Komponentenentwicklung für Hochtemperaturbrennstoffzellen für den stationären und mobilen Einsatz

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Outline

SOFCs

- State of the art and challenges

Cathodes

Oxygen exchange properties of **BSCF, NDN, LSCF, LSC** including

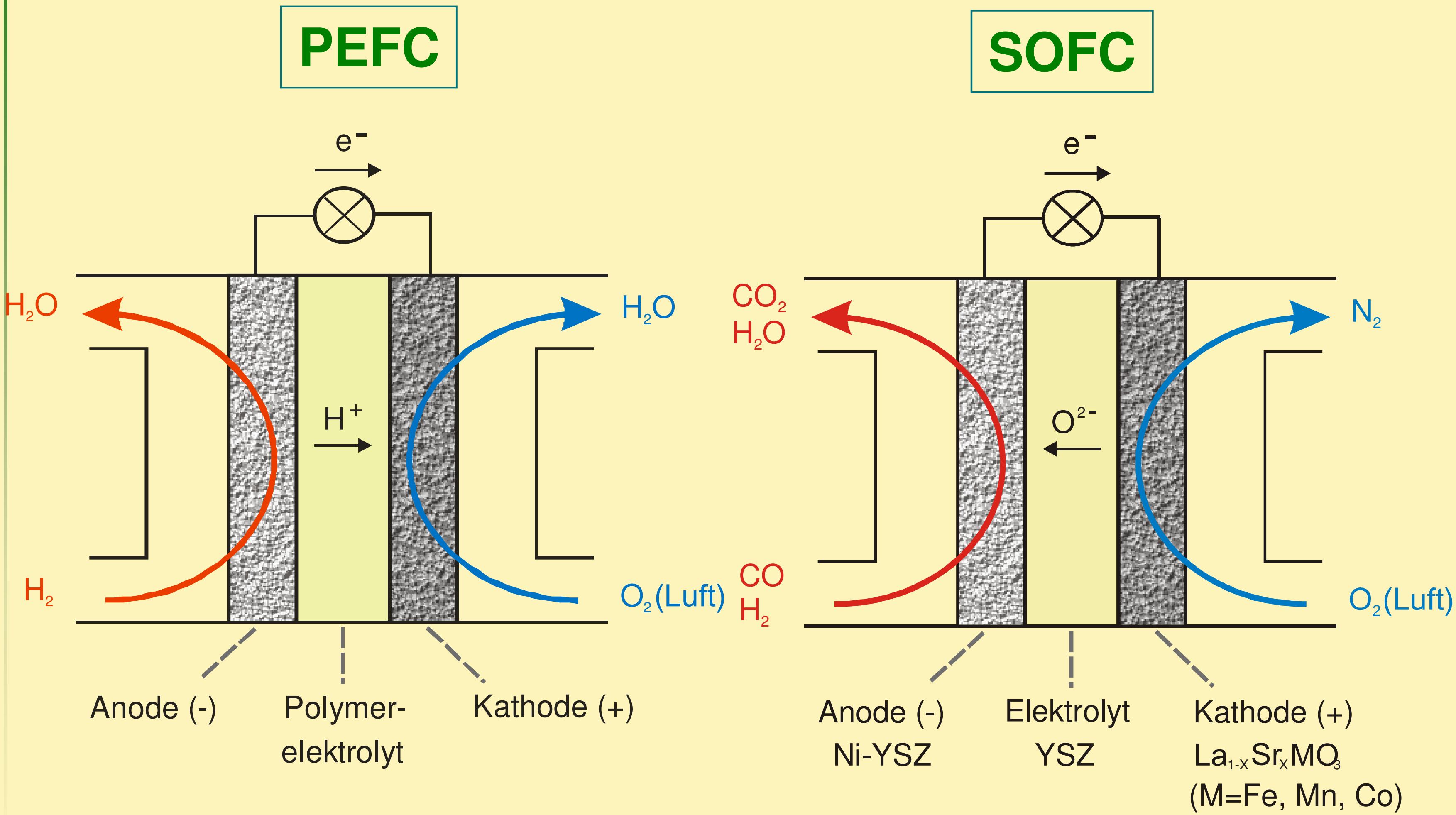
- long time stability in real atmospheres
- chromium and silicon poisoning

Electrolytes

Sc-ZrO_2

- bulk and grain boundary conductivity = f(T, pO_2)
- ageing studies

PEMFC - SOFC



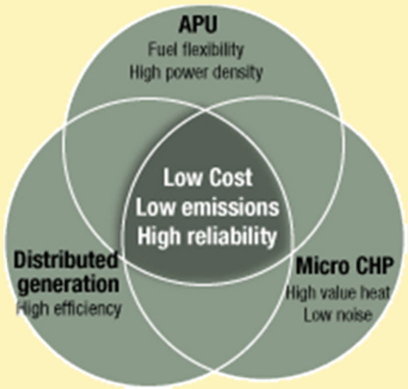
PEFC
e⁻
H₂O
H₂O
H⁺
H₂
O₂(Luft)
Anode (-)
Polymer-elektrolyt
Kathode (+)
SOFC
e⁻
CO₂
H₂O
N₂
O²⁻
CO
H₂
O₂(Luft)
Anode (-)
Ni-YSZ
Elektrolyt
YSZ
Kathode (+)
La1-xSrxMO3
(M=Fe, Mn, Co)

Development trends in SOFCs

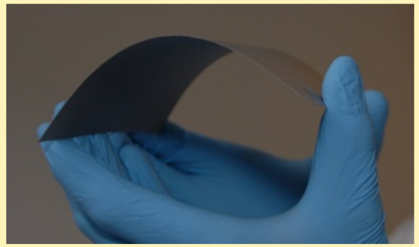
1000 ºC | 850 – 750 ºC | 700 – 600 ºC | 700 – 550 ºC

1000 ºC	850 – 750 ºC	700 – 600 ºC	700 – 550 ºC
LSM+YSZ	LSM+YSZ	MIEC	MIEC
YSZ	YSZ	CGO	ScYSZ
Ni+YSZ	Ni+YSZ	ScYSZ	Cermet - Infiltrate
		Ni+YSZ	FeCr

Ceramic-Supported
- Brittle

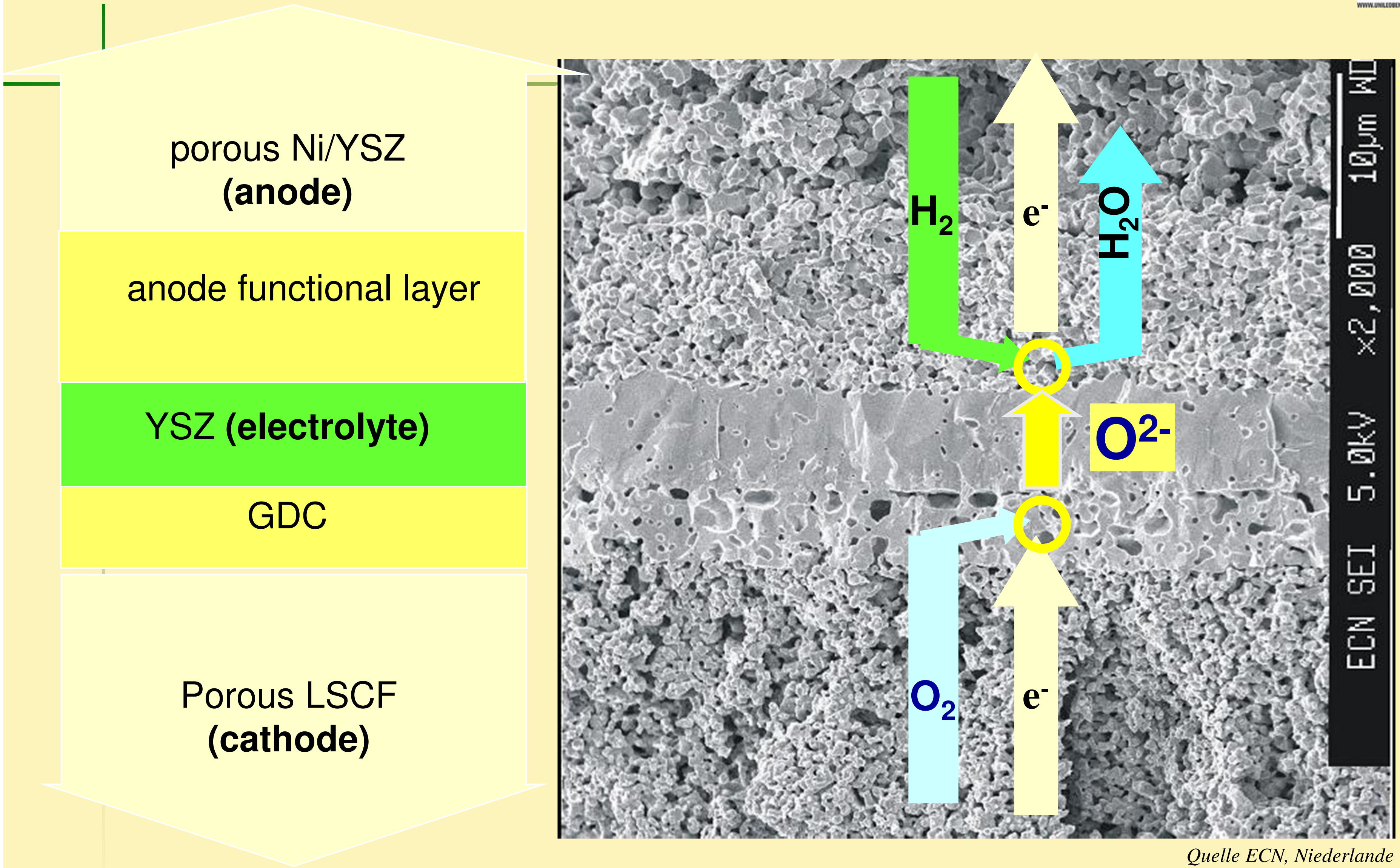


Metal-Supported
- Robustness
- Raw materials



Source: DTU Energy Conversion

SOFC



Quelle ECN, Niederlande

SOFC – state of the art

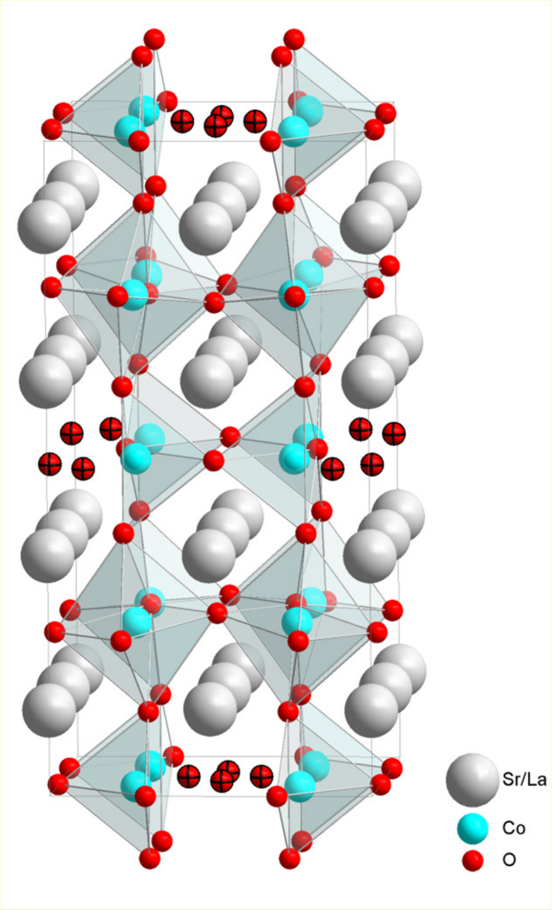
- SOFCs have the **highest efficiency** for conversion of chemical in electrical energy
- can be operated by **various fuels** (natural gas, gasoline, diesel, bio-fuels)
- allow to simultaneously generate **electricity and heat**
- **show low emissions and low noise**

Quelle Hexis AG

SOFCs - challenges

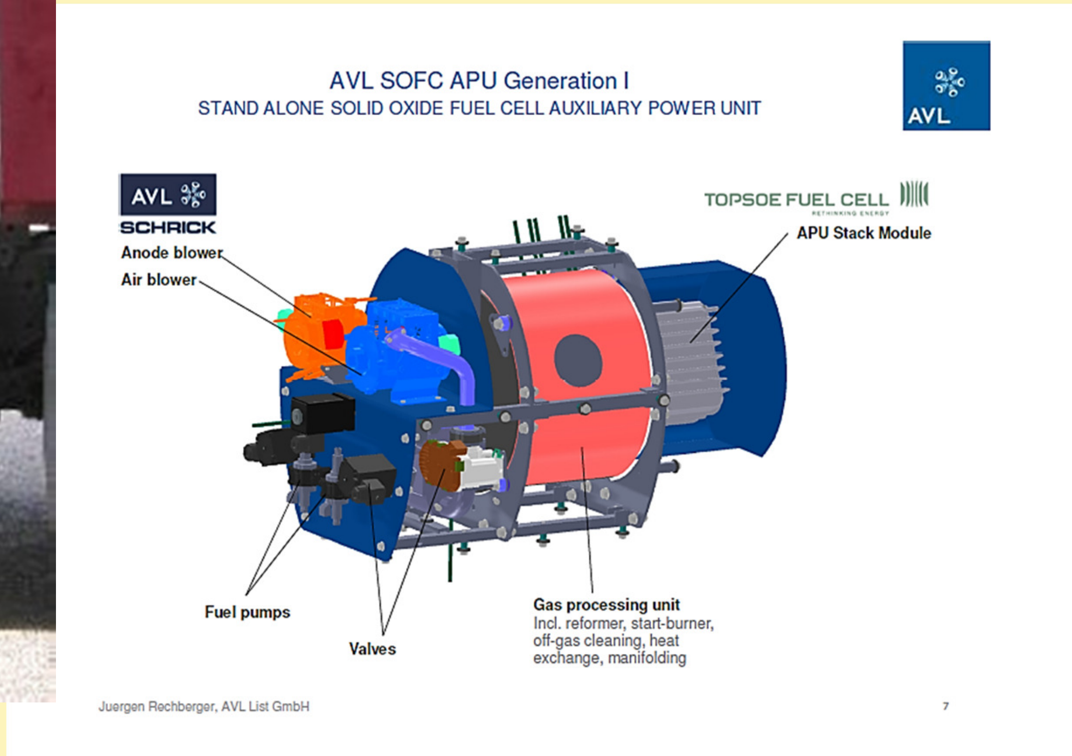
- **High operating temperatures** influence costs and reliability (chemical and thermo-mechanical **long-term degradation** of SOFC cells and stacks)

- With a **decrease of the operating temperature** to 600-700°C, new long-term **stable SOFC components** and cheaper **production technologies** are needed.



Quelle Hexis AG

SOFCs – mobile applications



Example: EU project SOFC600

- SOFC cell at 600°C
  - Area Specific Resistance (ASR) below 0,5 Ω.cm^2
  - Degradation rate below 0.05% / 1000 hours (1 mohm.cm^2/khr)
  - Robustness: 100 redox cycles, internal reforming capability, reduced coke formation activity

Aim for components:

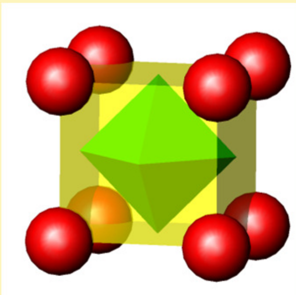
Anode	< 0.15 ohm.cm^2
Cathode	< 0.25 ohm.cm^2
Electrolyte	< 0.10 ohm.cm^2
Cell	**< 0.50 ohm.cm^2**

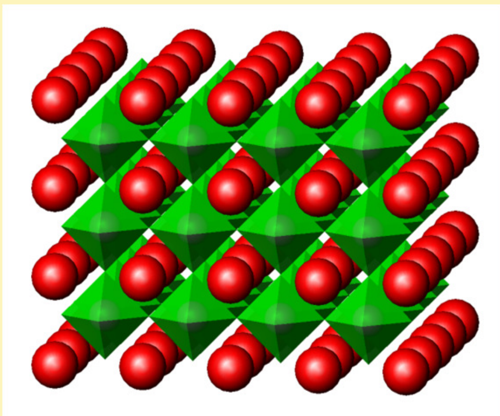
Characterization of cathodes

- Focus
  - Long-term behaviour ($t < 1000\,h$) of oxygen exchange properties of SOFC cathodes in various atmospheres
- Methods
  - thermogravimetry (δ)
  - dc conductivity relaxation measurements (k_{chem}, D_{chem}, σ_e)
  - surface and bulk characterisation by XPS
- Materials
  - $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)
  - $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)
  - $Nd_2NiO_{4+\delta}$ (NNO)
  - $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC)

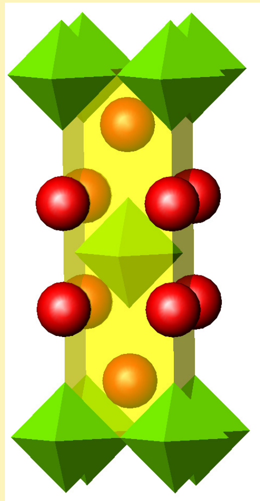
SOFC cathodes

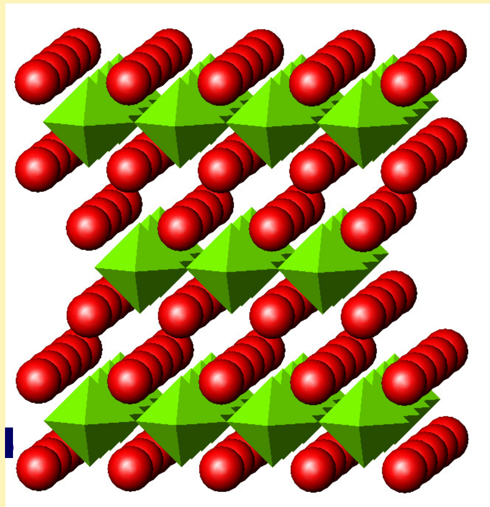
Perovskites ($ABO_{3-\delta}$):
A=(La,Sr,Ba) and B=(Co,Fe,Mn)
δ... oxygen nonstoichiometry
oxygen deficit (oxygen vacancies)





