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Quantifying the oxygen stoichiometry of Pr-doped ceria through X-ray diffraction

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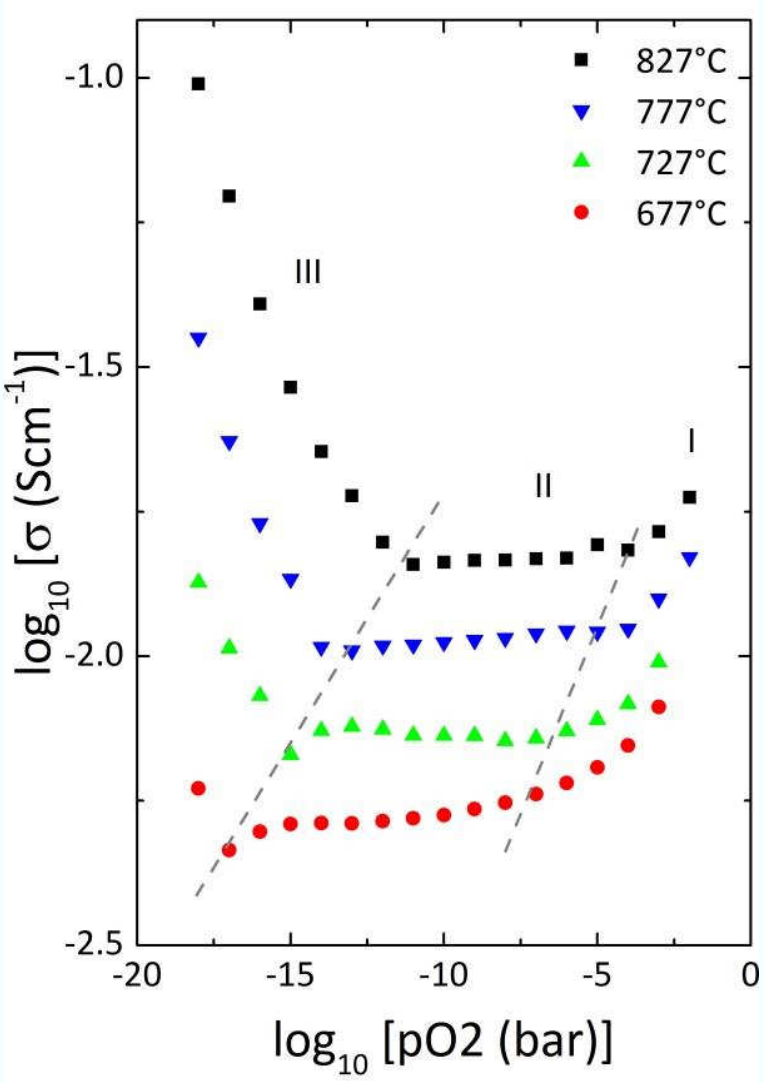
Institute for Energy- and Climate Research
IEK-1: Materials Synthesis and Processing

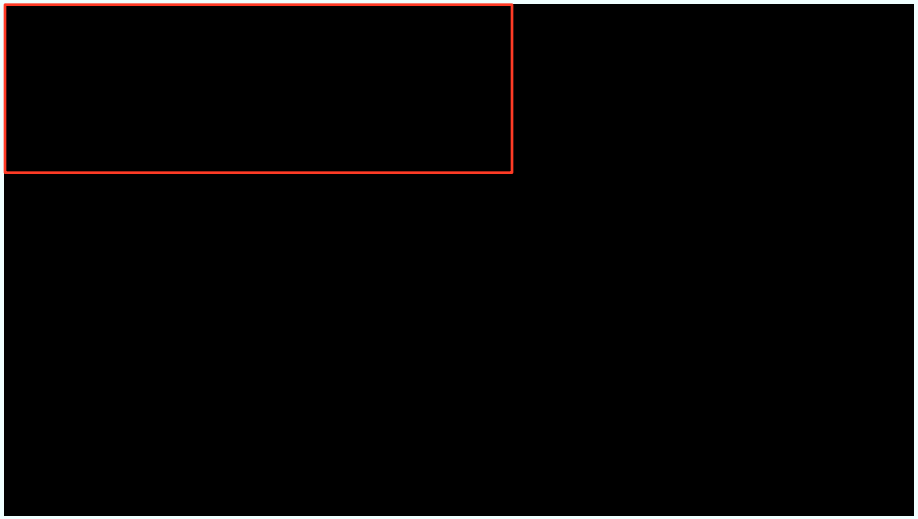
Outline

- **Background and Motivation**
- HT-XRD: oxygen stoichiometry and microstrain
- Impact of conductivity on cathode performance
- Summary

High Temperature Equilibrium Conductivity



HTEC of dense 20PCO ceramics



DC conductivity as expected for PCO[1,2]

