 7 ppm (mouse, 30 min)[3]

Plastic components

- Not hydroscopic:
  - PEEK
  - Polyethylene
  - Polypropylene
  - PTFE (Teflon) **Max temperature 170°C !**
  - PVC
  - Polyimide (Kapton)



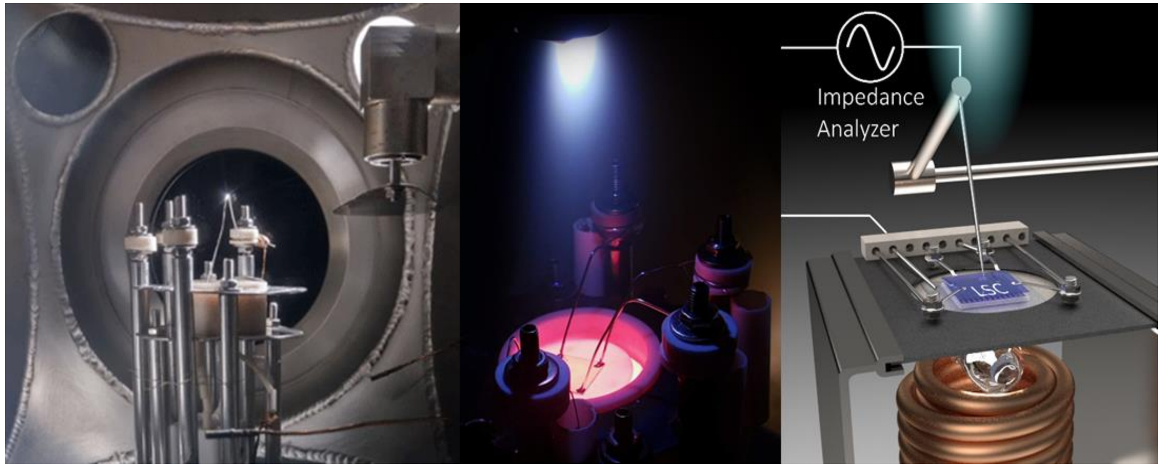
Using scroll vacuum pump with Teflon tip seal

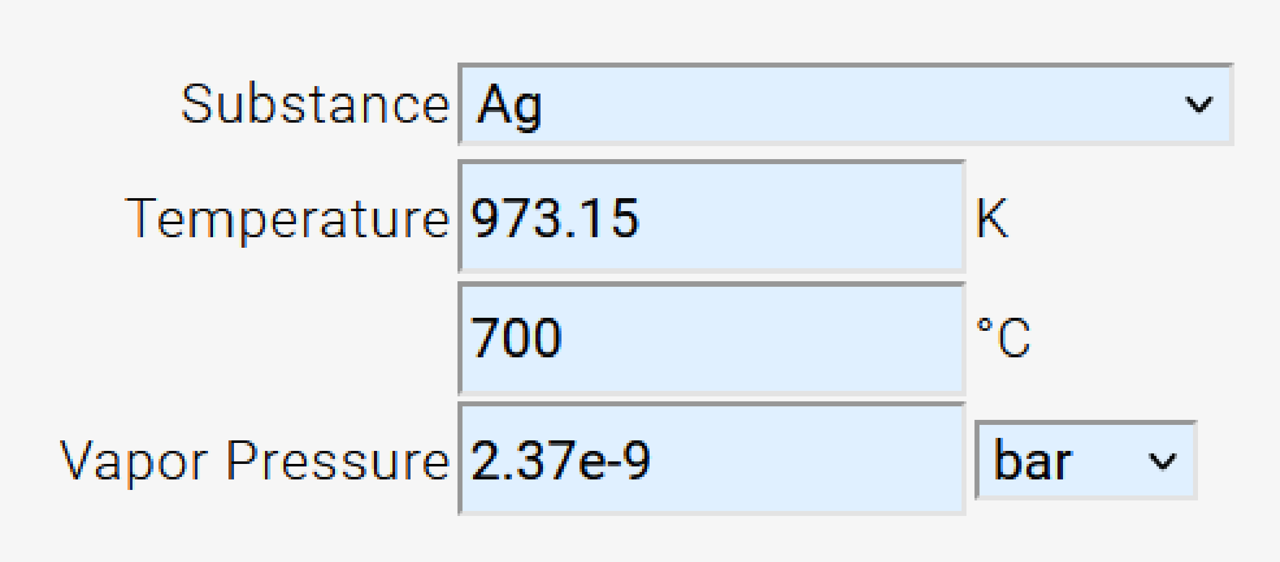
↓

Fluorine poisoned surface

Contacts and electrodes

- Platinum
  - Platinum Iridium alloys (better mechanical properties & harder)
  - Platinum Rhodium alloys (higher temperature stability)
- Tungsten, Tungsten Carbide
- Gold (very soft/ for sealing)
- Silver



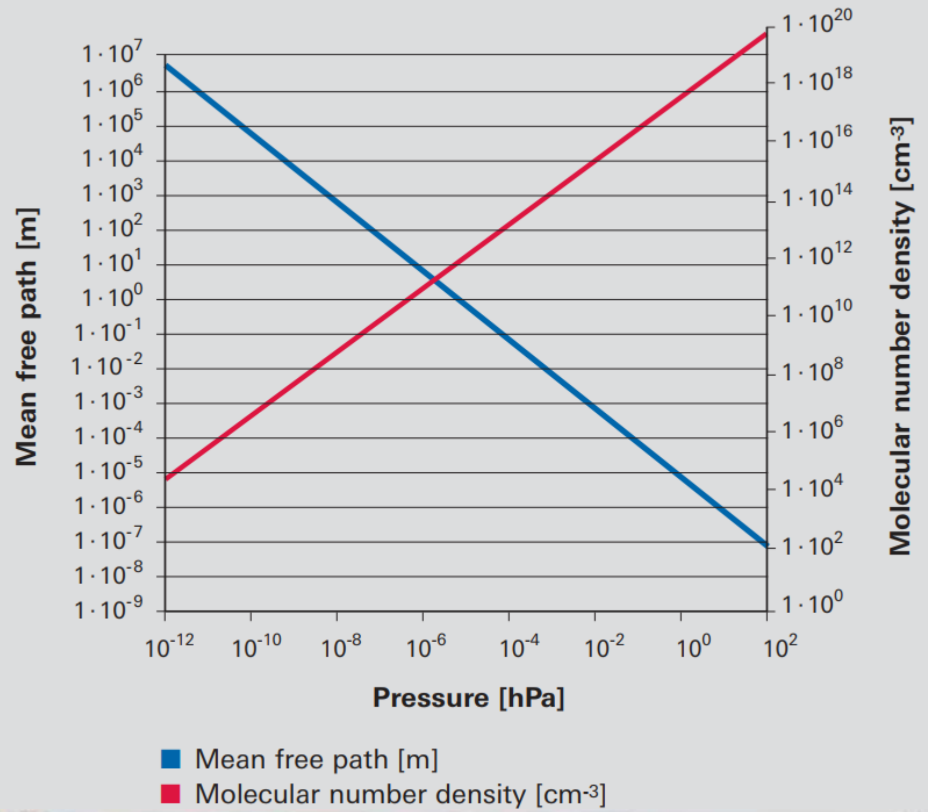


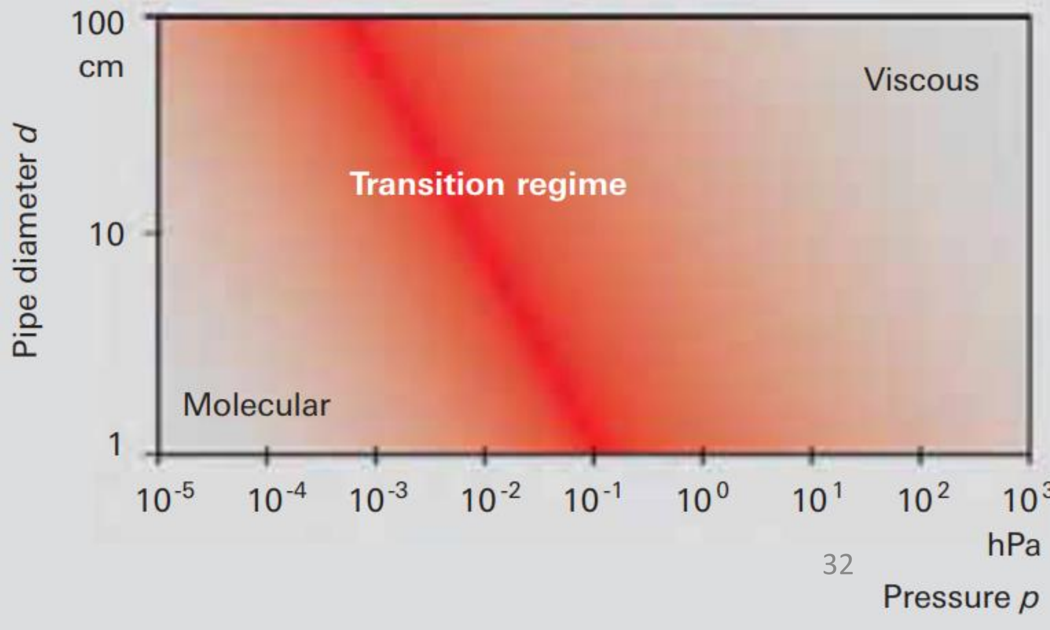
From: Michael Schmid, www.tuwien.at/en/phy/iap/tools/vapor-pressure-calculator

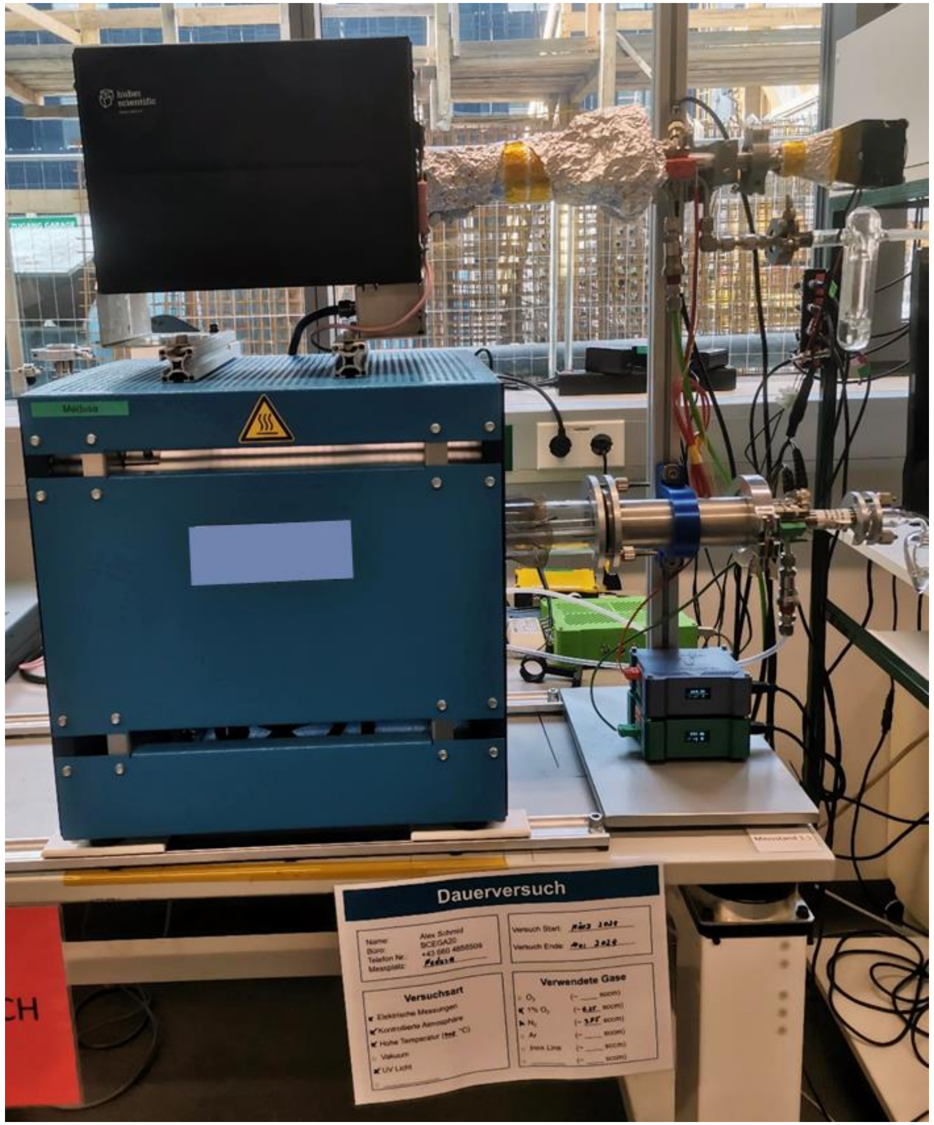
In situ / ex situ
Clean surface necessary?

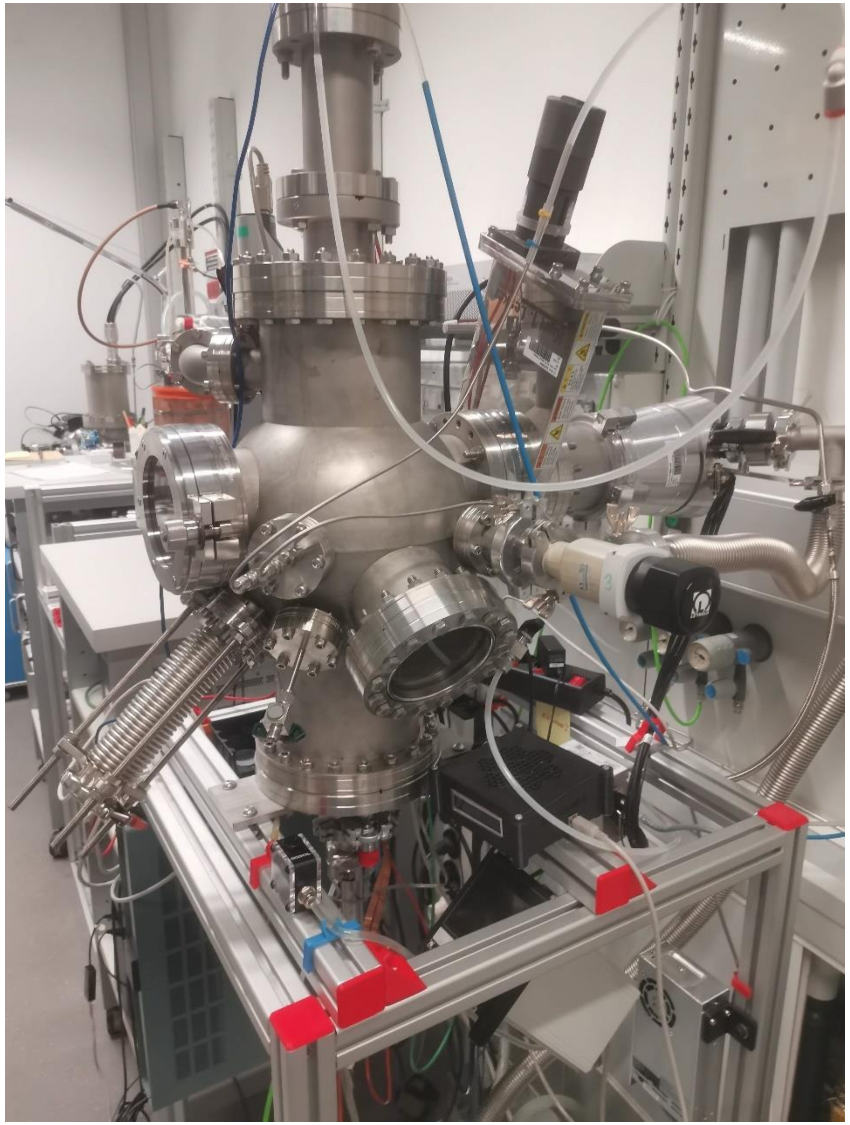
- In situ in same chamber/ transport?
- Mean free path at pressure regime?
- Temperature of components
  - Radiation
    - Parts in line of sight?
  - Convection
    - Mean free path at pressure regime?
    - Cooling effects!
  - Conduction
    - Cooling effects!
    - Sensitive parts connected?
- Simple leak test
  - Linear → leak
  - Asymptotical → outgassing

The Vacuum Technology Book Volume II



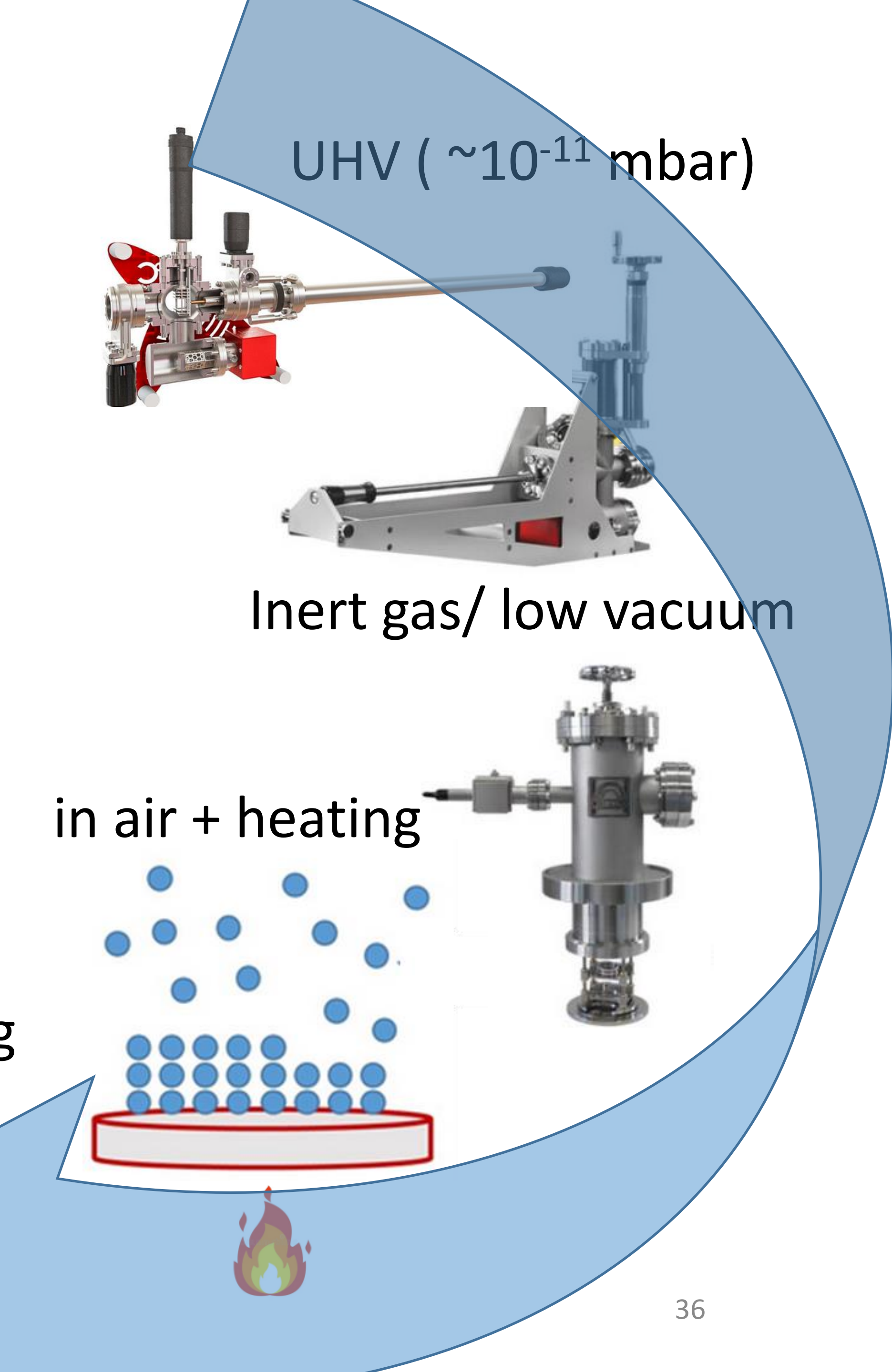


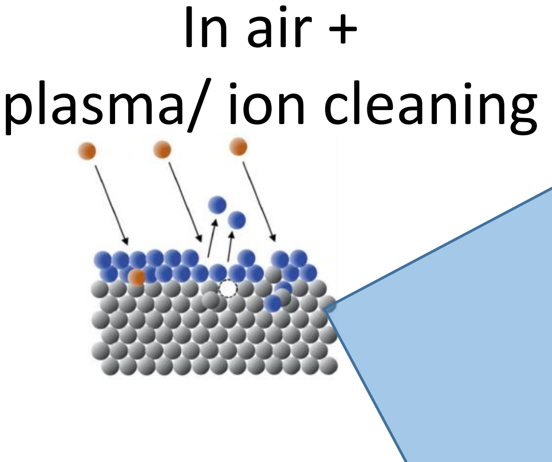

Dauerversuch
Versuchsart
Verwendete Gase



Transport

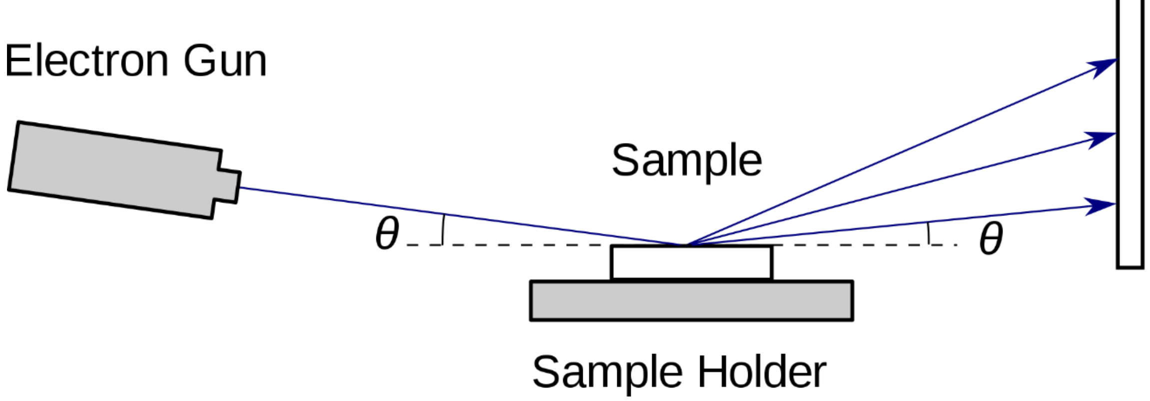
- Which contaminants are a problem?
- **Not from transport:** chromium, fluorine, silicon, heavy metals, …
- **From transport:** carbon, sulphur, water, CO_2, acidic gases, …
- **Cooling/heating:** cation diffusion, phase segregation, …
- **Surface cleaning:** changing the surface

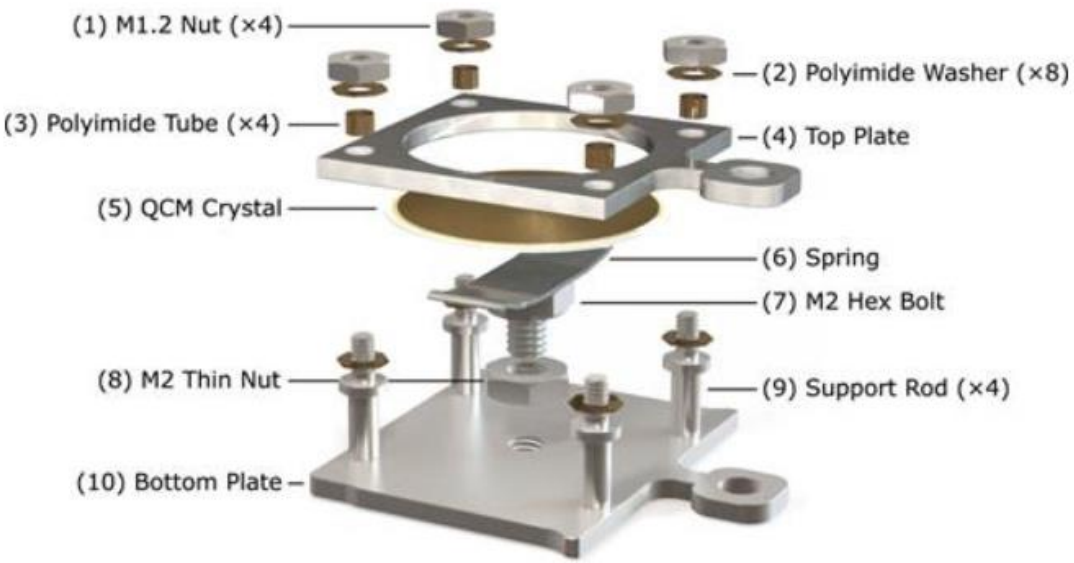




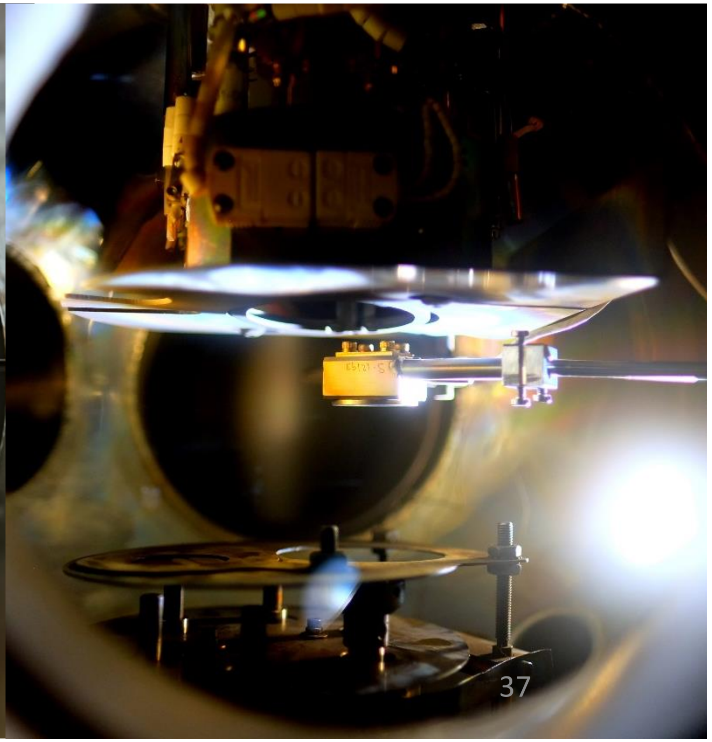
In situ thickness monitoring in PLD

- Rheed
- Quartz micro balance





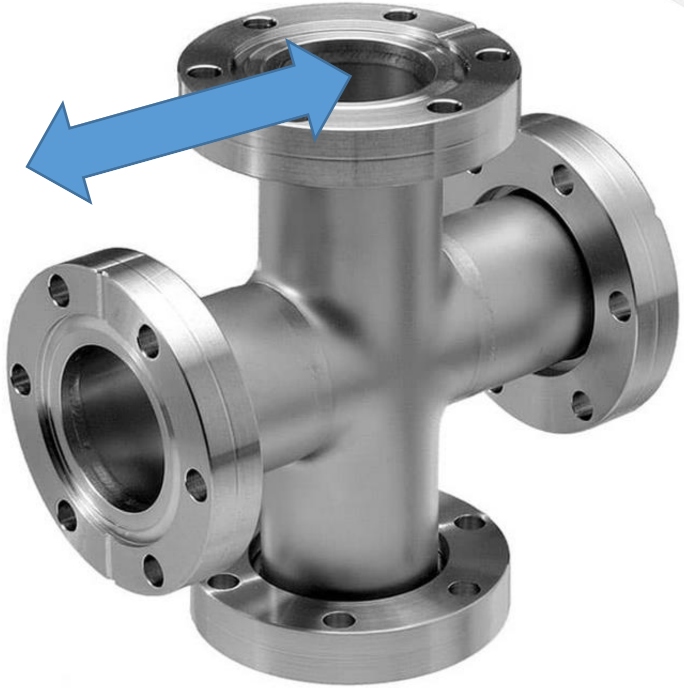
G. Franceschi, et al: Rev. Sci. Instrum. 91, 065003 (2020)

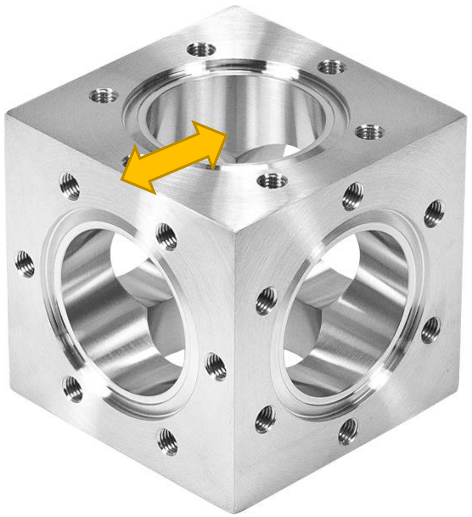


Important (small) points/problems

Transfer, chamber shape etc.

