ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

From Thin Films to Power Delivering Micro-Solid Oxide Fuel Cell Membranes

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Outline

Introduction

Results on µSOFC

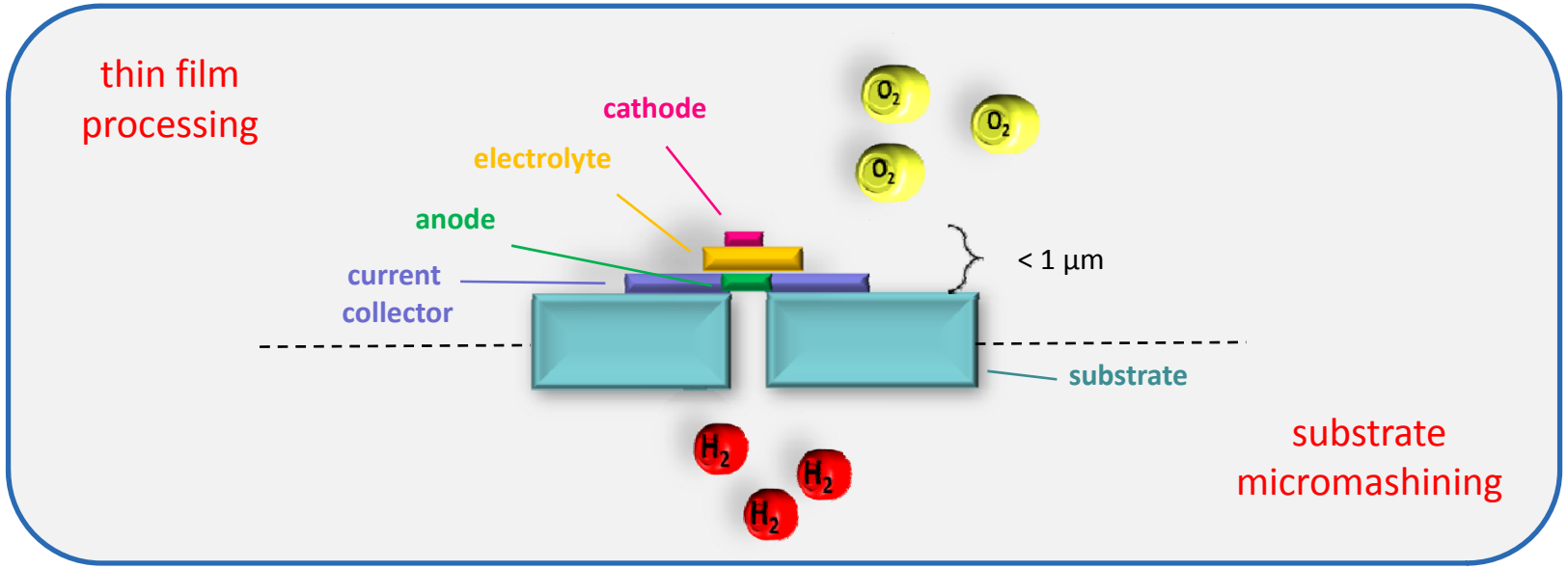
- Thin films
- Processing
- Power

Summary

Outlook

Micro-Solid Oxide Fuel Cell (µSOFC) Membranes

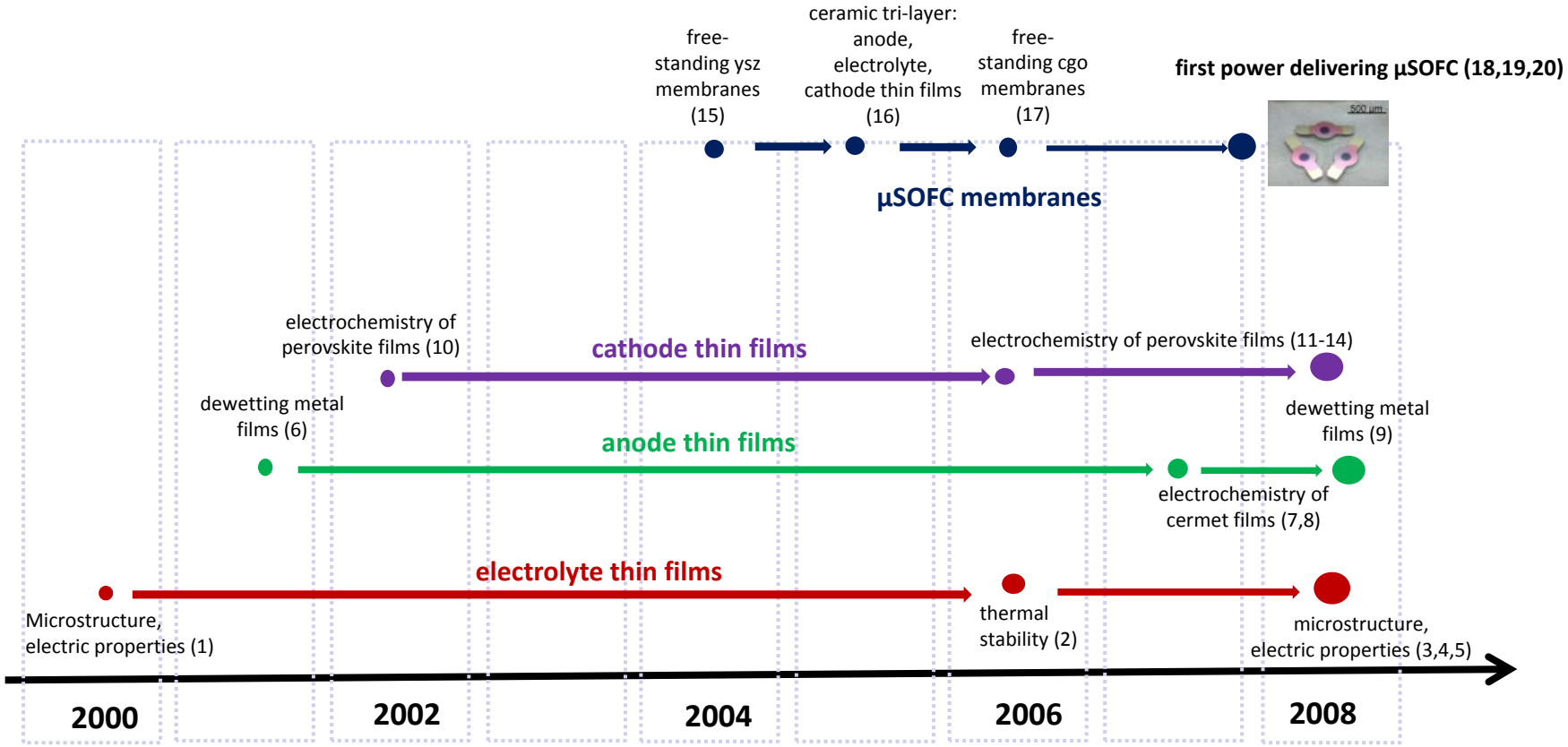
µSOFCs: Replacement of Li-ion batteries in portable electronics



- High efficiency & energy density, fuel flexibility, geographically independence
- Per membrane > 400 mW/cm^2 at 200-550°C

Bieberle-Hutter, A., et al., A micro-solid oxide fuel cell system as battery replacement. Journal of Power Sources, 2008. 177(1): p. 123-130.

From thin films to power delivering µSOFCs



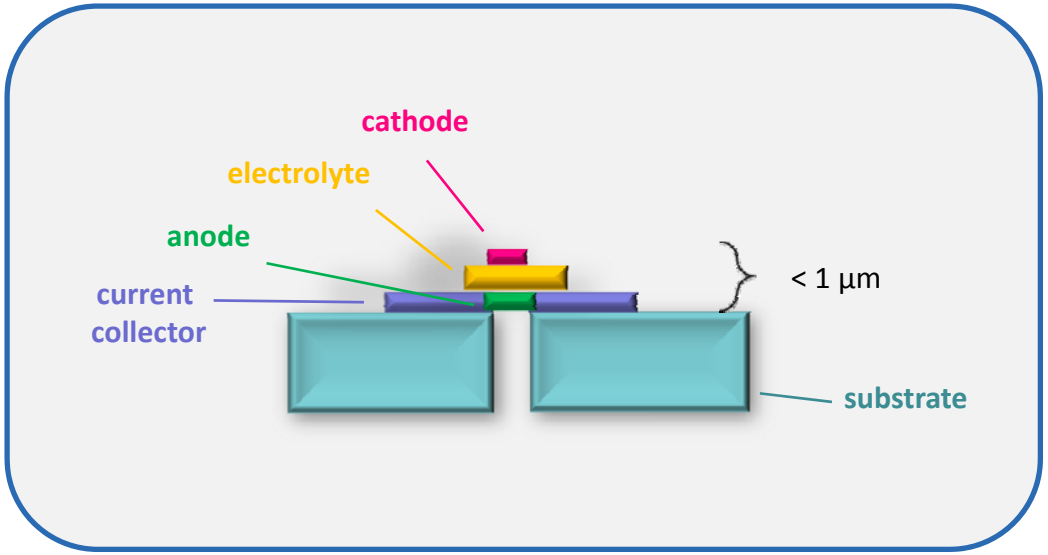
(1) I Kosacki et al., H Anderson, Solid State Ionics, 2000, 136: 1225.
(2) JLM Rupp et al., LJ Gauckler, Acta Materialia, 2006, 54(7): 1721.
(3) S Heiroth et al., T Lippert Appl. Physica A, 2008, in press.
(4) H Huang et al., F Prinz , Solid State Ionics, 2008, in press.
(5) JLM Rupp et al., LJ Gauckler, . J. of American Cer. Soc., 2007, 90(6): 1792
(6) X Hu et al., S. Averback , J. of Appl. Physics, 2001, 89(12): 7777.
(7) J Hertz , H Tuller, J of Electrochemistry, 2007, 154(4): B413.
(8) U Muecke, LJ Gauckler, Solid State Ionics 2008, 178: 1762.
(9) Wang et al., F Prinz , J. of Power Sources, 2008, 175: 75.
(10) V Brichzin, J Fleig, et al., J. Maier, Solid State Ionics 2002, 152: 499.
(11) A Bieberle-Hütter, M Søgaard, HL Tuller, Solid State Ionics , 2006, 177 : 1969.
(12) D Beckel et al., L J Gauckler, Solid State Ionics , 2007, 178 : 407.
(13) M Prestat et al., LJ Gauckler, J. of Electroceramics, 2007, 18: 111.
(14) C Peters, A Weber, E Ivers-Tiffée, J. of the Electrochemical Society, 2008, 155 [7]: B730
(15) CD Baertsch, H Tuller, J. of Material Research, 2004, 19(9)
(16) JLM Rupp, U Muecke, D. Beckel, LJ Gauckler, ETH Zurich, 2005
(17) M Greenberg et al., Adv. Funct. Materials, 2006, 16(1): 48.
(18) UP. Muecke et al., LJ Gauckler, Adv. Funct. Materials, accepted 2008.
(19) H Huang et. al., F Prinz, J. Electrochem. Soc., 2007, 154: B20.
(20) JH Shim, F Prinz, J. of the Electrochemical Society, 2007, 154 (1): B20

From thin films to power delivering µSOFCs

SOFC thin film properties: thermal, electric & thermodynamic ???