[1]: Bishop *et* al., J. Mater. Res., Vol. 27, No. 15, Aug 14, 2012

[2]: Bishop *et* al., Phys. Chem. Chem. Phys., 2011, **13**, 10165–10173

PCO as a cathode material

Figure of merit: $L_C = D^*/k^q$

D*: oxygen self-diffusion coefficient
k^q: oyxgen surface exchange coefficient

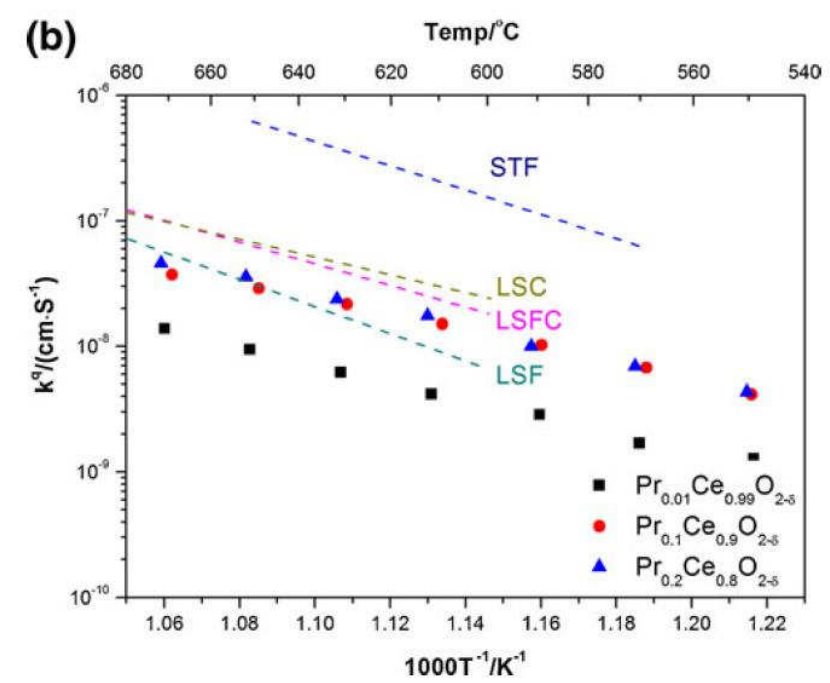
Model system suggests high k^q [1]

<u>Investigations on:</u>

PCO impregnated LSM-YSZ[2]

PCO interlayer for $LaNi_{0.6}Fe_{0.4}O_3$ [3]

PCO as an active material[4]



[1]: Chen *et* al., J. Electroceram. (2012) 28:62-69
[2]: Y. Ren, *et* al., *Journal of Materials Chemistry* **22** (2012) (48) 25042.
[3]: R. Chiba, *et* al., *Electrochemical and Solid-State Letters* **12** (2009) (5) B69.
[4]: R. Chiba, *et* al., *Solid State Ionics* **197** (2011) (1) 42.

Conductivity of $Pr_{1-x}Ce_xO_{2-\delta}$

Reduction

[redacted]

Conductivity

[redacted]

[redacted]

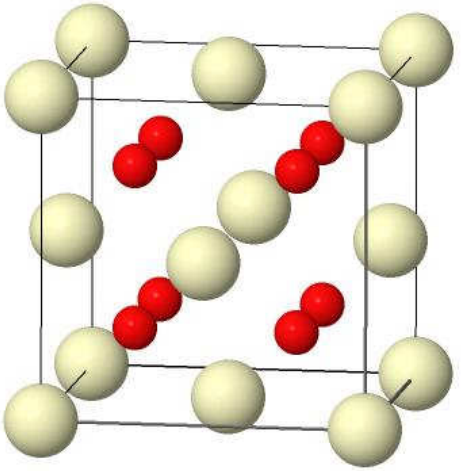
Charge neutrality

[redacted]

High pO_2

[redacted]

[redacted]



Ce^{4+}

O^{2-}

[redacted]