K_2NiF_4-type oxides ($A_2BO_{4+\delta}$):
A=(Nd,Pr) and B=Ni
δ... oxygen nonstoichiometry
oxygen excess (oxygen interstitials)





A-site ions (red)
BO_6-octahedra (green)

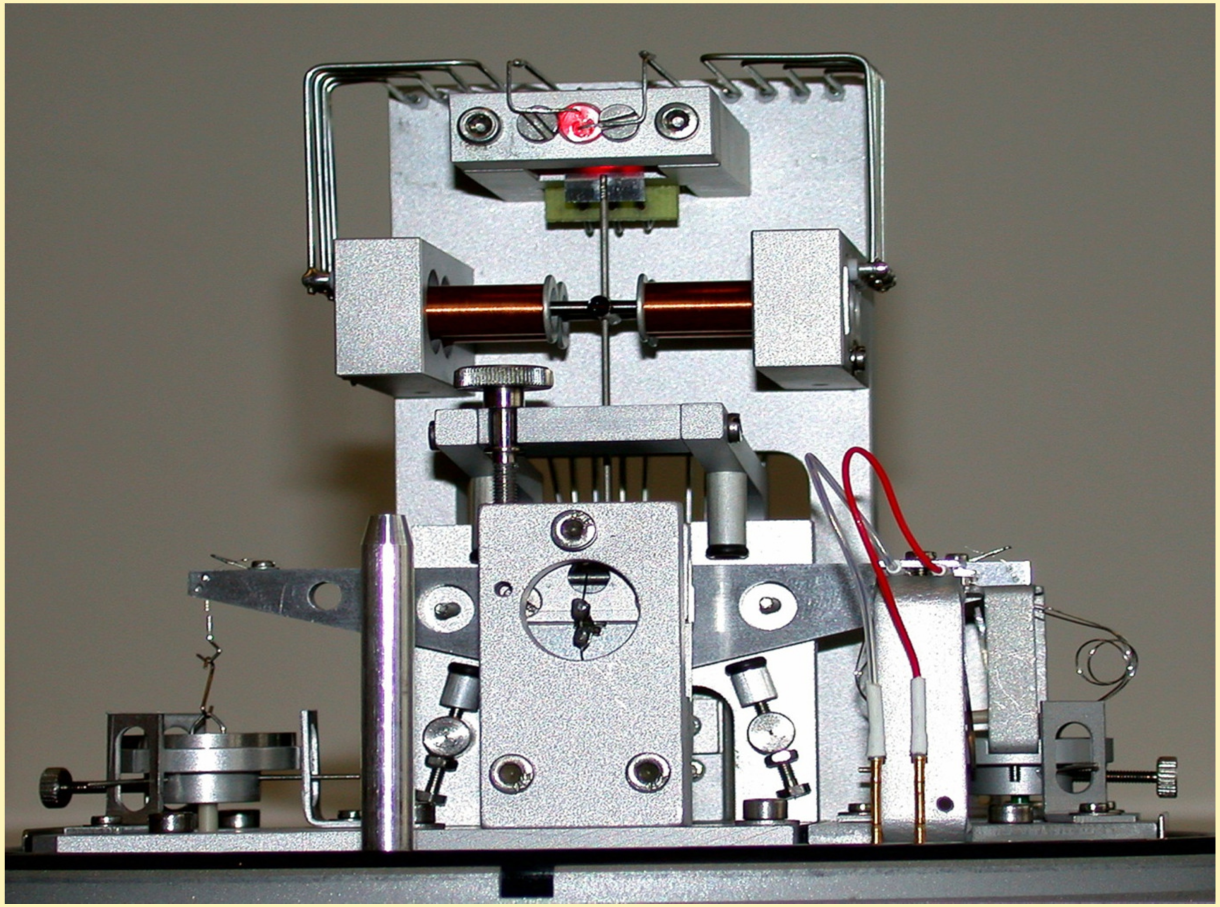
Long-term stability of

- $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)

in dry and CO_2-containing atmospheres

Experimental

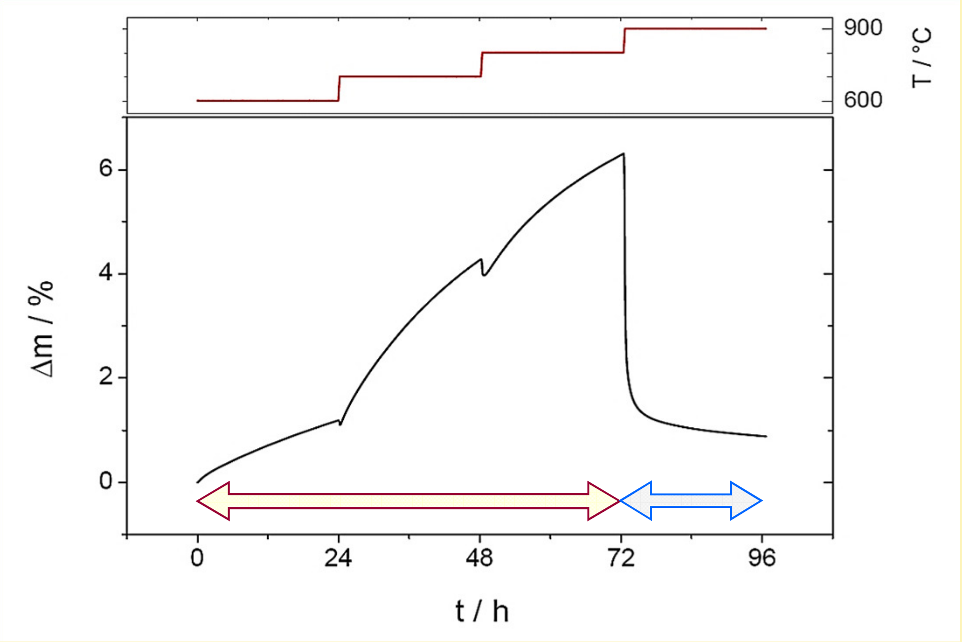
- **Thermoanalysis (TG, TG-MS)**
  - Ar-O_2 and CO_2-containing atmospheres



$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

BSCF in CO_2-rich atmosphere (20% O_2+5% CO_2, T=600-900°C)

- @ 600-800°C:
  Formation of $Ba_{1-x}Sr_xCO_3$ surface layer(1,2) separated from the bulk by an intermediate phase of Co/Fe-rich perovskite(3,4)
- T>800°C:
  Carbonate decomposition, regeneration



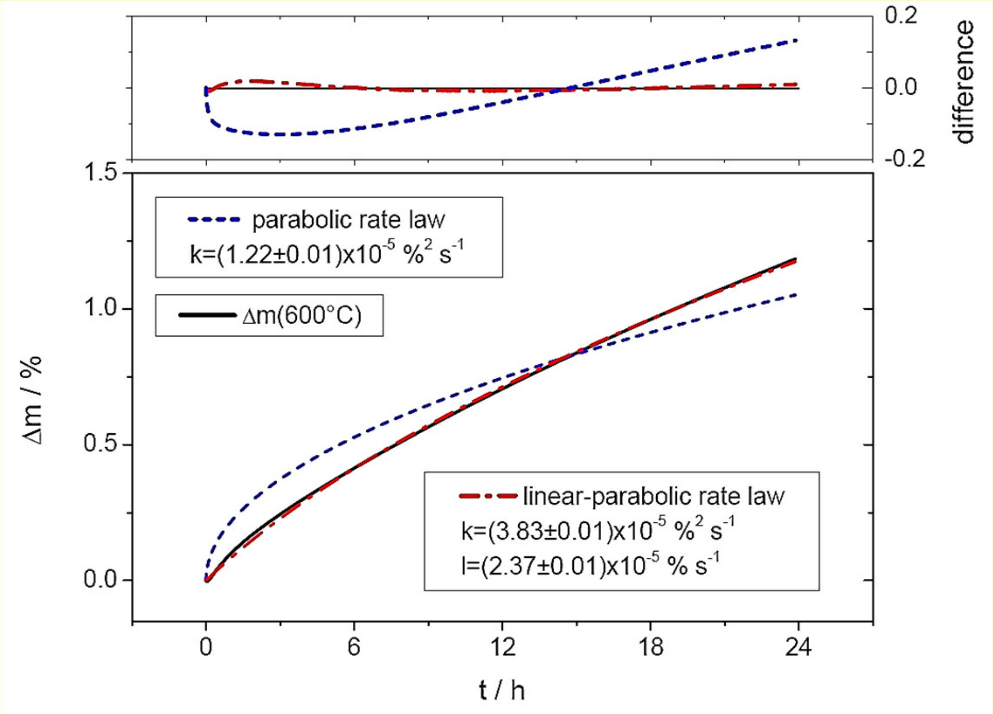
[1] Criado et al., *Thermochim. Acta*, 171 (1990) 229.
[2] Kiseleva et al., *Phys. Chem. Miner.*, 21 (1994) 392.
[3] Arnold et al., *J. Membr. Sci.*, 293 (2007) 44.
[4] Yan et al., *Appl. Catal. B*, 76 (2007) 320.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

BSCF in CO_2-rich atmosphere (20% O_2+5% CO_2, T=600°C)

- Mass increase follows a linear-parabolic rate law
- Kinetics of carbonate formation is simultaneously controlled by the solid-gas interface reaction and by diffusion through the surface (carbonate) layer

$$\frac{\Delta m}{l}+\frac{\Delta m^2}{k}=t$$



E. Bucher et al., *J. Electrochem. Soc.*, 155 (2008) B1218.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

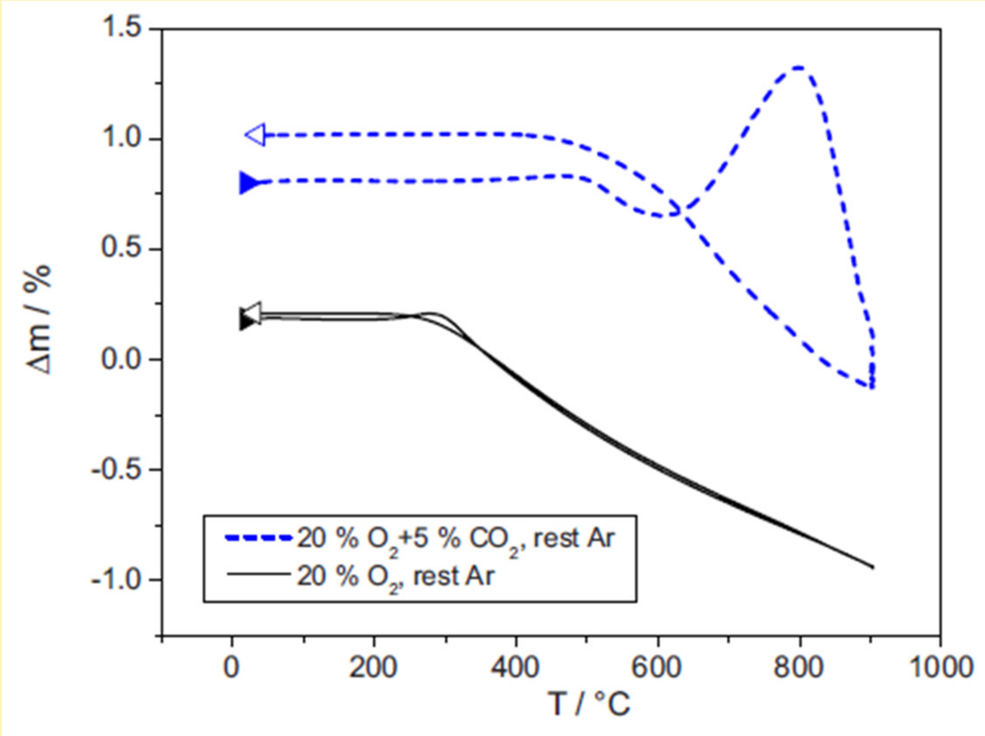
BSCF in different atmospheres

- CO_2-free atmosphere: Reversible oxygen exchange of perovskite phase ($ABO_{3-\delta}$)

$$\tfrac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e' \Leftrightarrow O_O^x$$

$$[V_O^{\bullet\bullet}] = \delta = f(T, pO_2)$$

- CO_2-rich atmosphere:
  - Onset of oxygen exchange shifted towards higher T



E. Bucher et al., in *Proc. 8th Eur. SOFC Forum*, 2008, p. A0603.

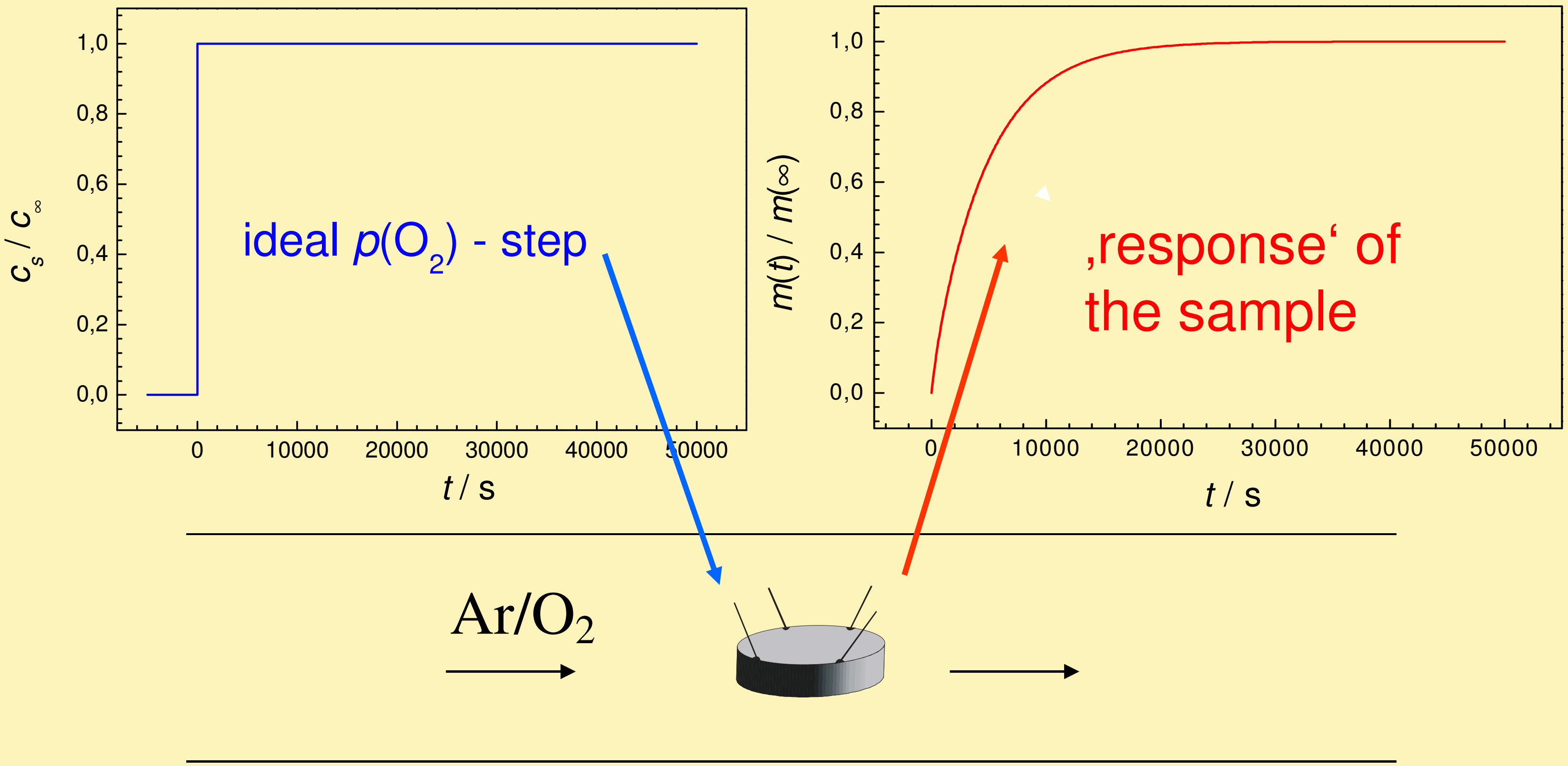
Long-term stabilities of

- $\mathbf{Nd_2NiO_{4+\delta}}$
- $\mathbf{La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}}$

in dry and humid O_2/Ar-atmosphere

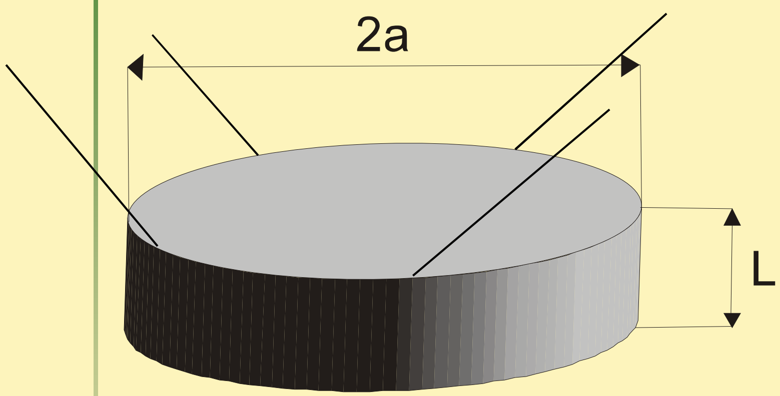
Experimental

- **Conductivity relaxation (CR)**



Experimental

- **Conductivity relaxation (CR)**



a >> L

$$\frac{\partial c}{\partial t} = \tilde{D}\frac{\partial^2 c}{\partial x^2}$$

$$\tilde{D}\frac{\partial c}{\partial x} = \pm\tilde{k}(c - c_s) \qquad x = 0, L$$

$\tilde{D}$... chemical diffusion coefficient

$\tilde{k}$ ... surface exchange coefficient

$$\frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = \frac{m(t)}{m(\infty)}$$