How to electrochemically test a µ-SOFC membrane ???

Maximum µSOFC power ???



Microstructering of SOFC thin films ???

Mechanical and thermal stability of µ-SOFC membranes ???

Plenty unsolved questions: From fundemental thin film properties to power delivering µSOFC

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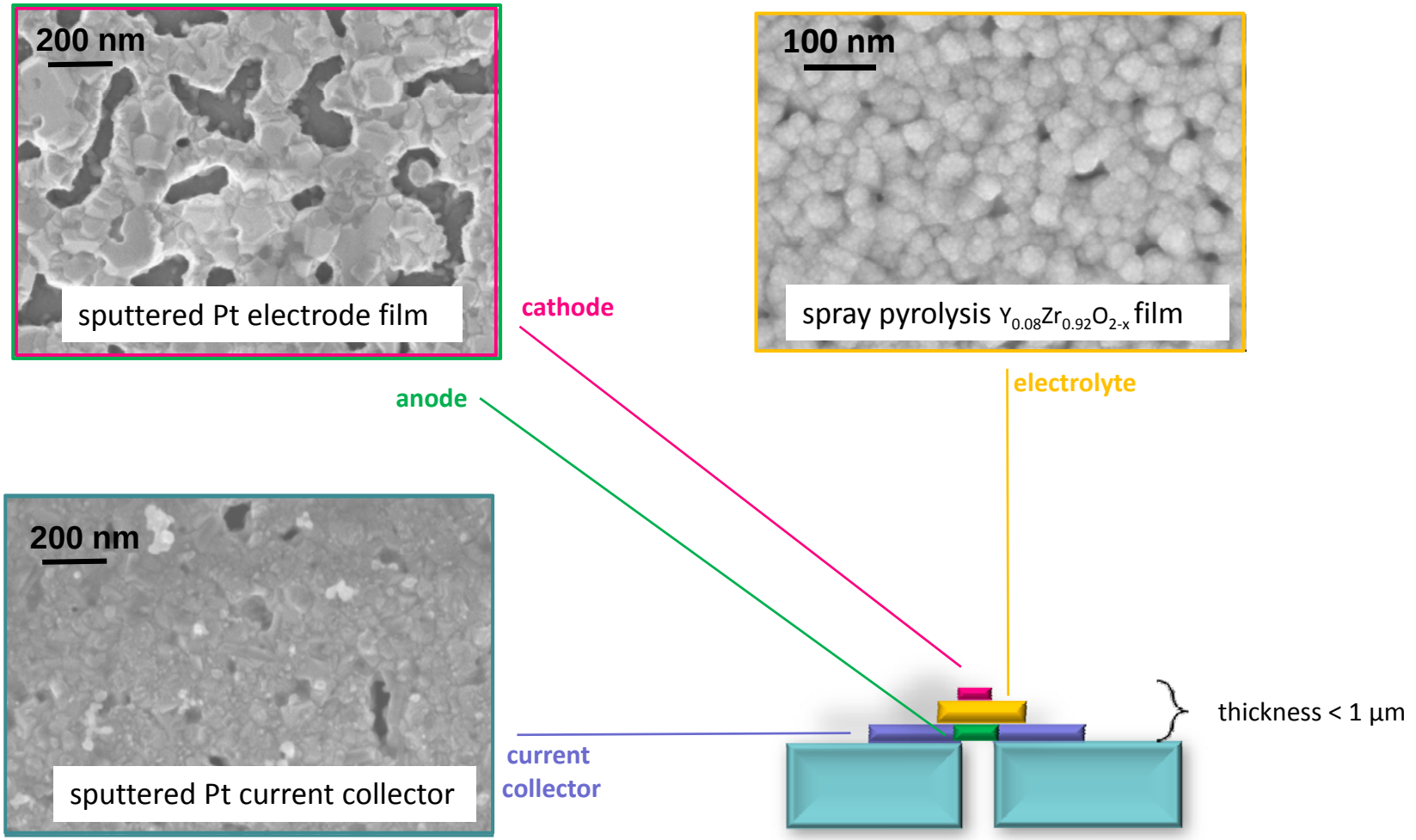
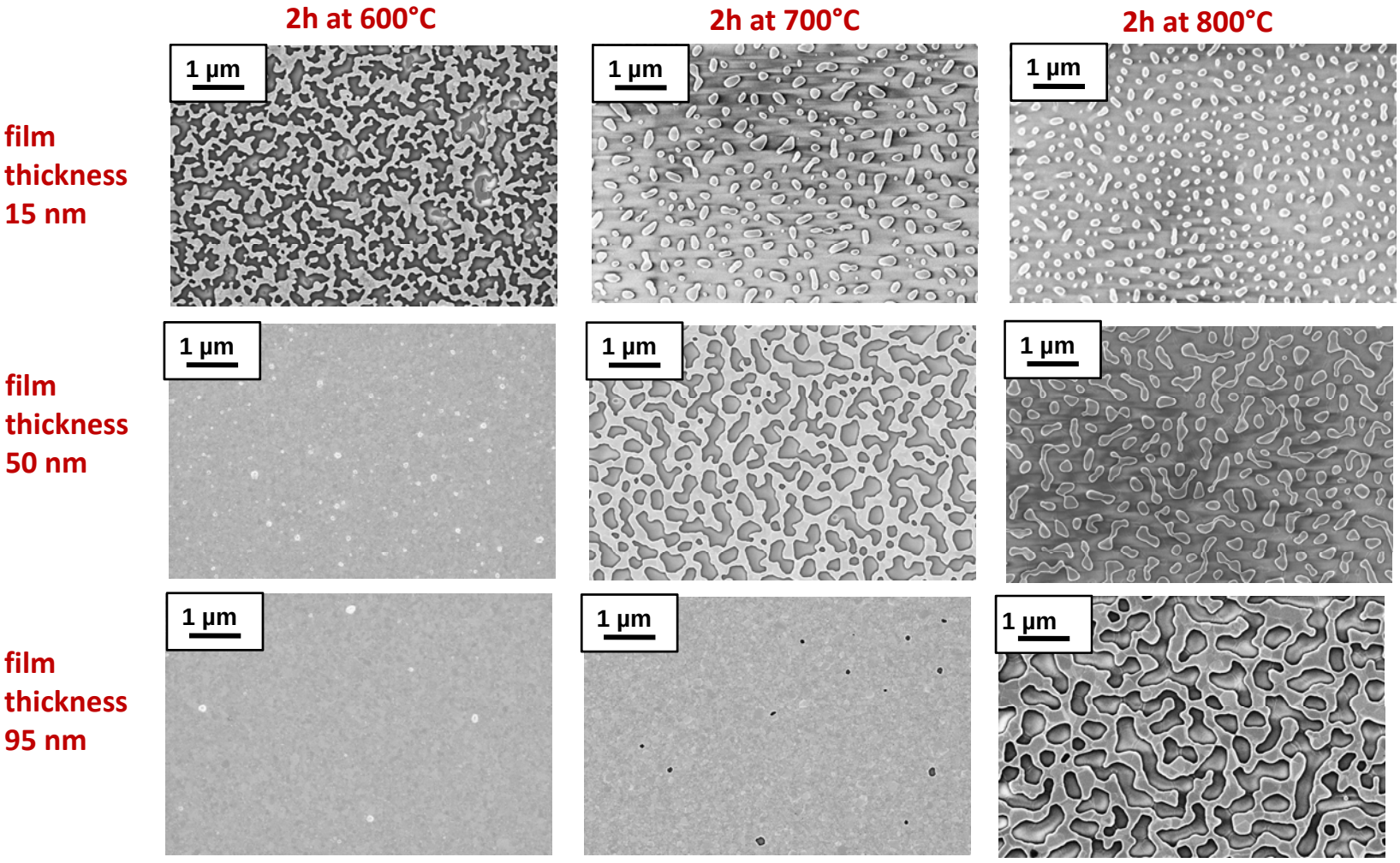
The simplest µSOFC thin film material concept