Bishop *et* al., J. Mater. Res., Vol. 27, No. 15, Aug 14, 2012

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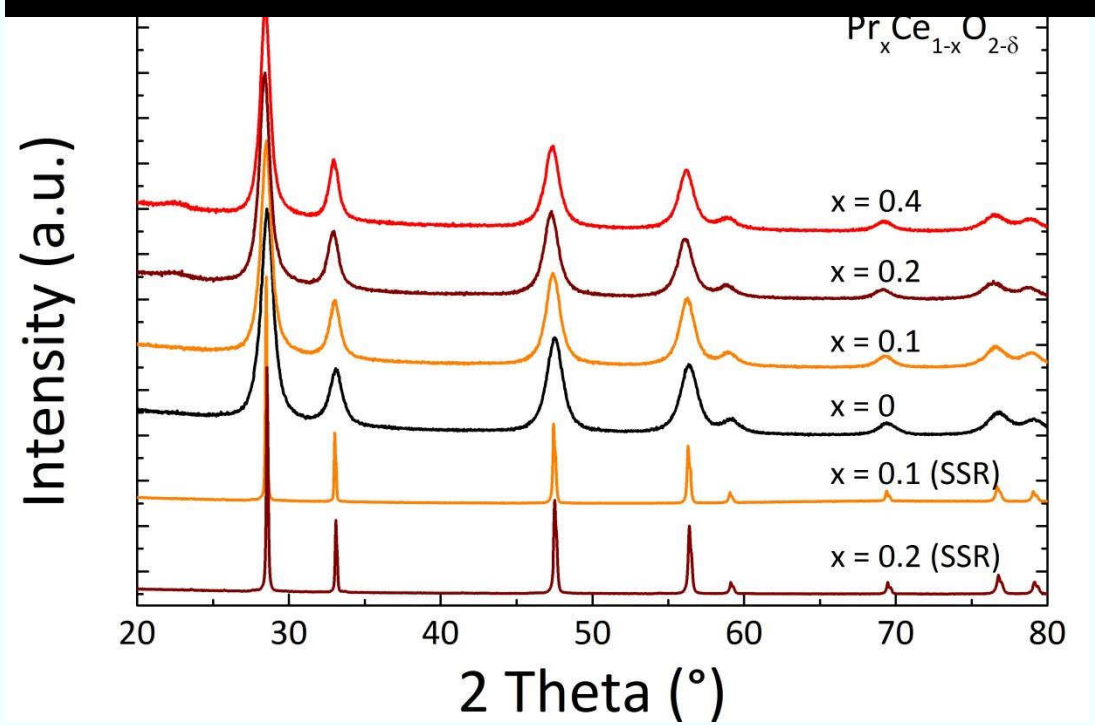
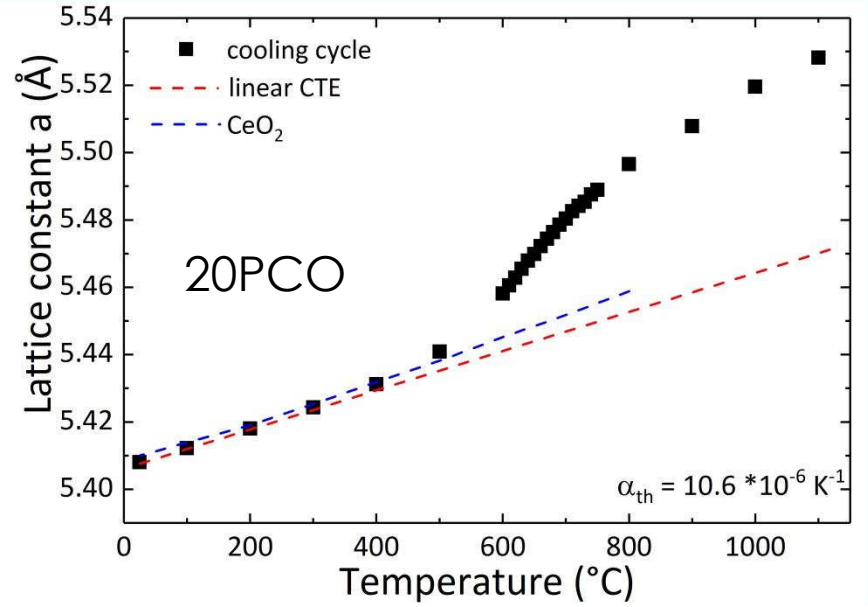
Synthesis



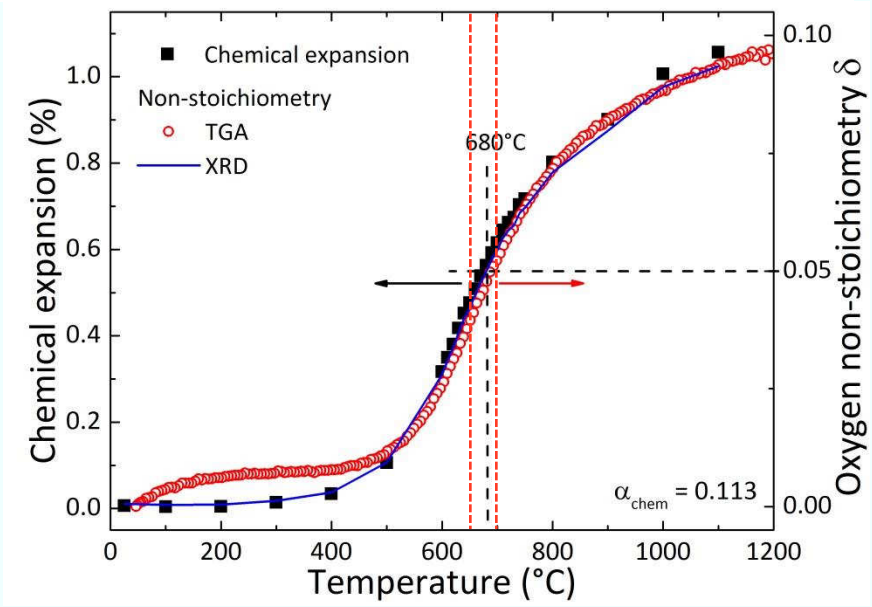
Line broadening:

- Crystallite size
- Microstrain (Δd_{hkl})