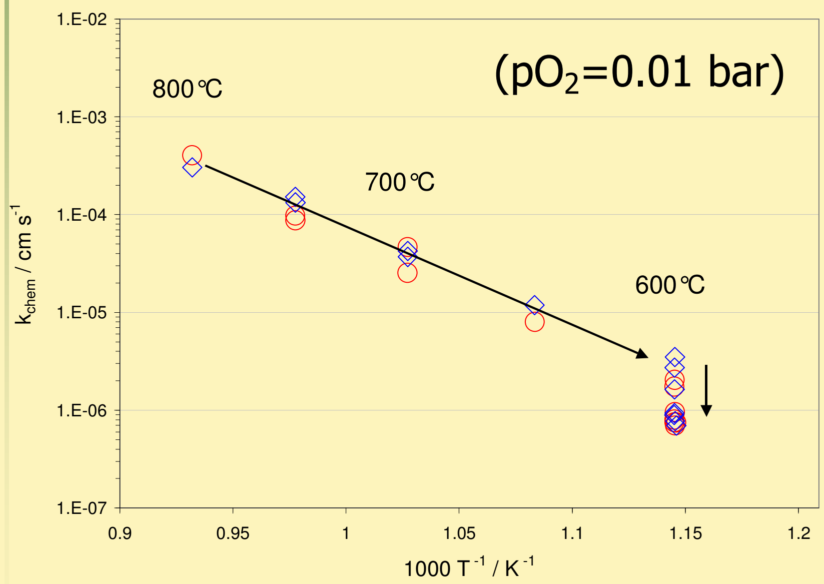
van der Pauw method $\rightarrow \sigma$

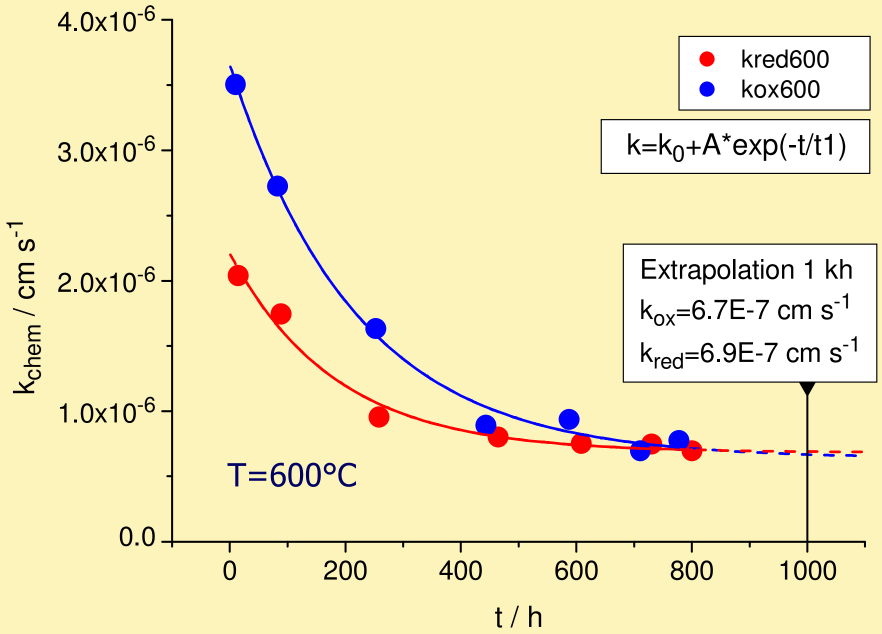
Results

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

Long term oxygen exchange kinetics of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in dry O_2/Ar

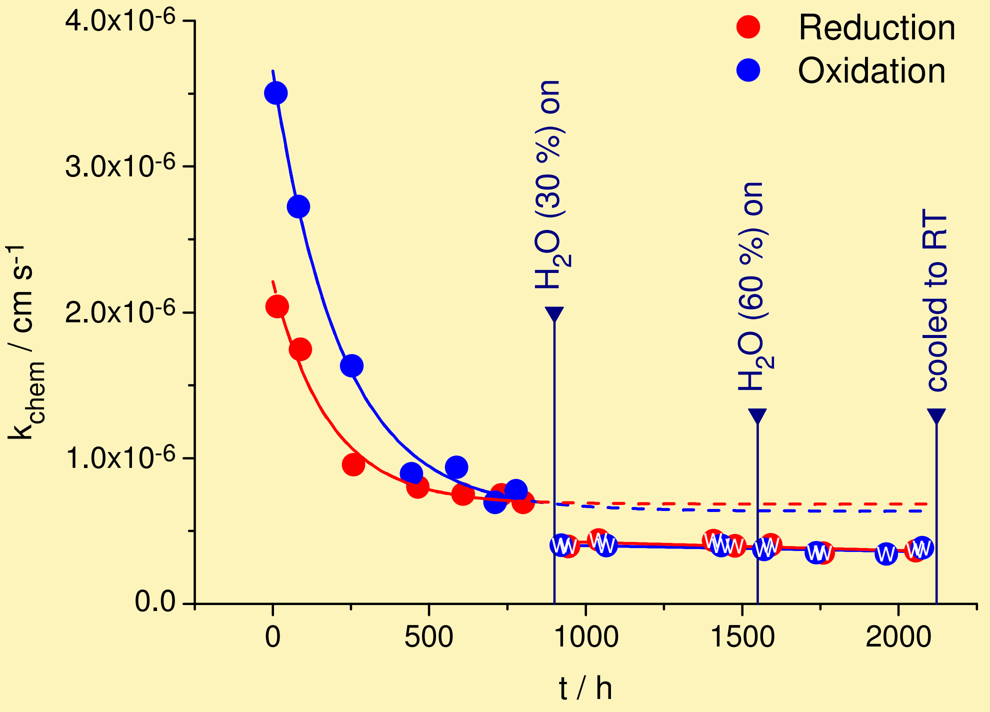
- LSCF shows fast oxygen exchange kinetics at 600-800°C in the short time scale
- long-term degradation of k_{chem} in dry O_2-Ar?





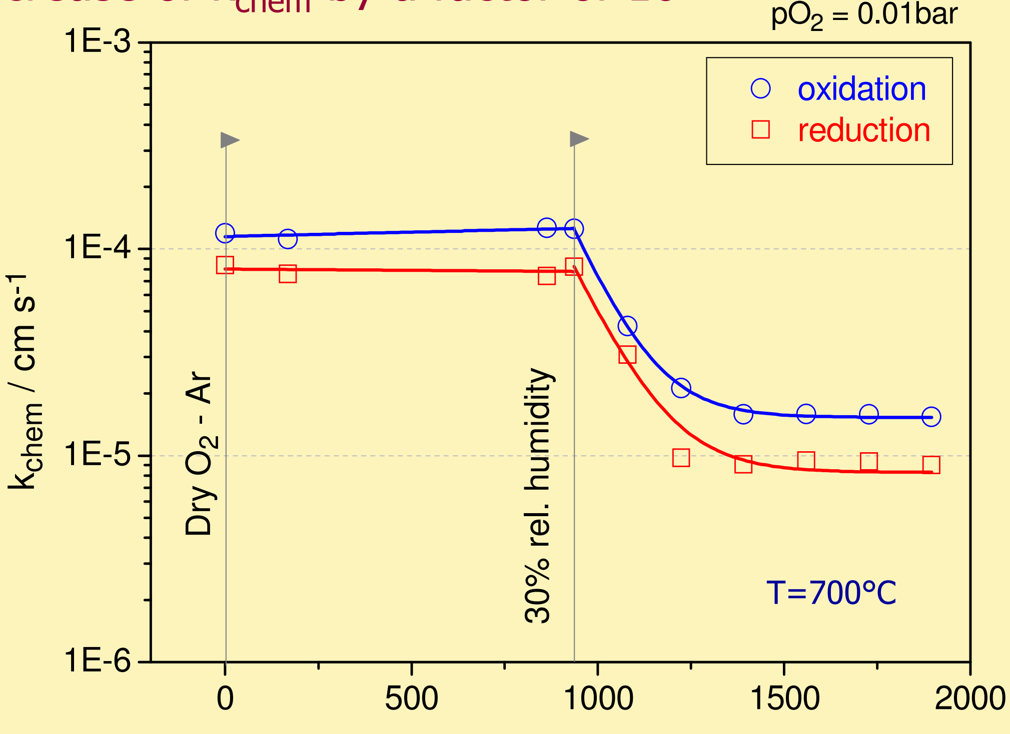
$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

- **Long term oxygen exchange kinetics of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in dry + wet atmospheres at 600°C**



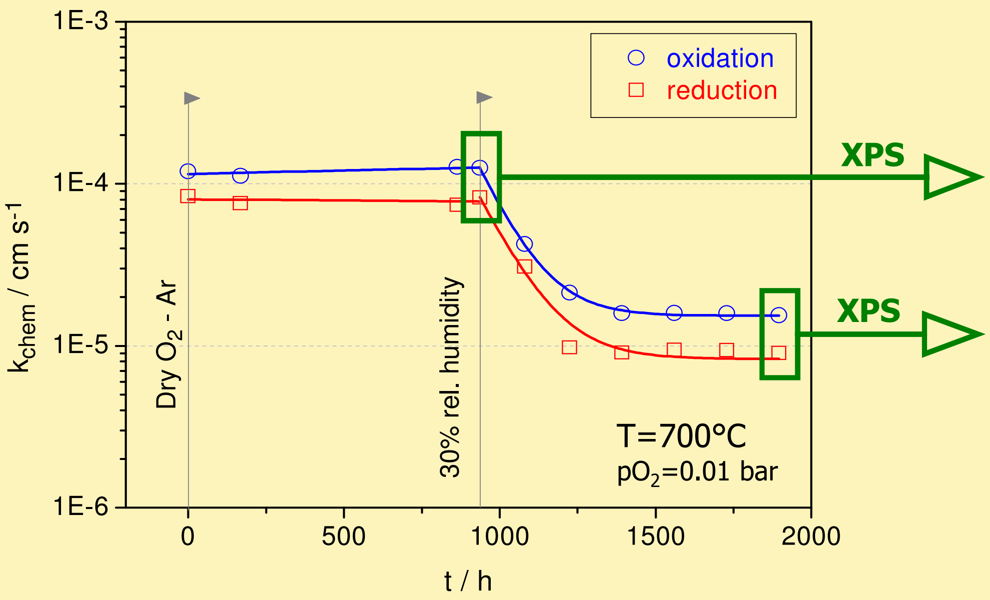
$Nd_2NiO_{4+\delta}$

- **Long term oxygen exchange kinetics of $Nd_2NiO_{4+\delta}$ in dry + wet atmospheres at 700°C**
  - excellent oxygen surface exchange kinetics at 700°C
    → no degradation during 1 kh at 700°C in **dry** atmosphere (O_2/Ar)
  - **wet** atmosphere (pH_2O=1E-2bar; 30% relative humidity)
    → decrease of k_{chem} by a factor of 10



$Nd_2NiO_{4+\delta}$

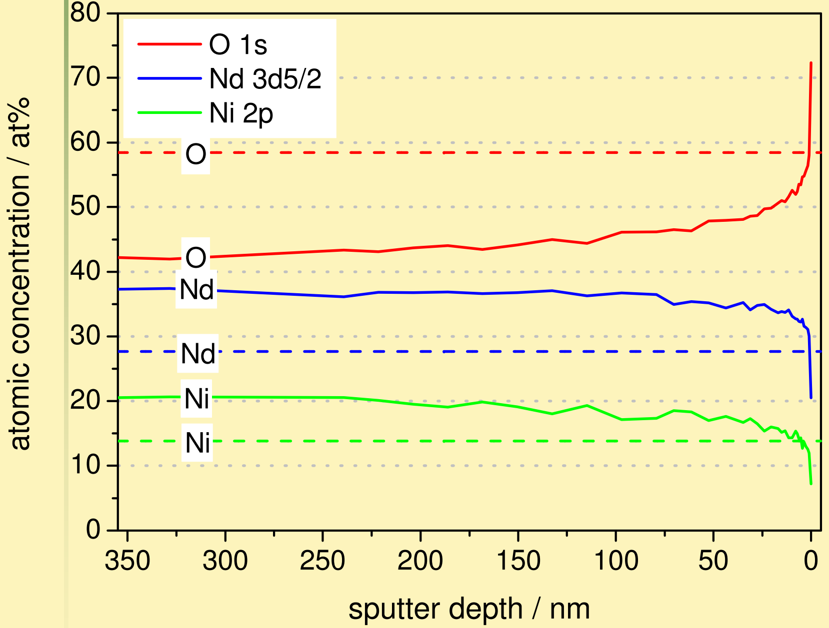
- **Long term stability of k_{chem} of $Nd_2NiO_{4+\delta}$ in dry + wet atmospheres (700°C)**

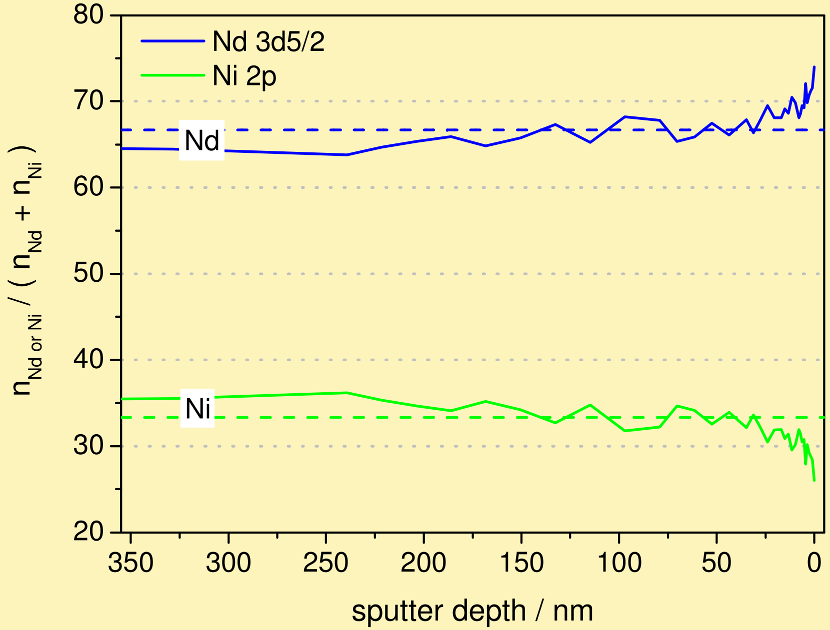


XPS elemental depth profiles

$Nd_2NiO_{4+\delta}$: XPS elemental depth profiles

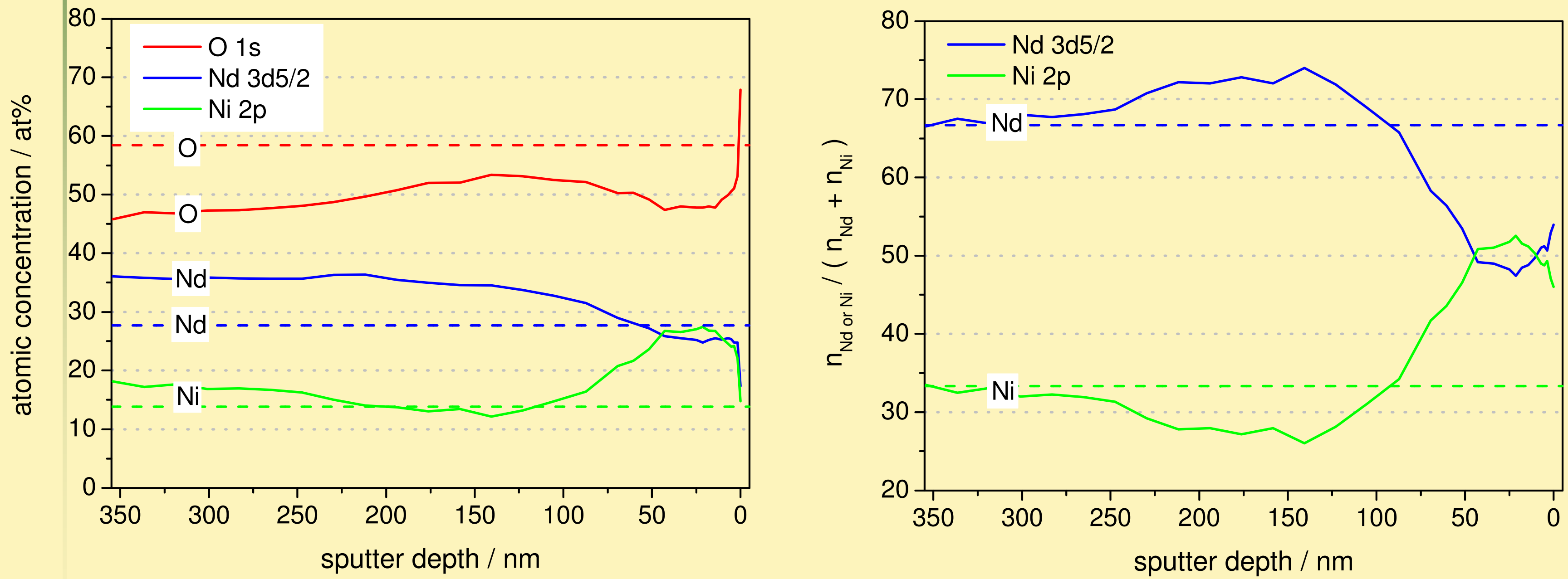
$Nd_2NiO_{4+\delta}$ 1000h **dry atmosphere**
T = 700° C pO_2 = 0.01 bar