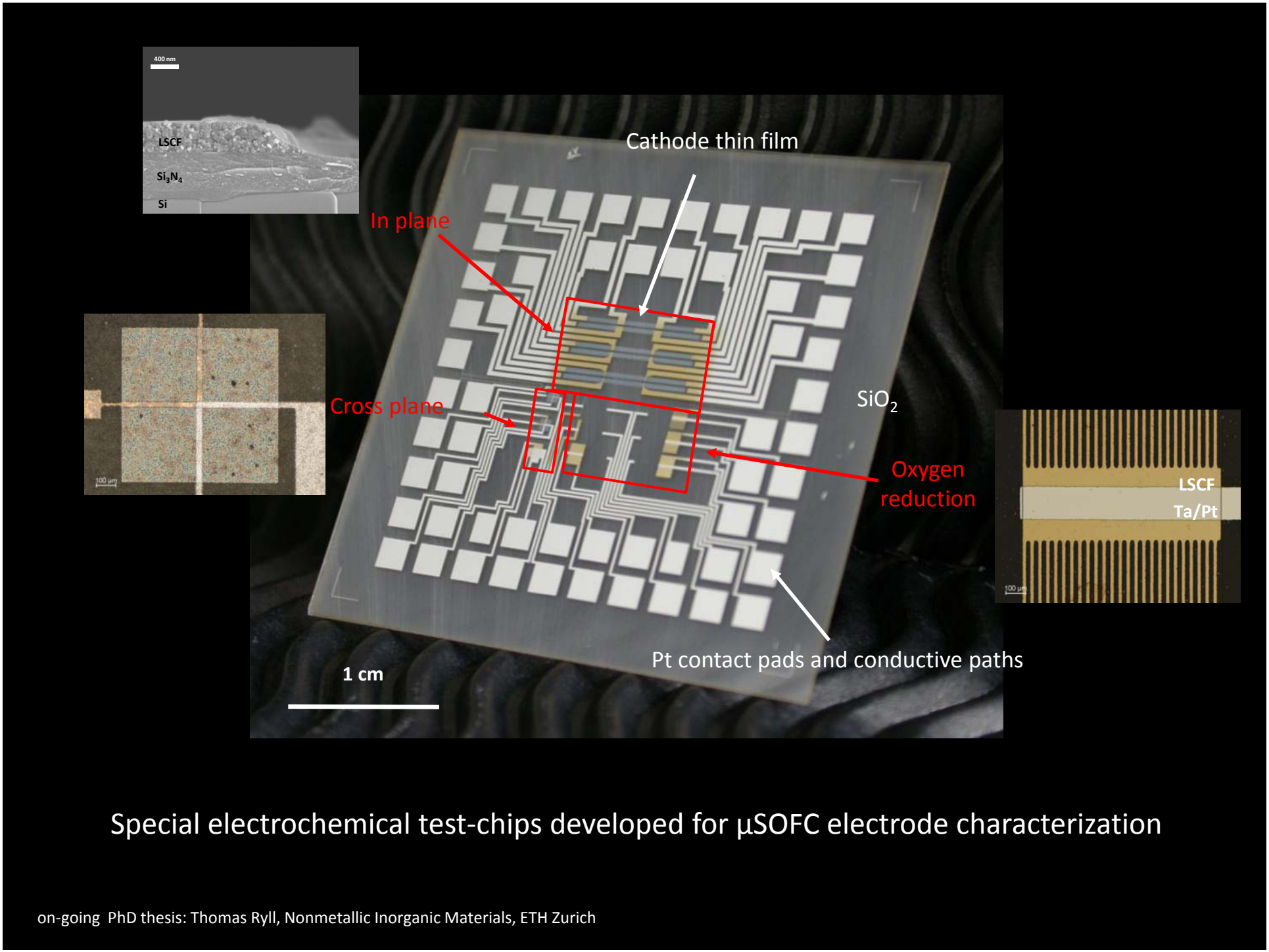
Only 2 film materials Pt and $Y_{0.08}Zr_{0.92}O_{2-x}$: Microstructures & electric properties triggered via annealing.

Platinum Thin Film Electrodes



Pt thin film dewetting is strongly f(film thickness, temperature) → trigger the electrode ASR

on-going PhD thesis: Henning Galinski & Thomas Ryll, P. Elser, Nonmetallic Inorganic Materials, ETH Zurich

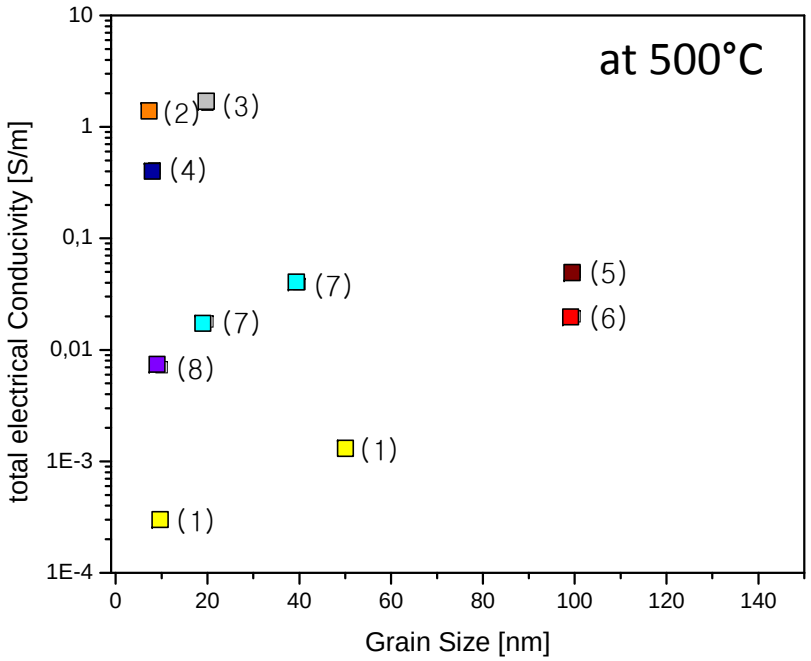


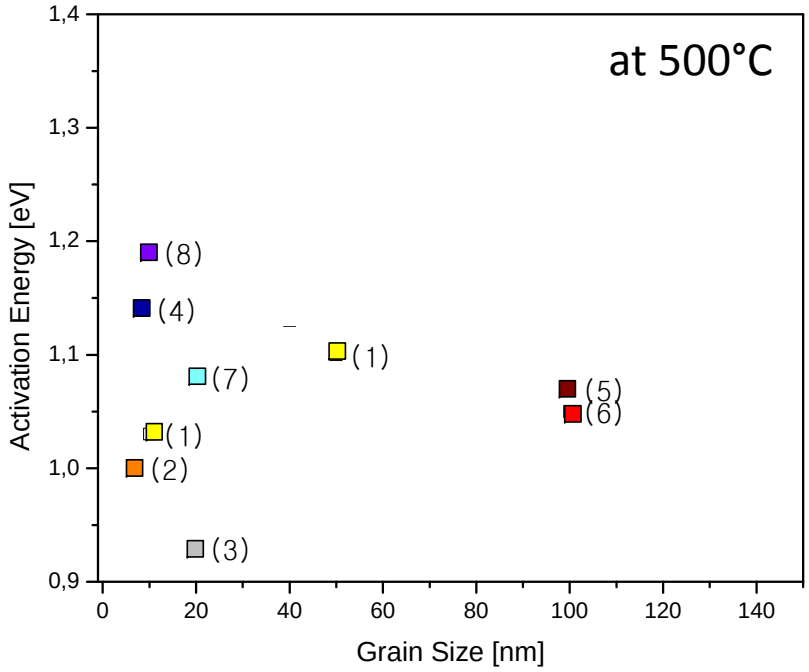
Special electrochemical test-chips developed for µSOFC electrode characterization

on-going PhD thesis: Thomas Ryll, Nonmetallic Inorganic Materials, ETH Zurich

$Y_{0.08}Zr_{0.92}O_{2-x}$ Electrolyte – Electrical Conduction

on-going PhD thesis: Barbara Scherrer, Nonmetallic Inorganic Materials, ETH Zurich





[1] Infortuna, A., A.S. Harvey, and L.J. Gauckler, *Advanced Functional Materials*, 2008. 18: p. 127-135.
[2] Hertz, J.L. and H.L. Tuller, *Journal of Electroceramics*, 2004. 13(1-3): p. 663-668.
[3] Kosacki, I., et al., *Solid State Ionics*, 2000. **136-137**: p. 1225-1233.
[4] Garcia-Sanchez, M.F., et al., *Solid State Ionics*, 2008. 179(7-8): p. 243-249.
[5] J. H. Joo and G. M. Choi, *Solid State Ionics,* vol. 177, pp. 1053-1057, 2006.
[6] T. Petrovsky, H. U. Anderson, and V. Petrovsky, *Solid State Ionics - 2002. Symposium (Mater. Res. Soc. Symposium Proceedings Vol.756),* pp. 515-20|xvi+575, 2003.
[7] S. Heiroth, Th. Lippert, A.Wokaun and M. Döbeli, *Applied Physics A,* [in press]
[8] D. Perednis, PhD, ETH Zurich, Nr. 15190, 2003.