Chemical expansion in air



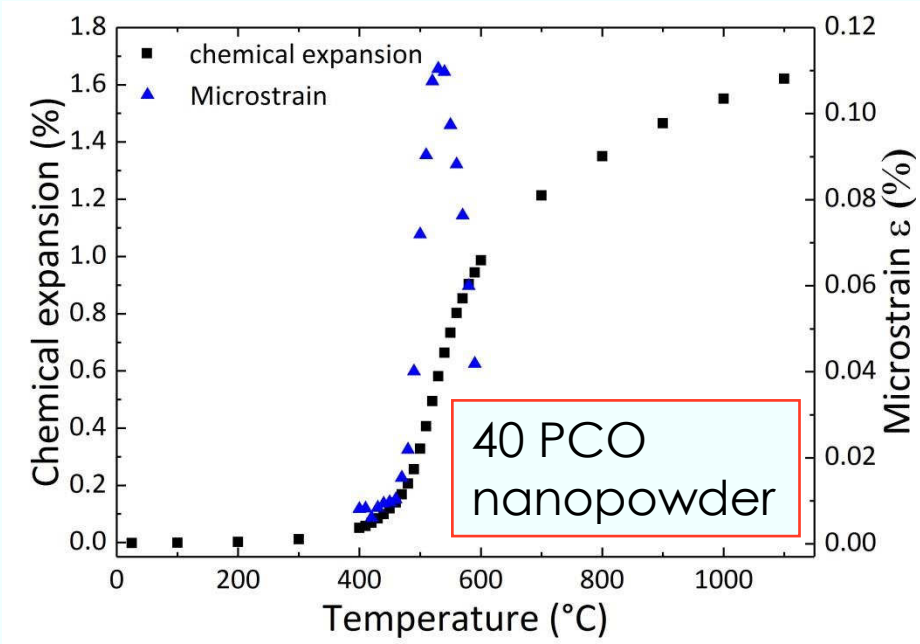
[redacted]

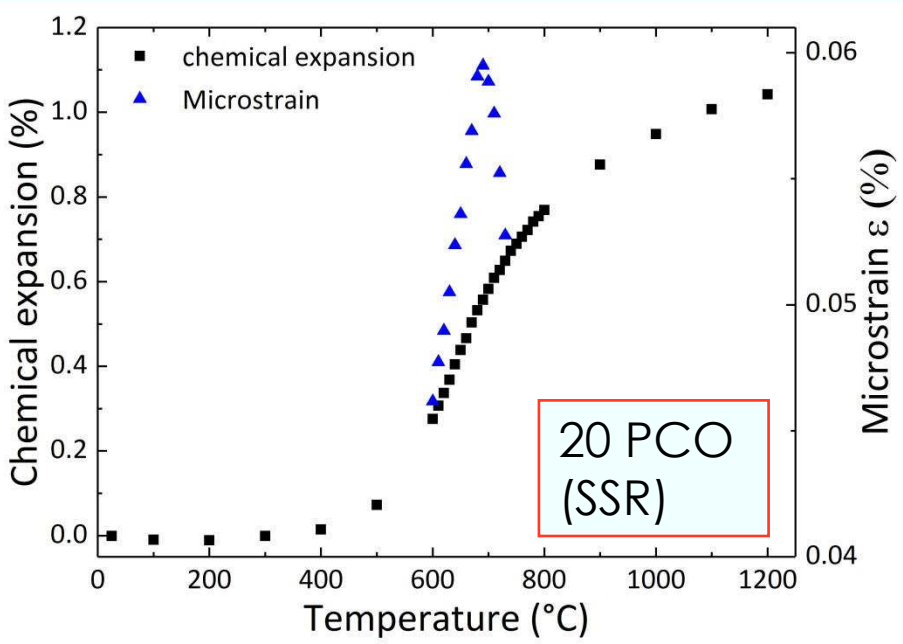


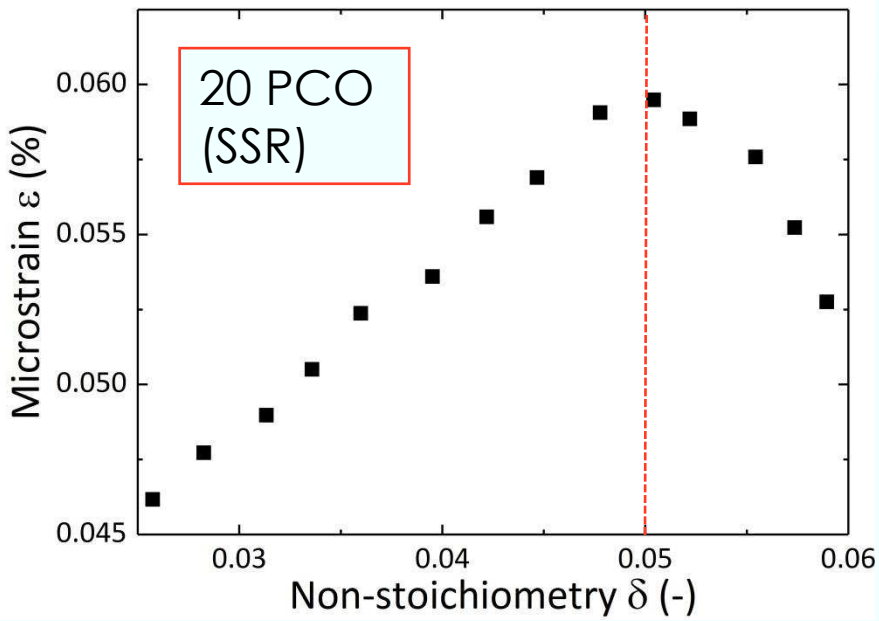
[redacted]