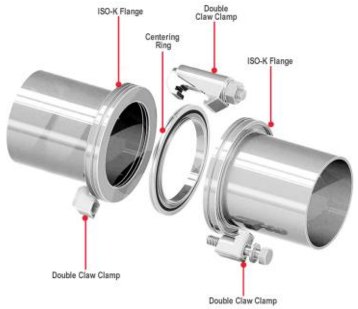
+





< $1 \cdot 10^{-7}$ mbar?

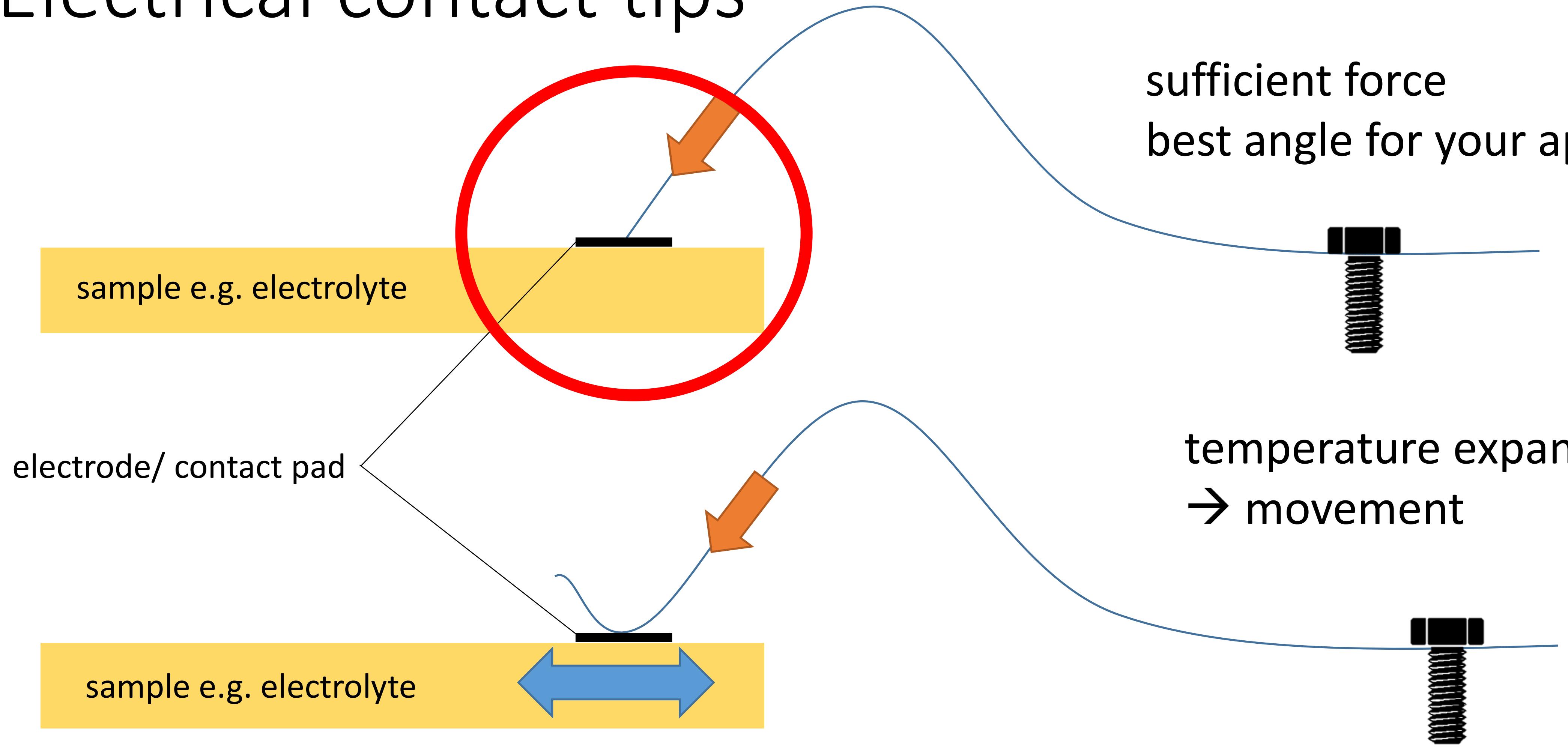
Pressure range?



Don't shoot sparrows with cannons!

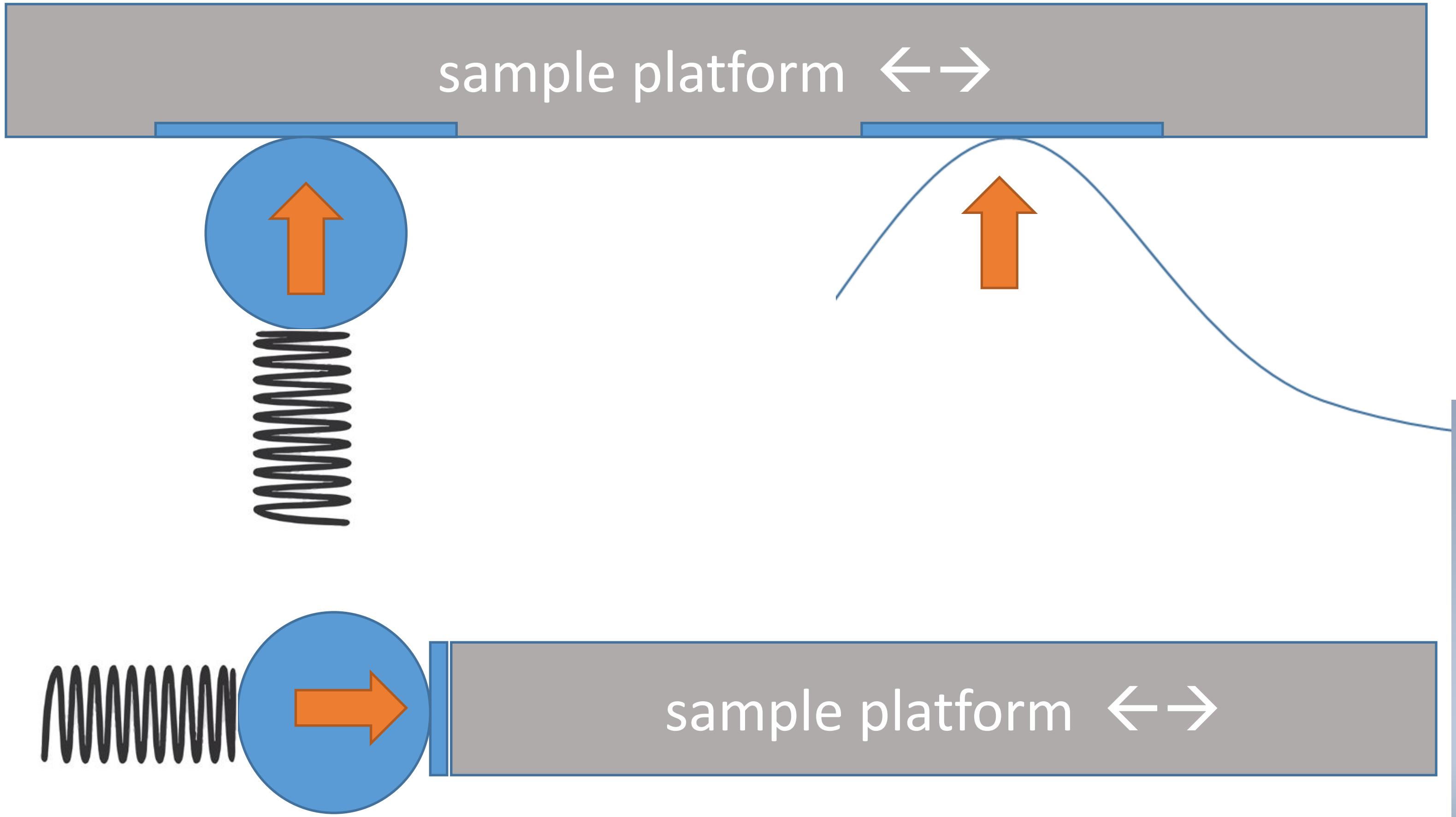
material compatibility

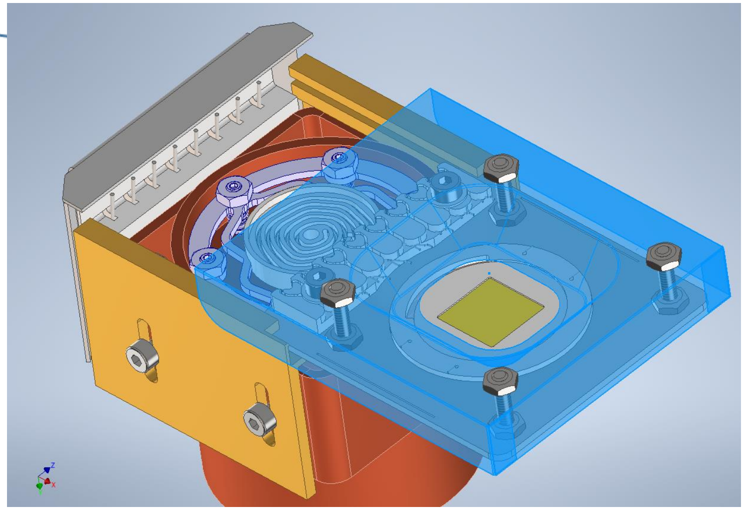
Electrical contact tips



Spring loaded sliding contacts

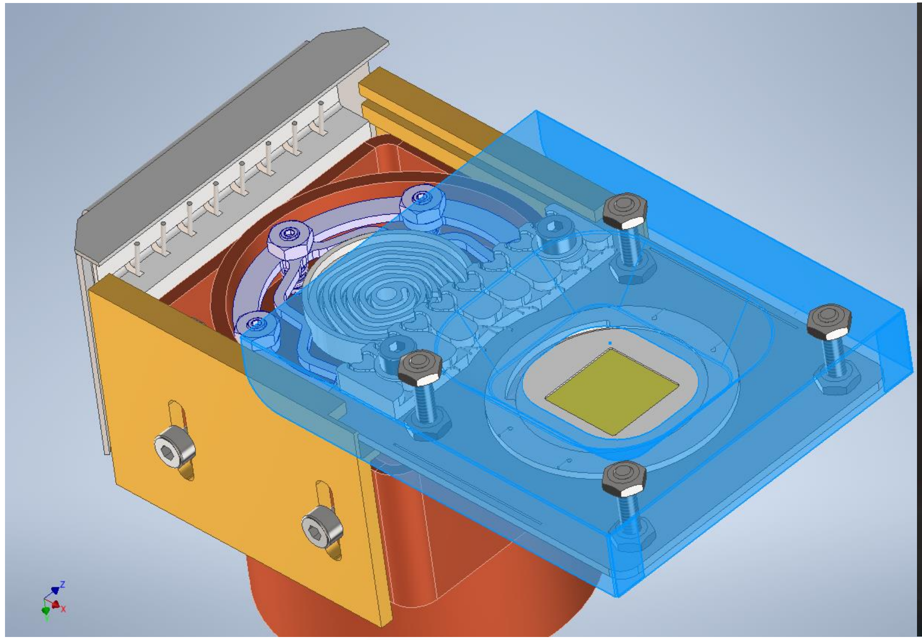
Corrosion issues!
Use TC type S



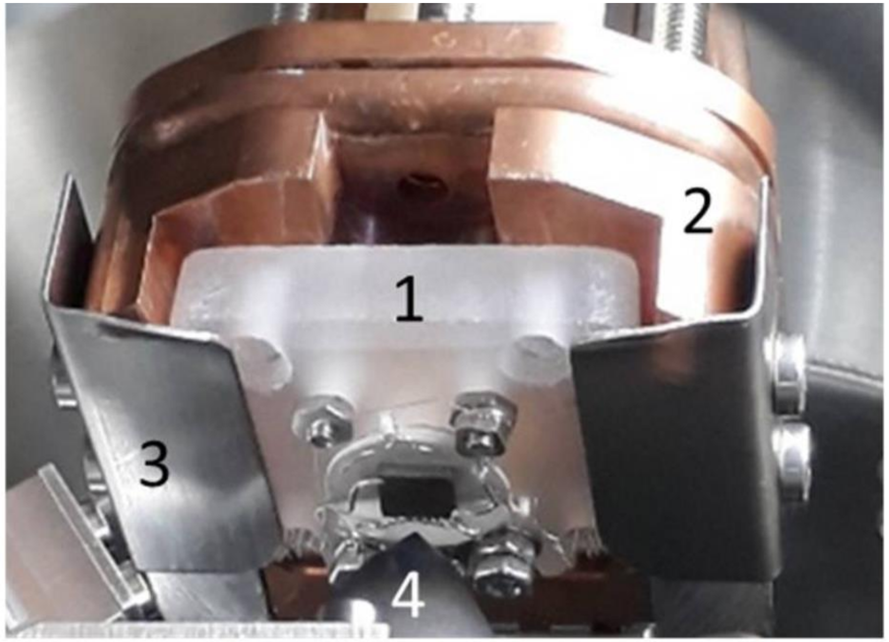


Sample platforms

PVD systems (HV)



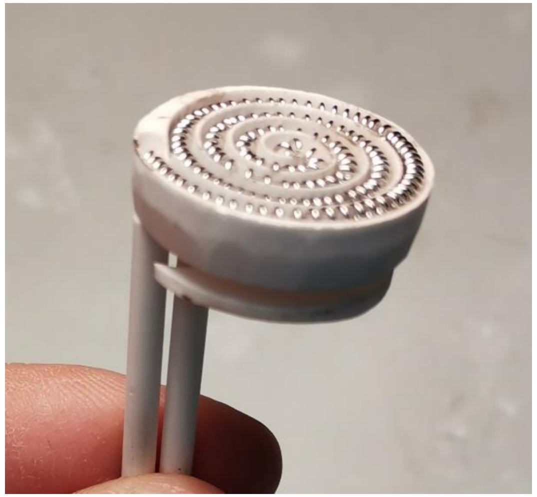
NAP-XPS (UHV)




+

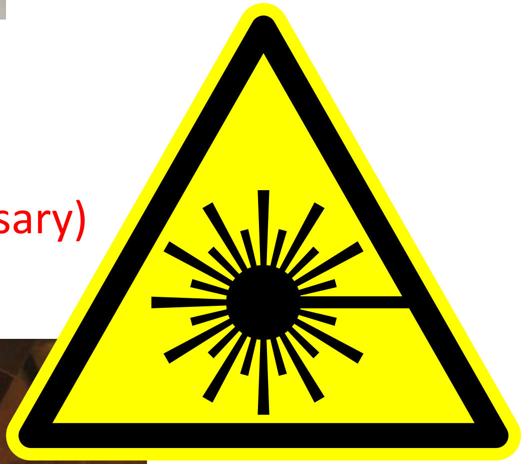

Heating

- **conduction, convection and radiation**
- **1000 → 10 mbar (laminar flow)**
- **$10e^{-4}$ mbar thermal conductivity of the gas low**
  - Radiation → line of sight, distance
  - Convection → gas pressure & gravity
  - Heat conduction → material properties



resistive

Small is beautiful
(only heat what's necessary)



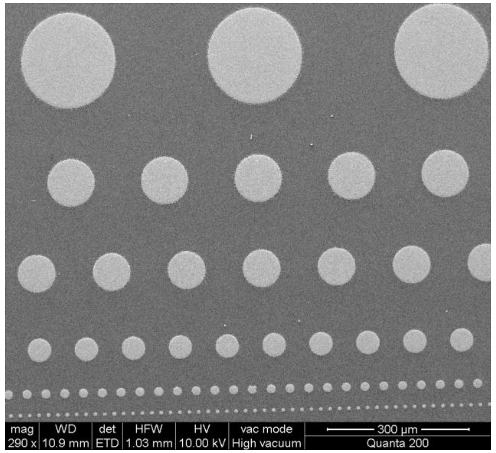
laser

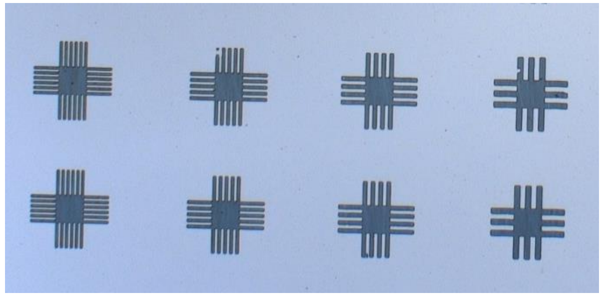
radiation

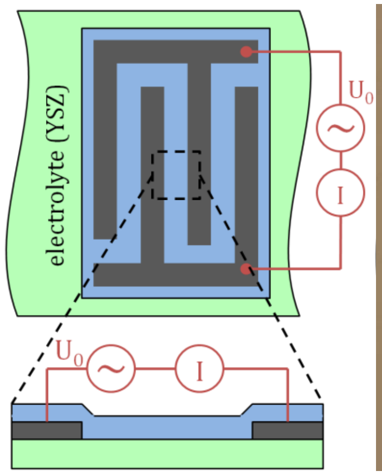
Electrode shapes & electrical measurements

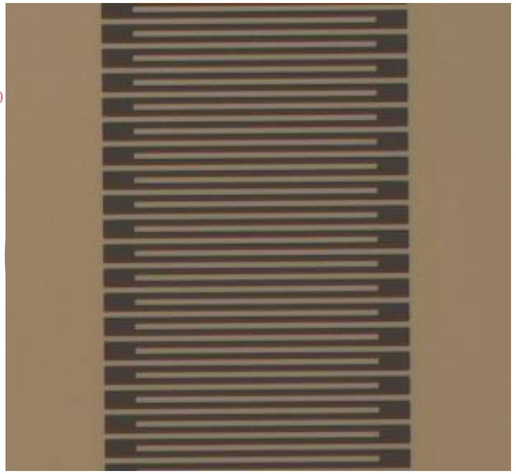
Electrical measurements

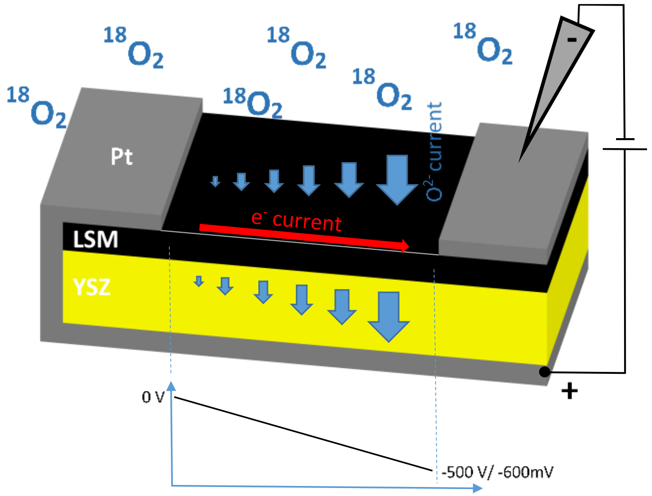
- Symmetric cell
- Asymmetric cell
  - Large difference in R and C of WE & CE
  - Microelectrode
  - Reference electrode
- Special geometries

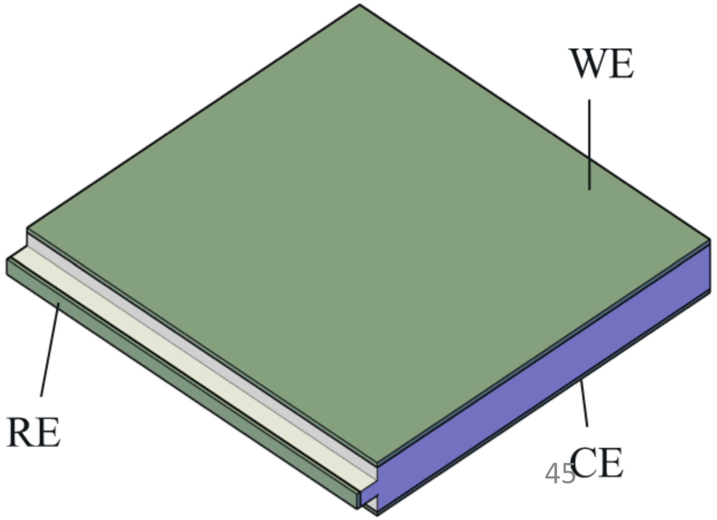






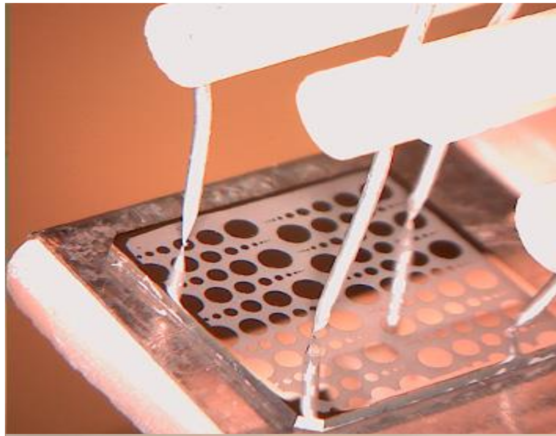


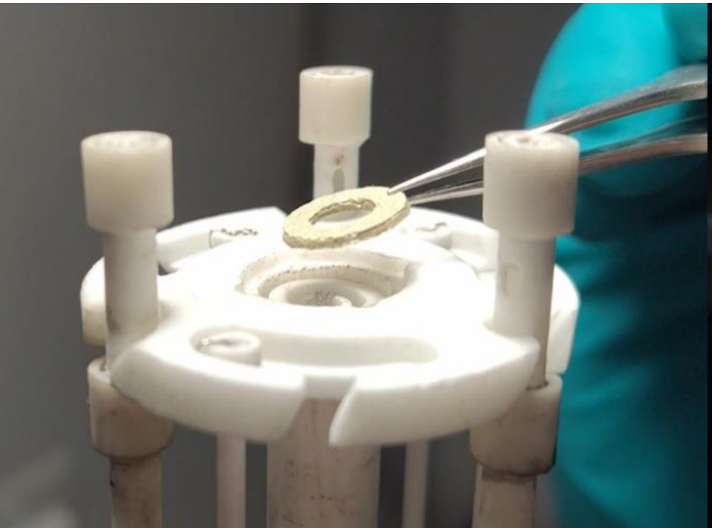


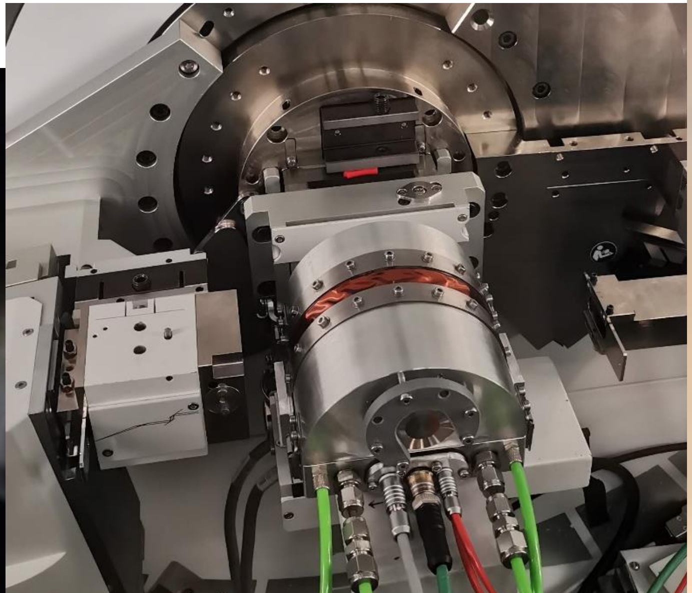


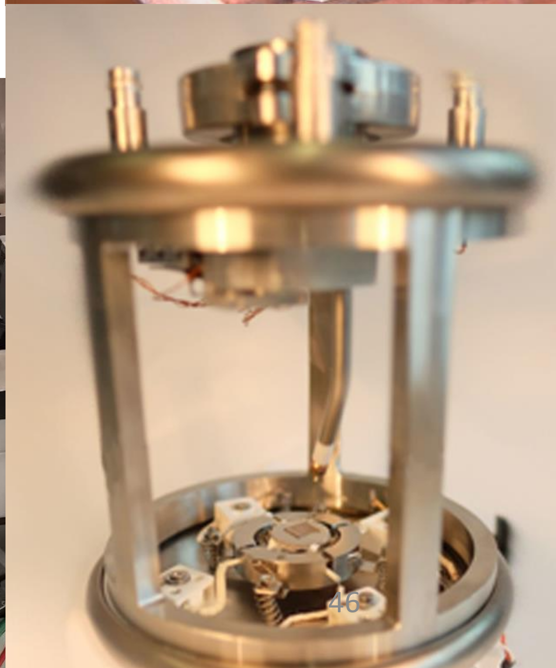
Advantages of micro patterned thin film electrodes

- Well-defined geometry (variable L3PB, …)
- No reference electrode
- Large number of electrodes
- Direct access to active surfaces
- Current voltage measurements