$Y_{0.08}Zr_{0.92}O_{2-x}$ Electrolyte – Electrical Conduction

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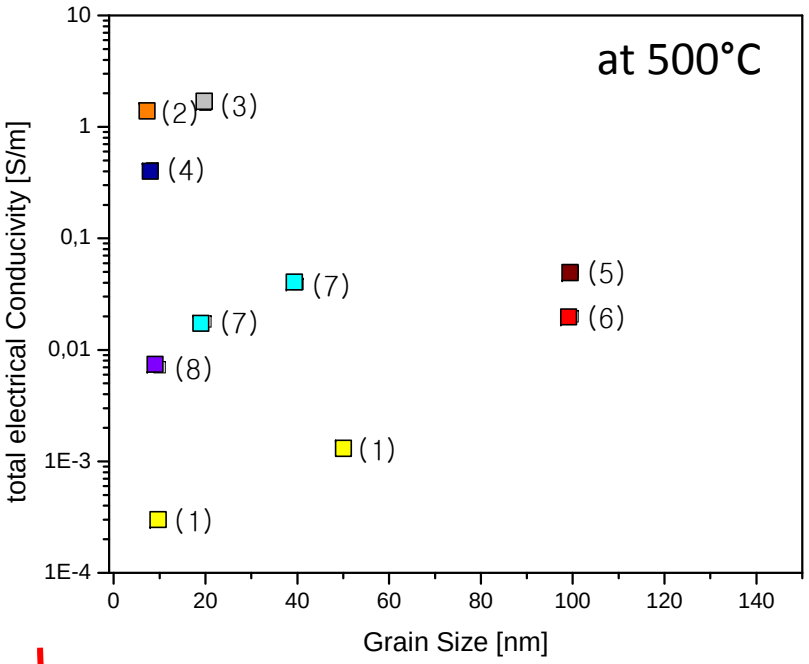
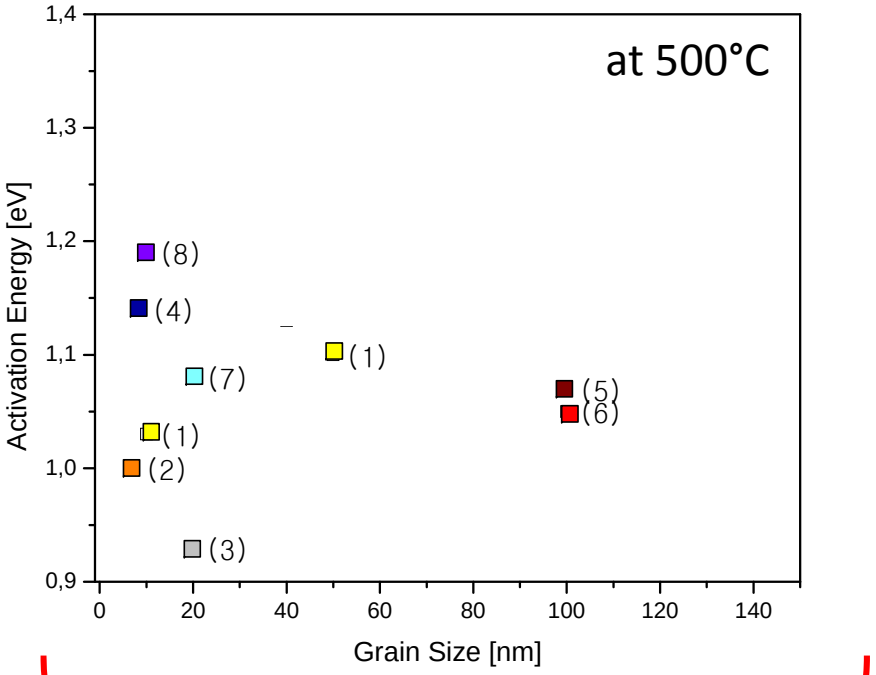


Conduction scatters 3 orders of magnitude



eV scatters up to 30 %

[1] Infortuna, A., A.S. Harvey, and L.J. Gauckler, *Advanced Functional Materials*, 2008. 18: p. 127-135.
[2] Hertz, J.L. and H.L. Tuller, *Journal of Electroceramics*, 2004. 13(1-3): p. 663-668.
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[6] T. Petrovsky, H. U. Anderson, and V. Petrovsky, *Solid State Ionics - 2002. Symposium (Mater. Res. Soc. Symposium Proceedings Vol.756),* pp. 515-20|xvi+575, 2003.
[7] S. Heiroth, Th. Lippert, A.Wokaun and M. Döbeli, *Applied Physics A,* [in press]
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$Y_{0.08}Zr_{0.92}O_{2-x}$ Electrolyte – Electrical Conduction

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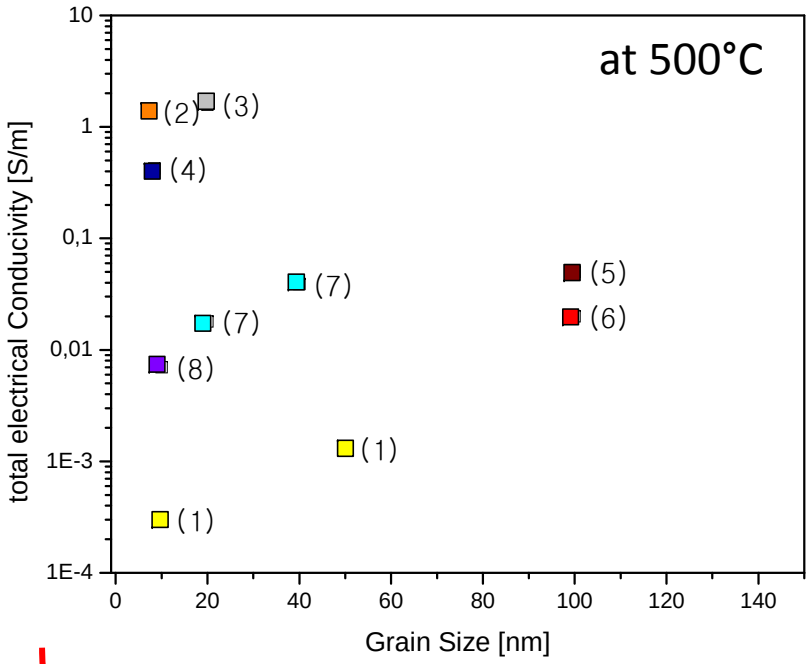
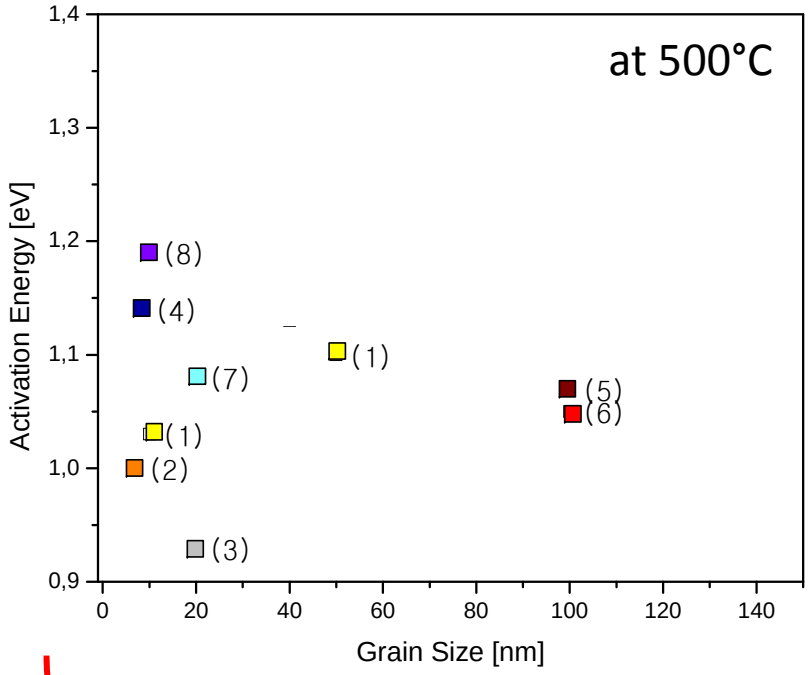


Conduction scatters 3 orders of magnitude

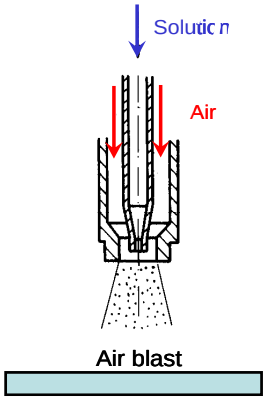


eV scatters up to 30 %

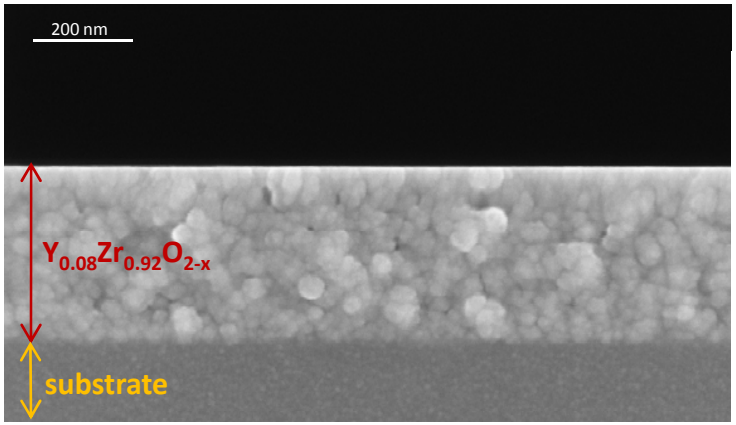
one material, but differencent: grain size, degree of crystallinity, strain…

$Y_{0.08}Zr_{0.92}O_{2-x}$ Electrolyte

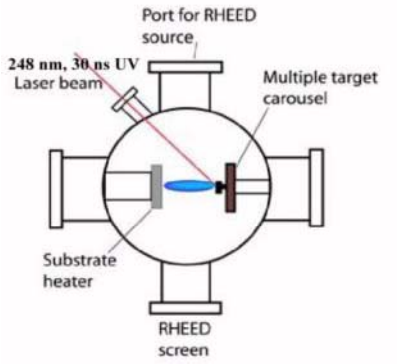
Spray pyrolysis

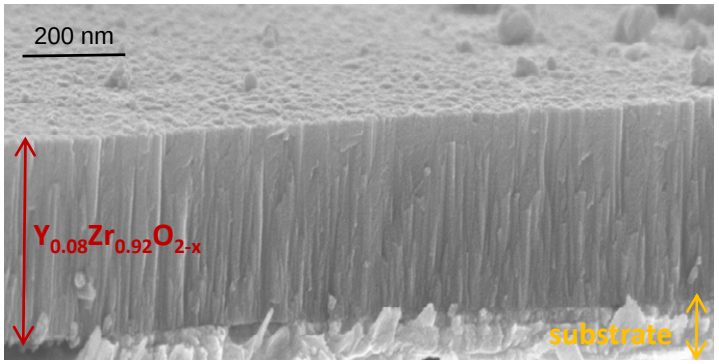


annealed 4h at 600 °C



Pulsed laser deposition (PLD)





Dense films result after annealing, but grain microstructure is influenced by initial processing.