$Nd_2NiO_{4+\delta}$: XPS elemental depth profiles

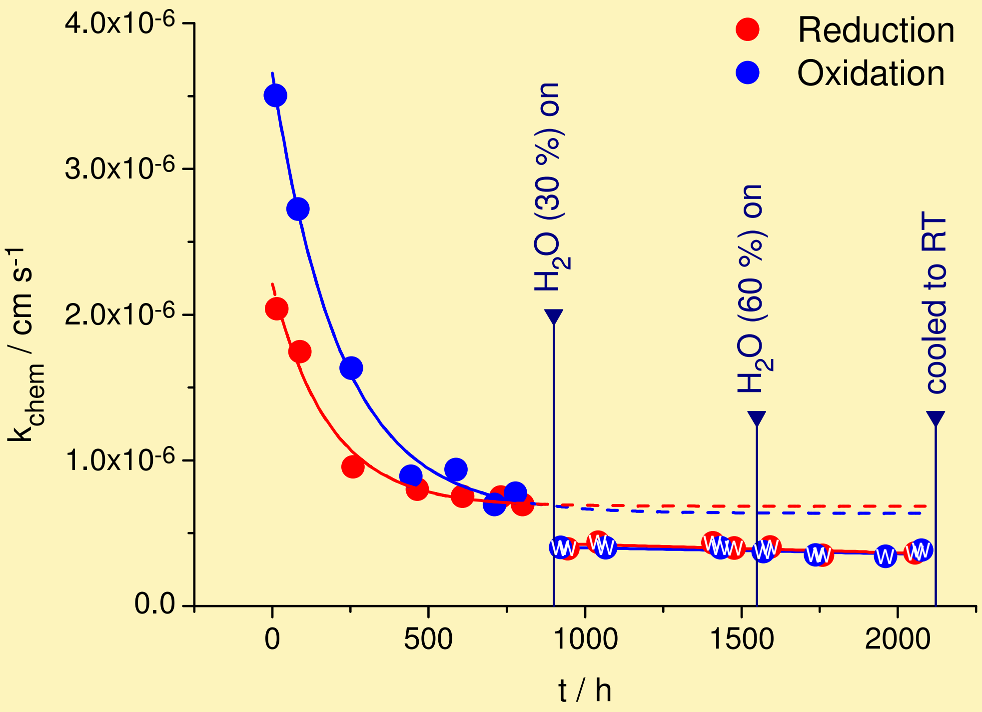
$Nd_2NiO_{4+\delta}$ 1000h **dry** + 1000h **humid atmosphere**
T = 700° C pO_2 = 0.01 bar

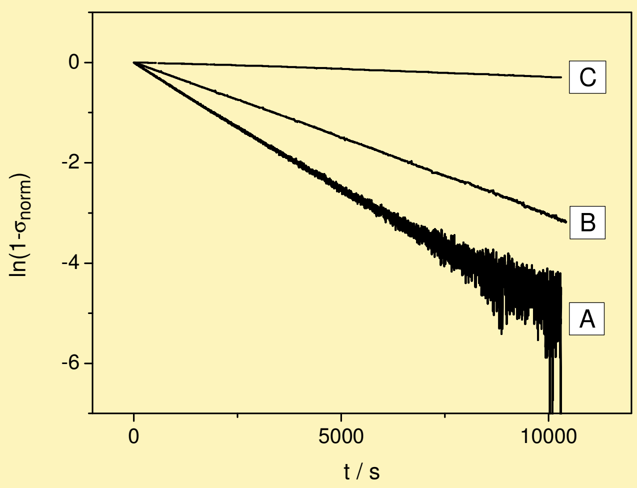


E. Bucher, W. Sitte, F. Klauser, E. Bertel, J. Electrochem. Soc. 157 (2010) B1537-B1541

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

- Long term oxygen exchange kinetics of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in dry and wet atmospheres at 600°C





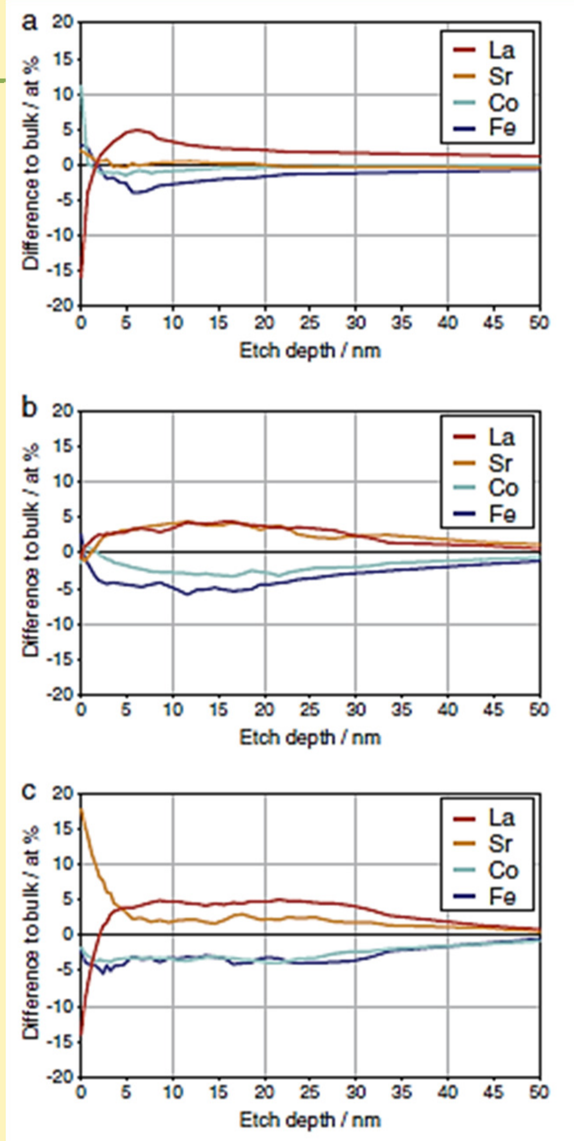
$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ elemental depth profiles

fresh sample

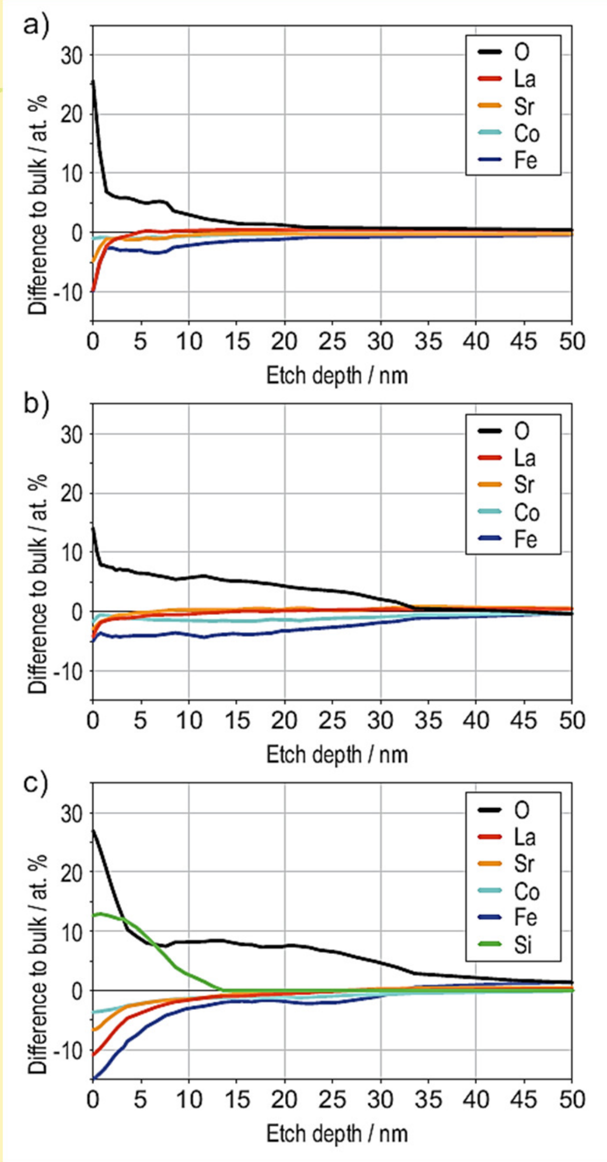
1000h dry 1% O_2/Ar atmosphere

1000h dry + 1000h humid 1% O_2/Ar-atmosphere

La, Sr, Co, Fe



+ O and Si

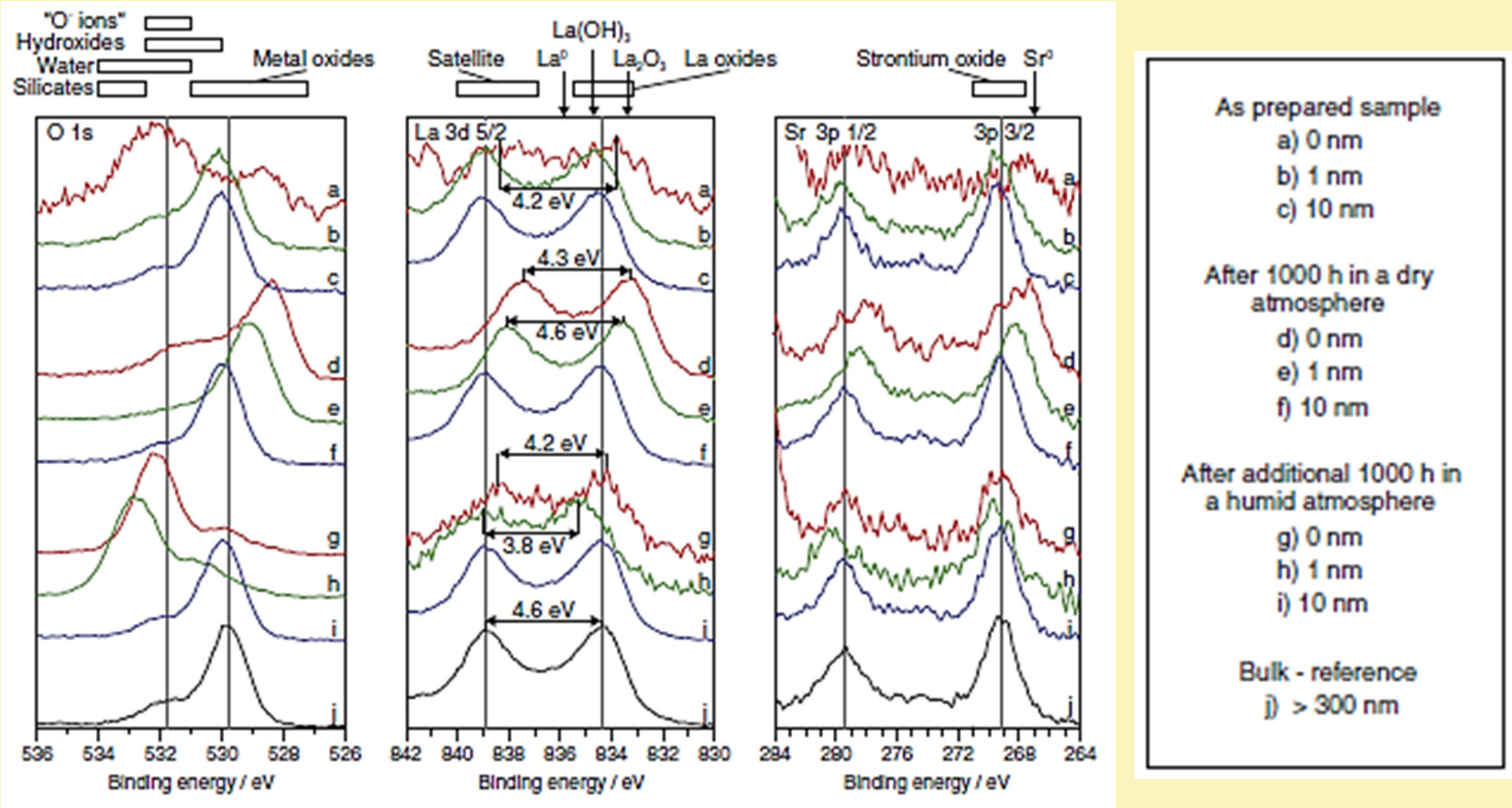


E. Bucher, W. Sitte, F. Klauser, E. Bertel, Solid State Ionics, 191 (2011) 61-67

constant cation composition : ~ 50 nm.

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ core level spectra

O 1s, La 3d, Sr 3p

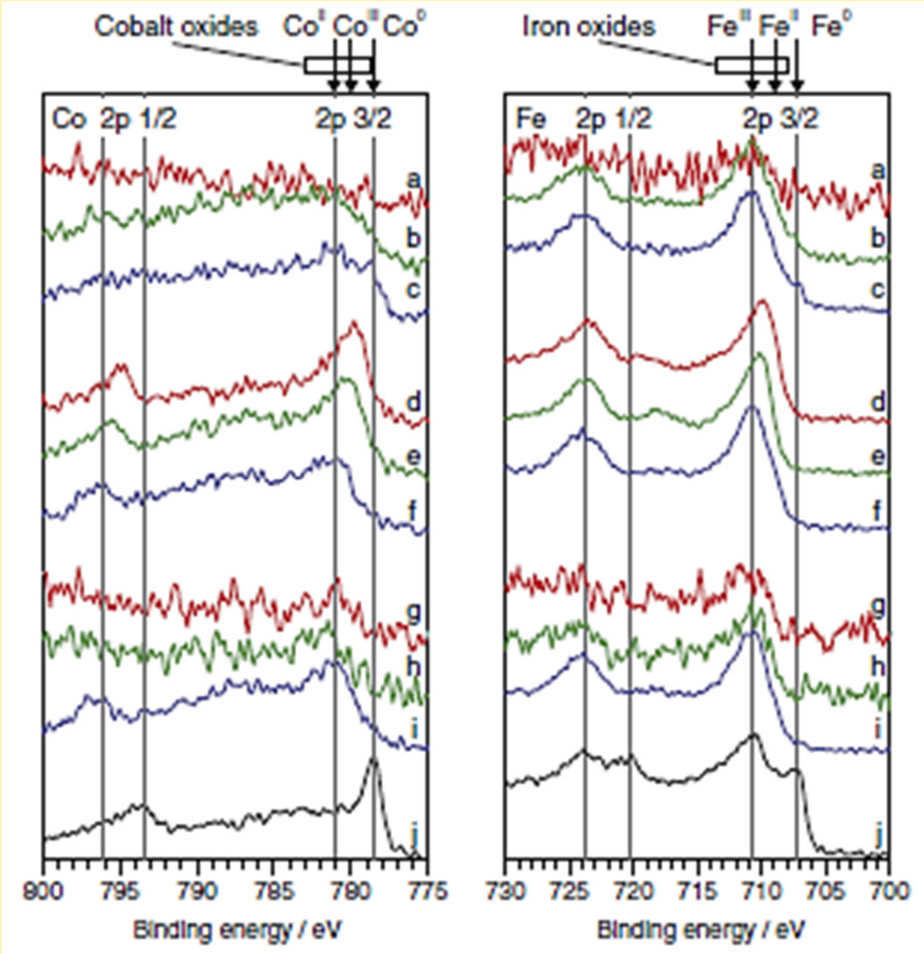


XPS core level spectra of the O 1s, La 3d, Sr 3p peaks of the three different samples, obtained from immediate surface (0 nm), at etch depths of 1 nm and 10 nm, and from bulk (depth > 300 nm).

E. Bucher, W. Sitte, F. Klauser, E. Bertel, Solid State Ionics, 191 (2011) 61-67

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ core level spectra

Co 2p, Fe 2p



As prepared sample
a) 0 nm
b) 1 nm
c) 10 nm

After 1000 h in a dry atmosphere
d) 0 nm
e) 1 nm
f) 10 nm

After additional 1000 h in a humid atmosphere
g) 0 nm
h) 1 nm
i) 10 nm

Bulk - reference
j) > 300 nm

XPS core level spectra of Co 2p and Fe 2p peaks of the three different samples, obtained from immediate surface (0 nm), at etch depths of 1 nm and 10 nm, and from bulk (depth > 300 nm).

$La_{0.6}Sr_{0.4}CoO_{3-\delta}$ surface morphology

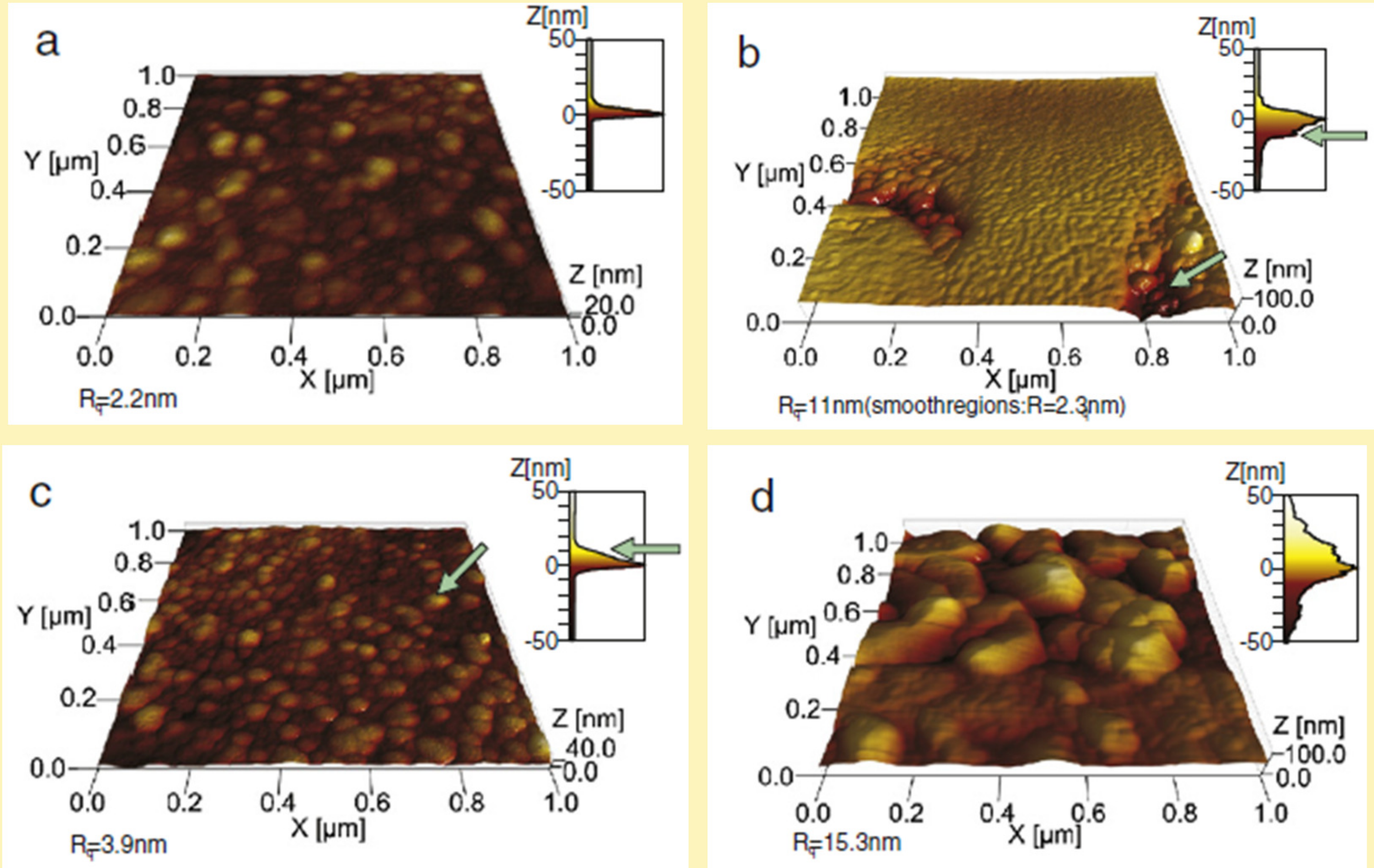


Fig. 7. Surface topography of different $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ samples; AFM high resolution scans ($1\times1\ \mu m^2$) of (a) the fresh surface, (b) after 1000 h in a dry atmosphere, (c) after an additional 1000 h in a moderately humidified atmosphere (30% r.h.), and (d) after a further 2000 h in a strongly humidified atmosphere (75% r.h.) including 1000 h of exposure to a saturated NaCl solution; R_q values represent the root-mean-square roughness. Height histograms are given as insets with each image.