Kuru et al., Solid State Ionics 193 (2011, 1-4)

Microstrain analysis







- Microstrain: Δd_{hkl}

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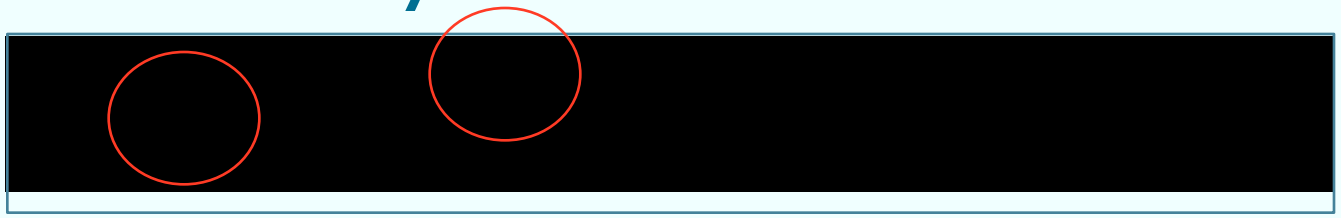
Conductivity of 20PCO in air

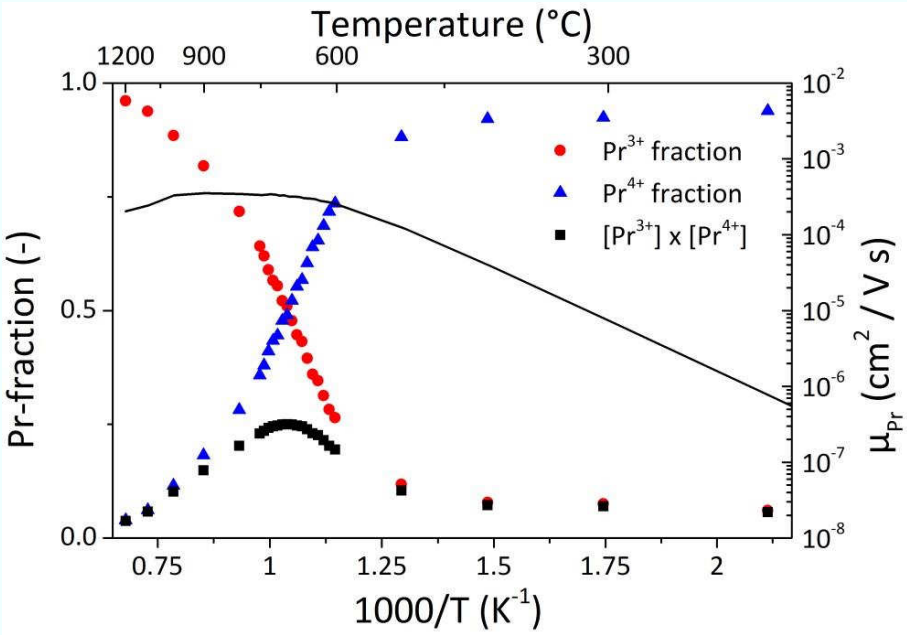


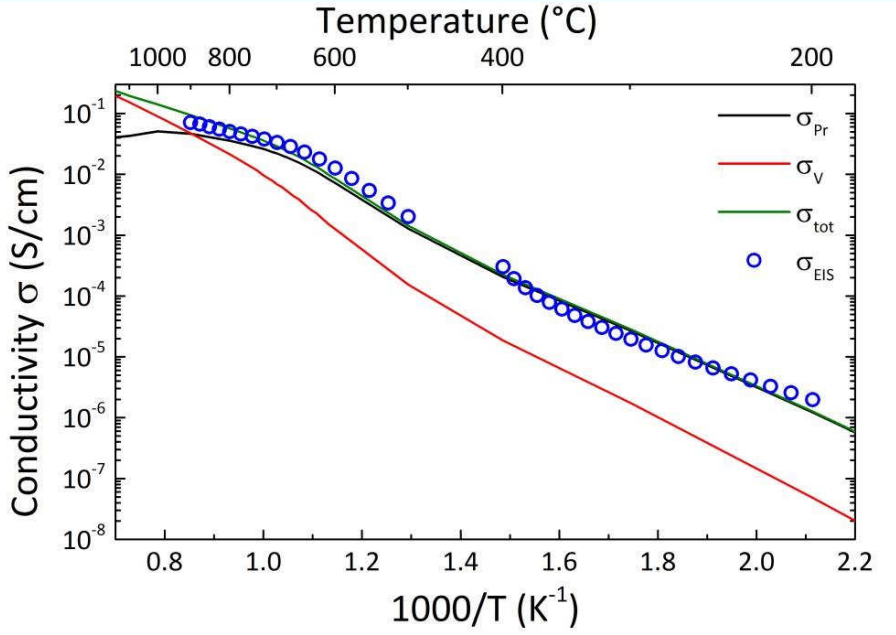
Ionic plateau ($pO_2 = 10^{-12}$ bar)