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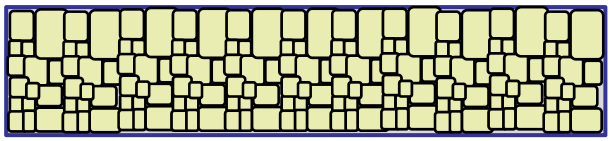
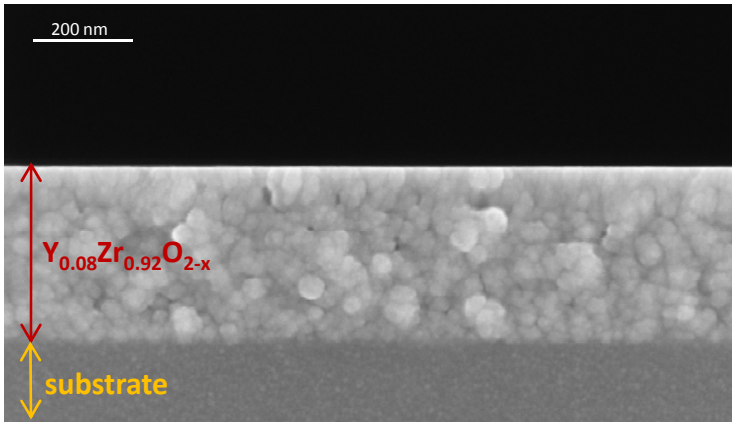
$Y_{0.08}Zr_{0.92}O_{2-x}$ Electrolyte

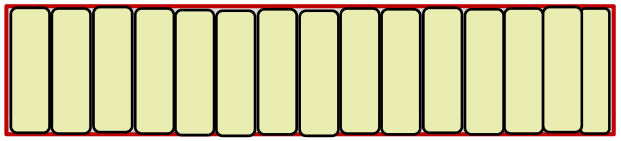
Non-Vaccuum-technique:
Spray pyrolysis



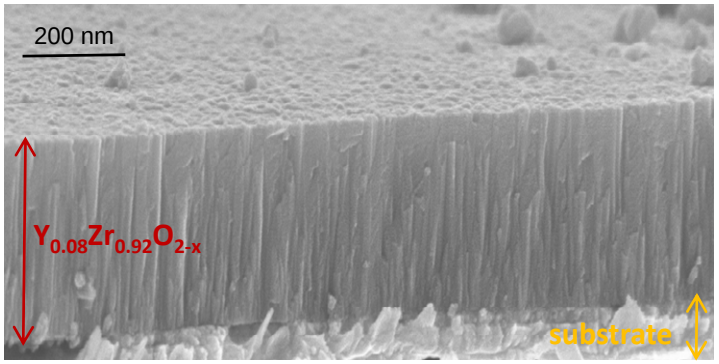
brick-layer grained microstructure
- after annealing of amorphous film



Vaccuum-technique:
Pulsed laser deposition (PLD)



columnar grained thin films
- after annealing of crystalline film



µSOFC electrolyte microstructures is engineerable via annealing and use of different deposition techniques

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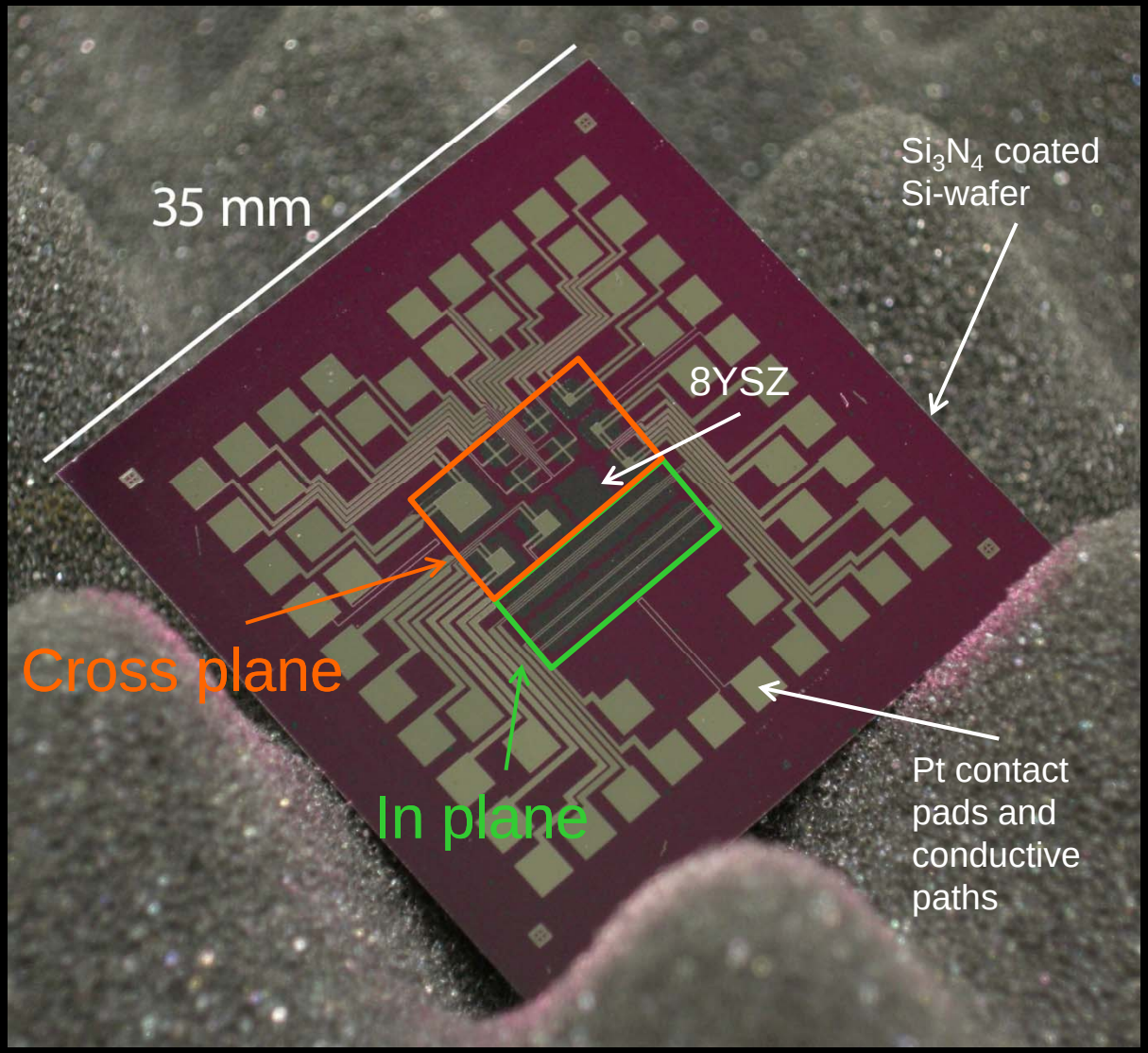

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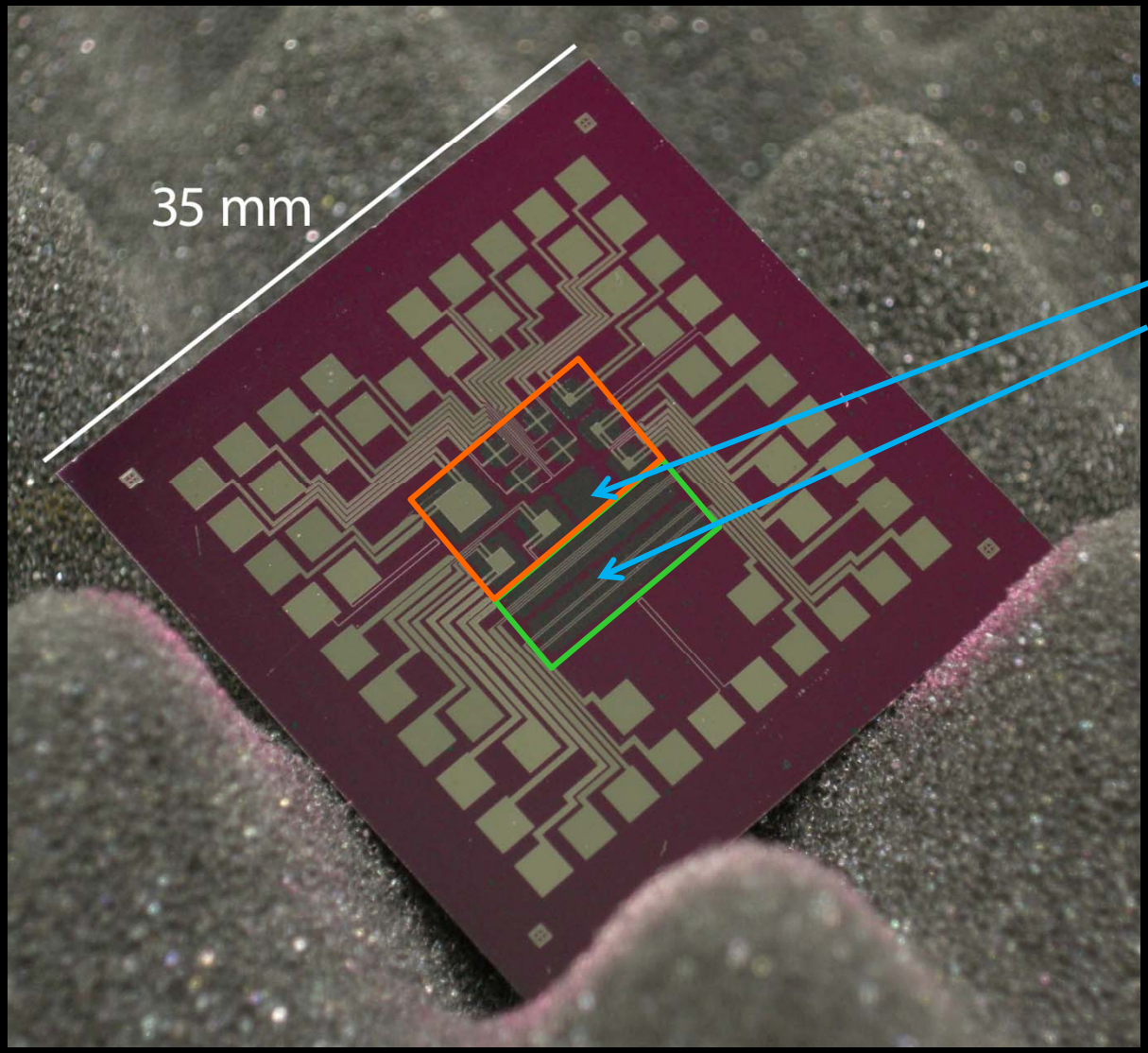
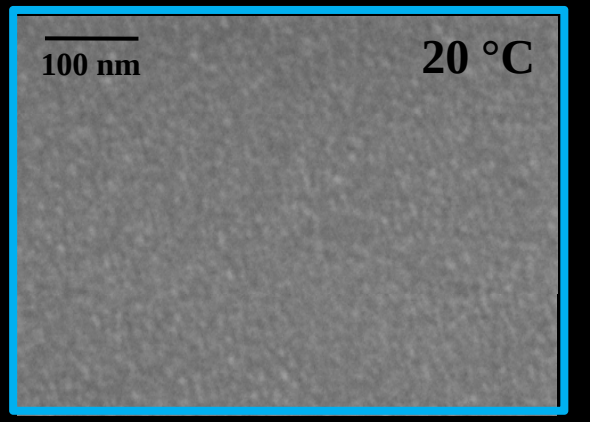
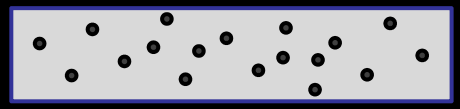