Long-term degradation of the IT-SOFC cathode material

- $La_{0.6}Sr_{0.4}CoO_3$

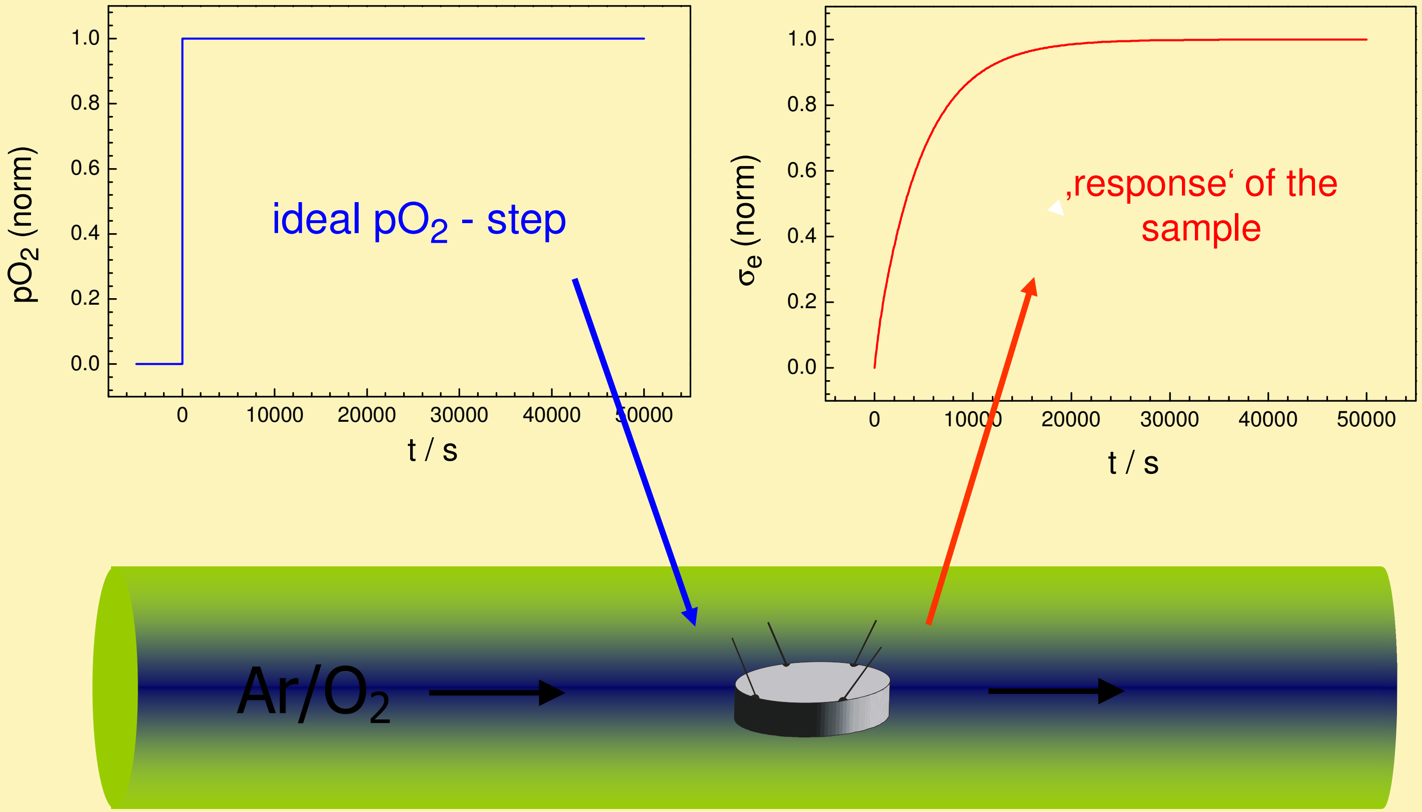
in dry and humid O_2/Ar-atmosphere

in the presence of Cr and Si

- Interconnects of IT-SOFCs are Cr-based alloys (stainless steels)

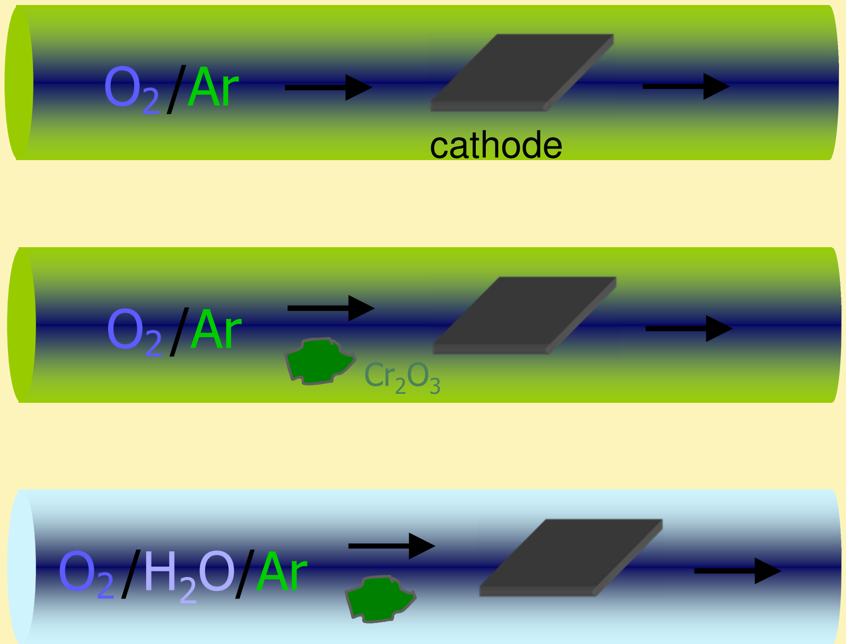
  → stability of the cathode vs. Cr-poisoning is a key issue

Experimental: dc-Conductivity relaxation



Oxygen exchange measurements

- Cr-source: Chromium pellet placed in vicinity to the sample
- Si-source: Quartz sample holder/reactor
- Experimental conditions: T=600°C; $p(O_2)=0.10$ bar; $0<p(H_2O)/bar<0.01$

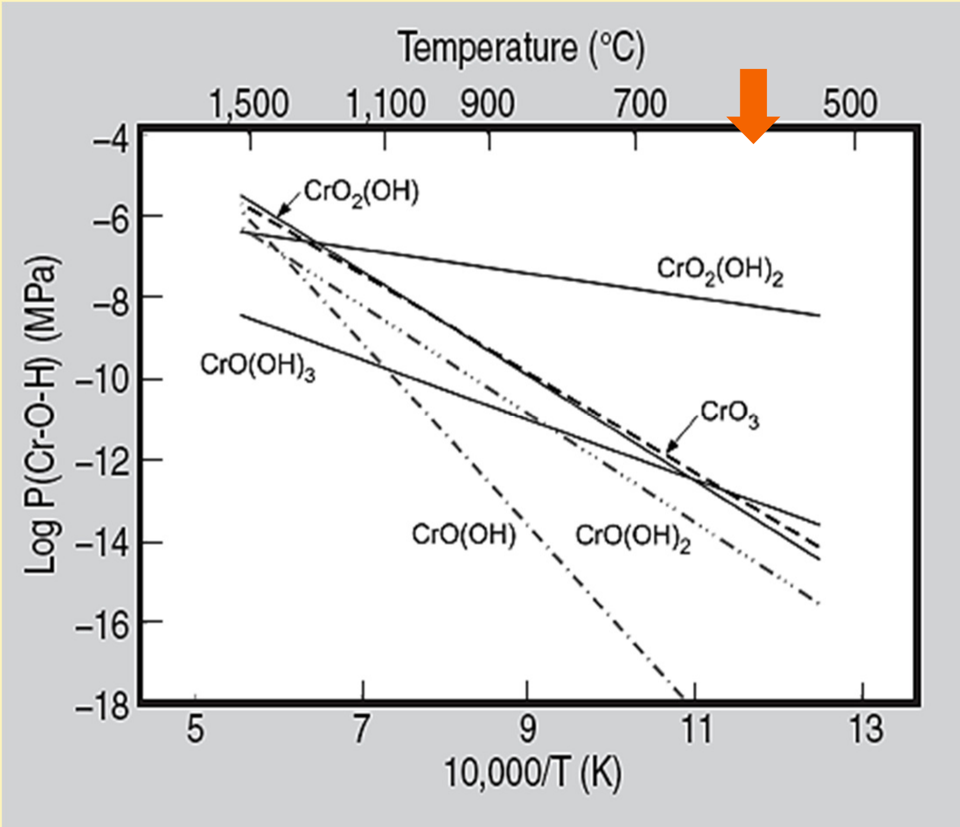


Sequence of cathode testing:

1. 1000 h without Cr-source in a dry atmosphere
2. 1000 h with Cr-source in a dry atmosphere
3. 1000 h with Cr-source in a humidified atmosphere

Gas phase equilibria

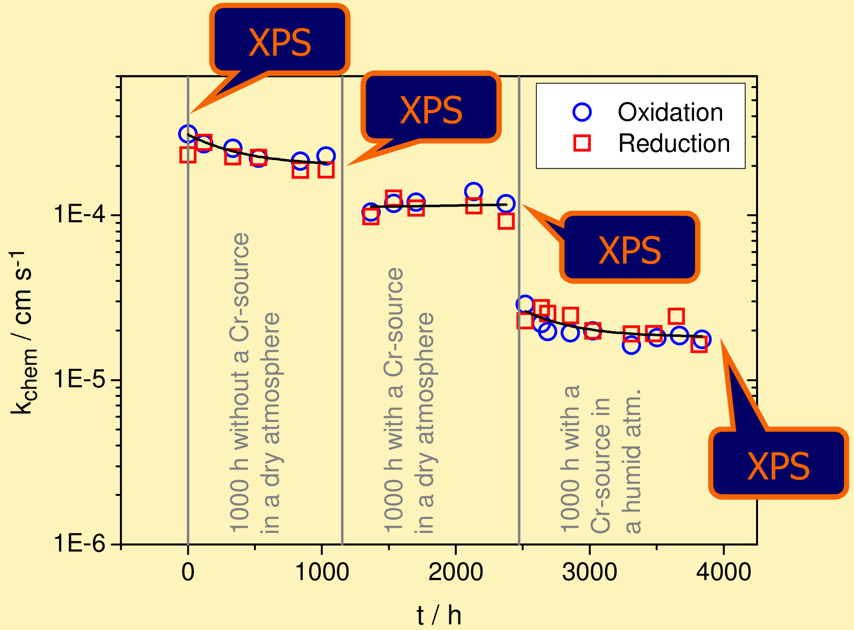
- Poisoning (degradation) is caused by reaction of the cathode with volatile species which are transported via the gas phase
- The predominating gas phase species depend on T, $p(O_2)$, $p(H_2O)$
- Under the present experimental conditions:
  - ½ $Cr_2O_3(s) + H_2O(g) + 3/4\ O_2(g) \rightarrow$ **$CrO_2(OH)_2(g)$**
  - ½ $Cr_2O_3(s) + 3/4\ O_2(g) \rightarrow CrO_3(g)$
  - $SiO_2(s) +\ 2\ H_2O(g) \rightarrow$ **$Si(OH)_4(g)$**



E. Opila et al., JOM 58 (2006) 22.

Oxygen exchange measurements

- At 600°C in dry atmosphere without/with a Cr-source $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ shows only a minor decrease of the kinetic parameters
- In humidified atmosphere (30 % rel. humidity) with a Cr-source at 600°C a pronounced decrease of k_{chem} and D_{chem} occurs

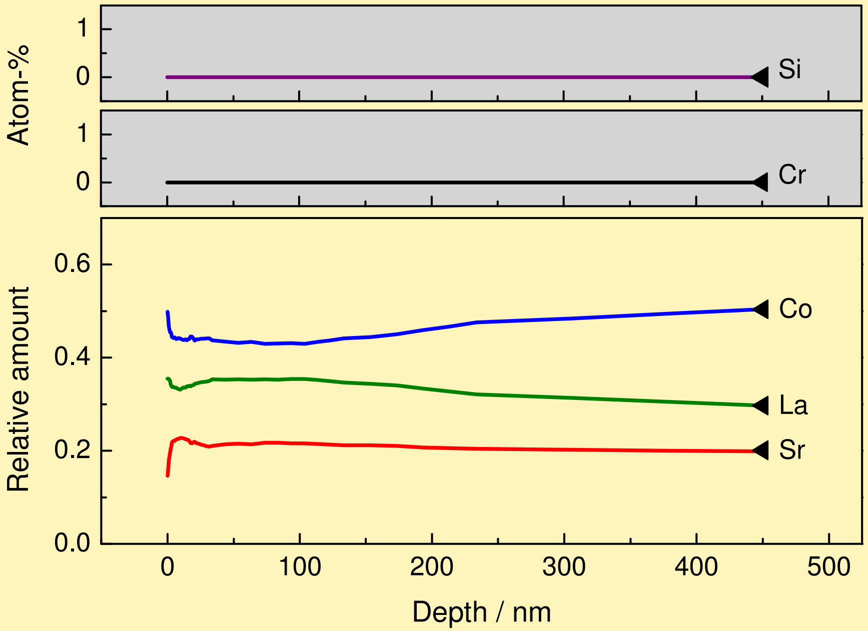


E. Bucher et al., Proc. SOFC-XII, 2011.

XPS post-test analysis (1)

- $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ after 1000 h at 600°C in vicinity of a Cr-source in dry atmosphere
- Only small deviations from the nominal La/Sr/Co ratio
- No Cr- or Si-contamination detected
- Correlates with stable oxygen exchange kinetics
- Elemental depth profiles are comparable to those obtained after 1000 h in dry atmosphere without a Cr-source

$(La,Sr)CoO_{3-\delta}$ with Cr-source
1000 h dry atmosphere

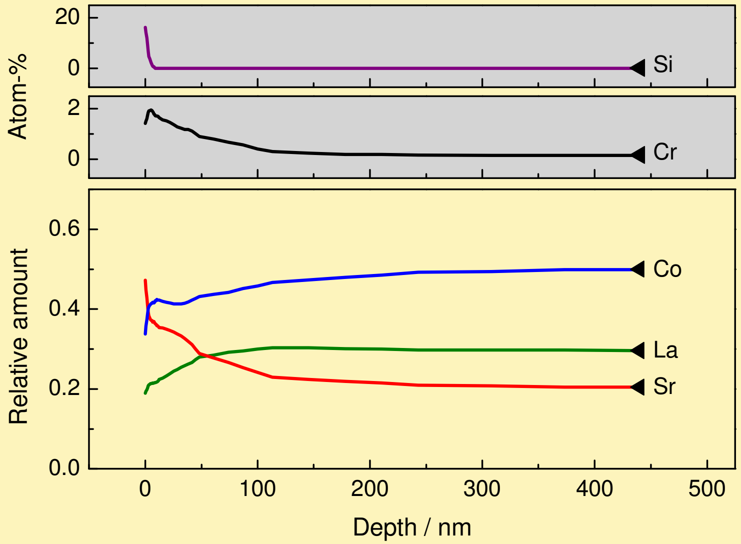


E. Bucher et al., Proc. SOFC-XII, 2011.

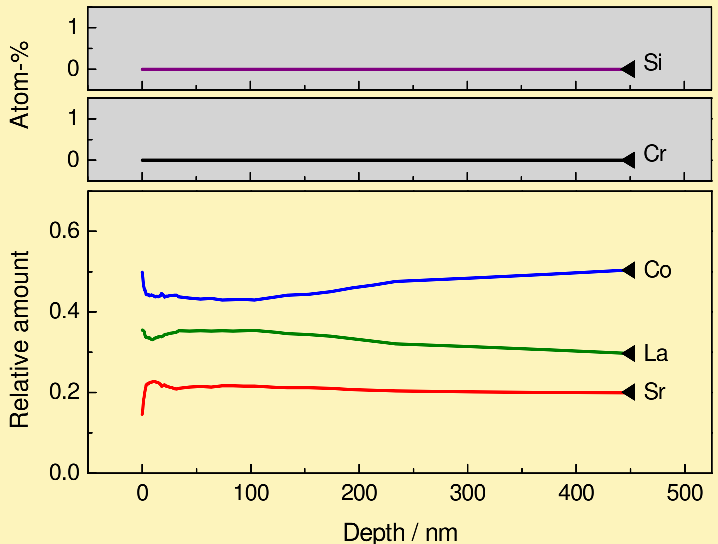
XPS post-test analysis (2)