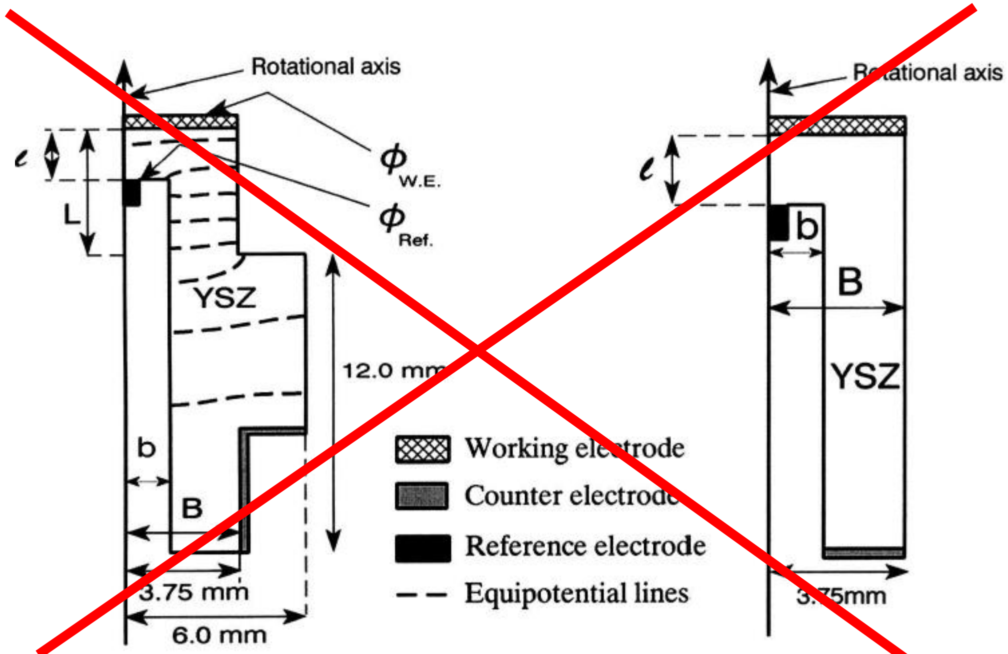




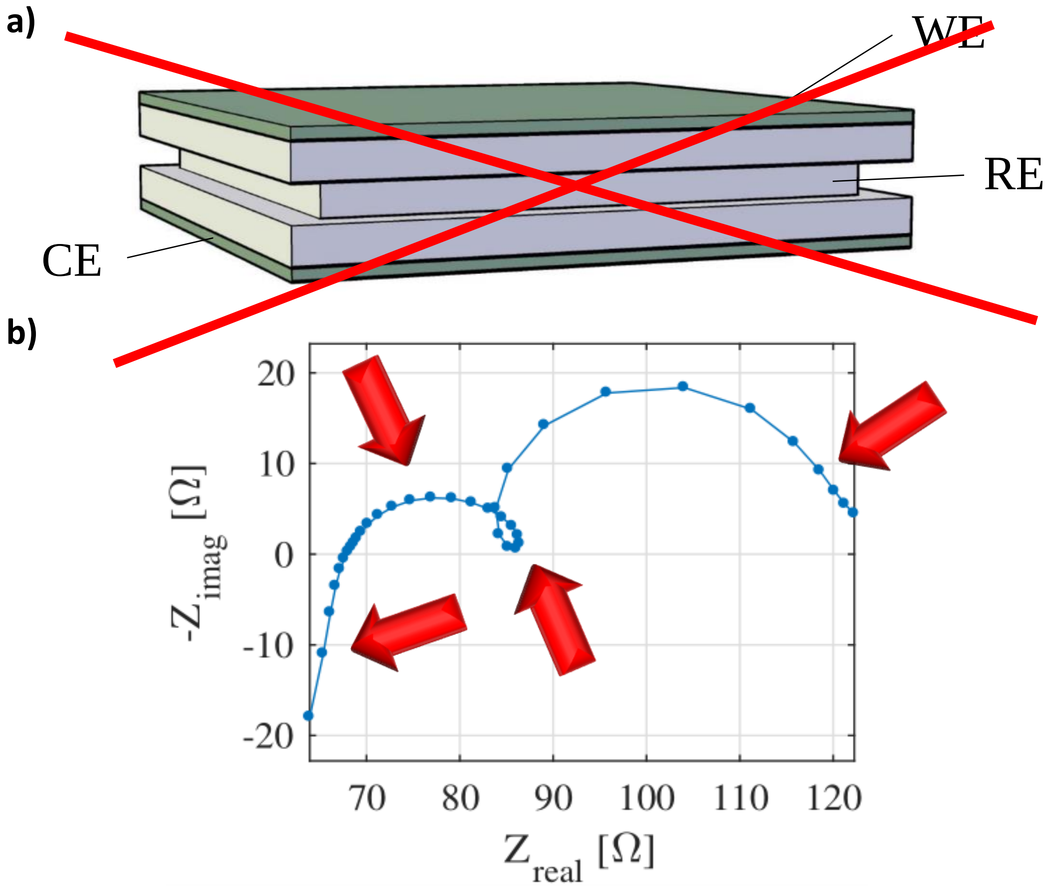




Reference electrodes

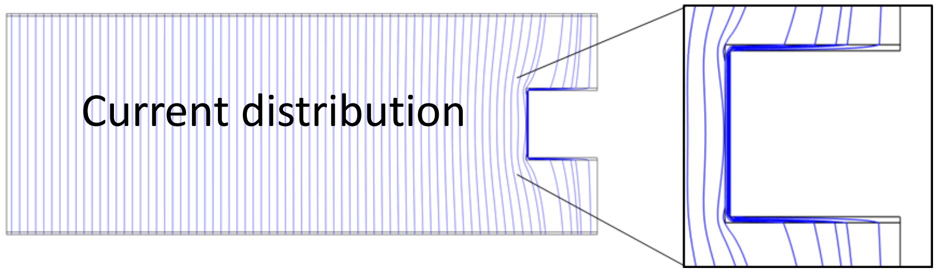


J. Winkler et al., Journal of The Electrochemical Society 145.4 (1998), pp. 1184-1192

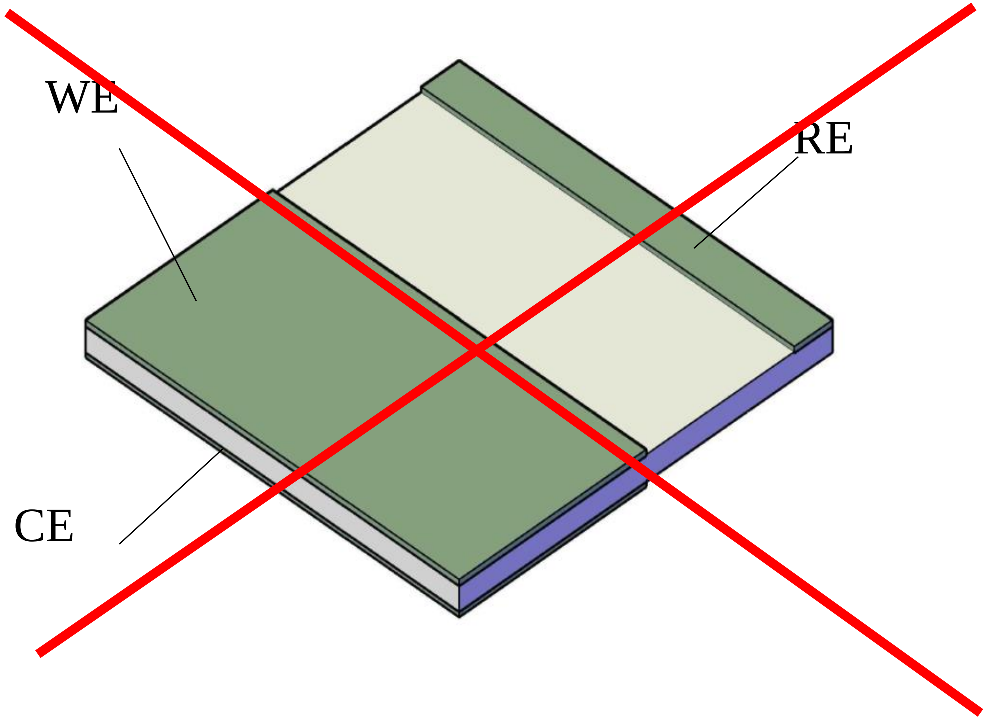


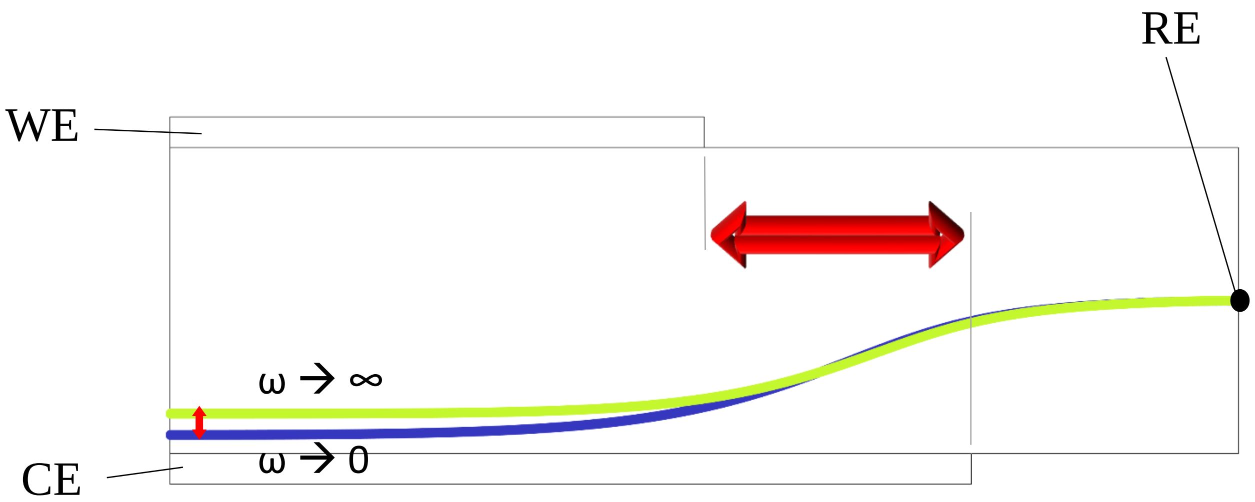
a) **Ring geometry** arrangement with carved reference electrode

b) Impedance spectra of LSF on YSZ single crystal sample indicating **four measurement errors**



Widely used 3-terminal measurements



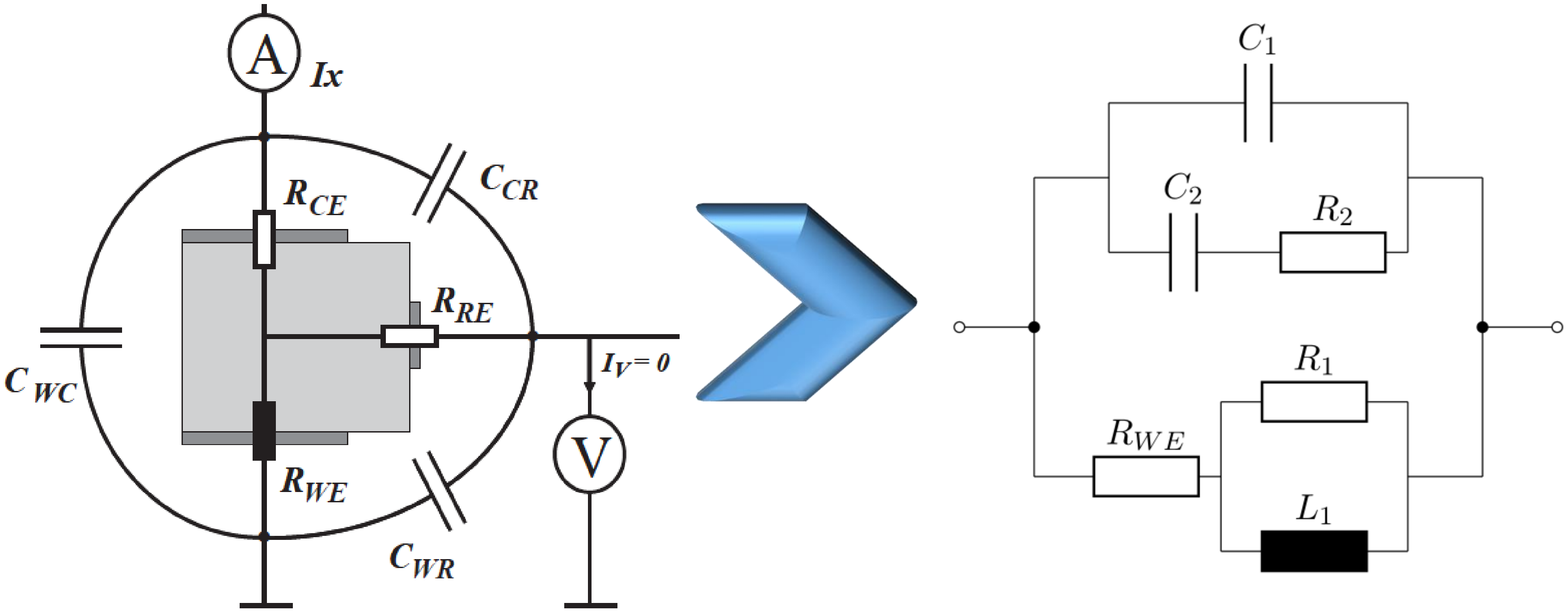


effect of misaligned electrodes

→ asymmetric WE and CE

→ potential shift in the reference potential from high to low measurement frequency

High resistive samples/ High frequencies



3-point transfer characteristic

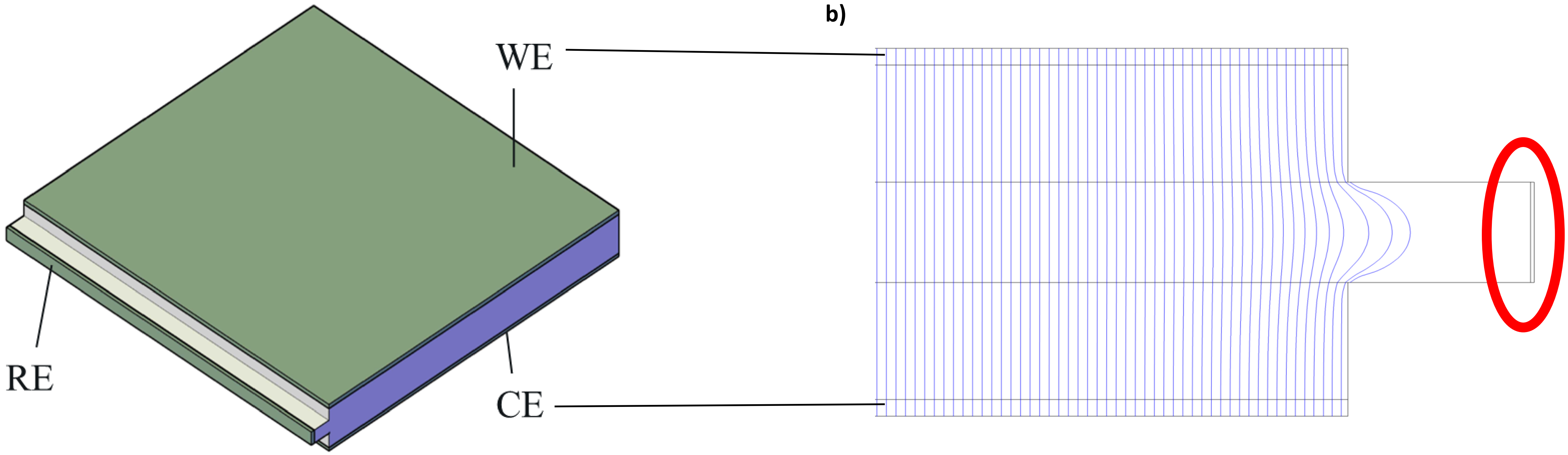
$$\underline{Z}(\omega)_{\text{3-point}} = \frac{\underline{V}}{\underline{I}} = \underline{Z}(\omega)_{\text{2-point, equivalent}}$$

S. Fletcher, Electrochemistry Communications 3.12 (2001), pp. 692-696

The novel "WING GEOMETRY"

a)

b)



a) Wing geometry

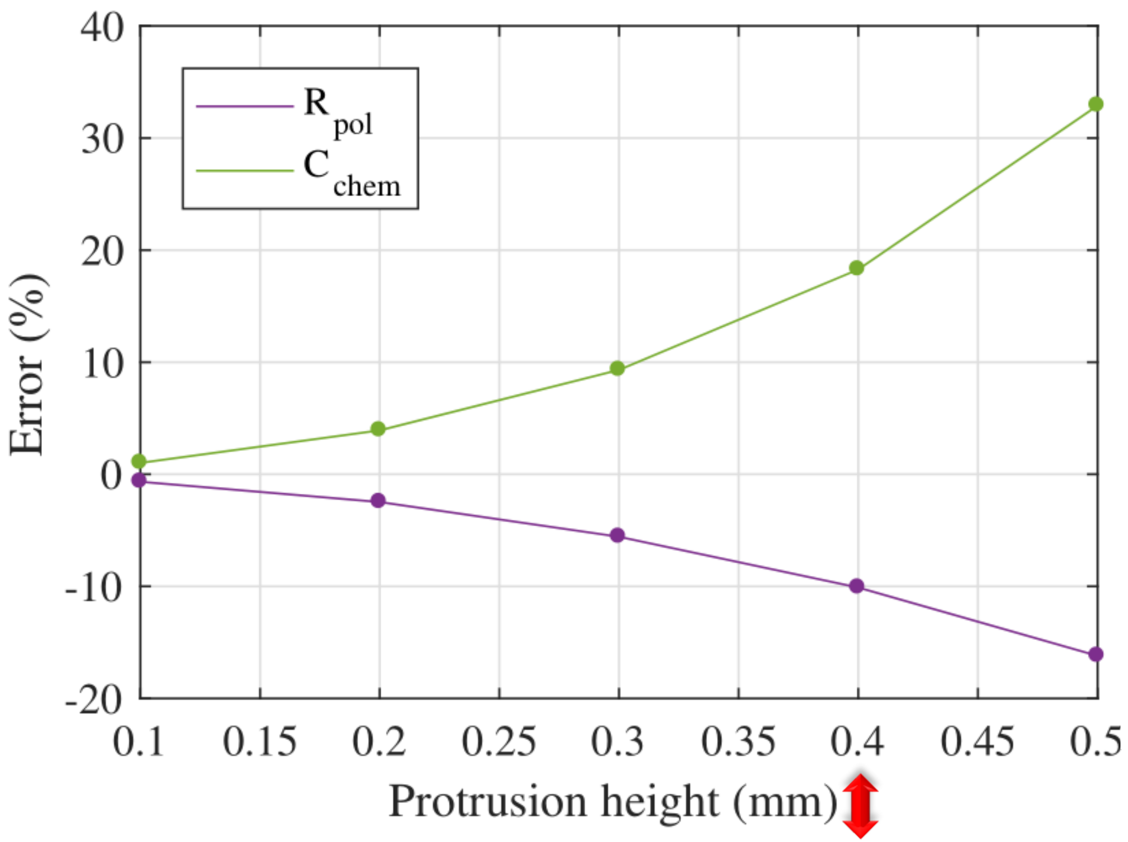
b) Current distribution (ω → ∞)

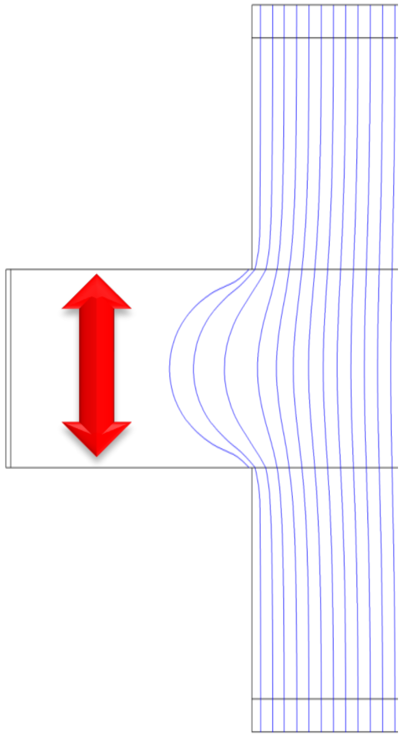
Alexander Schmid

- minimal measurement errors
- affordable
- suitable for different applications

Andreas Nenning *et al* 2022 *J. Electrochem. Soc.* **169** 094508

The novel "WING GEOMETRY"





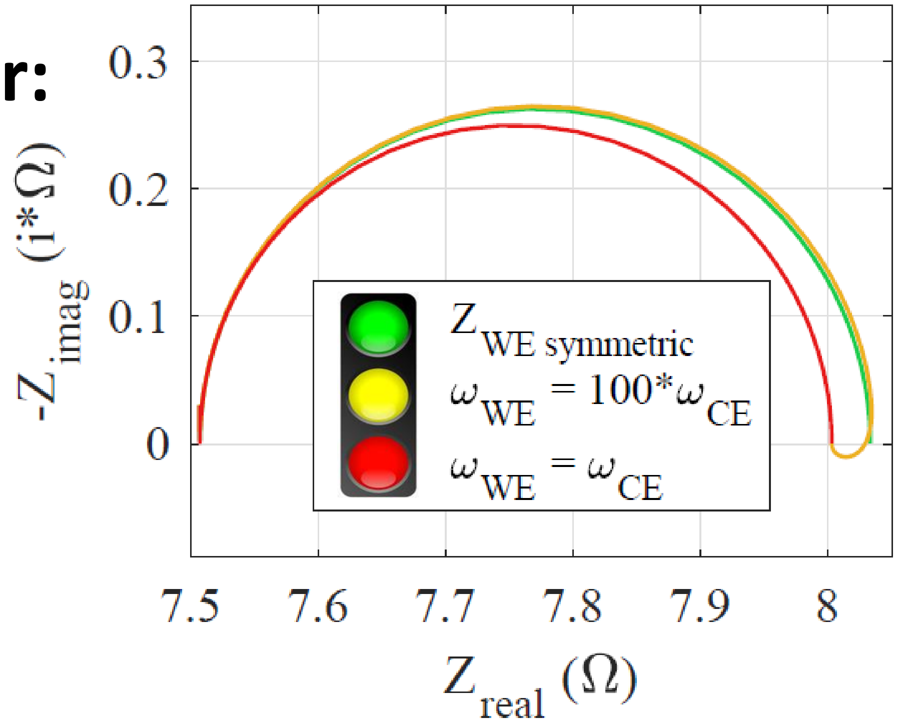
Measurement errors for worst case scenario (low-resistive electrodes and identical relaxation times)

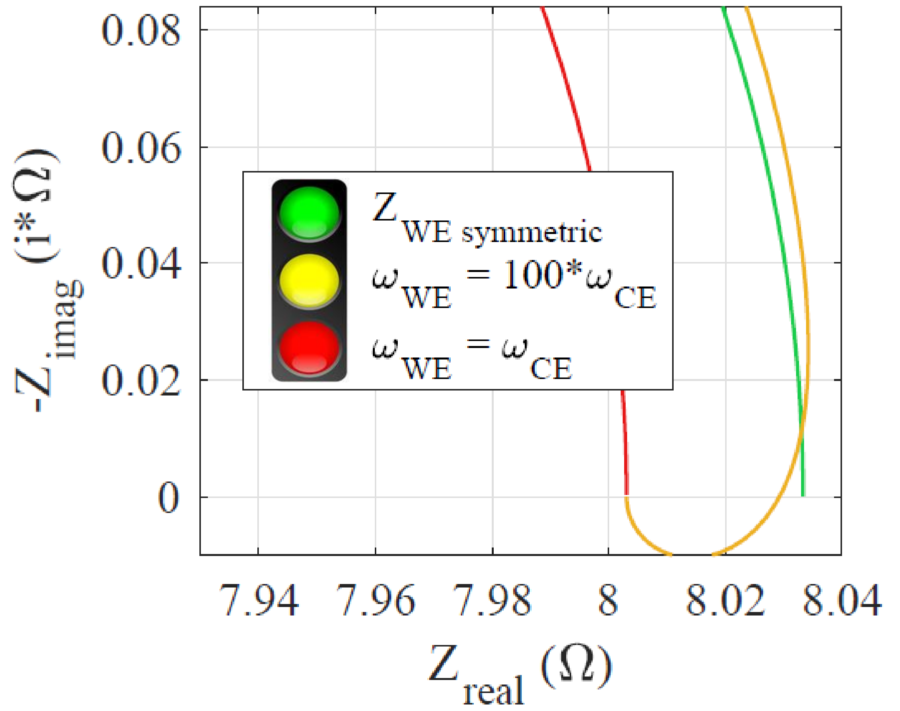
3 Error sources:

1. **3-point transfer characteristic** (high ohmic electrodes and high frequencies)
2. **Reference potential shift caused by WE/CE**
   - Geometrical asymmetry
   - Resistive asymmetry
   - Capacitive asymmetry
3. **Short circuit effect**

Low frequency error:

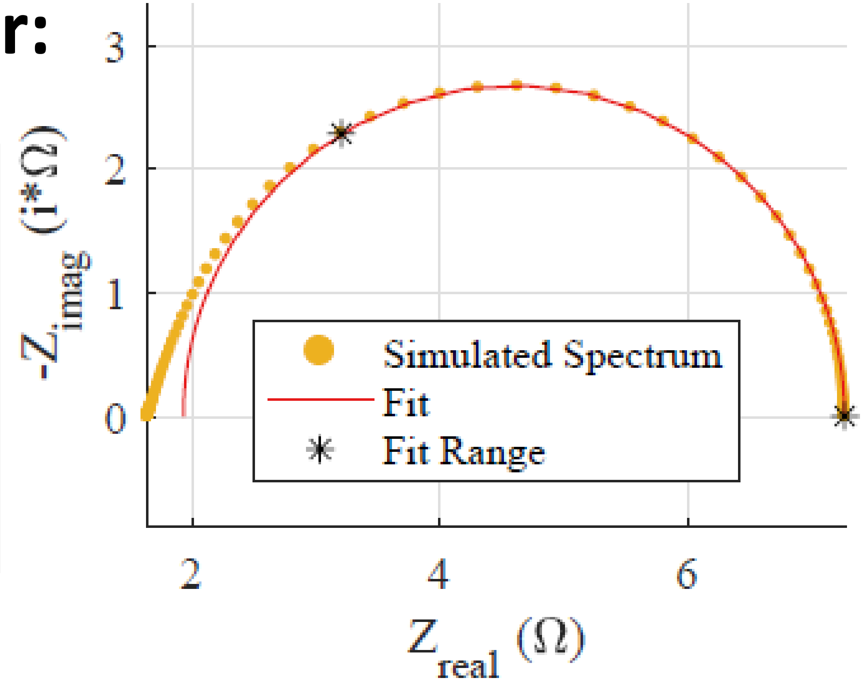
$$\omega = \frac{1}{RC}$$

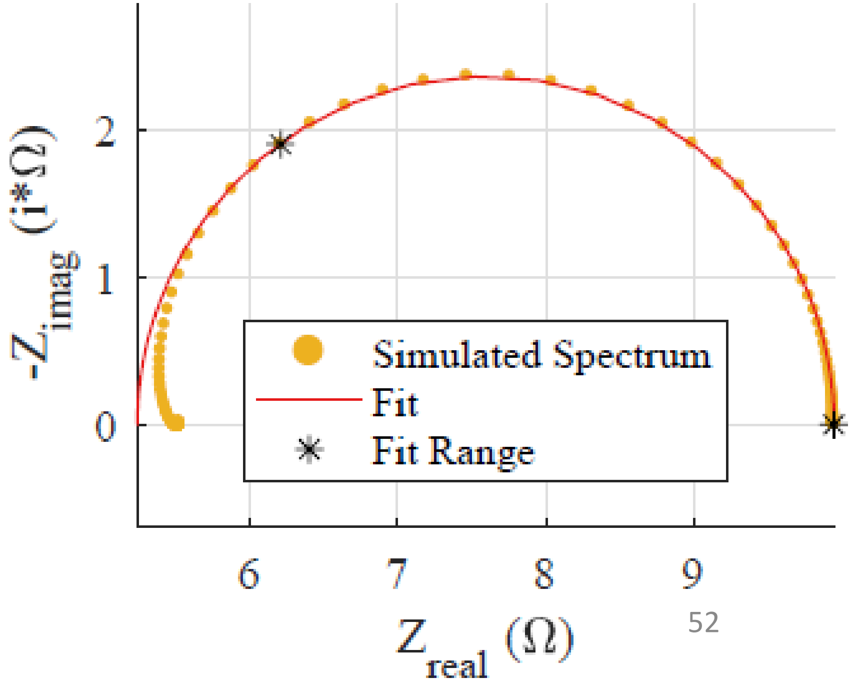




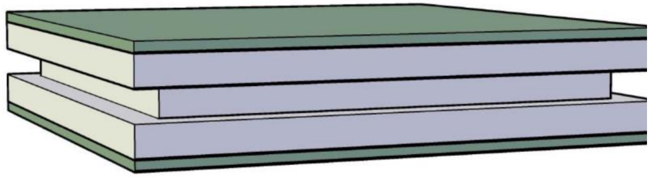
High frequency error:

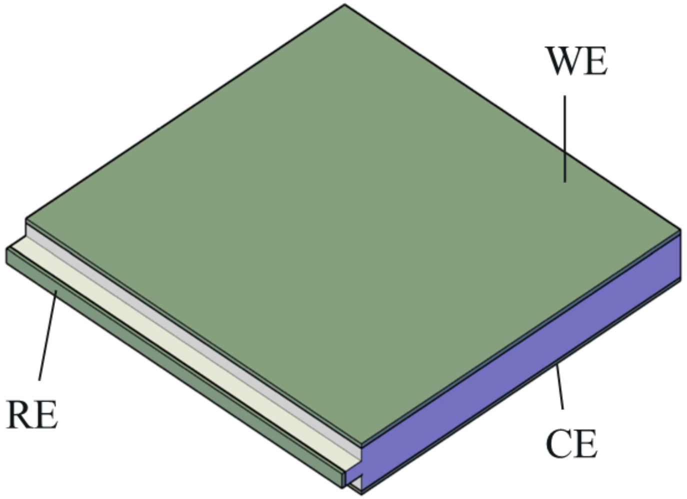
-cross check CE vs RE
-switch WE, CE
-get an idea of WE/CE asymmetry

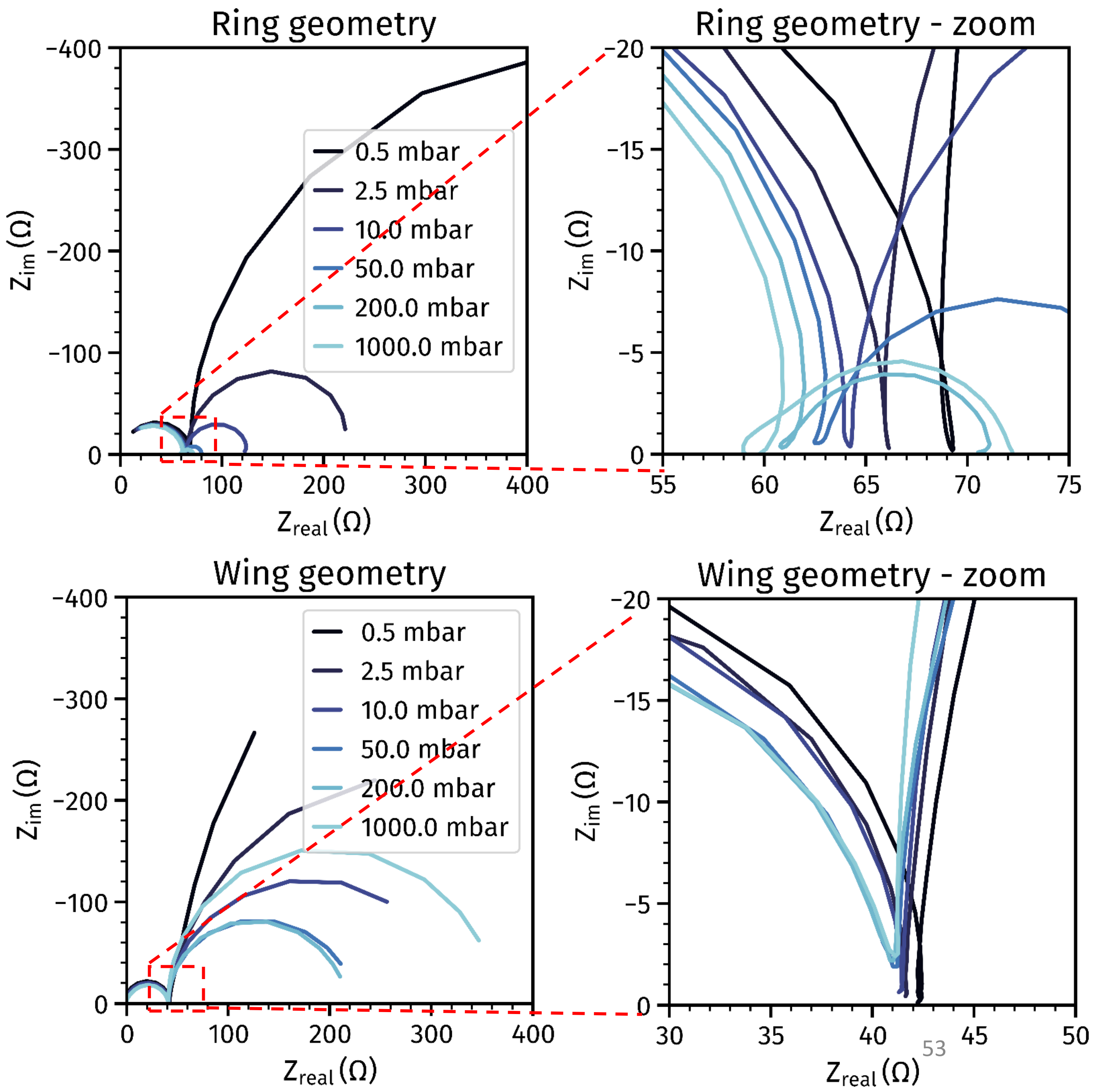




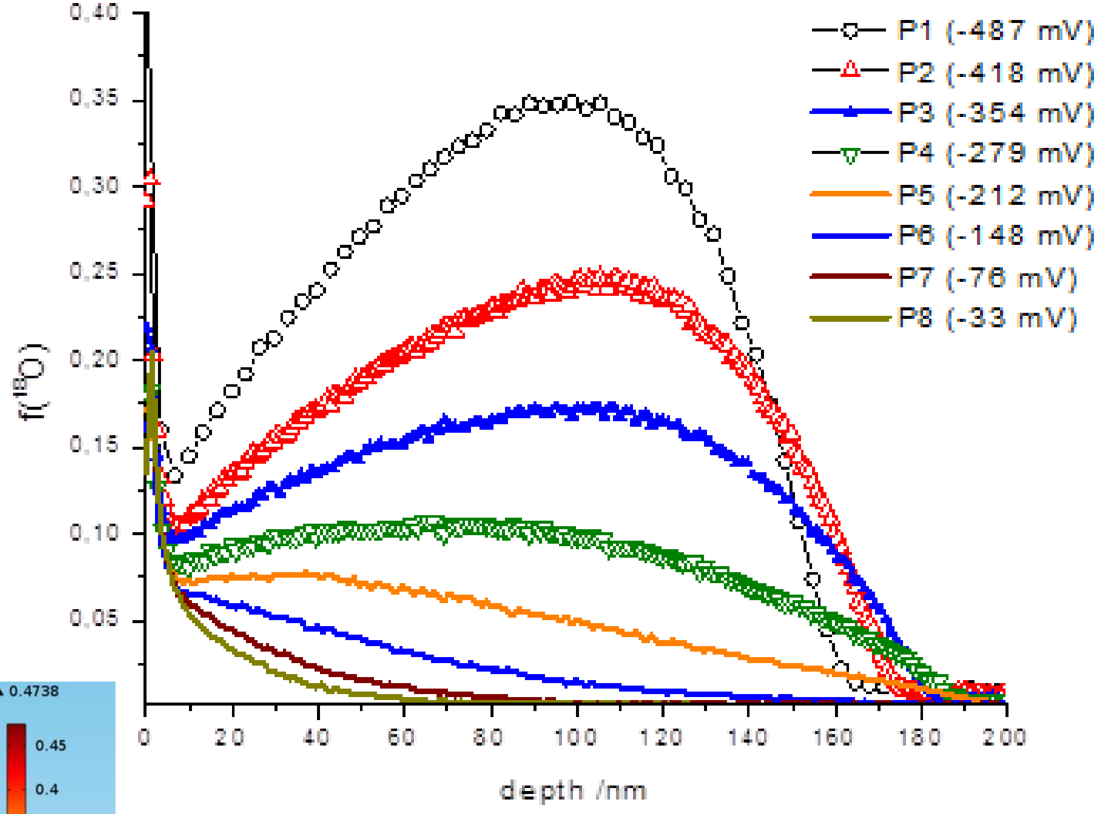
The novel “WING” vs. “RING GEOMETRY”

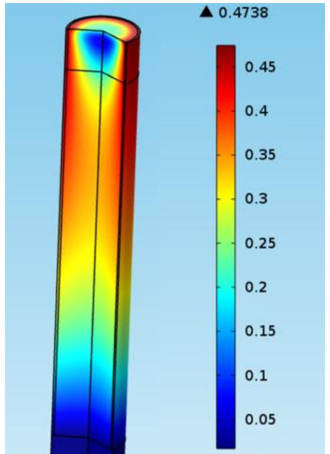


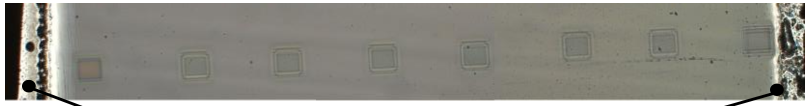




New experimental design for polarization experiments

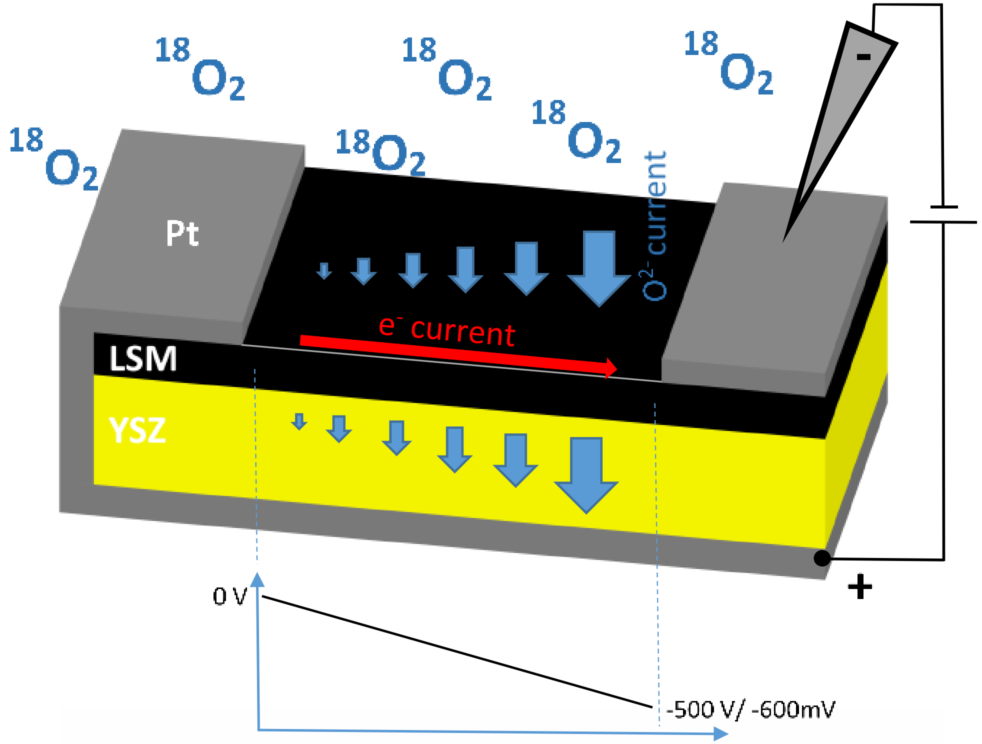


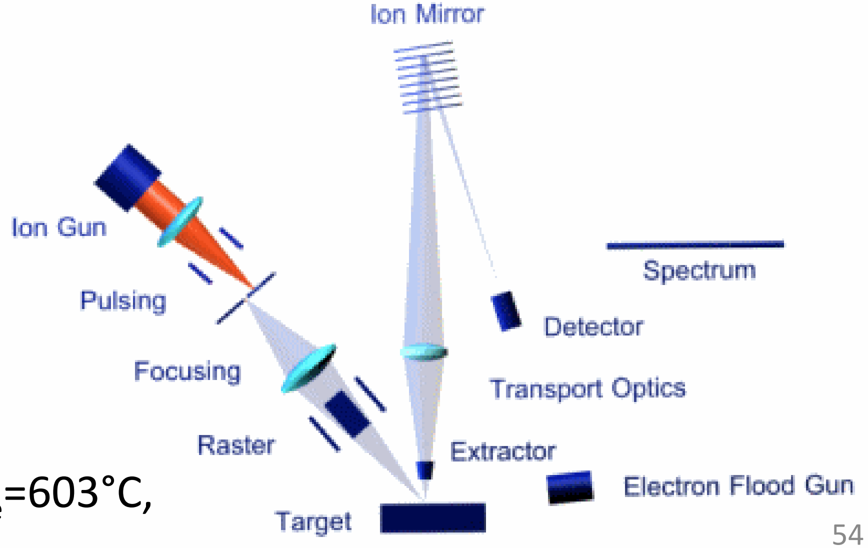




Platinum electrodes

(distance=7.865 mm)

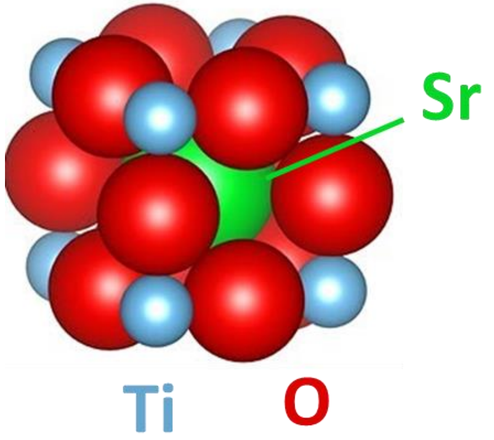




LSM_{600}, $T_{exchange}$=603°C, V=-500 mV;

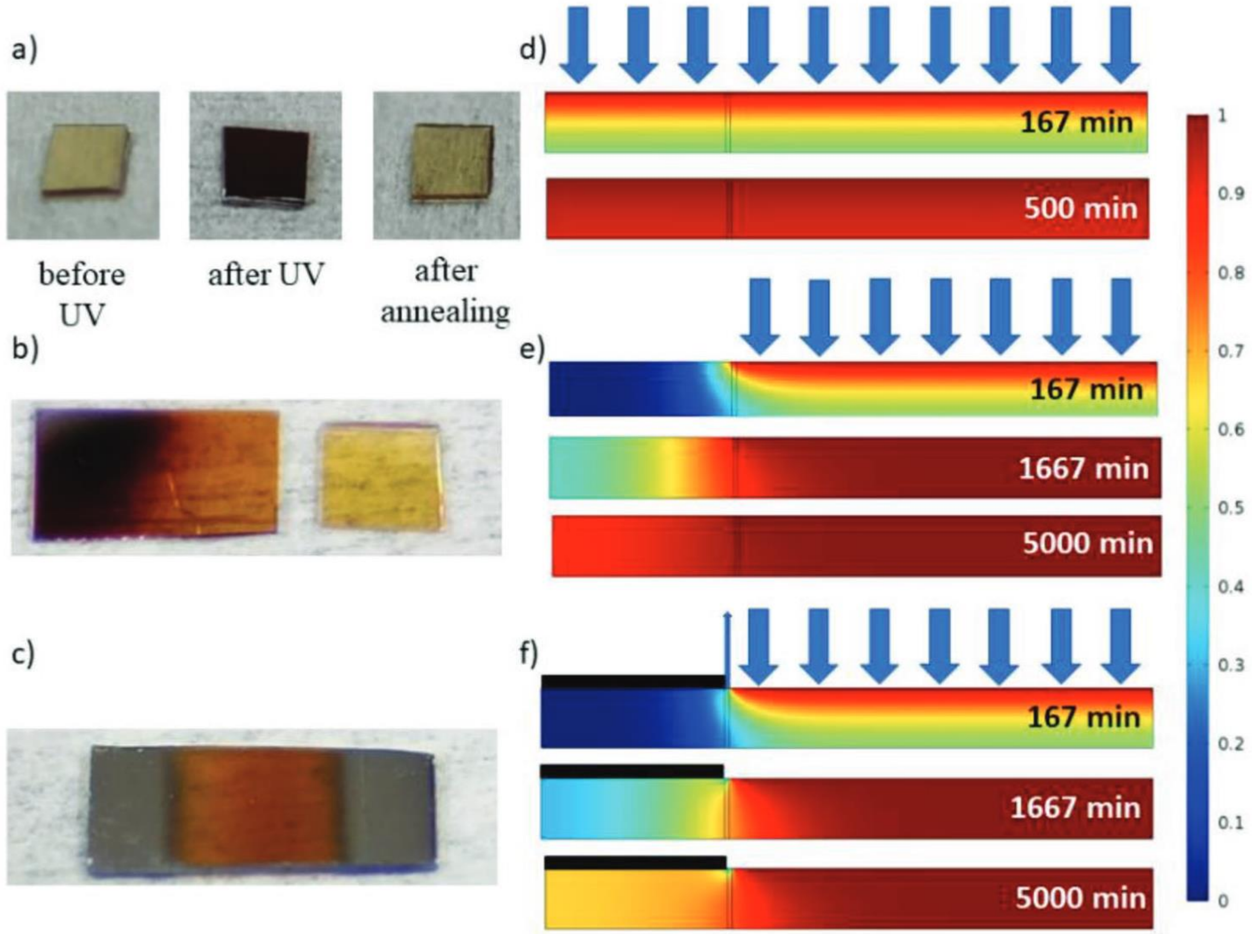
Temperature & light gradient issues

Light experiments (shadowing problem)



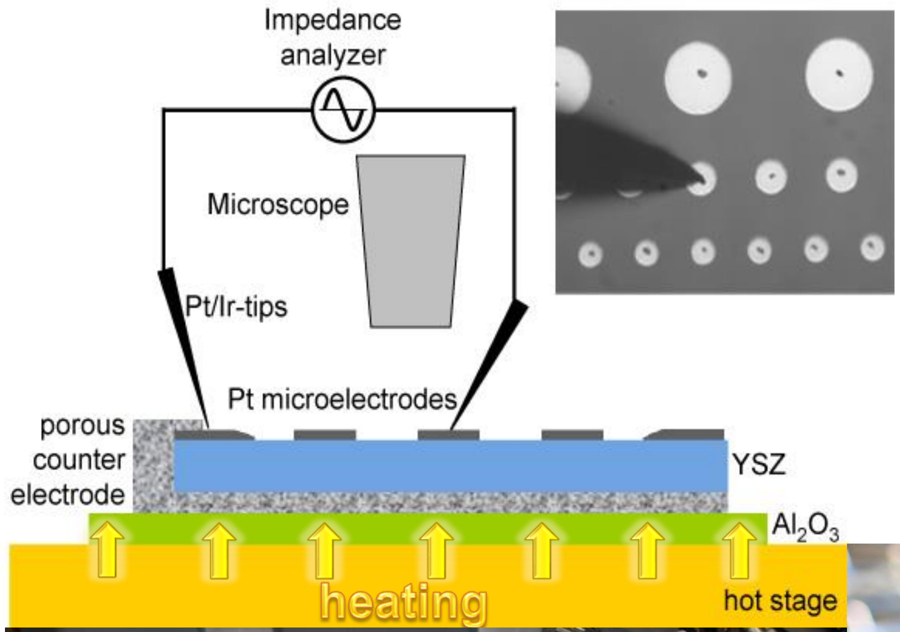
Opto-Ionic effects in $SrTiO_3$

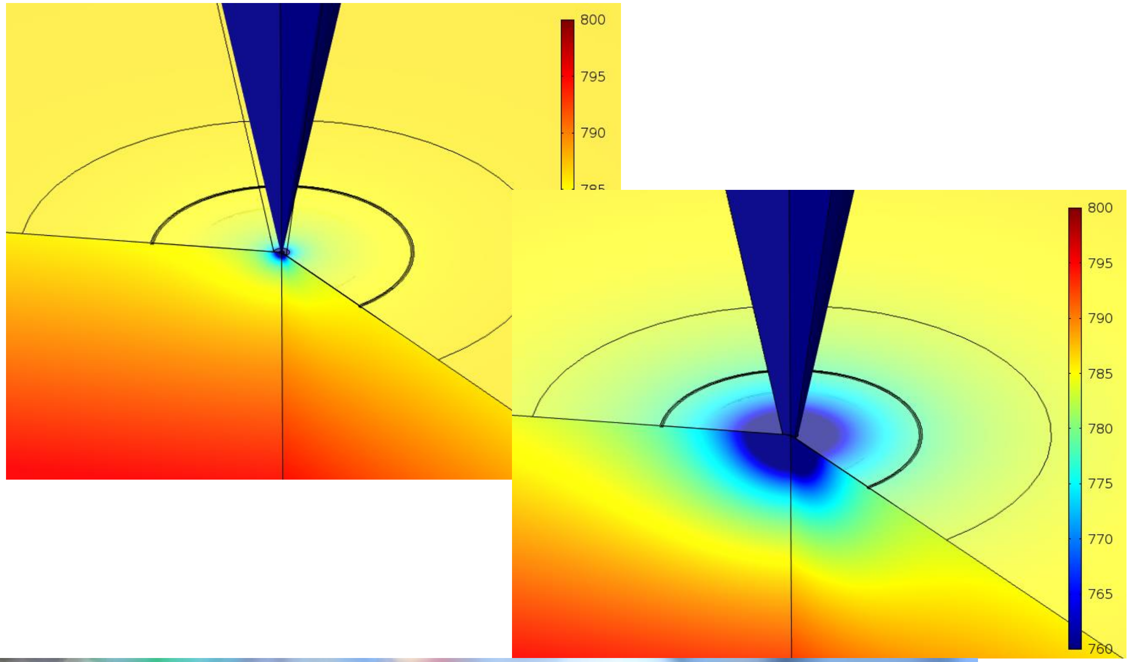
- Perovskite structure
- Model electroceramic
- Indirect bandgap ~3.2 eV

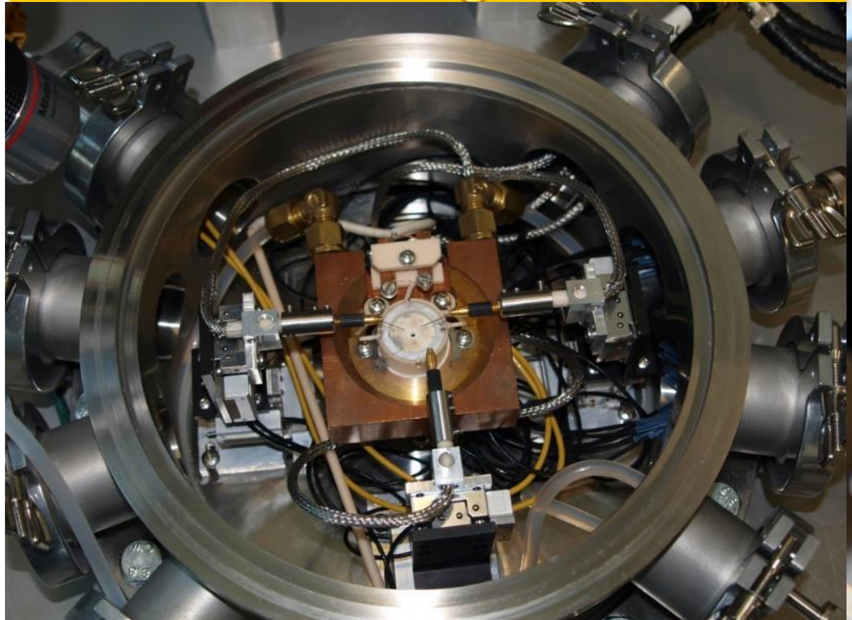


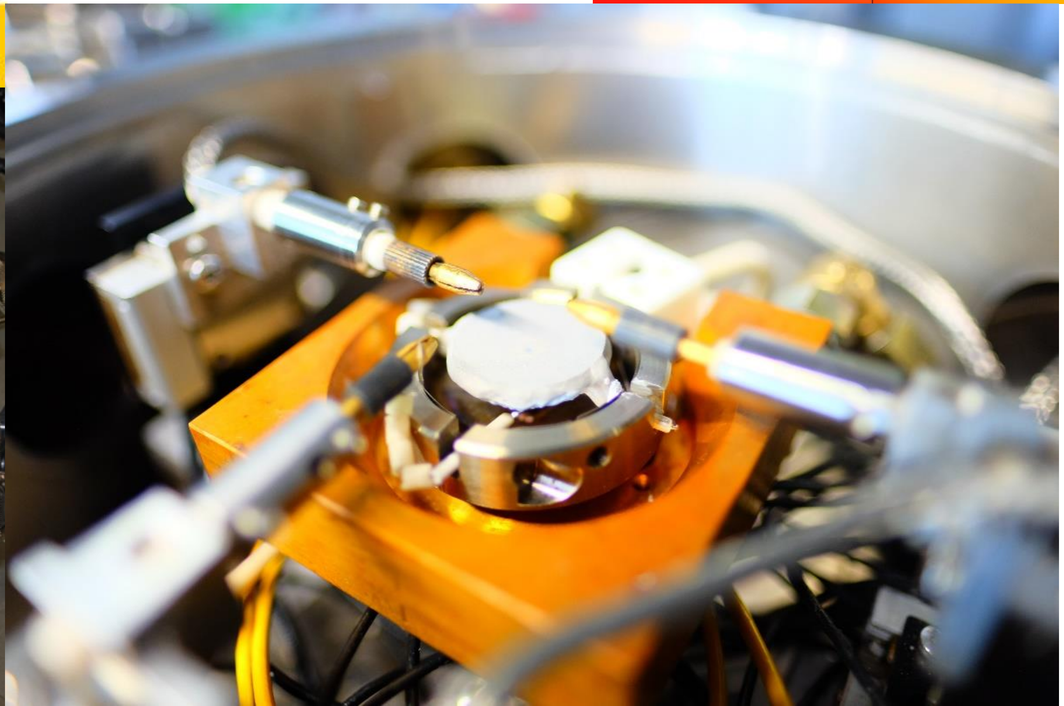
Viernstein, A., Kubicek, M et al., Adv. Funct. Mater. (2019), 29, 23, 1900196C.