amorphous spray pyrolysis films at deposition



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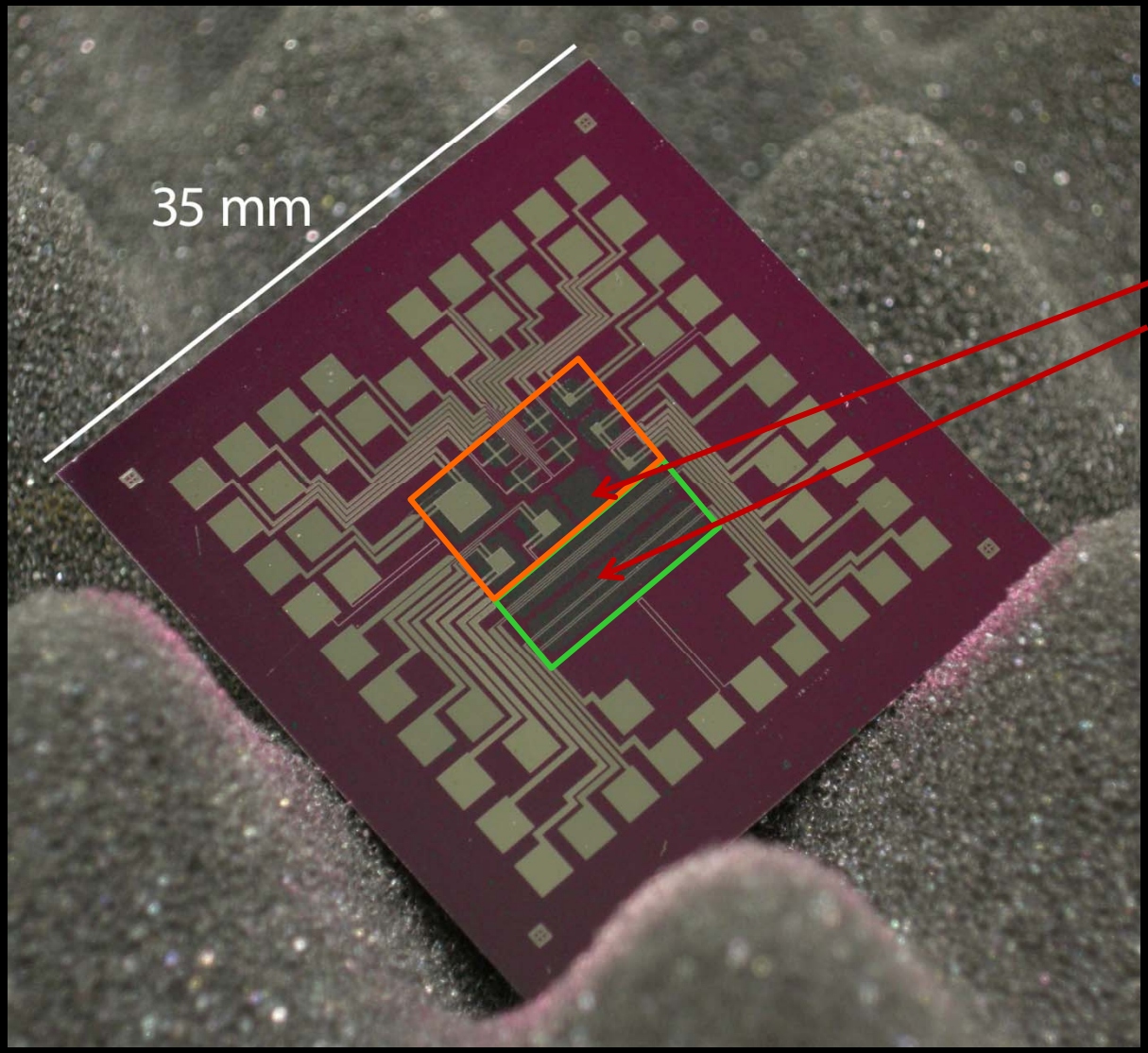

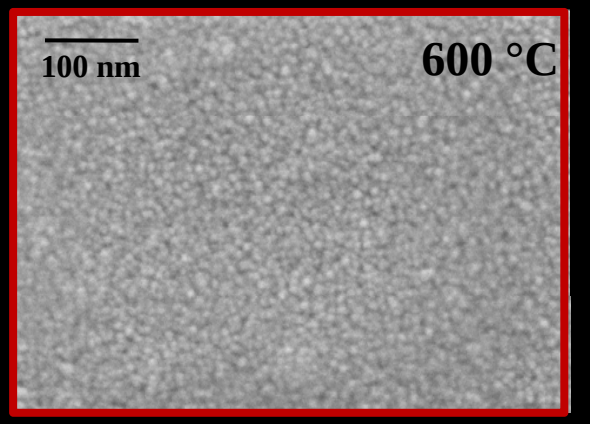

nanocrystalline
spray pyrolysis film
after annealing

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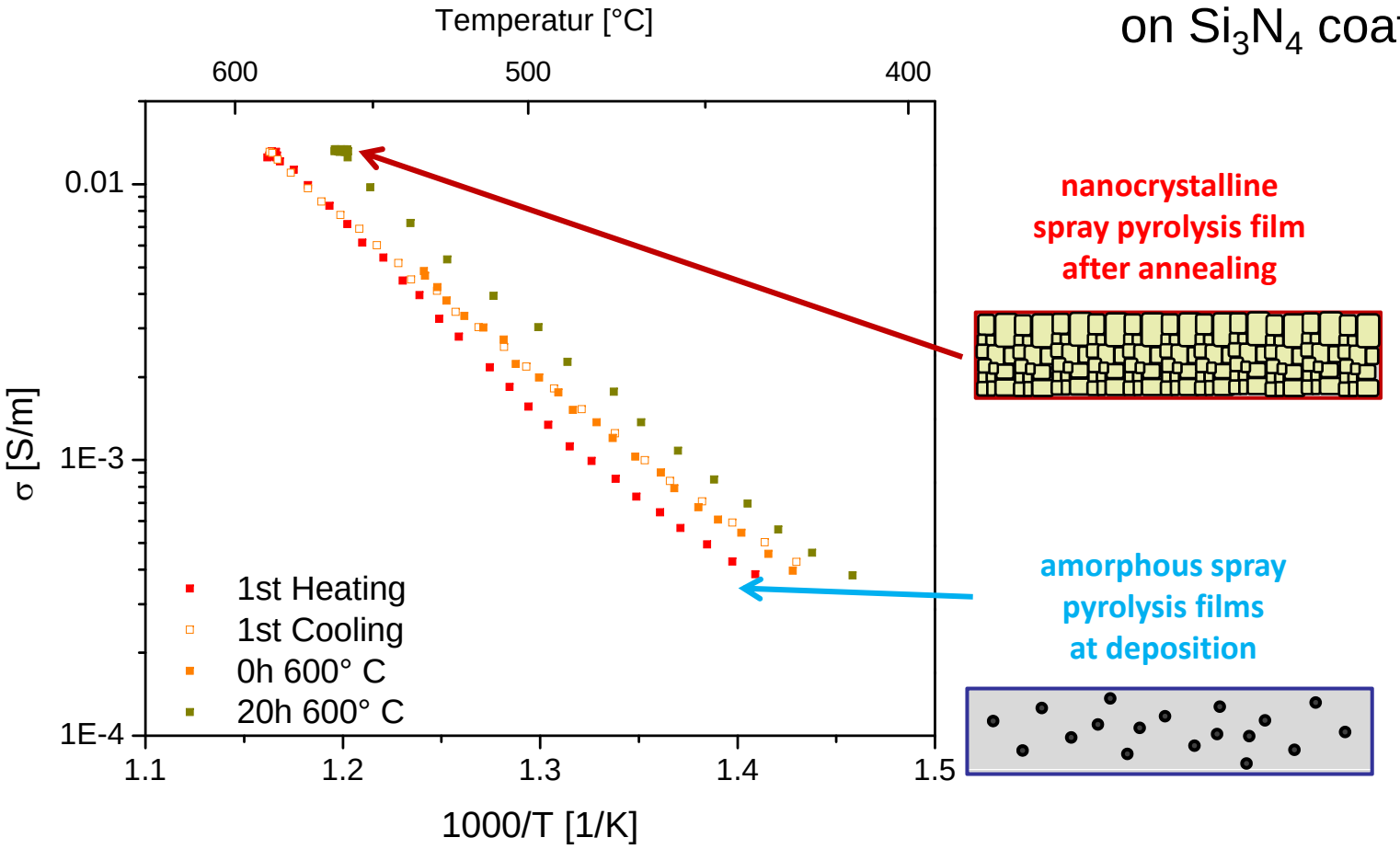
$Y_{0.08}Zr_{0.92}O_{2-x}$ Electrolyte

on Si_3N_4 coated Si-wafer



➢ Total electrical conductivity increases with increasing crystallinity.