- $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ in vicinity of a Cr-source, 1000 h at 600°C in humidified atmosphere (30% relative humidity)
- XPS shows Cr-poisoning and Sr-enrichment : 0 - 100-150 nm
- In addition Si-impurities: 0 - 10 nm nm
- Cr- and Si-poisoning correlates with decrease in oxygen exchange kinetics

(La,Sr)$CoO_{3-\delta}$ with Cr-source
1000 h humidified atmosphere



(La,Sr)$CoO_{3-\delta}$ with Cr-source
1000 h dry atmosphere



E. Bucher et al., Proc. SOFC-XII, 2011.

Characterization of electrolyte materials

Electrical properties of scandia-stabilized zirconia co-doped with yttria and ceria

Characterization of electrolyte materials

- Investigation of $Ce_xY_{0.2-x}Sc_{0.6}Zr_{3.2}O_{8-d}$ $(0<x<0.2)$:
  systematic variation of yttria and ceria content

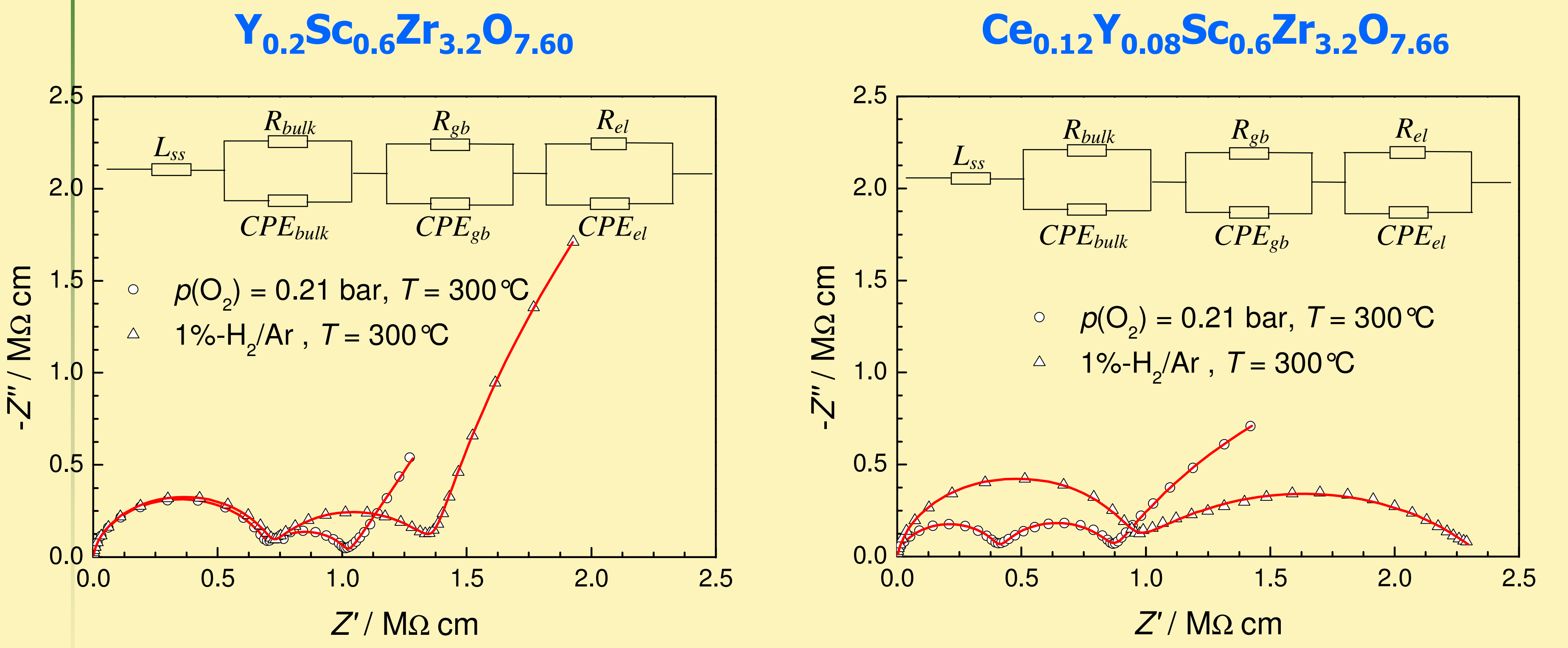
- Determination of bulk and grain boundary conductivities as a function of
  - temperature
  - oxygen partial pressure

- Thermal analysis
  - thermogravimetry
  - dilatometry

- Ageing studies in reducing atmospheres for more than 5000 hours by application of both dc and ac measurements

Characterization of electrolyte materials

Impedance spectra in oxidizing and reducing atmospheres (300°C)

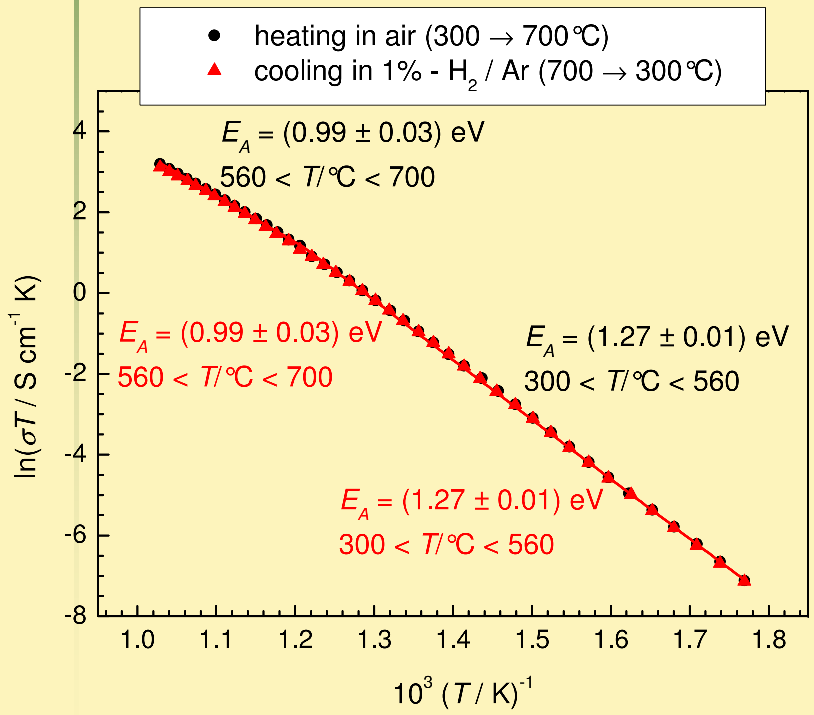


Characterization of electrolyte materials

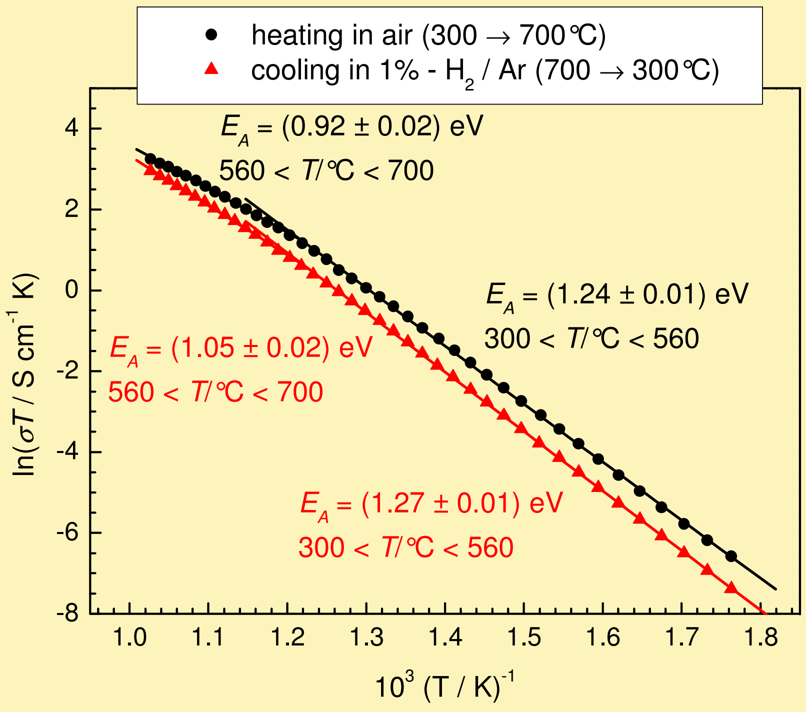
Bulk conductivity as a function of temperature in oxidizing and reducing atmospheres

Comparison between $Y_{0.2}Sc_{0.6}Zr_{3.2}O_{7.60}$ and $Ce_{0.12}Y_{0.08}Sc_{0.6}Zr_{3.2}O_{7.66}$: heating in air (oxidizing conditions) and cooling in 1%-H_2/Ar after reduction at 700° C for approx. 4 days

$Y_{0.2}Sc_{0.6}Zr_{3.2}O_{7.60}$



$Ce_{0.12}Y_{0.08}Sc_{0.6}Zr_{3.2}O_{7.66}$

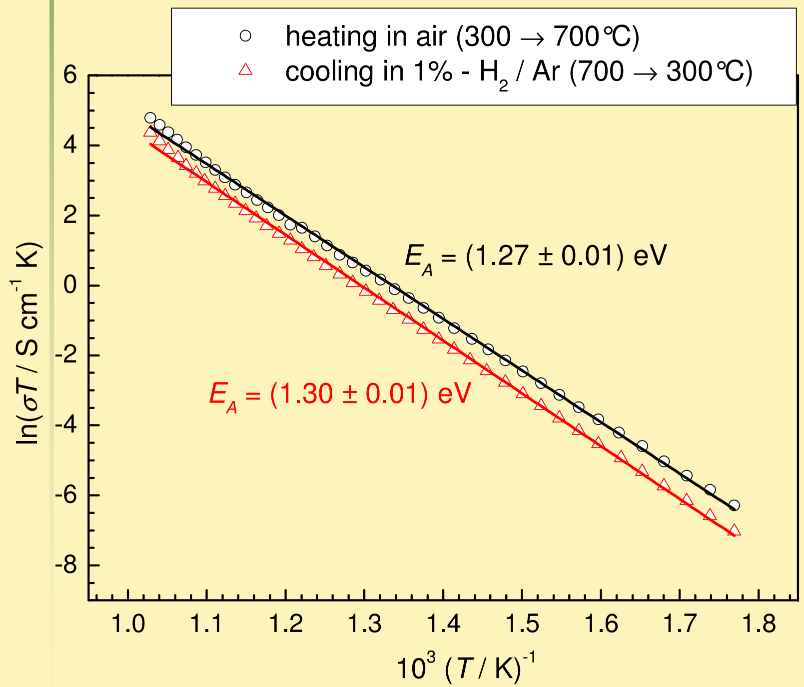


Characterization of electrolyte materials

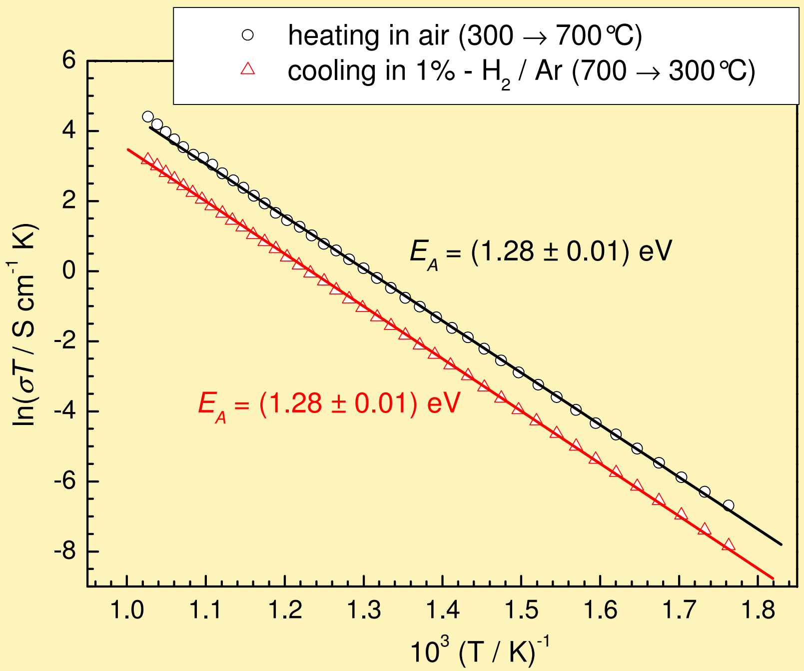
Grain boundary conductivity as a function of temperature in oxidizing and reducing atmospheres

Comparison between $Y_{0.2}Sc_{0.6}Zr_{3.2}O_{7.60}$ and $Ce_{0.12}Y_{0.08}Sc_{0.6}Zr_{3.2}O_{7.66}$: heating in air (oxidizing conditions) and cooling in 1%-H_2/Ar after reduction at 700° C for approx. 4 days

$Y_{0.2}Sc_{0.6}Zr_{3.2}O_{7.60}$



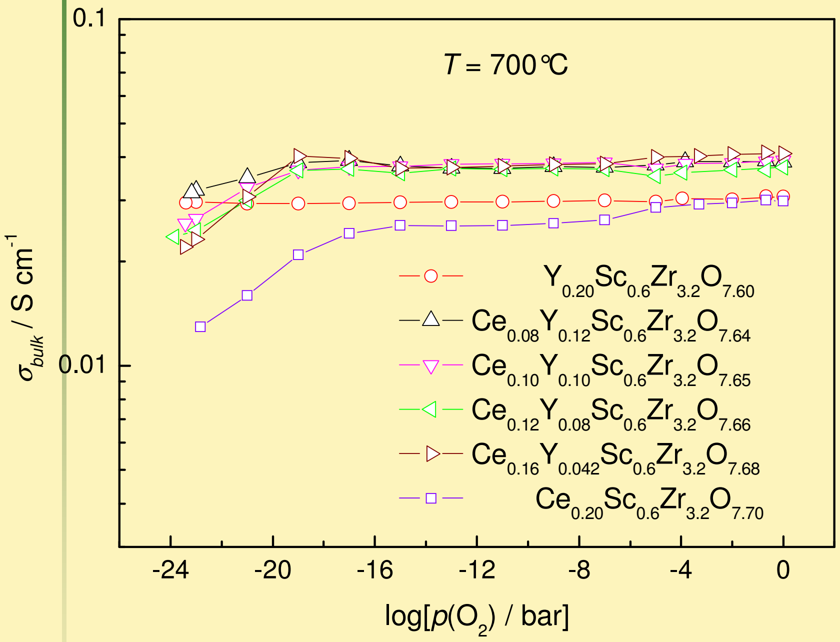
$Ce_{0.12}Y_{0.08}Sc_{0.6}Zr_{3.2}O_{7.66}$



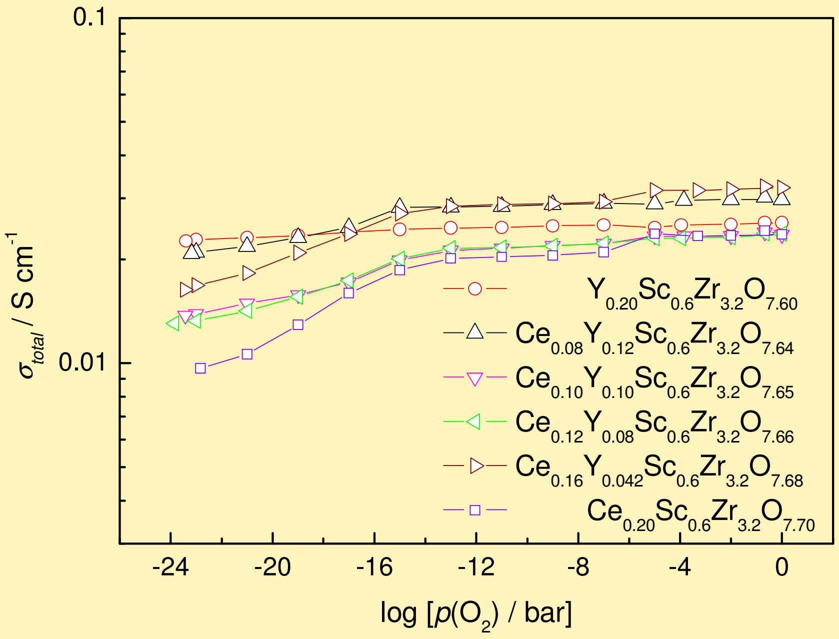
Characterization of electrolyte materials

Electrical conductivity as a function of oxygen partial pressure at 700°

Bulk conductivity



Total (bulk + gb) conductivity



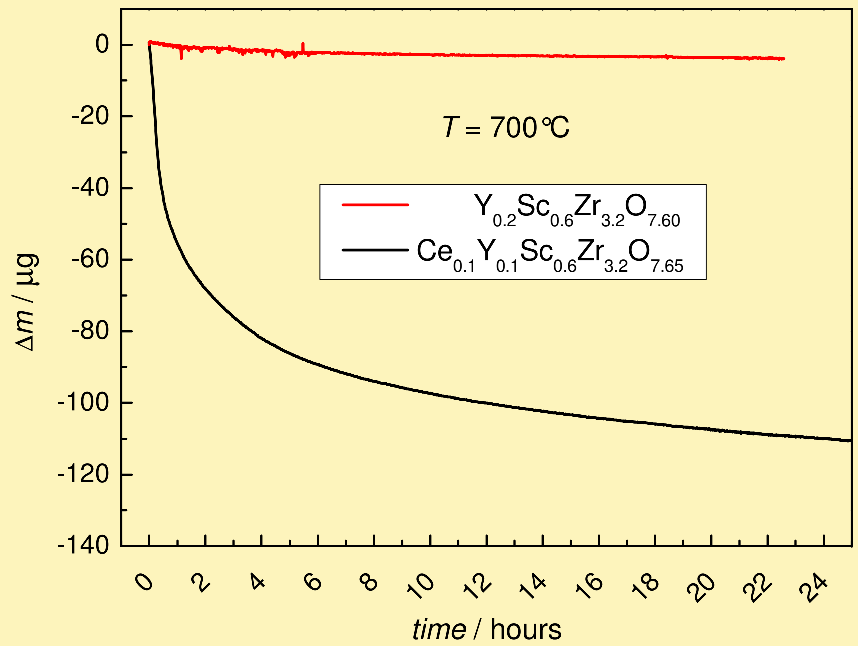
- **All samples containing ceria show a remarkable decrease of the ionic conductivity at $p(O_2) < 10^{-15}$ bar**
- **This effect is even more pronounced for grain boundaries**