$H_{m,V} = 0.83$ eV
$\mu_{0,V} = 327$ cm²/Vs

$\sigma_{Pr} = \sigma_{tot} - \sigma_{ion}$

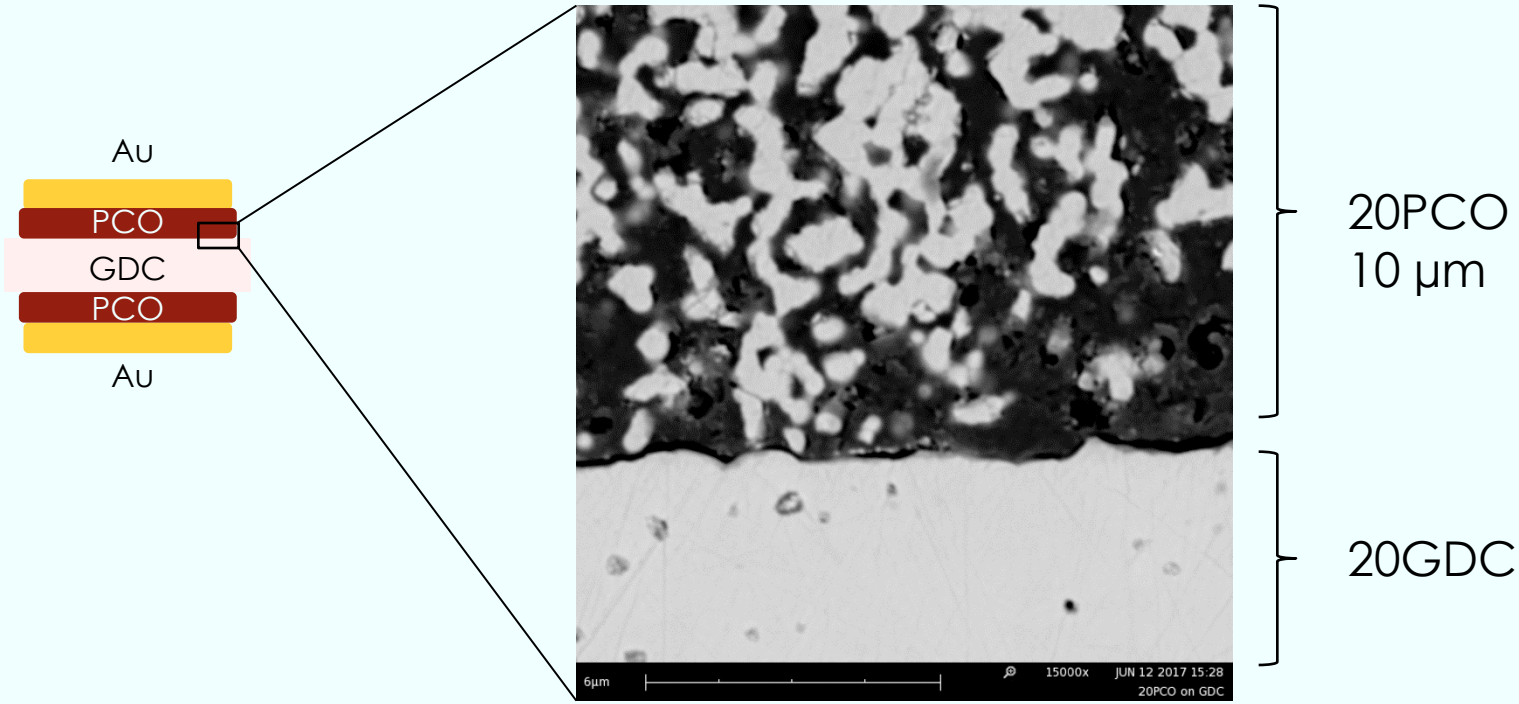
$H_{m,Pr} = 0.72$ eV
$\mu_{0,Pr} = 589$ cm²/Vs