Asymmetric heating

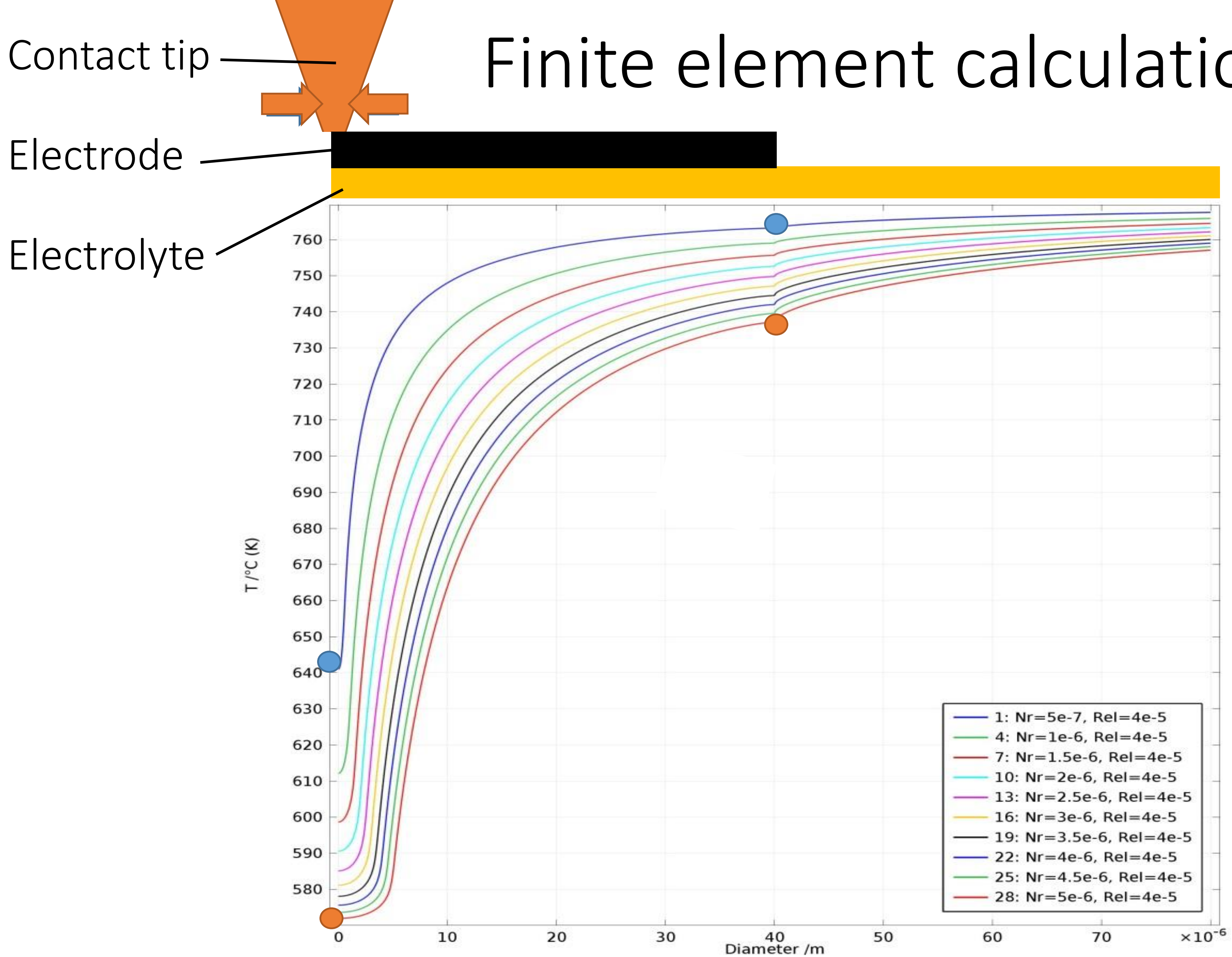






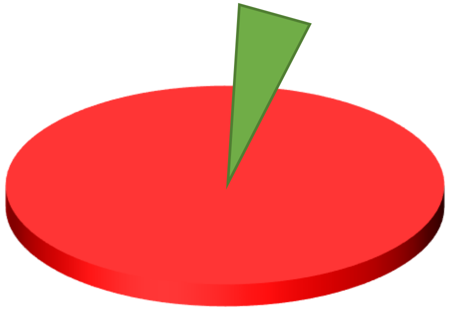


Finite element calculations

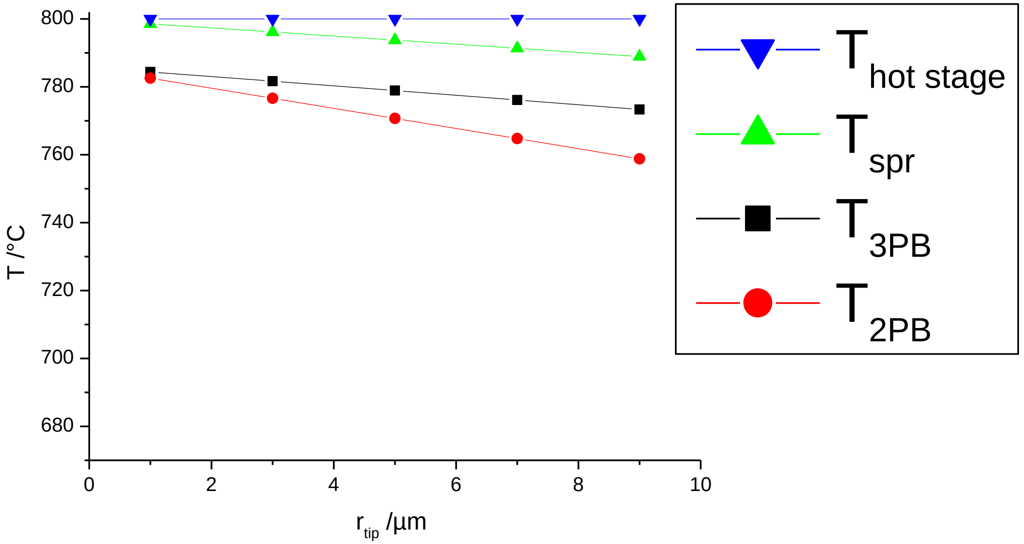


T. M. Huber, et. al. Solid State Ionics 268 (2014): 82-93

Temperatures at differently sized electrodes

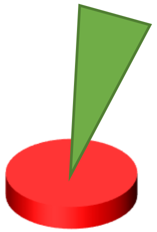


Ø=200 µm

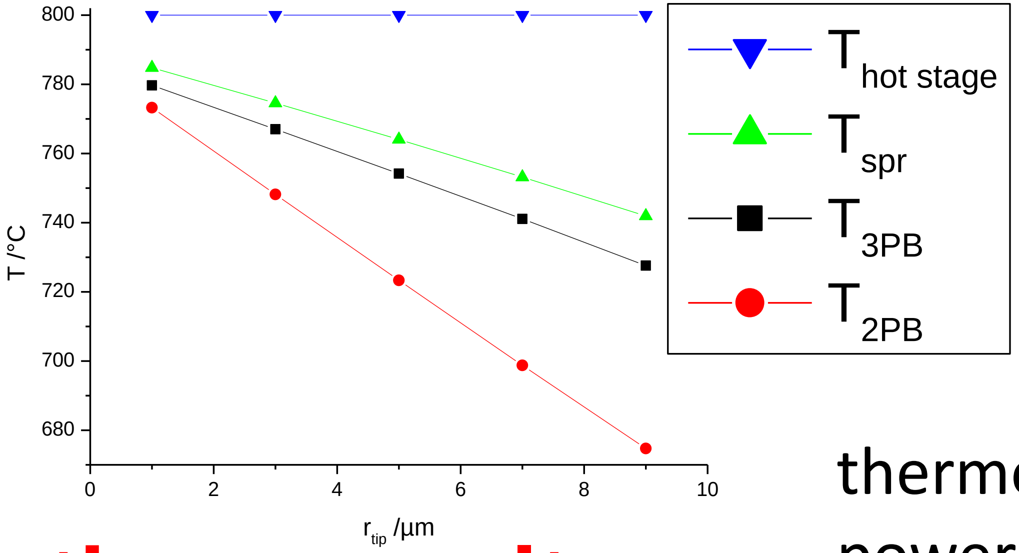


$$\sigma_{ion} = \frac{1}{2d_{ME}R_0} = \sigma^* \cdot e^{-\frac{E_a}{k_B T}}$$

$$T_{spr} = \frac{E_a}{k_B \cdot \ln(2d_{ME}R_0)}$$



Ø=50 µm



$$T_{2PB} = \frac{4}{d_{ME}^{\;2}} \int T(r) \cdot r \cdot 2 \cdot dr$$

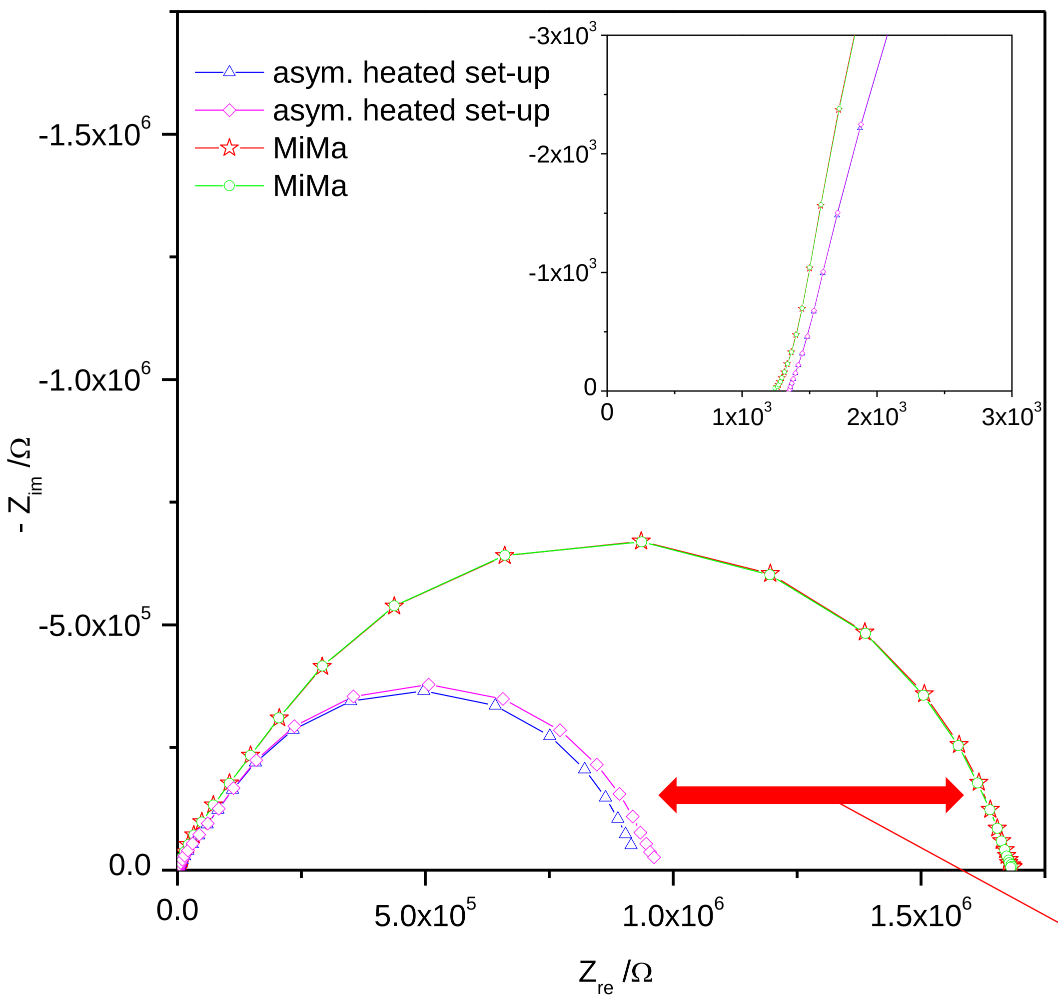
thermoelectric power (0.486 mV/K YSZ in air [1])

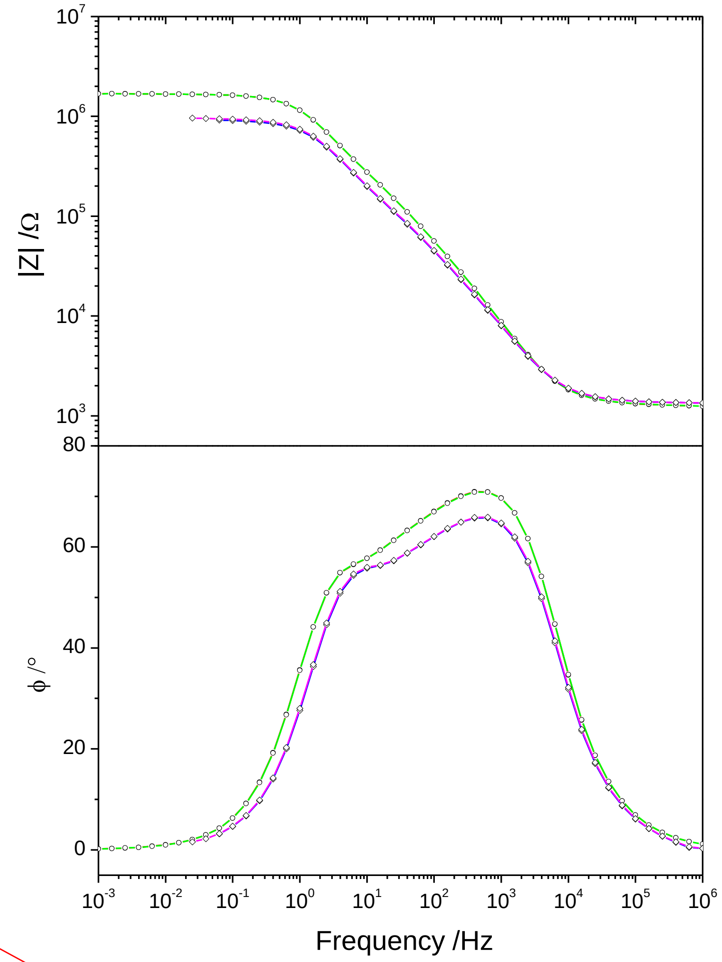
problem: ΔT→ thermo voltage

E. Ahlgren, F. W. Poulsen; Solid State Ionics 70/71(1994) 528-532

Impedance spectroscopy on microelectrodes

145 µm squared LSM microelectrode at 760 °C





error induced by thermovoltage

T. M. Huber, et. al. Solid State Ionics 268 (2014): 82-93

Institute of Chemical Technologies and Analytics

huber scientific

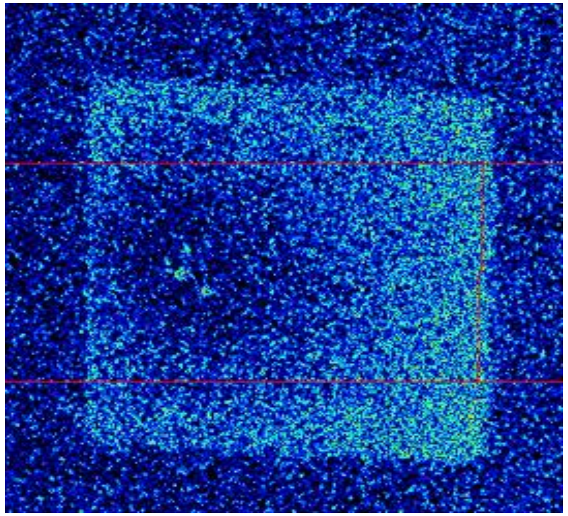
novel measurement solutions

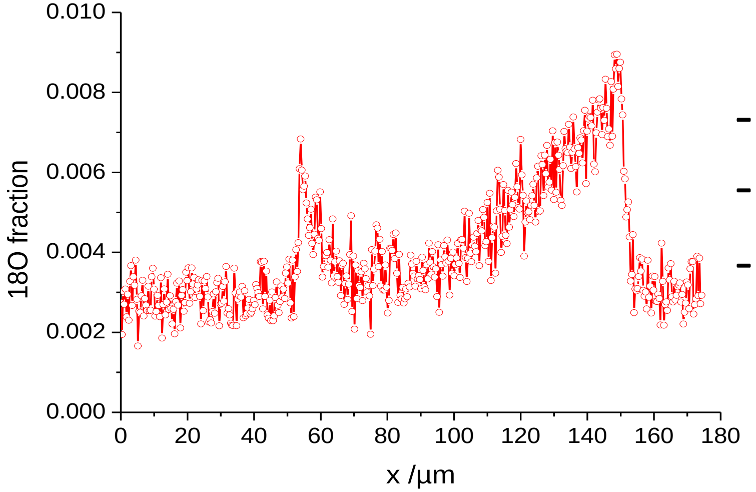
PIZZA

- Surface de wetting → Mozarella

DC-polarization with ^{18}O tracer

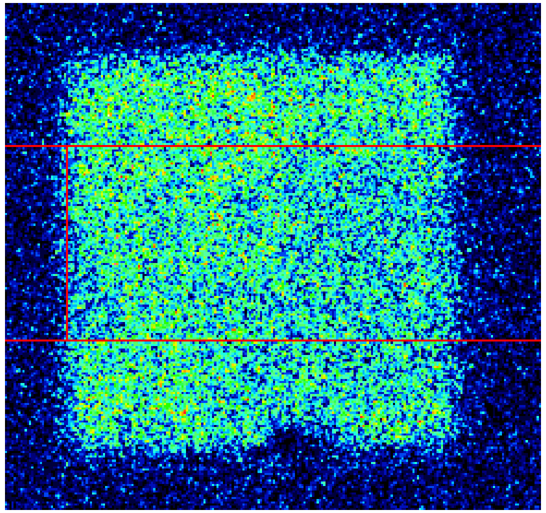
asymmetrically heated set-up

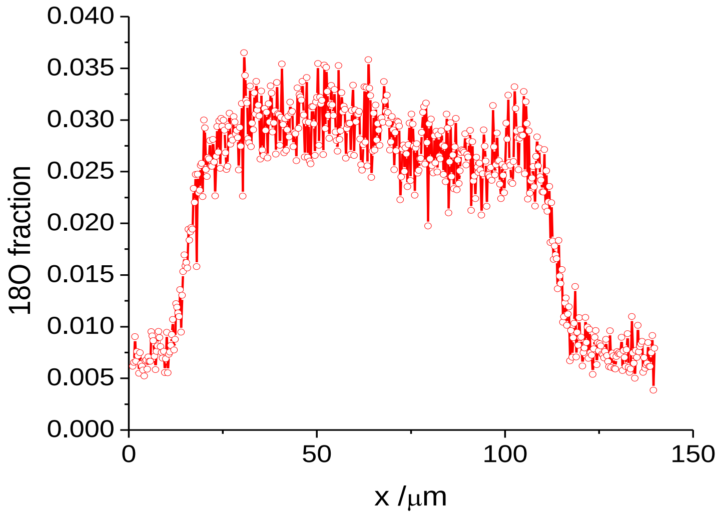




- 369°C
- -850 mV bias
- $5 \cdot 10^{-8}$ A

symmetrically heated set-up

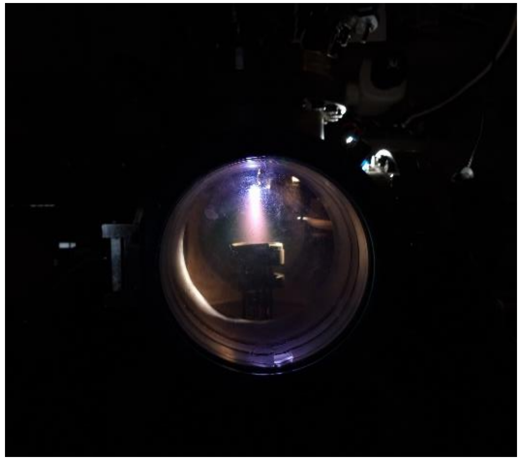


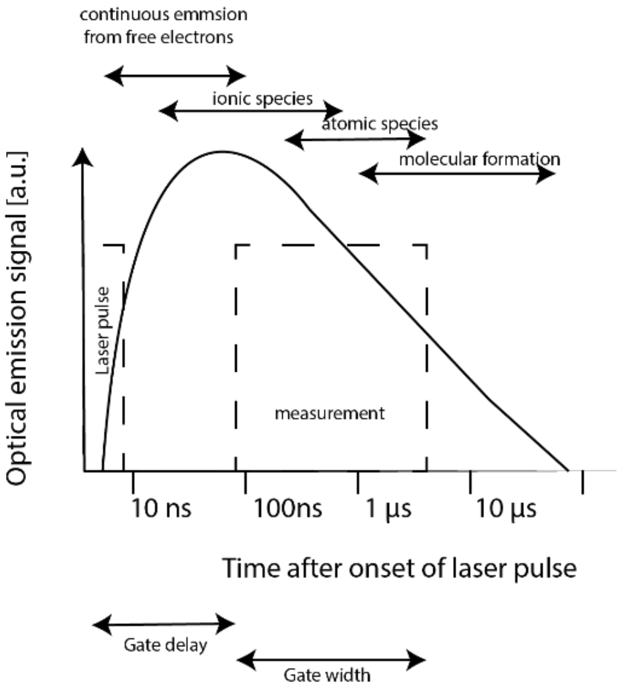


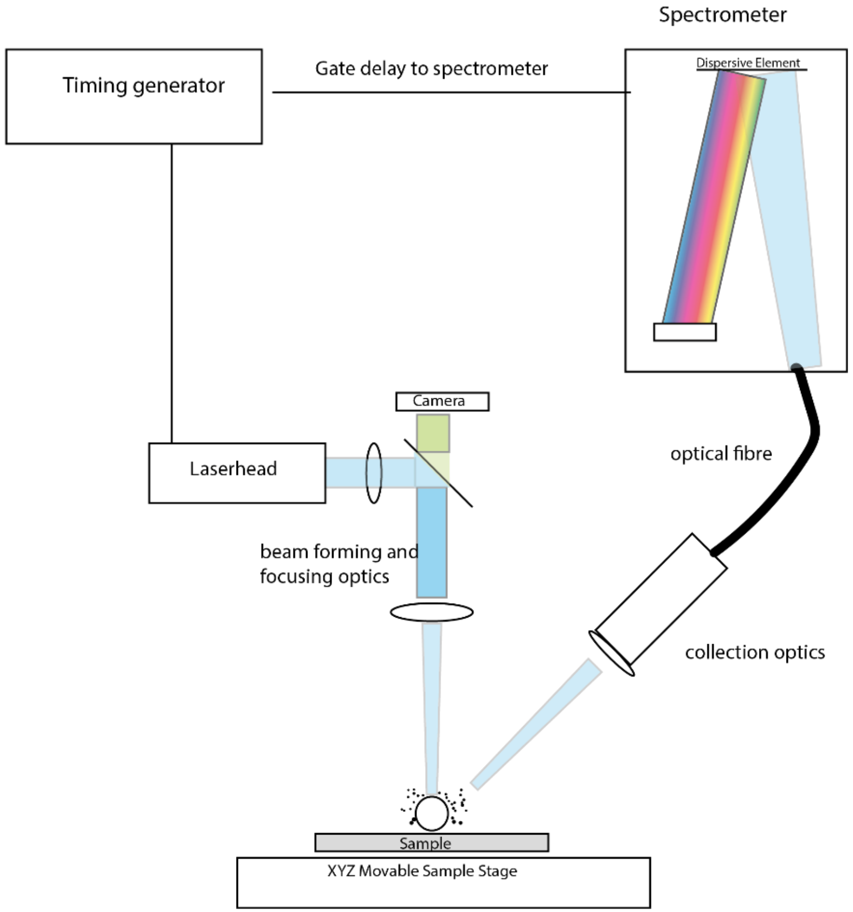
- 466°C
- -900 mV bias
- $7.5 \cdot 10^{-7}$ A

Laser induced breakdown spectroscopy

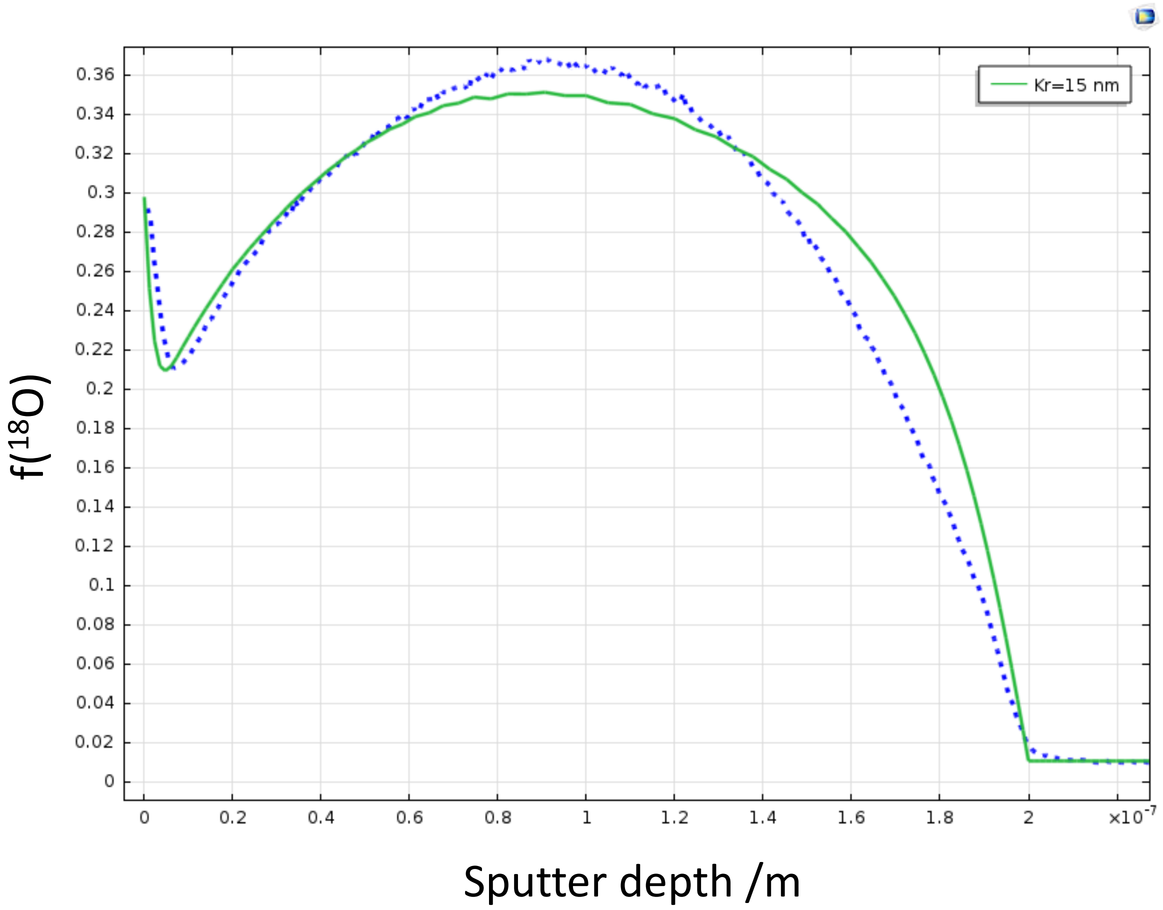
- **Laser pulse evaporates sample**
  - **(same mechanism as PLD)**
- **Removed material forms plasma**
- **Plasma emits characteristic elemental emission → detected and quantified**