[W. Preis, A. Egger, J. Waldhäusl, W. Sitte, E. de Carvalho, J.T.S. Irvine, ECS Transactions 25 (2009) 1635-1642]

Characterization of electrolyte materials

Thermogravimetry as a function of pO_2 at 700°

$Ce_{0.1}Y_{0.1}Sc_{0.6}Zr_{3.2}O_{8-\delta}$ vs. $Y_{0.2}Sc_{0.6}Zr_{3.2}O_{8-\delta}$



- **approx. 66% of ceria in $Ce_{0.1}Y_{0.1}Sc_{0.6}Zr_{3.2}O_{8-\delta}$ is reduced ($Ce^{4+} \rightarrow Ce^{3+}$) after 250 h in 1%-$H_2$/Ar at 700° C**
- **negligible effect for $Y_{0.2}Sc_{0.6}Zr_{3.2}O_{8-\delta}$ (no ceria)**

Characterization of electrolyte materials

Doping with rare earth elements

Highest ionic concutivity with Sc-doping

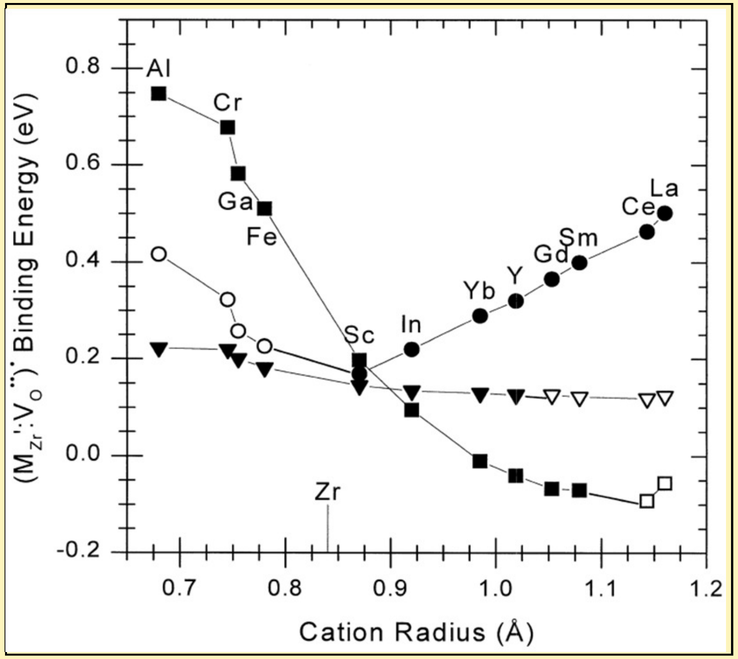
→ similar ionic radius as Zr

→ smallest lattice strain

→ maximum oxygen vacancy concentration

→ lowest association energy of defect clusters formed with oxygen vacancies

Association energy of defect clausters as function of the radius of various cations (M^{3+})

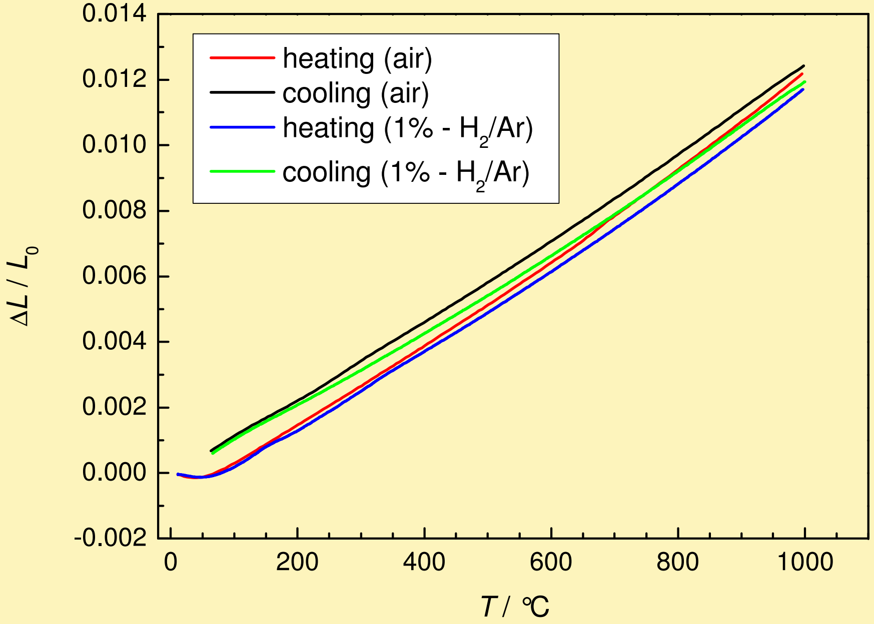


[M.O. Zacate, L. Minervini, D.J. Bradfield, R.W. Grimes, K.E. Sickafus, Solid State Ionics 128 (2000) 243-254]

Characterization of electrolyte materials

Dilatometry in oxidizing and reduzing atmospheres

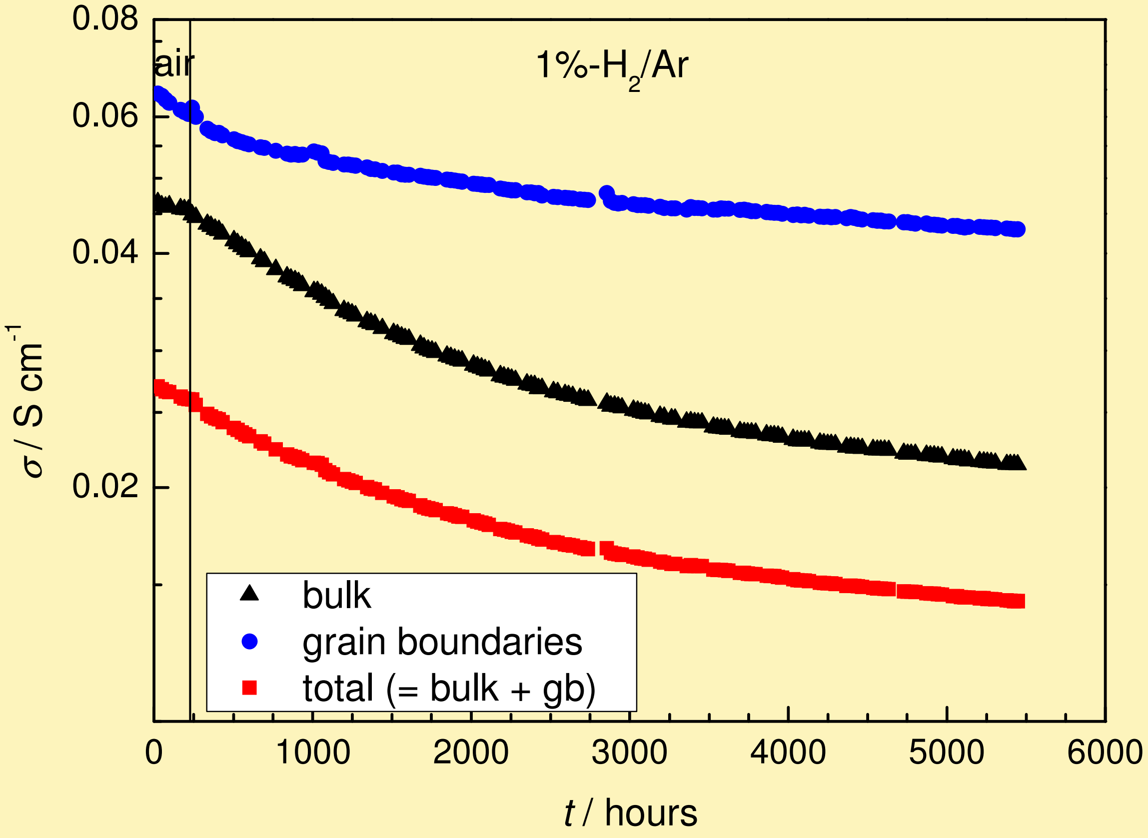
Thermal expansion of $Ce_{0.1}Y_{0.1}Sc_{0.6}Zr_{3.2}O_{8-\delta}$



- thermal expansion seems to be unaffected by reduction in 1% - H_2/Ar (200 hours at 700° C)
- thermal expansion coefficient of $Ce_{0.1}Y_{0.1}Sc_{0.6}Zr_{3.2}O_{8-\delta}$ at 600° C: $\alpha \approx 12.5 \times 10^{-6}$ K^{-1}

Characterization of electrolyte materials

Aging study of $(CeO_2)_{0.01}(Sc_2O_3)_{0.10}(ZrO_2)_{0.89}$ at 700° under 1%-H_2/Ar



Summary

Cathodes

Oxygen exchange properties of **BSCF, LSCF, LSC, NDN** including

- Long-term stability in real (humid) atmospheres
- chromium and silicon poisoning

Humid atmospheres strongly enhance transport of Cr and Si via the gas phase, even at temperatures as low as 600°C.
→ dry air can significantly increase life-time of SOFC cathodes

Electrolytes (doped Sc-Zr)

- bulk and grain boundary conductivity = f(T, pO_2)
- ageing studies

All ceria-containing electrolytes show a decrease of the ionic conductivity (bulk and grain boundaries) under reducing conditions

Acknowledgment (I)

Support by co-workers and partners

- Montanuniversität Leoben
  W. Preis, J. Bugajski,
  P. Gsaxner
- Universität Innsbruck
  F. Klauser, E. Bertel
- MPI FKF Stuttgart
  J. Maier, R. Merkle
- Partners of SOFC600

Acknowledgment (II)

Research Co-operations

Financial Support

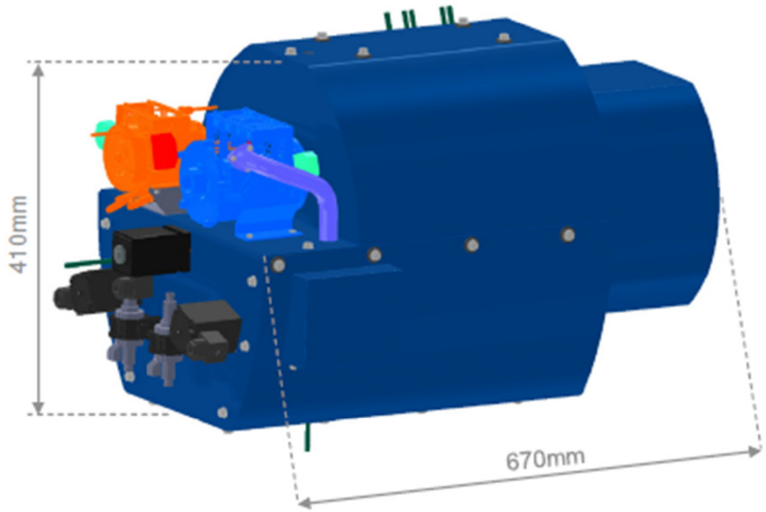
Thank you for your attention!

Zusätzliche Folien

AVL

AVL SOFC APU Generation I

STAND ALONE SOLID OXIDE FUEL CELL AUXILIARY POWER UNIT



Status: Design Freeze AVL APU GEN 1.0

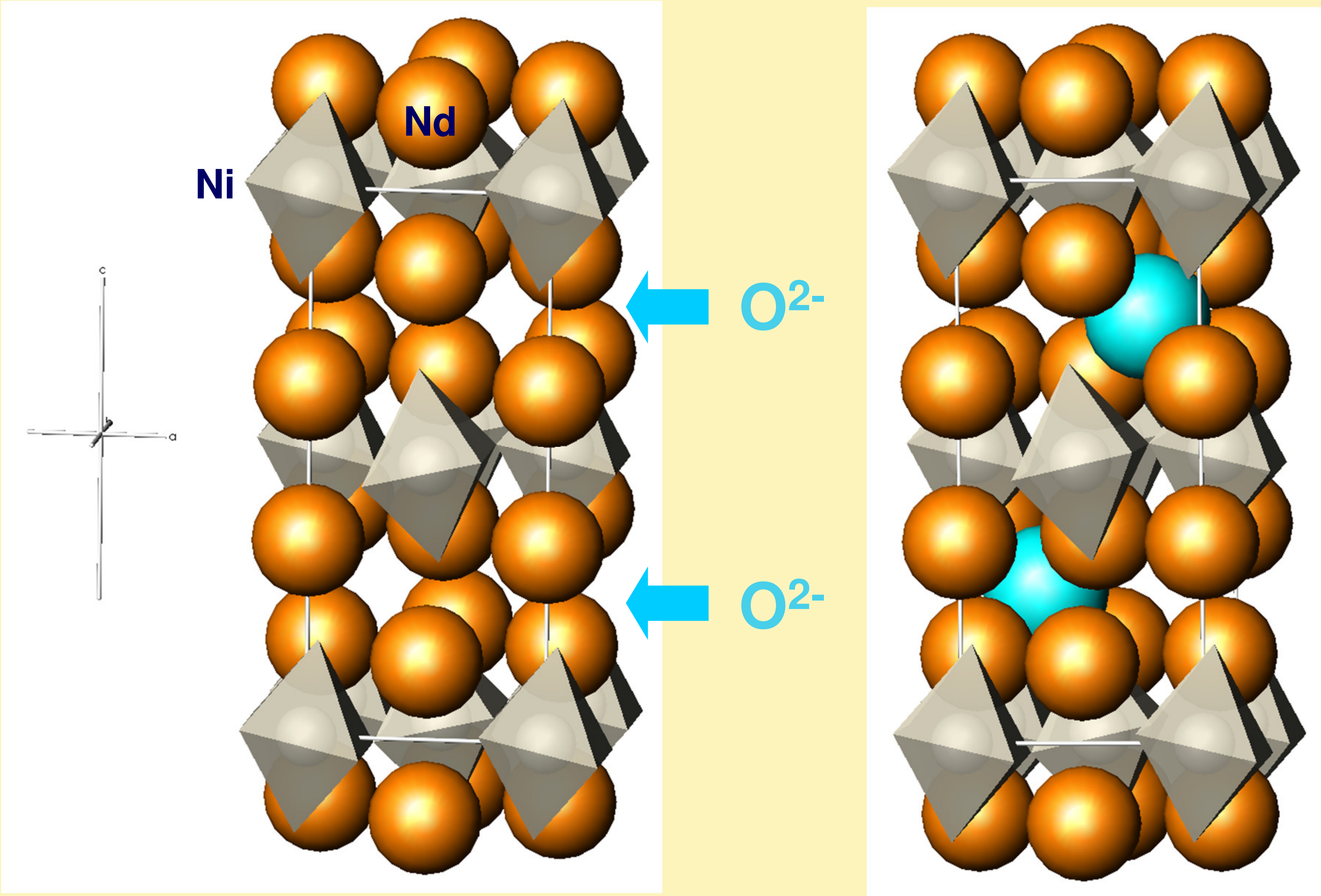
Design Targets:

- → 3kW electrical power
- → 10kW thermal power
- → el. efficiency ~35%
- → Fuel: european road diesel (< 10 ppm S)
- → 80L, 65kg
- → ~ 55dB(A) noise

Technology:

- → Solid Oxide Fuel Cell
- → anode-supported stack
- → hot-gas anode recirculation
- → auto thermal reforming
- → highly efficient radial-blowers for media supply
- → system internal regeneration approaches