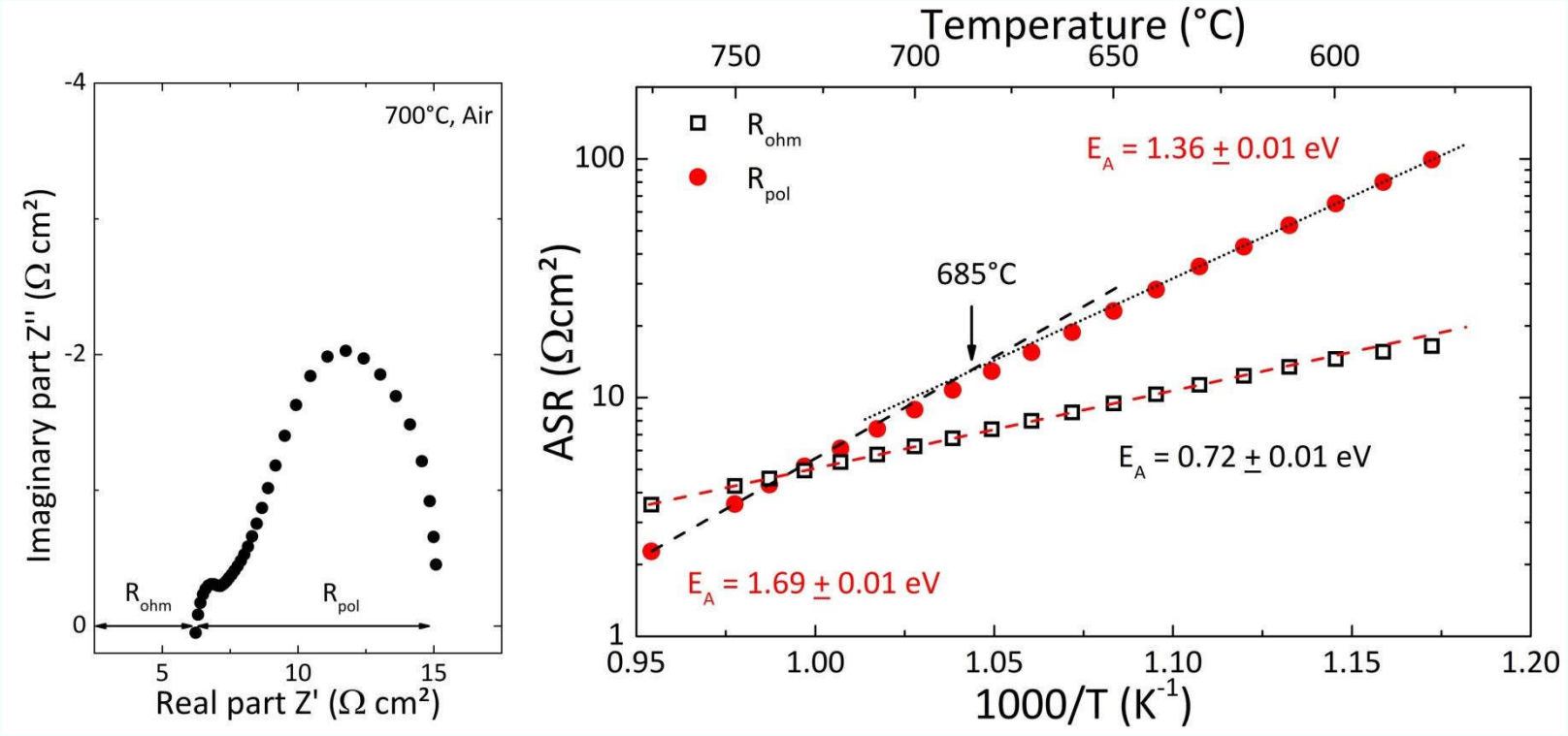
Sample preparation

Screen printed samples on 1 mm 20GDC pellet



Cathode sintering at 1300°C

Electrochemical impedance spectroscopy



Assumptions:

R_{ohm} = ionic resistance of electrolyte

R_{pol} = oxygen surface exchange resistance of electrode

Summary

- Conductivity of 20PCO sensitive to Pr-valence state
- Mixed valence of Pr induces microstrain – maximum at $[Pr^{3+}] = [Pr^{4+}]$
- Polaron mobility has maximum at $\delta = 0.05$ – 680°C for 20PCO in air
- Polaron mobility influences polarization resistance R_{pol}
- Activation energy of 20PCO cathodes increases with T
- Chemical expansion a problem for processing

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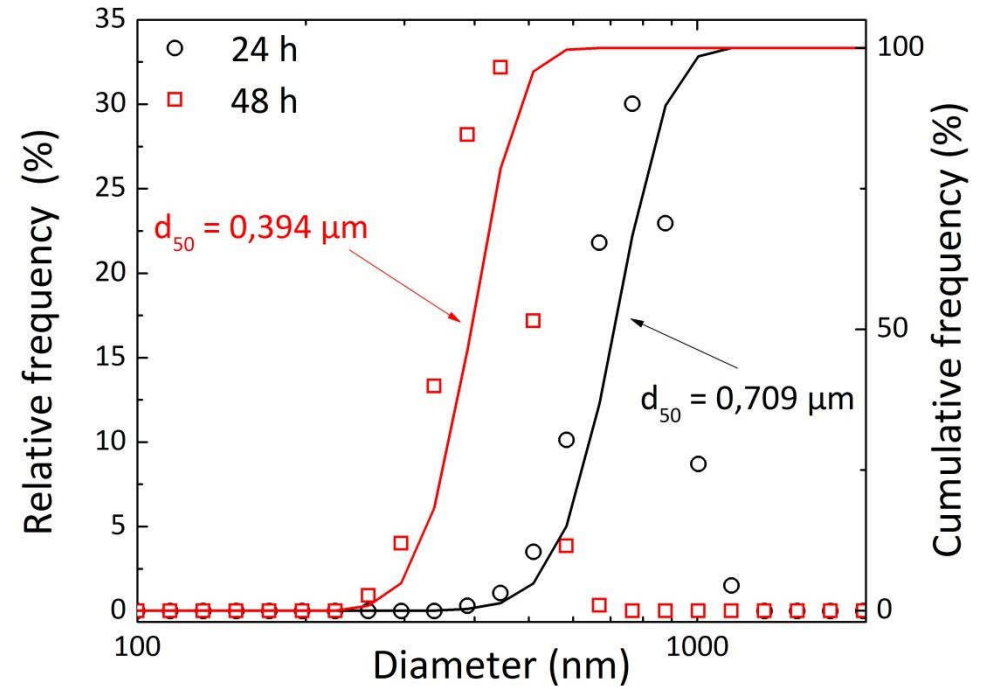
Thank you for your attention!