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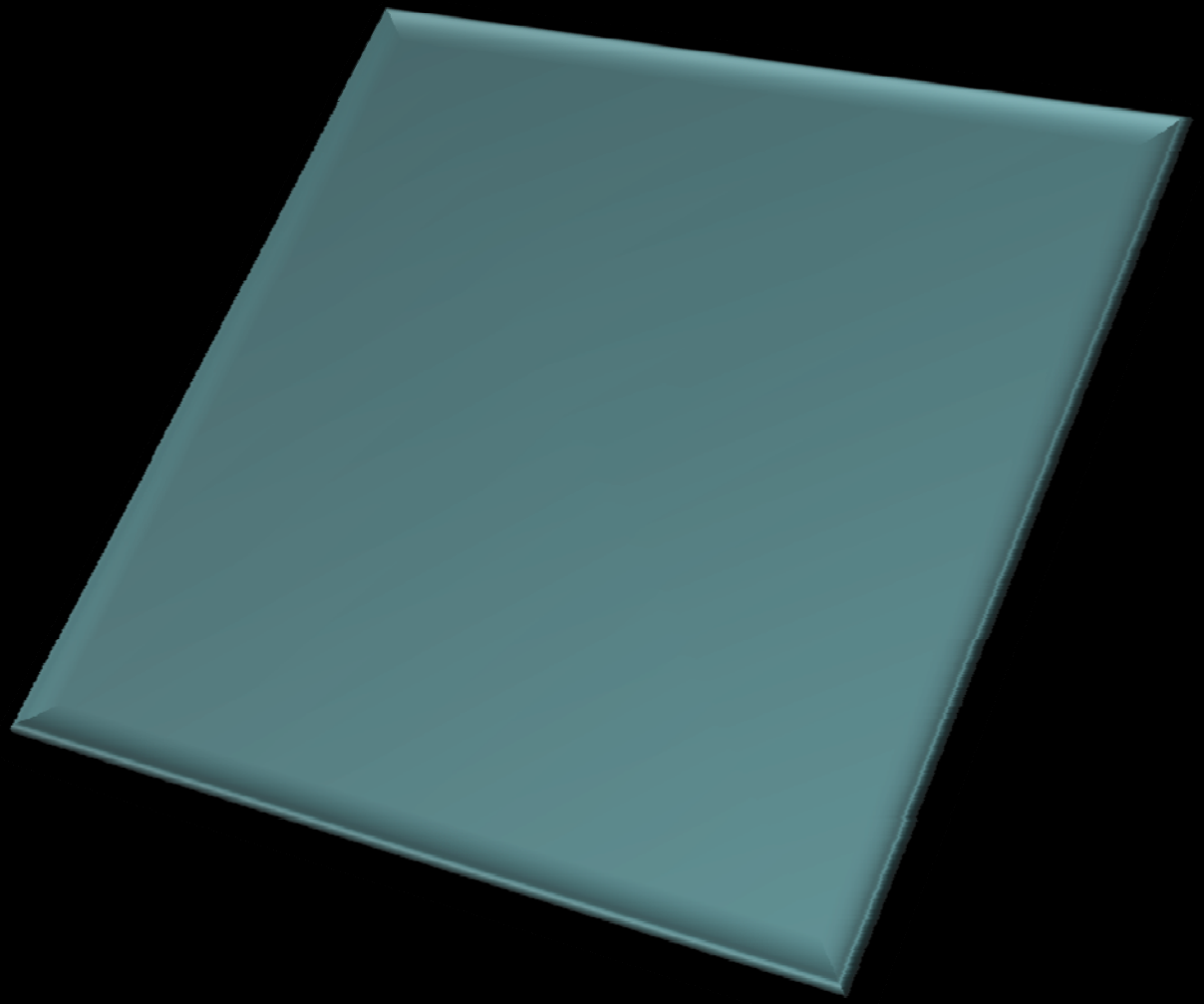
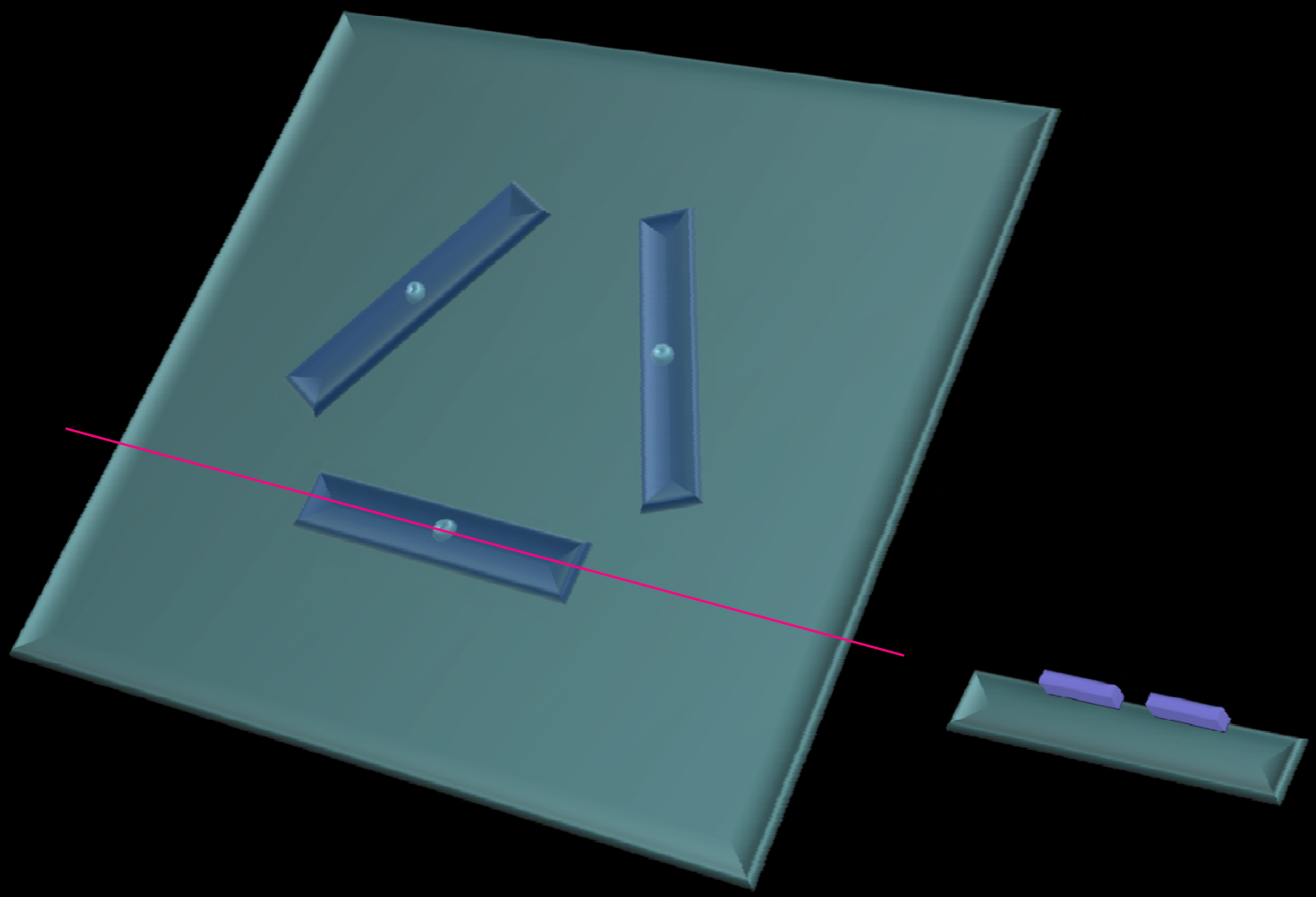
Foturan glass-ceramic wafer piece



U.P. Muecke, D. Beckel, A. Bernard, A. Bieberle-Hütter, S. Graf, A. Infortuna, P. Müller, J.L.M. Rupp, J. Schneider and L. J. Gauckler, Advanced Functional Materials, accepted 2008
L.J. Gauckler, D. Beckel, U. Mücke, P. Müller and J.L.M. Rupp, PCT patents: PCT /CH 2006/000573, PCT /CH 2006/000575, PCT /CH 2006/000605, 2006