$Nd_2NiO_{4+\delta}$



$La_{0.6}Sr_{0.4}CoO_{3-\delta}$ elemental depth profiles

La, Sr, Co

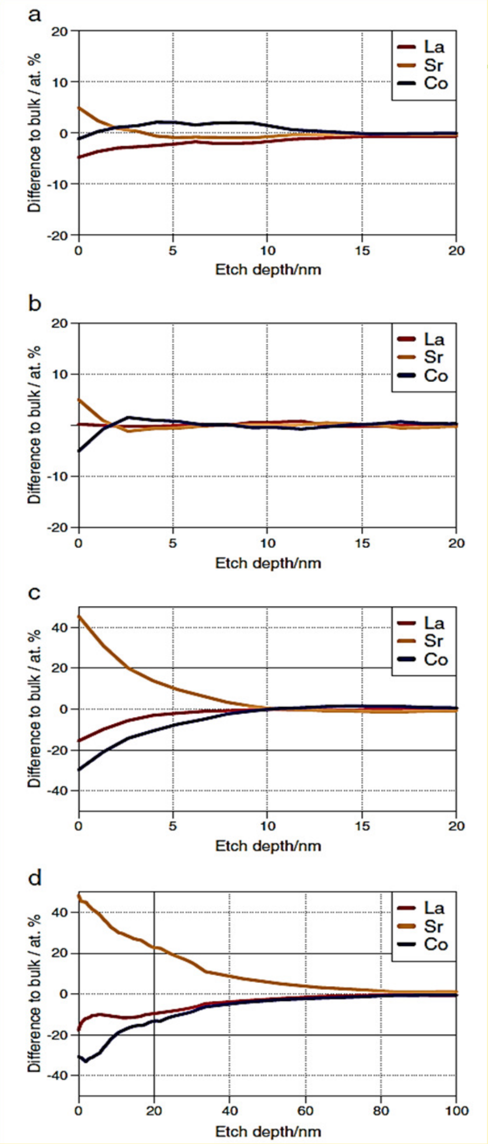
+ O, Si, Na

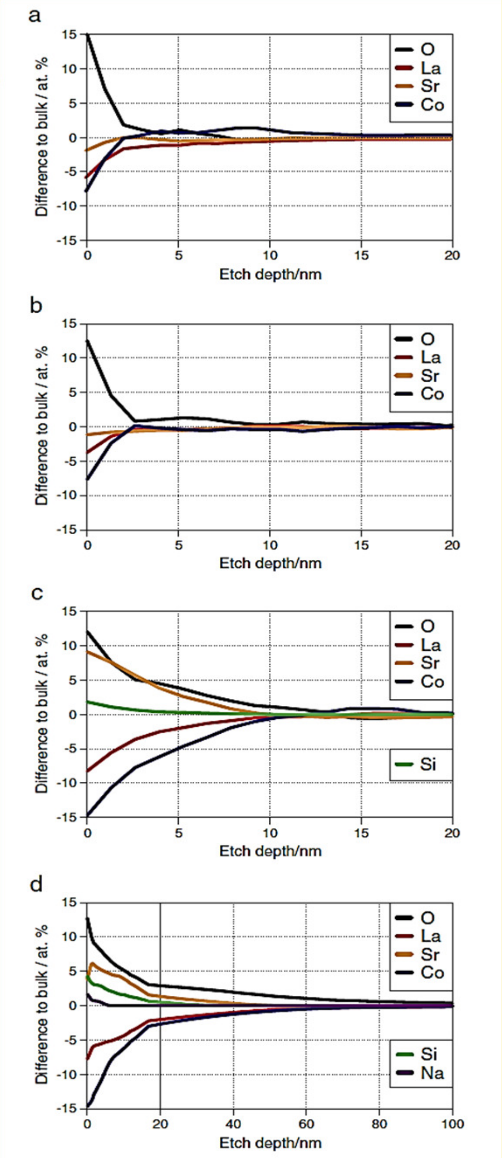
fresh sample

1000h dry 1% O_2/Ar atmosphere

1000h dry + 1000h humid 1% O_2/Ar-atmosphere

1000h dry + 2000h humid + 1% NaCl sol. O_2/Ar-atmosphere

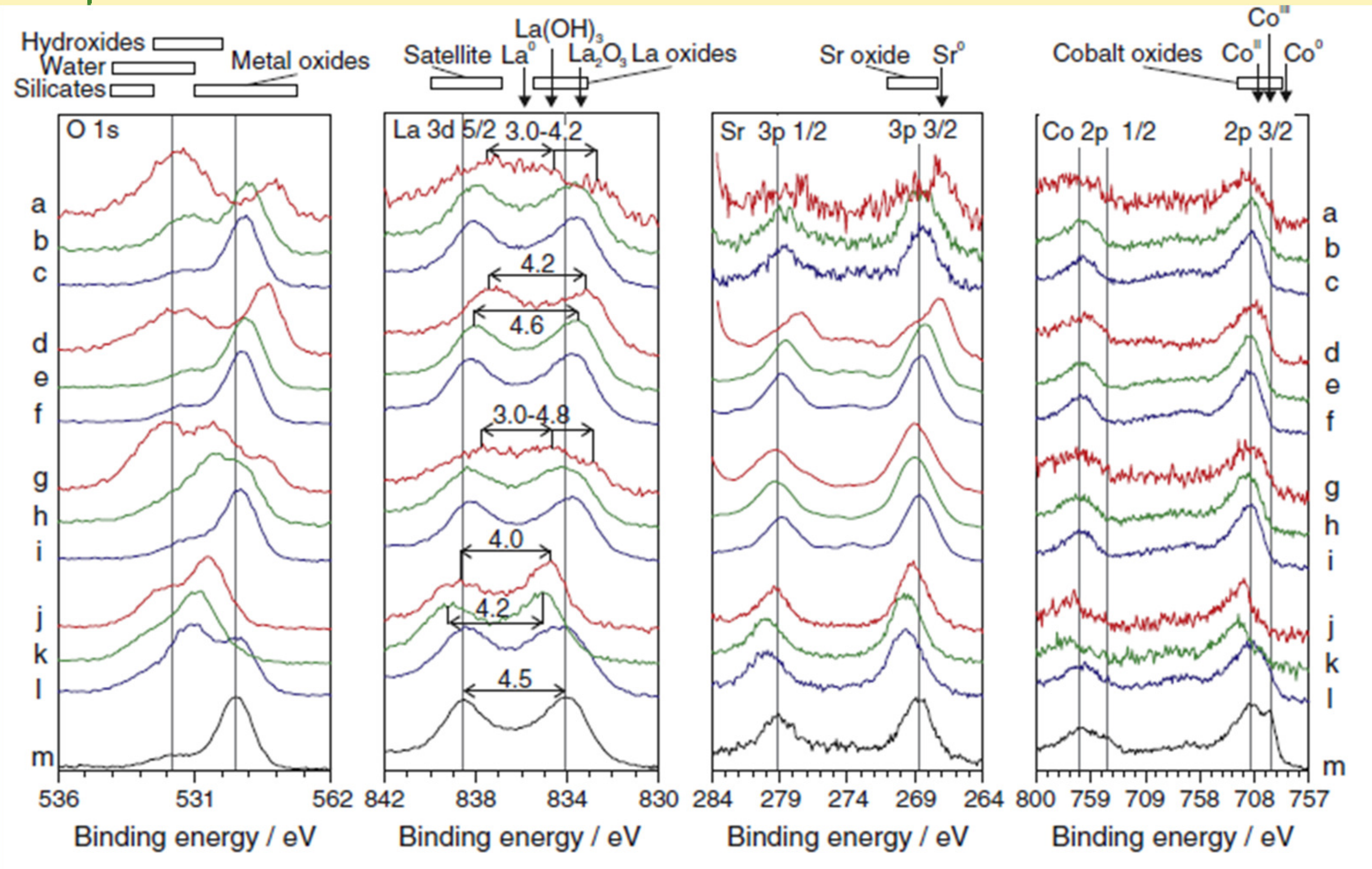




E. Bucher, W. Sitte, F. Klauser, E. Bertel, Solid State Ionics, *in press* (2012)

$La_{0.6}Sr_{0.4}CoO_{3-\delta}$ core level spectra

O 1s, La 3d, Sr 3p



As prepared sample
a) 0 nm
b) 1 nm
c) 10 nm

After 1000 h in a dry atmosphere
d) 0 nm
e) 1 nm
f) 10 nm

After additional 1000 h in a humid atmosphere
g) 0 nm
h) 1 nm
i) 10 nm

Bulk - reference
j) > 300 nm

E. Bucher, W. Sitte, F. Klauser, E. Bertel,
Solid State Ionics, *in press* (2012)

$La_{0.6}Sr_{0.4}CoO_{3-\delta}$ surface morphology

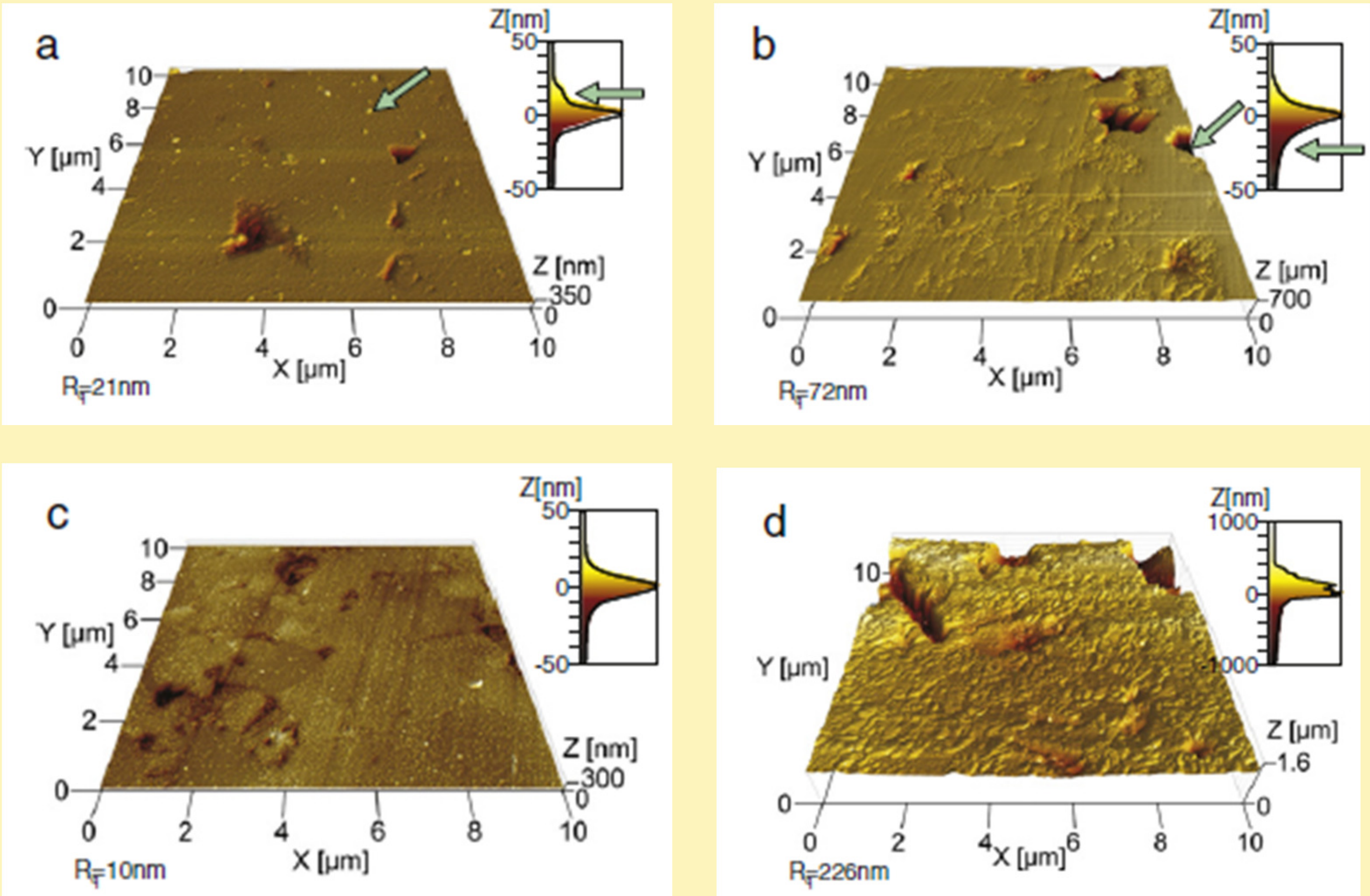
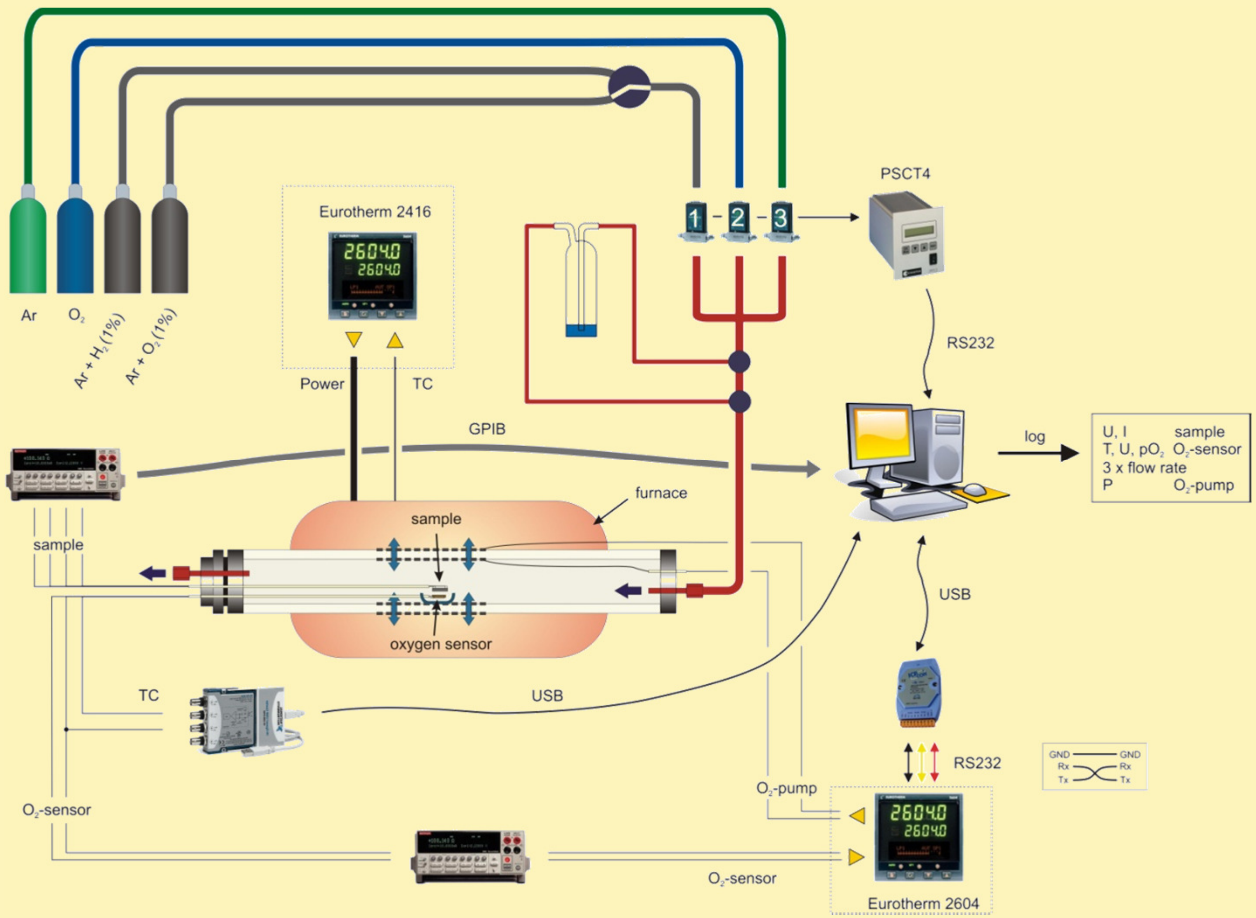


Fig. 6. Surface topography of different $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ samples; AFM large area scans ($10\times10\,\mu m^2$) of (a) the fresh surface, (b) after 1000 h in a dry atmosphere, (c) after an additional 1000 h in a moderately humidified atmosphere (30% r.h.), and (d) after a further 2000 h in a strongly humidified atmosphere (75% r.h.) including 1000 h of exposure to a saturated NaCl solution; R_q values represent the root-mean-square roughness. Height histograms are given as insets with each image.

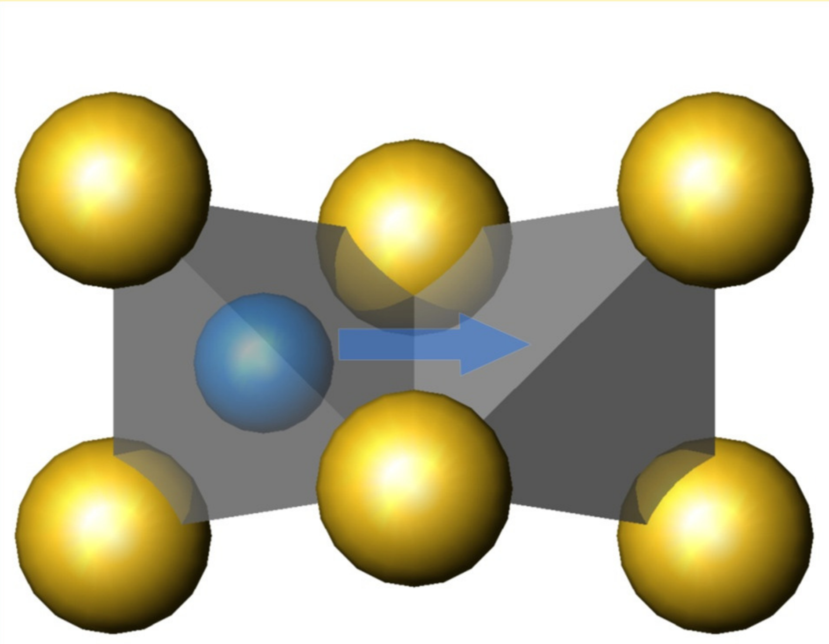
Characterization of electrolyte materials

Electrical conductivity as a function of pO_2 - electrochemical oxygen pump



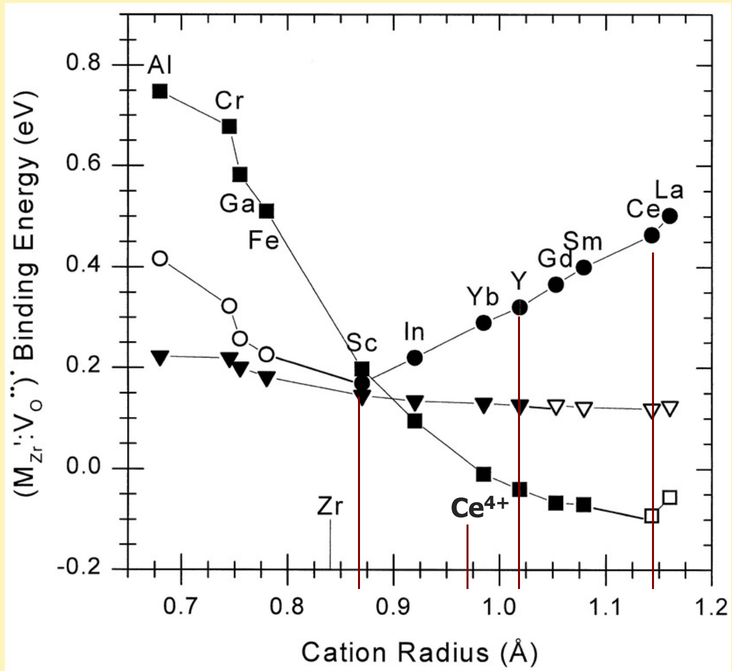
Characterization of electrolyte materials

Reduction of $Ce^{4+} \rightarrow Ce^{3+}$:
- increase of oxygen nonstoichiometry
- decrease of ionic conductivity
- increase of activation energy



Jump of oxygen ion through a common edge of two adjacent tetrahedra in the fluorite structure

Association energy versus cation (M^{3+}) radius



[M.O. Zacate, L. Minervini, D.J. Bradfield, R.W. Grimes, K.E. Sickafus, Solid State Ionics 128 (2000) 243-254]