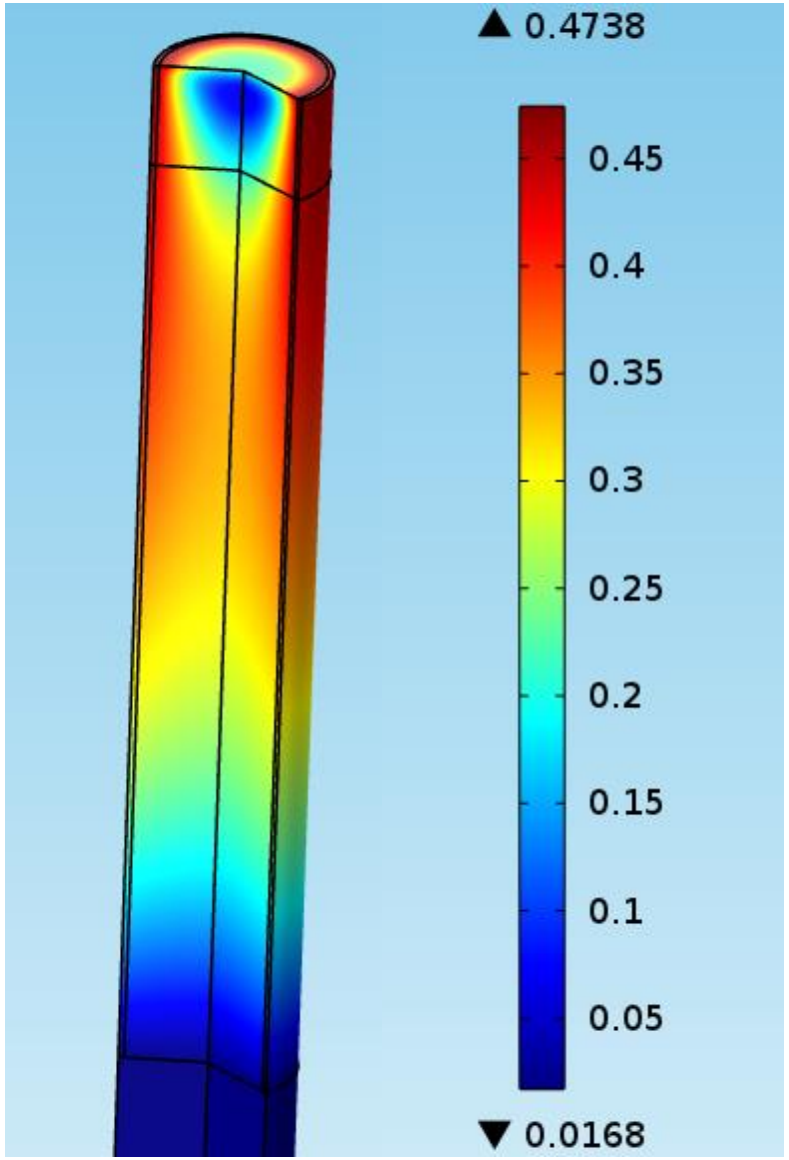






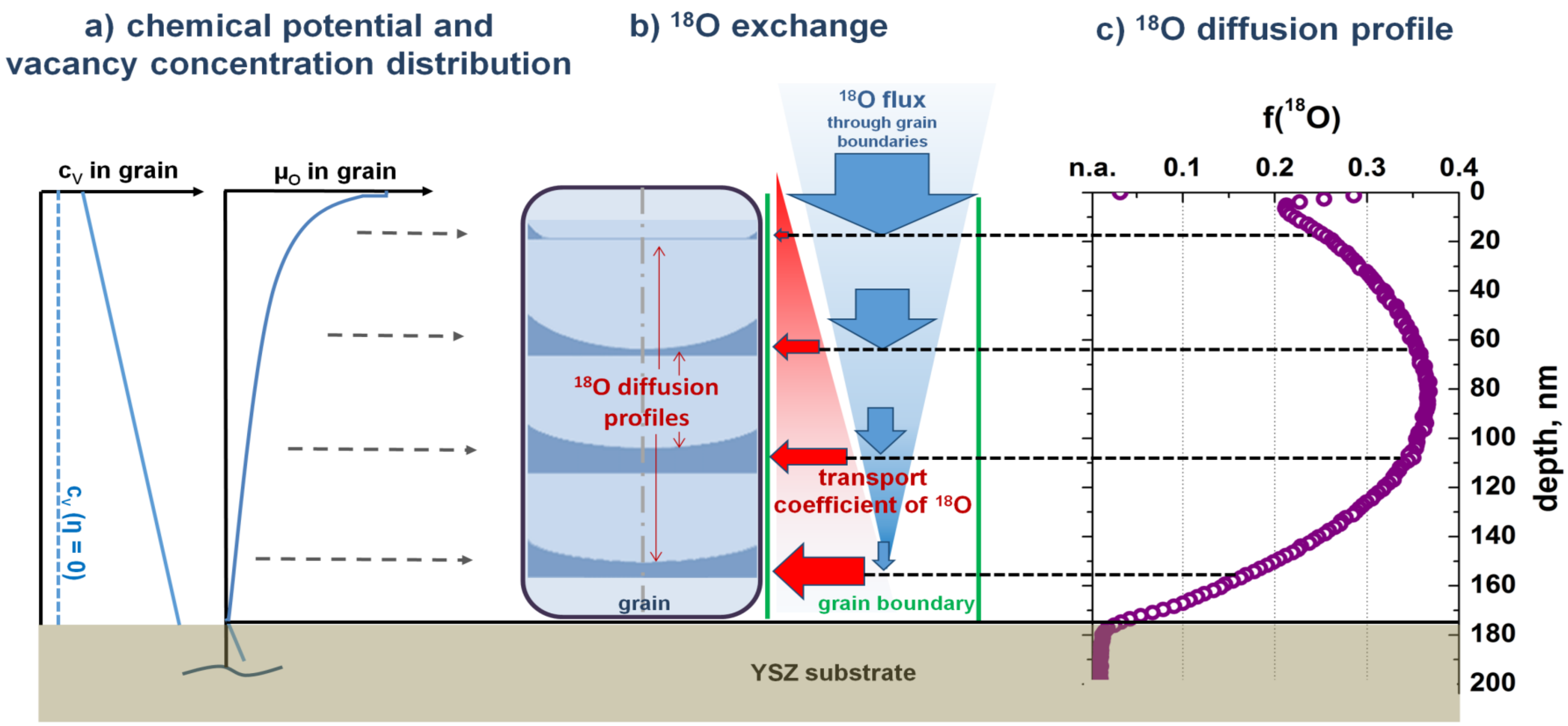
Apparent uphill diffusion /finite element fitting





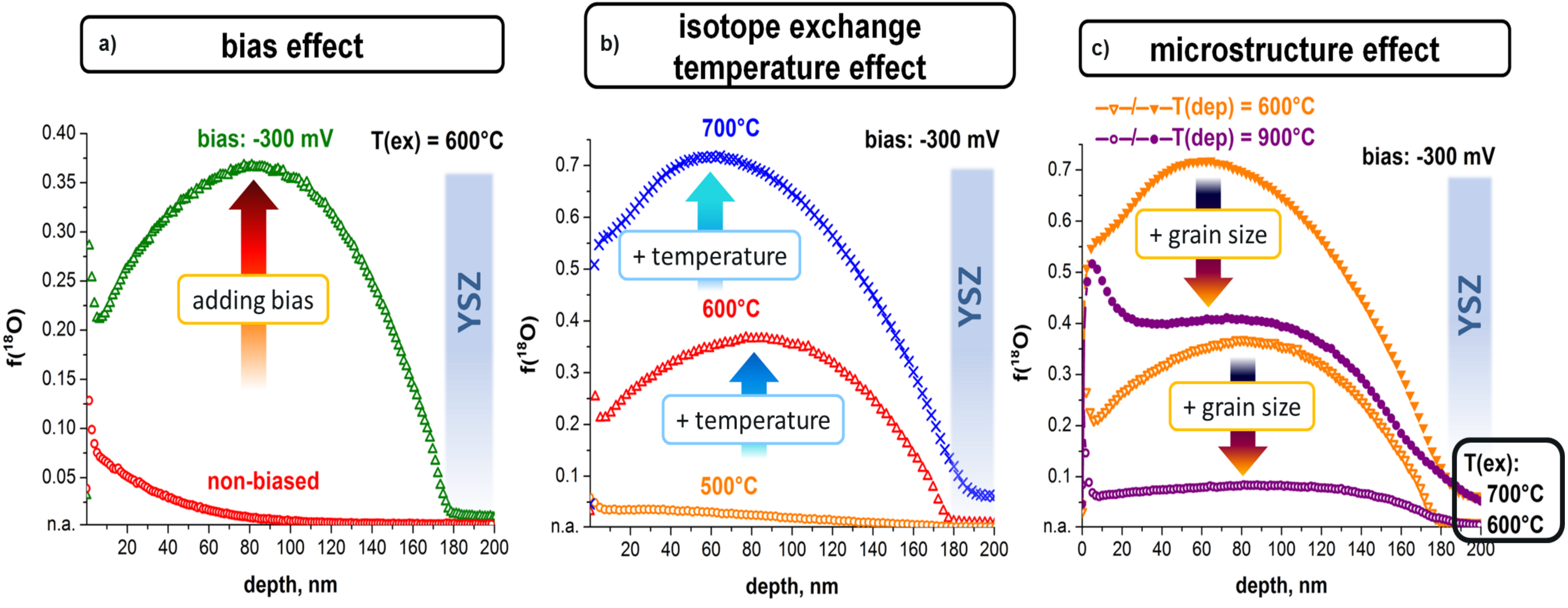
T. M. Huber & E. Navickas et al. ChemElectroChem, 2, 10, 1487–1494, 2015

Evolution of apparent uphill diffusion



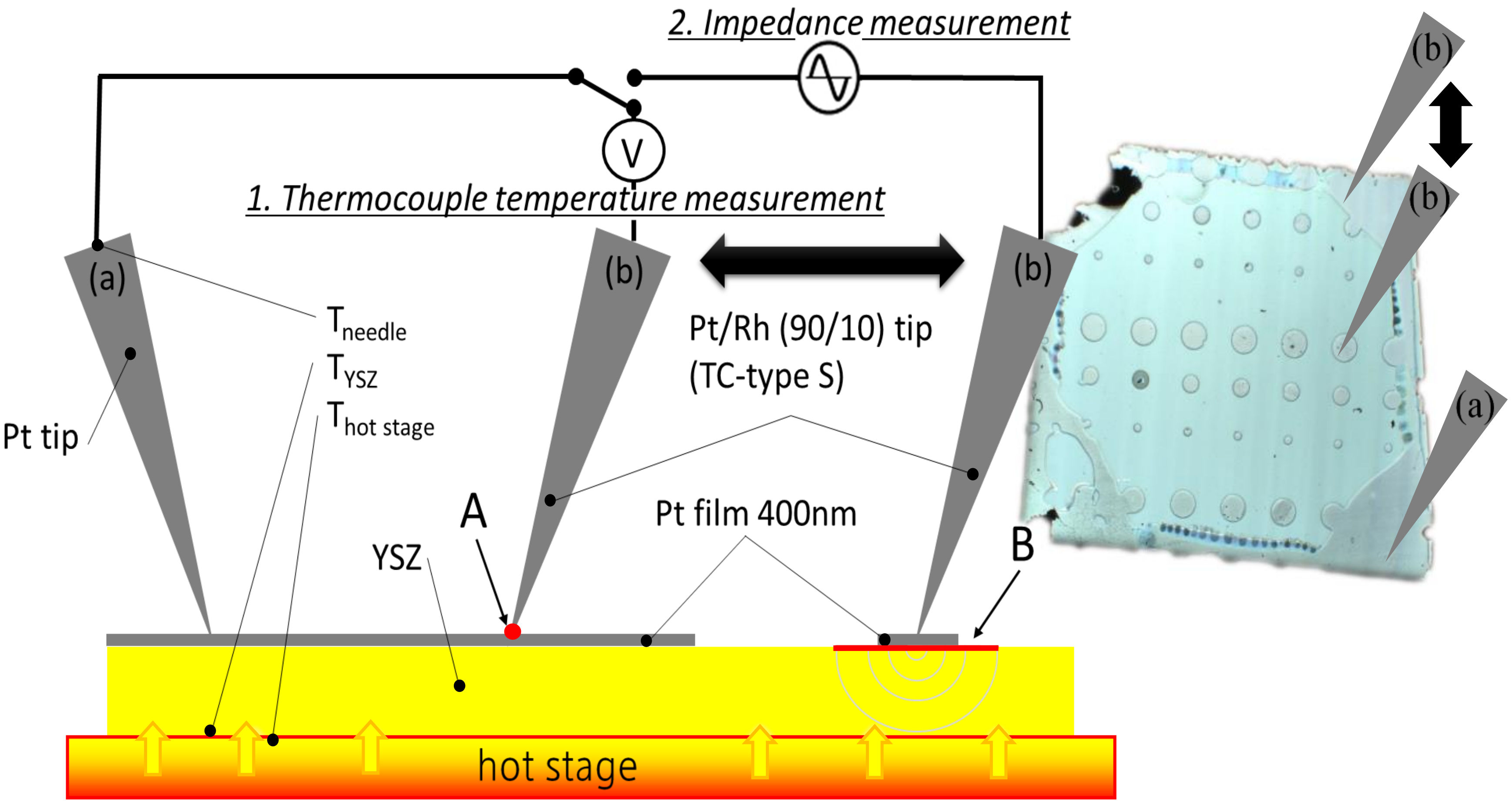
$$D_b(z) = D_b(z=0)\cdot\left(1+\Delta\frac{z}{h}\right)$$

Voltage effect on oxygen tracer diffusion



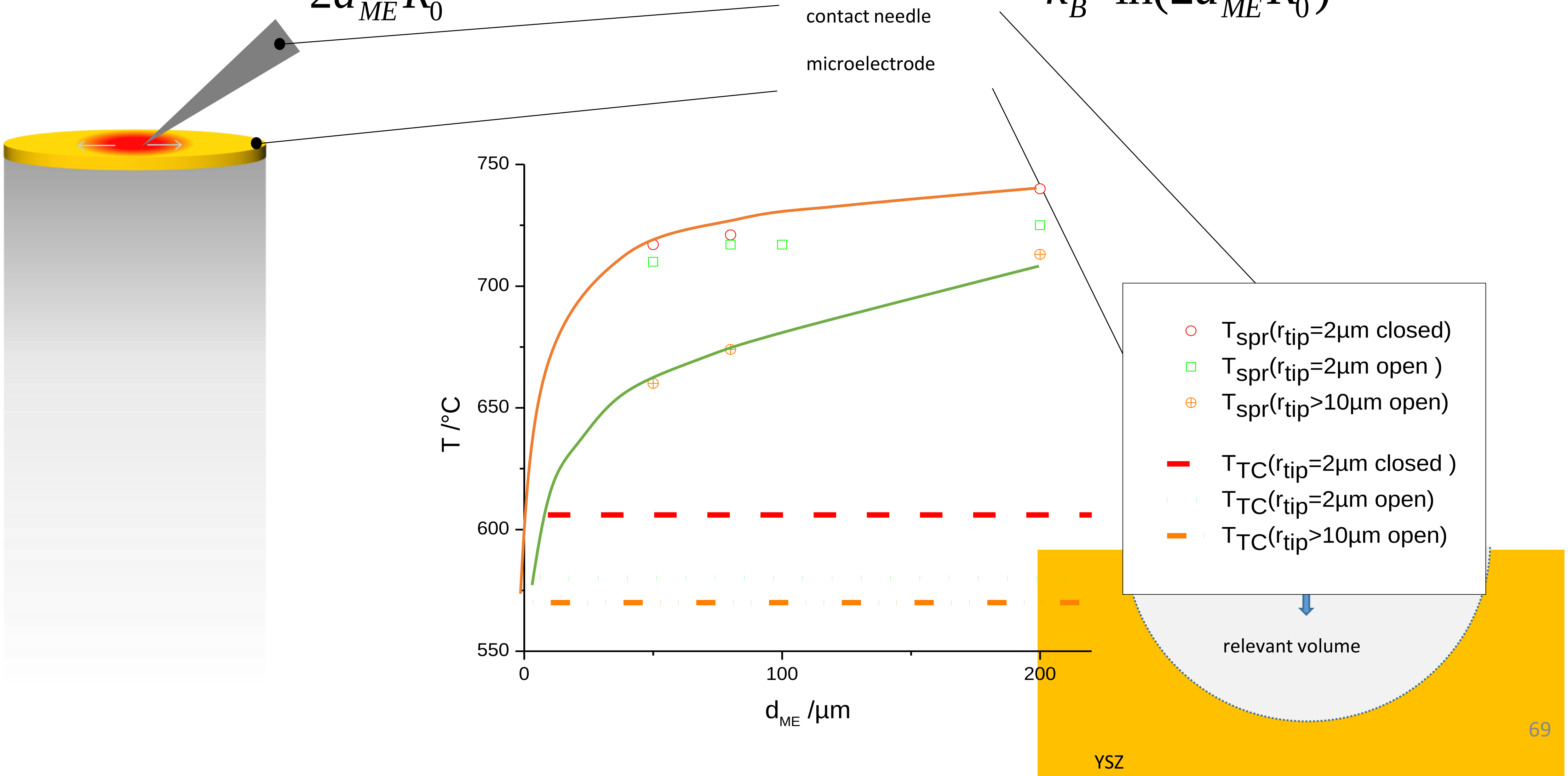
T. M. Huber & E. Navickas et al. ChemElectroChem, 2, 10, 1487–1494, 2015

Micro-thermocouple

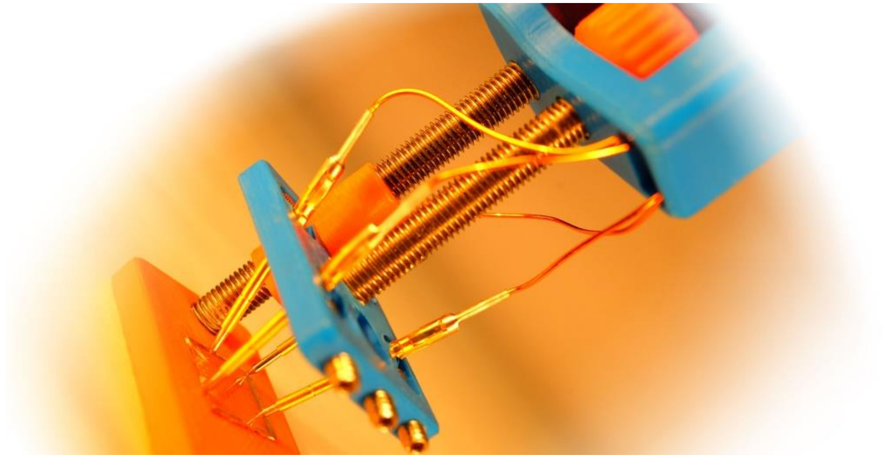


Visualization of temperature gradients

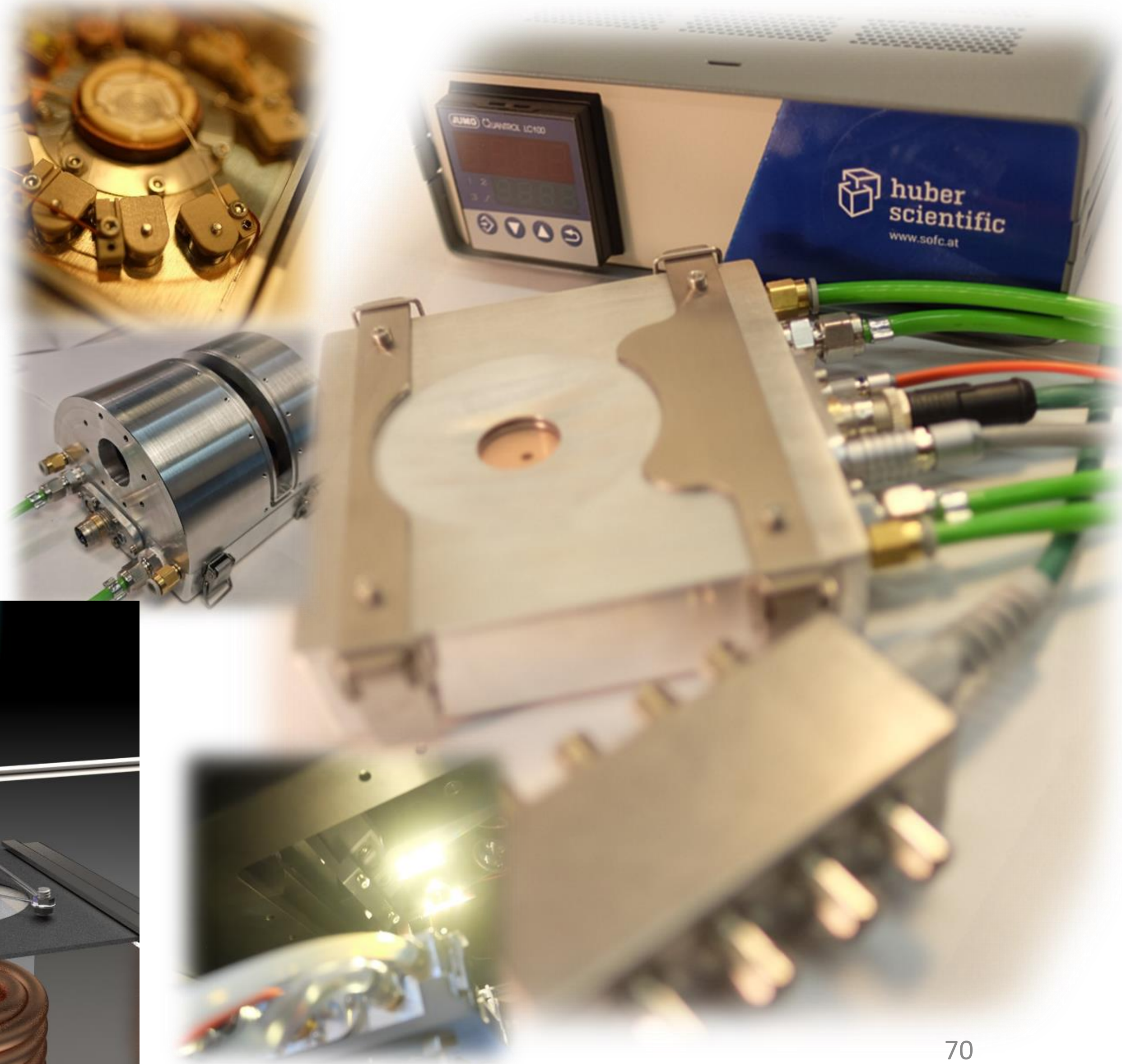
$$\sigma_{ion} = \frac{1}{2d_{ME}R_0} = \sigma^* \cdot e^{-\frac{E_a}{k_B T}} \Rightarrow T_{spr} = \frac{E_a}{k_B \cdot \ln(2d_{ME}R_0)}$$



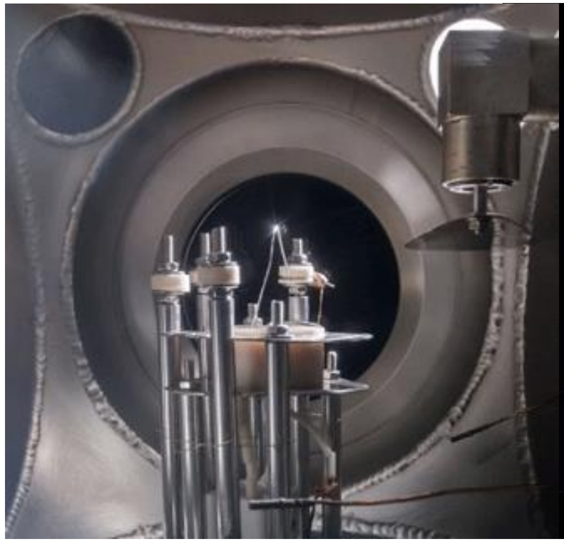
IN SITU NEUTRON REFLECTIVITY

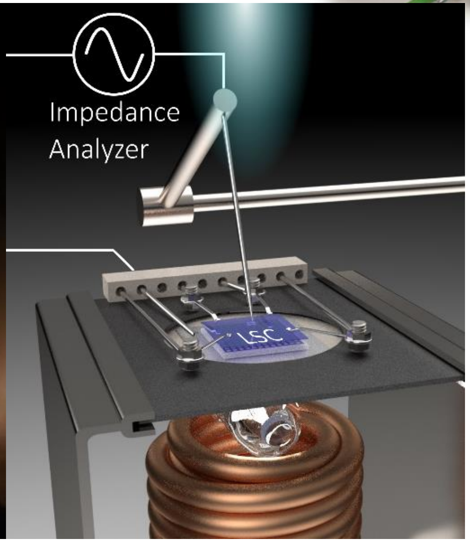


MINI CHAMBER
FOR THIN FILMS & DEVICES



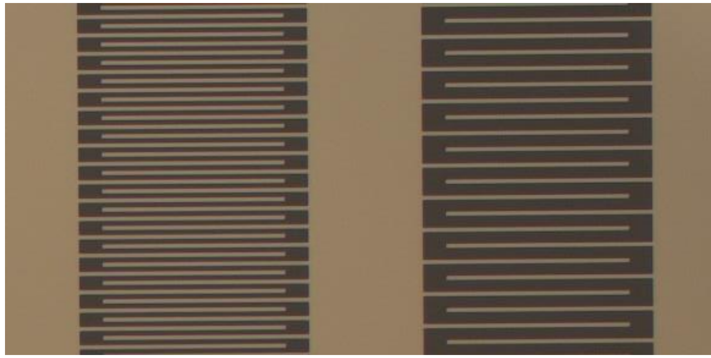
IN SITU I-PLD & I-PVD HEATER

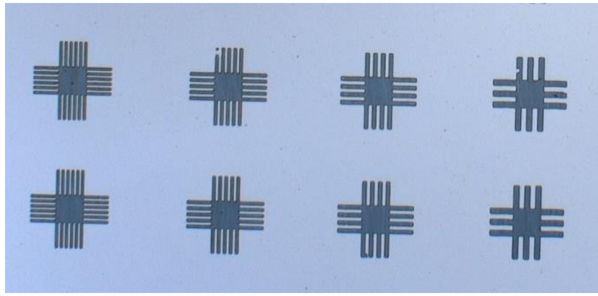


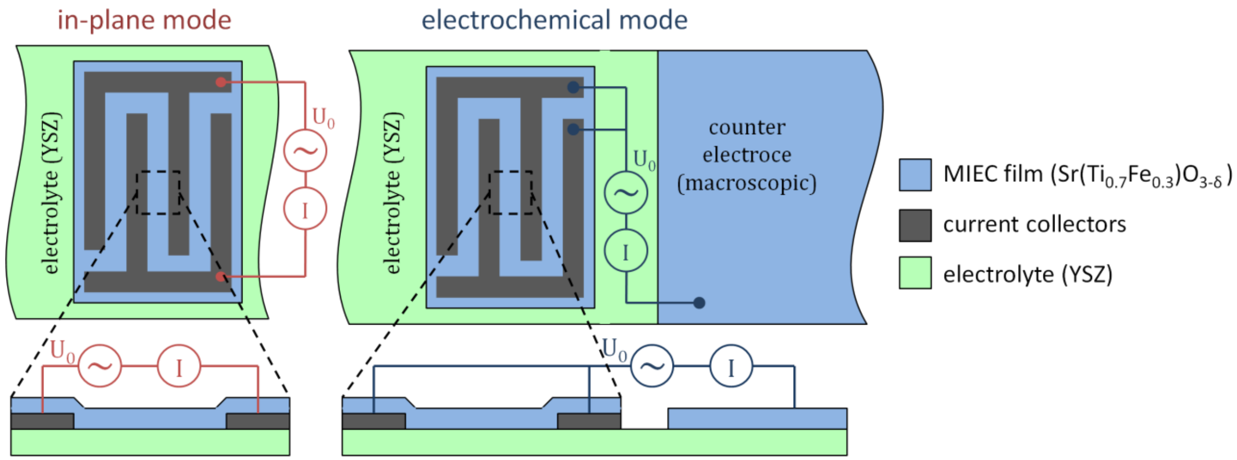


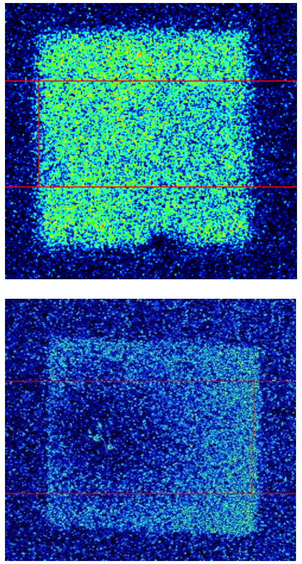
Advantages of micro patterned thin film electrodes