Preparation of screen printing pastes

Grain size is very important for properties of ceramic

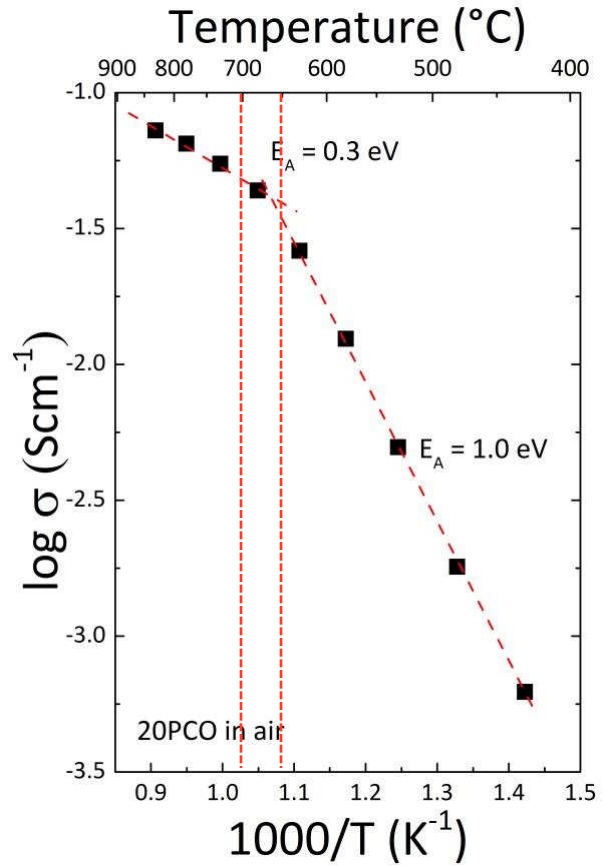
Control of particle size via ball-milling for solid state powders



Screen printing pastes: powders in terpineol mixing the pre-suspension with ethylcellulose solved in terpineol.
Layers were printed on 150 µm 8YSZ foils (Kerafol), using a circular geometry with Ø = 12 mm for PCO and Ø = 10 mm for LSCF. Symmetric and asymmetric cells were prepared for EIS and microscopy.

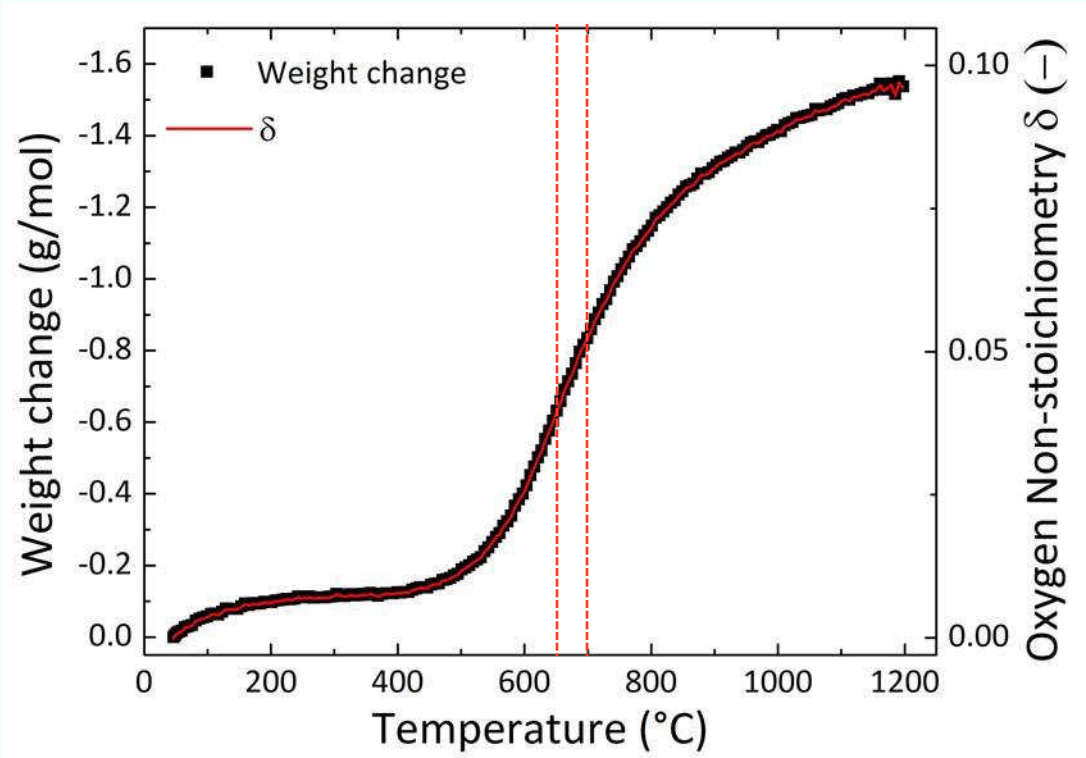
PCO in air

4-point conductivity



- Change in E_A

Thermogravimetry



- Temperature interval close to $\delta = 0.05$