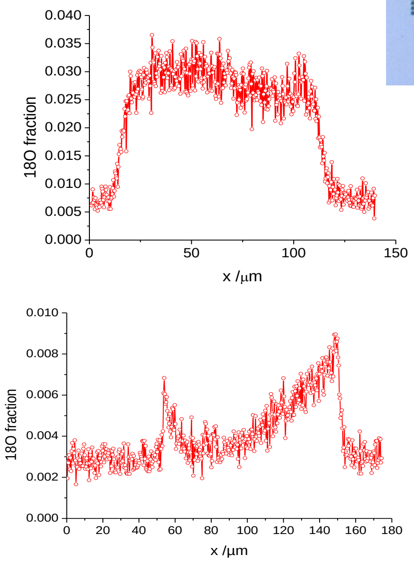
- Well-defined geometry (variable L3PB, …)
- Reference electrode can be omitted
- Large number of electrodes on each sample
- Direct access to active surfaces in SIMS-studies, …
- Current voltage measurement measurements

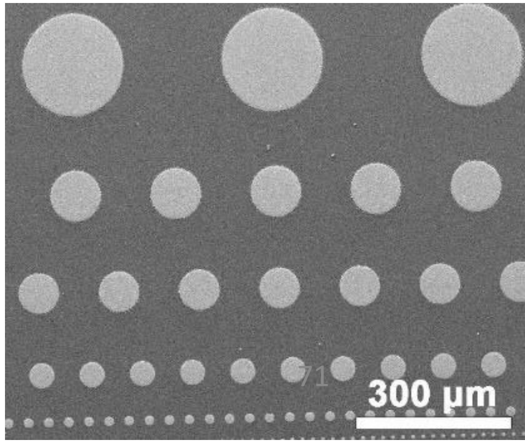


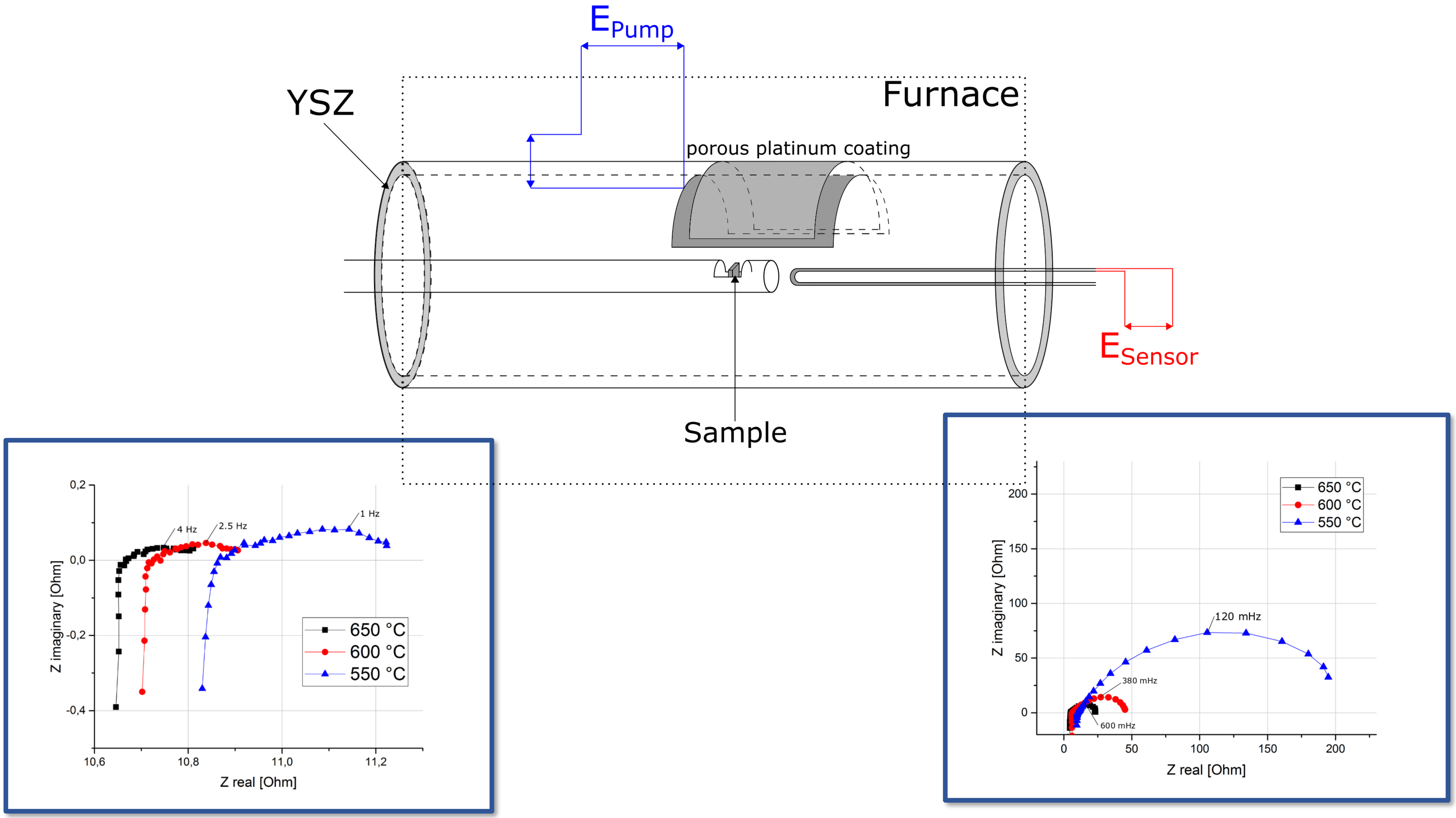






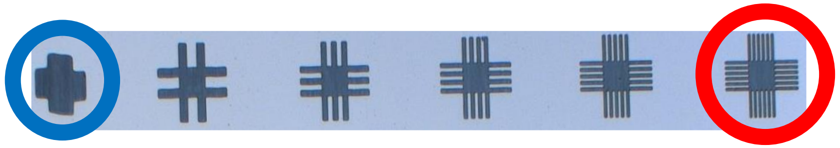


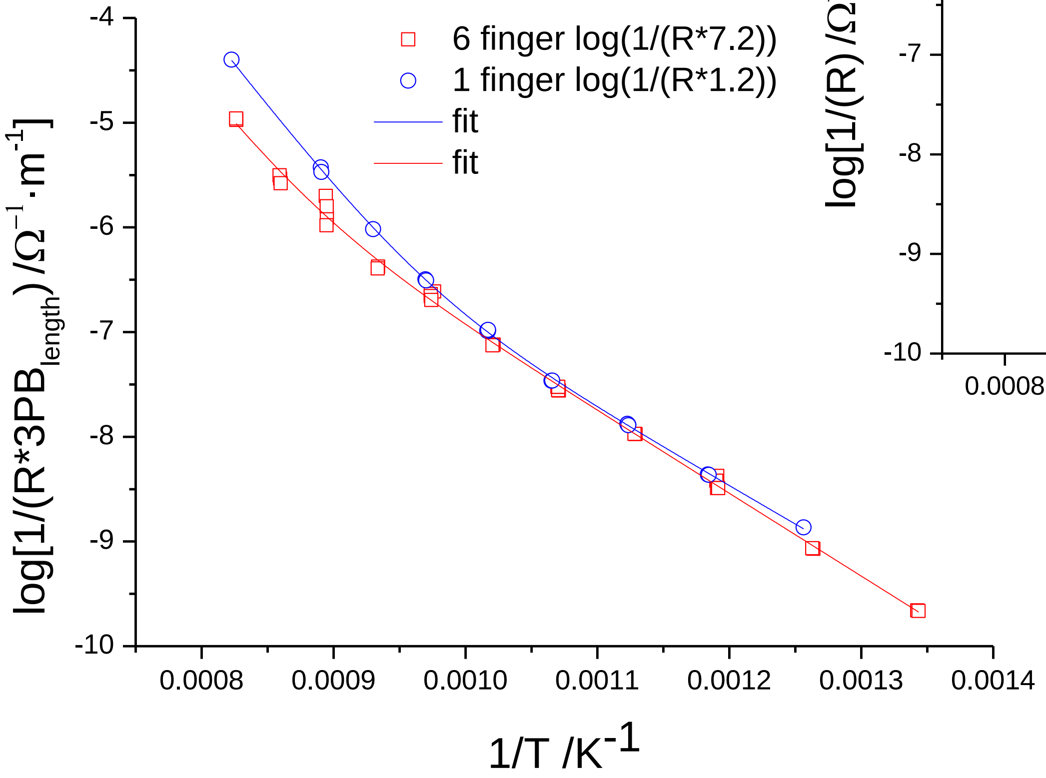


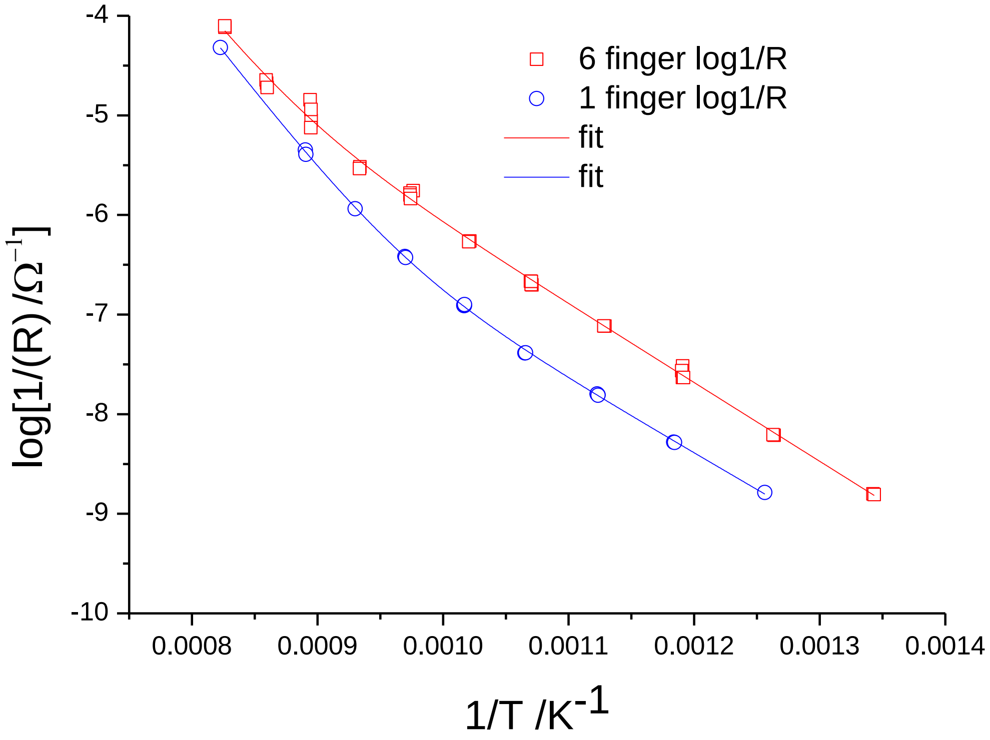


E Pump
YSZ
Furnace
porous platinum coating
E Sensor
Sample
Z imaginary [Ohm]
Z real [Ohm]
4 Hz
2.5 Hz
1 Hz
650 °C
600 °C
550 °C
120 mHz
380 mHz
600 mHz

Ridge electrodes, variation of 3PB



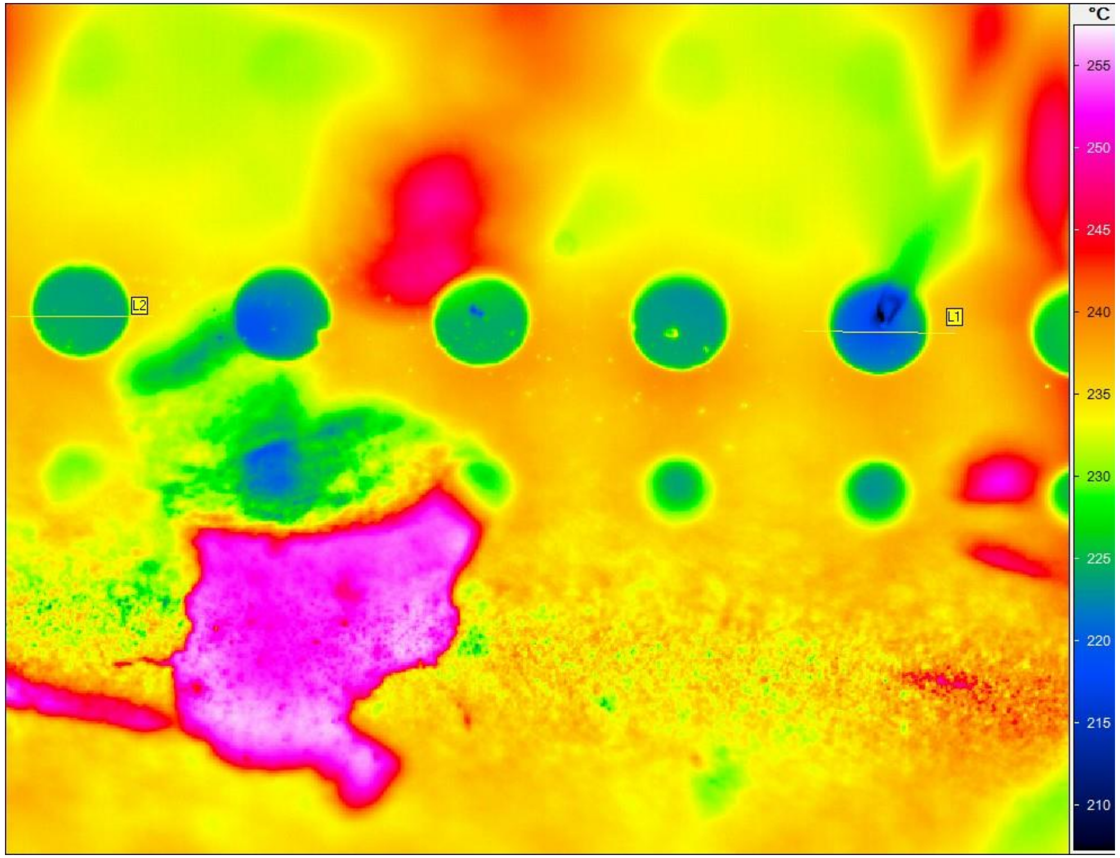




thickness: 240 nm

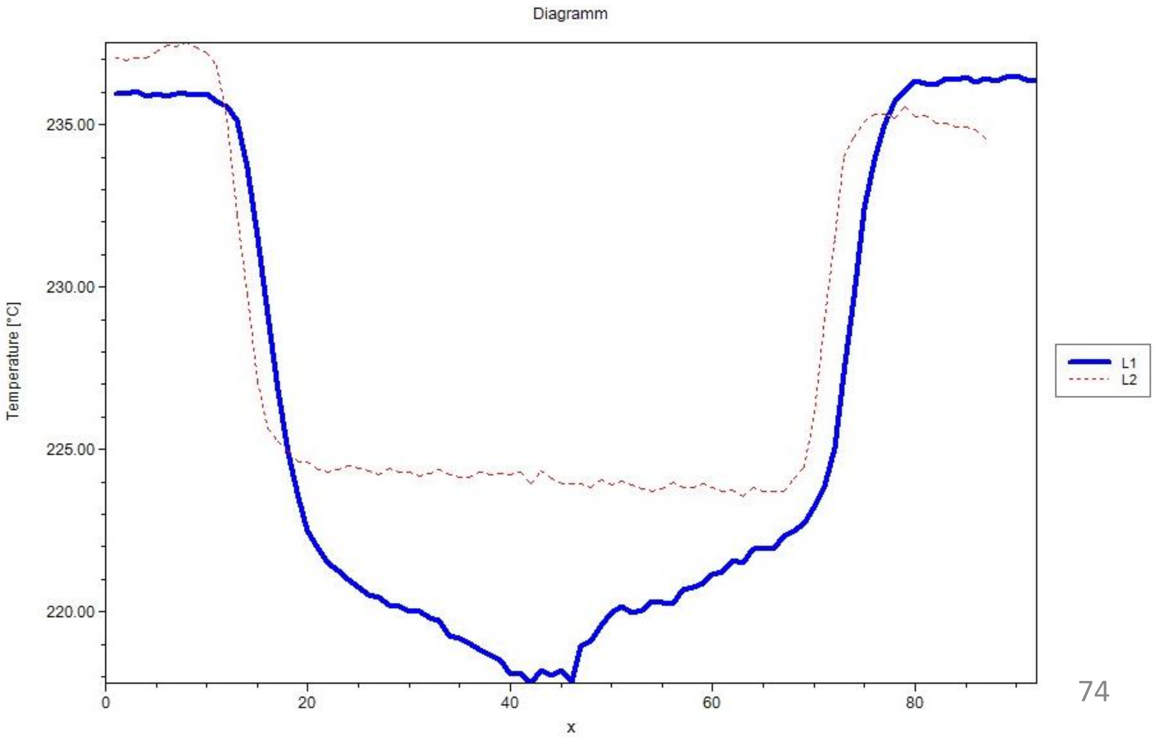
all electrodes have the same surface area

Infrared camera

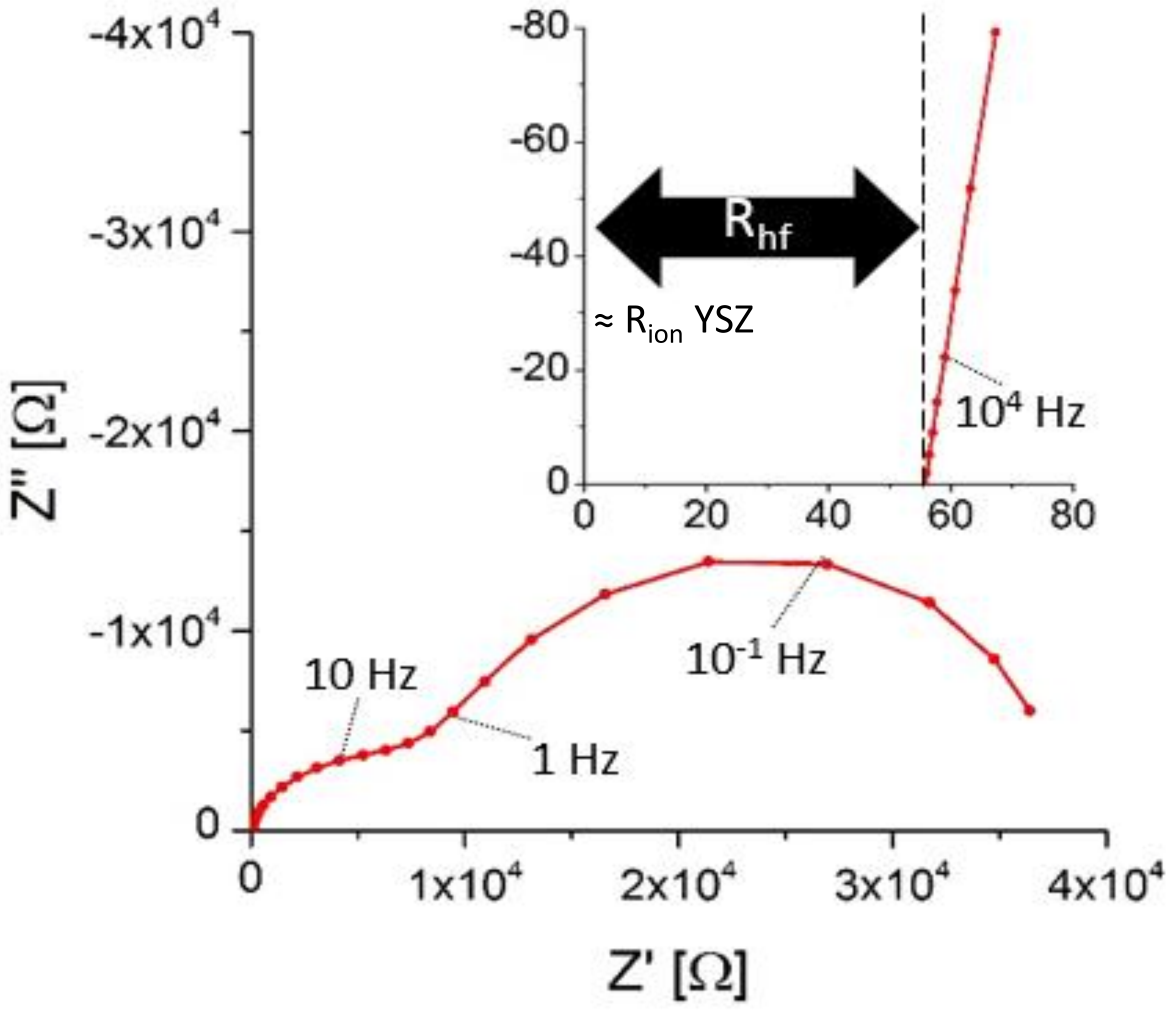


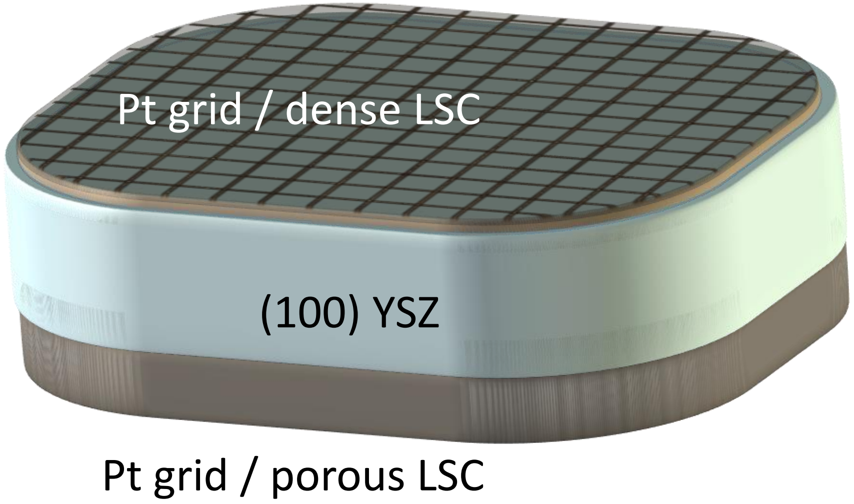
Infratec, ImageIR ®9300

- 200 µm LSM electrode
- 300 °C furnace temperature
- visualizing temperature gradient



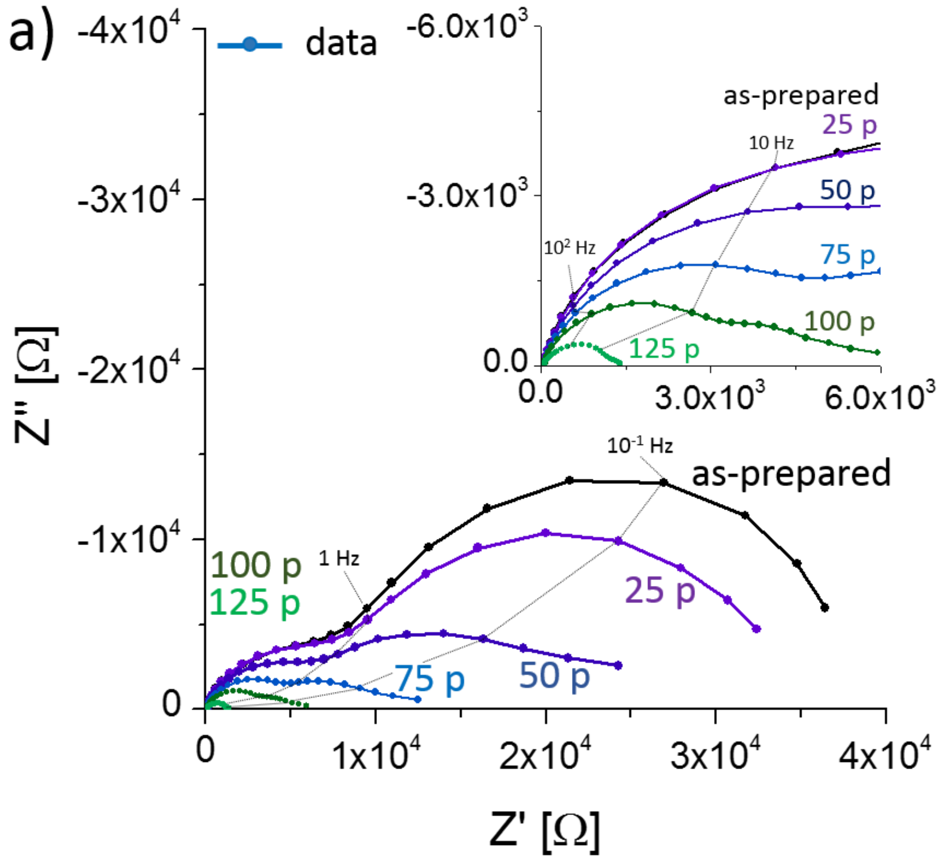
Temperature control

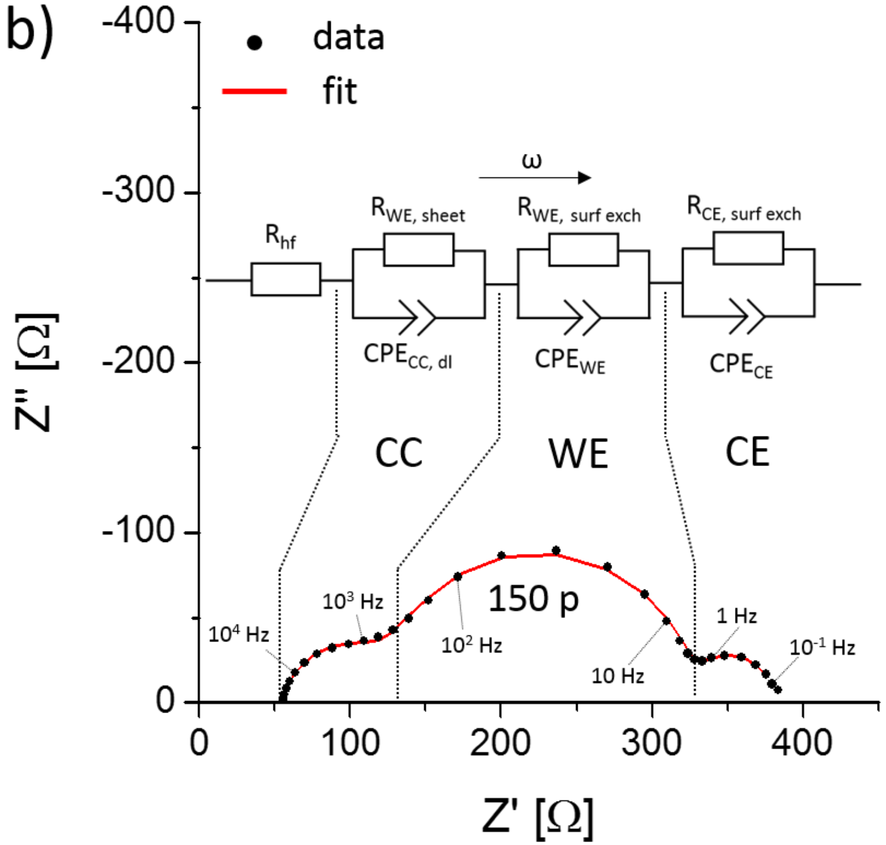




- High frequency resistance R_{hf} is dominated by the ionic oxygen transport resistance of (100) YSZ
- Calibration via reference measurements of YSZ

Impedance in the first 3 nm LSC

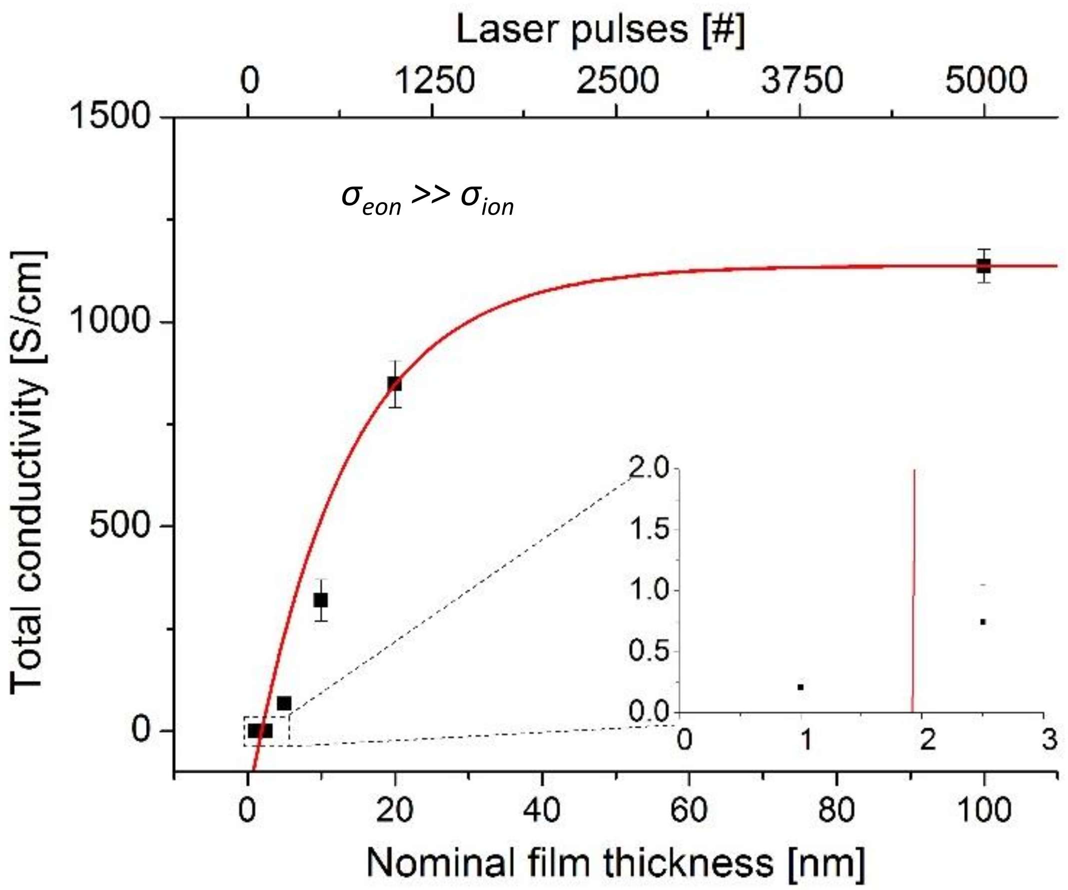


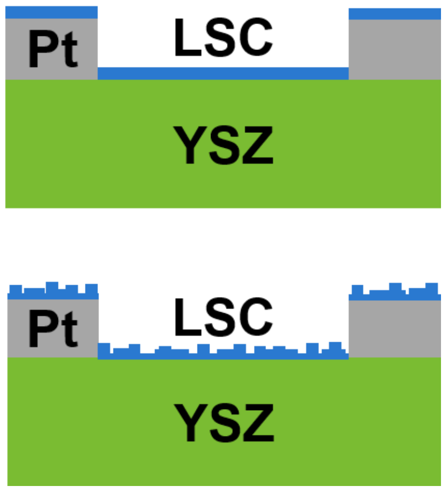


- PLD at 600°C and $4 \cdot 10^{-2}$ mbar p(O2), 10 mVAC for impedance
- At the beginning impedance is dominated by Pt grid
- > 125 pulses: 4 resistive contributions can be distinguished

150 pulses = 3 nm

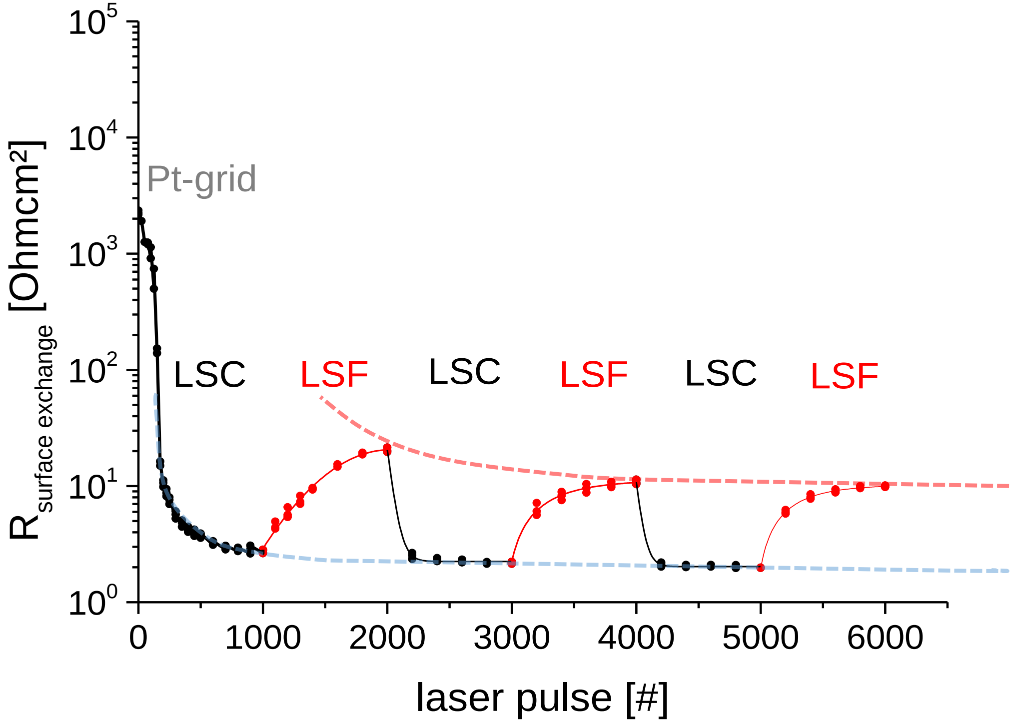
Sheet resistance of the growing film

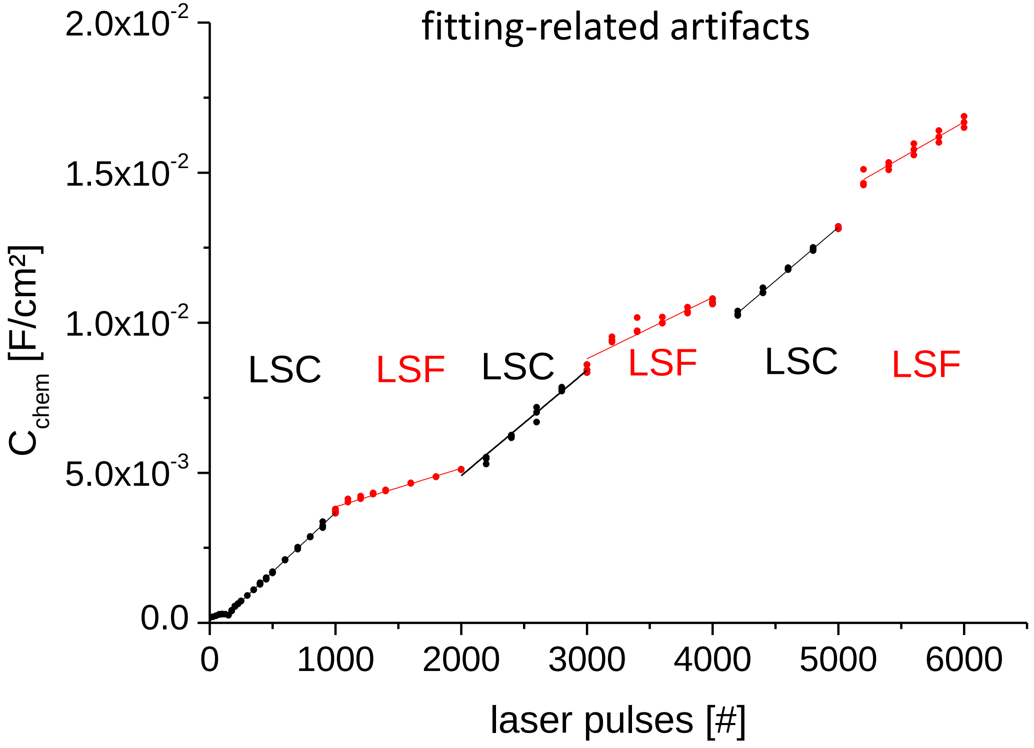




- Ex situ 4-point Van-der-Pauw measurements
- Expected LSC conductivity
- Slight deviation from ideal behavior → non-ideal growth

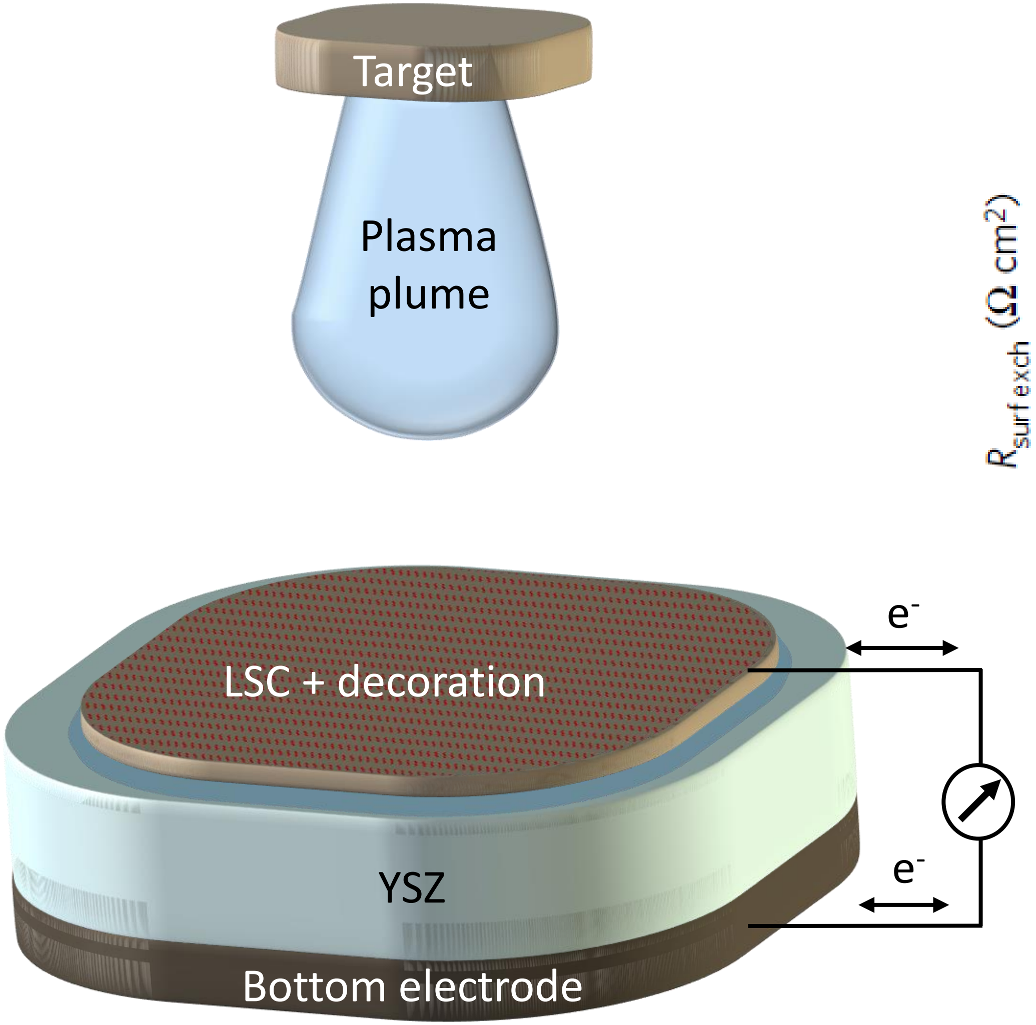
Multilayers of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $La_{0.6}Sr_{0.4}FeO_{3-\delta}$

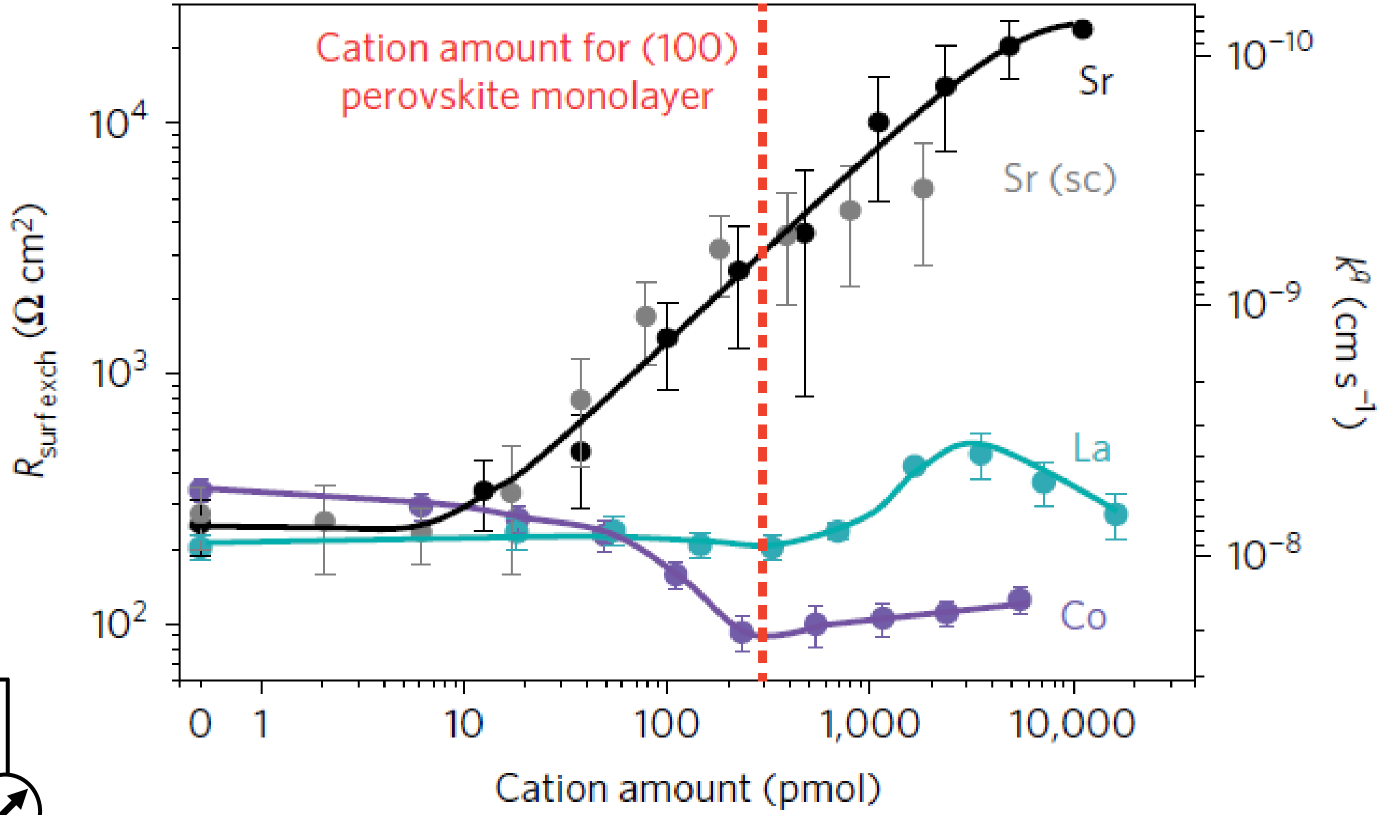




- Multilayers show transition between different surfaces (R_s)
- Charge carrier concentration from C_{chem}

Sub-monolayer decoration layers

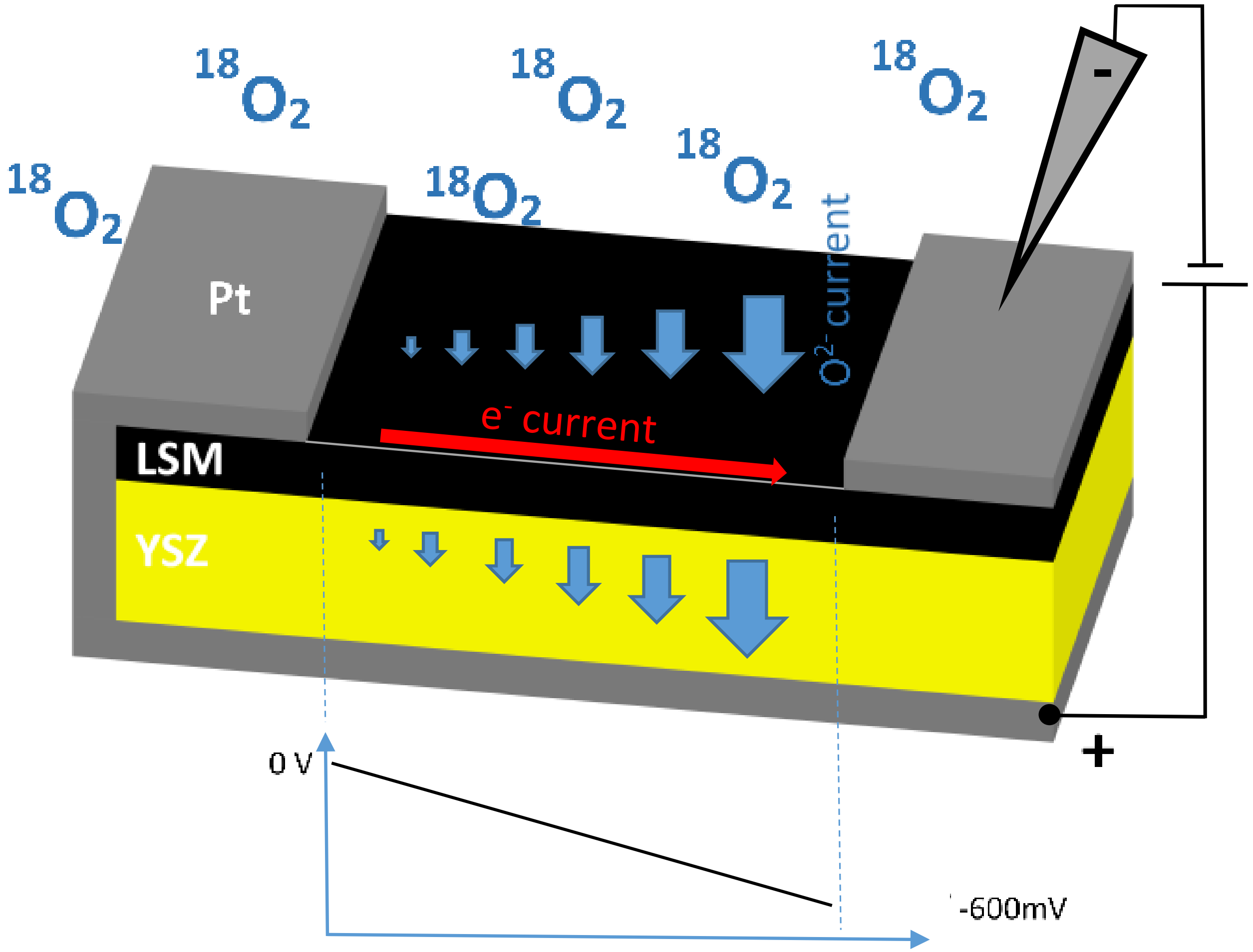




Rupp G.M. et al. Nature Mat. 2017 16(6), 640

- **Huge impact:**
  add 13% of a ML → +100% resistance
- **Few active centers on the surface**
- **Co enhances, Sr reduces activity**

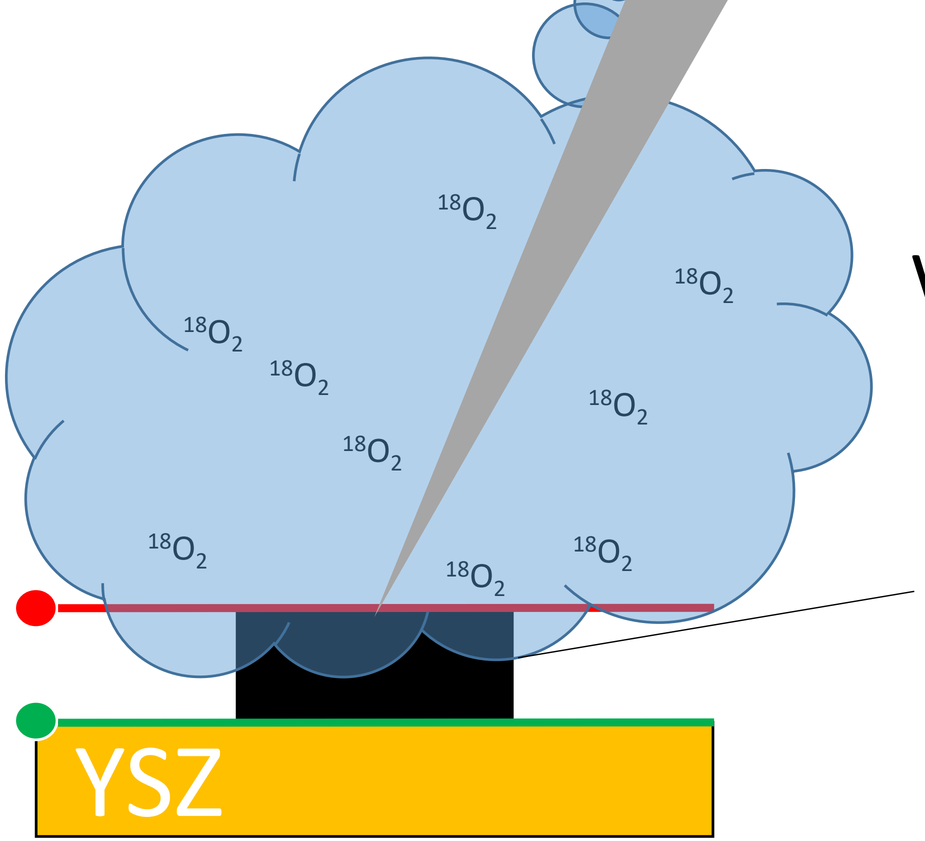
New experimental design for polarization experiments

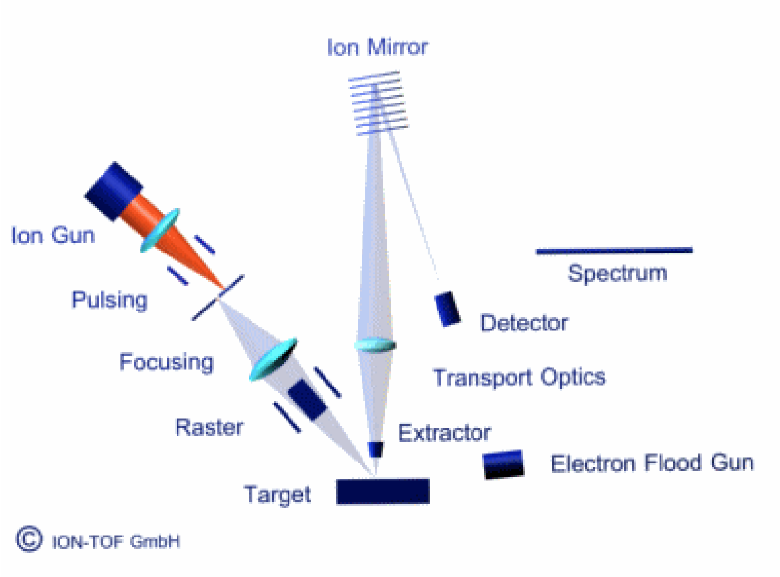


motivation:

- Develop a simple method to study voltage assisted tracer exchange
- Easy to contact
- Highly accurate applied voltage
- Different polarized thin film on one and the same sample

SIMS and ^{18}O exchange with polarization





in situ ⇔ ex situ

sufficient resources? (time & money)

cooling down changes experiment

surface with analytic tools accessible

in situ ex situ same surface process?

process only visible under experimental conditions

data possible to interpret?

impurities cause problems

oxidation → reductions make it visible

switch the catalyst on and off

observe the process. e.g. from the interface

expert in two fields … e.g. deposition and measuring at the same time