Sputtered current collectors



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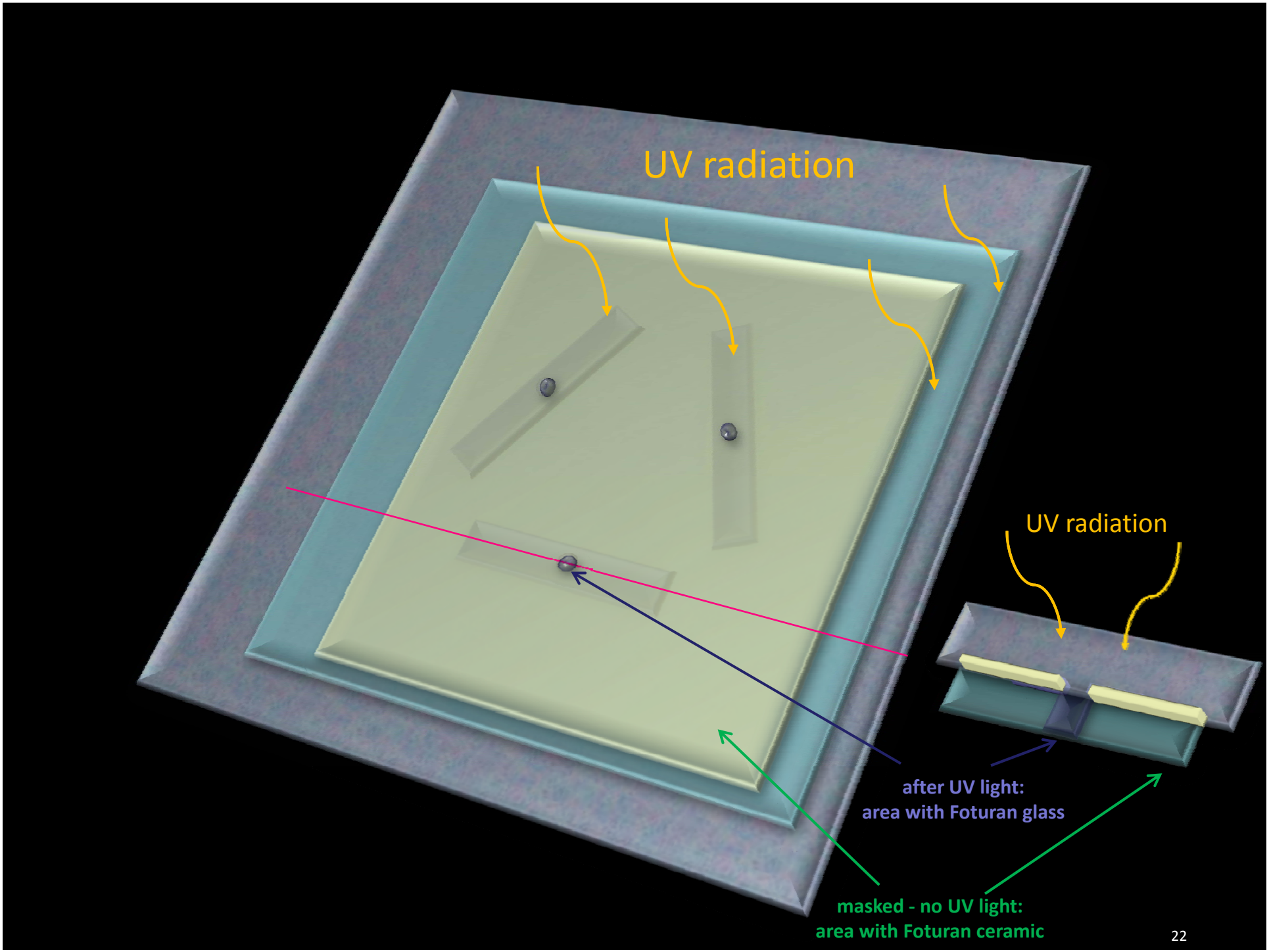
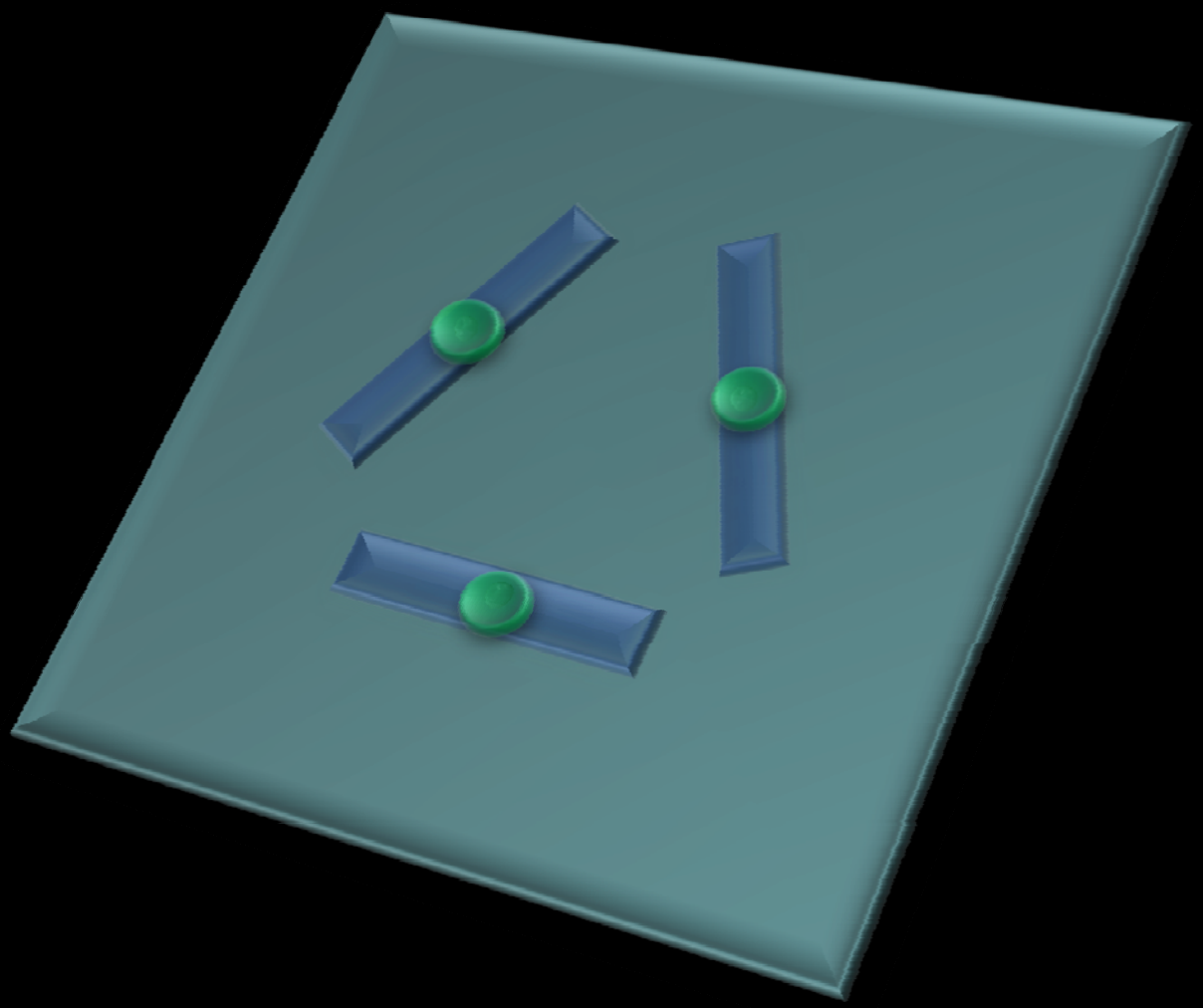

UV radiation
UV radiation
after UV light:
area with Foturan glass
masked - no UV light:
area with Foturan ceramic

anode thin film depositions



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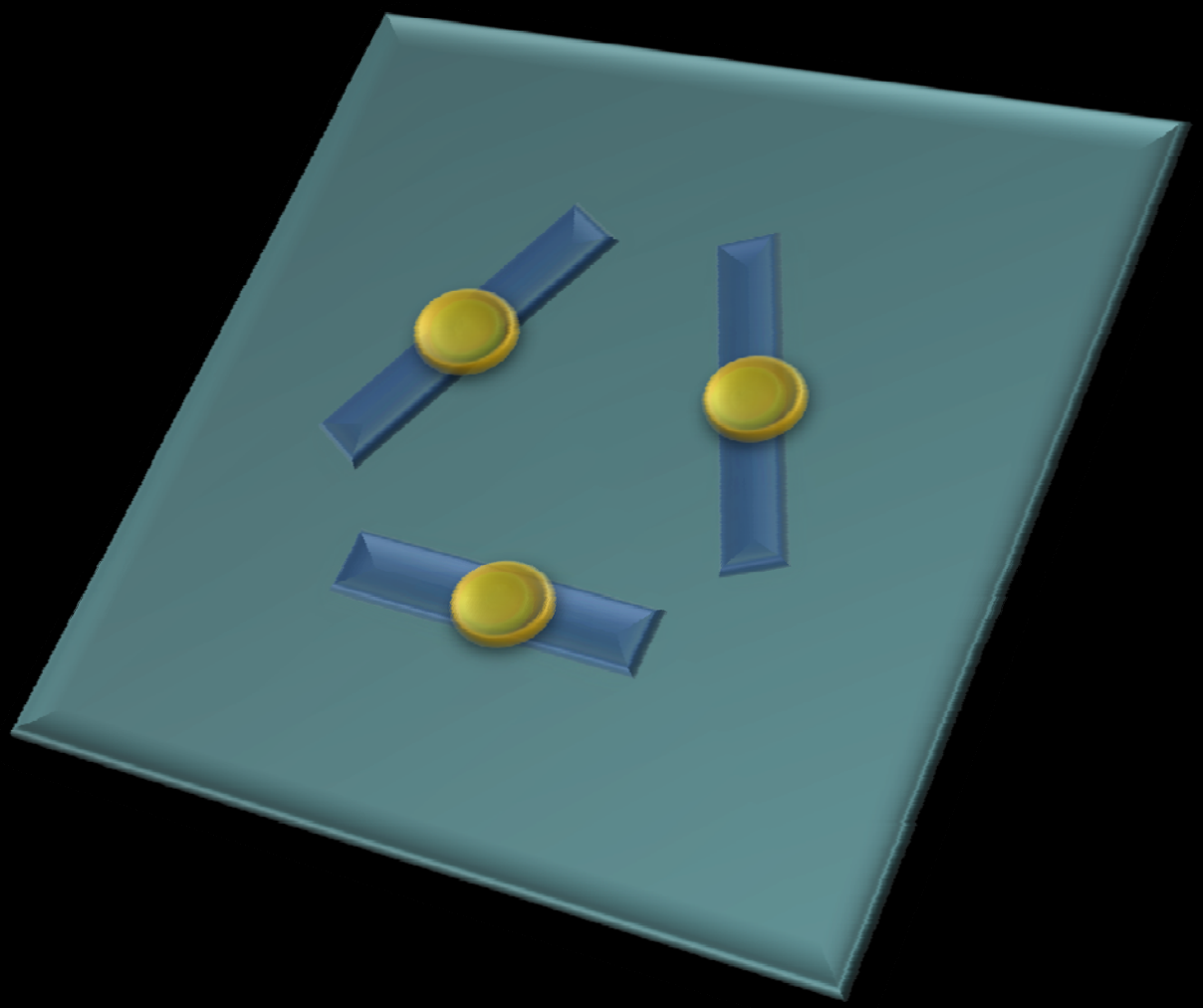
electrolyte thin film depositions



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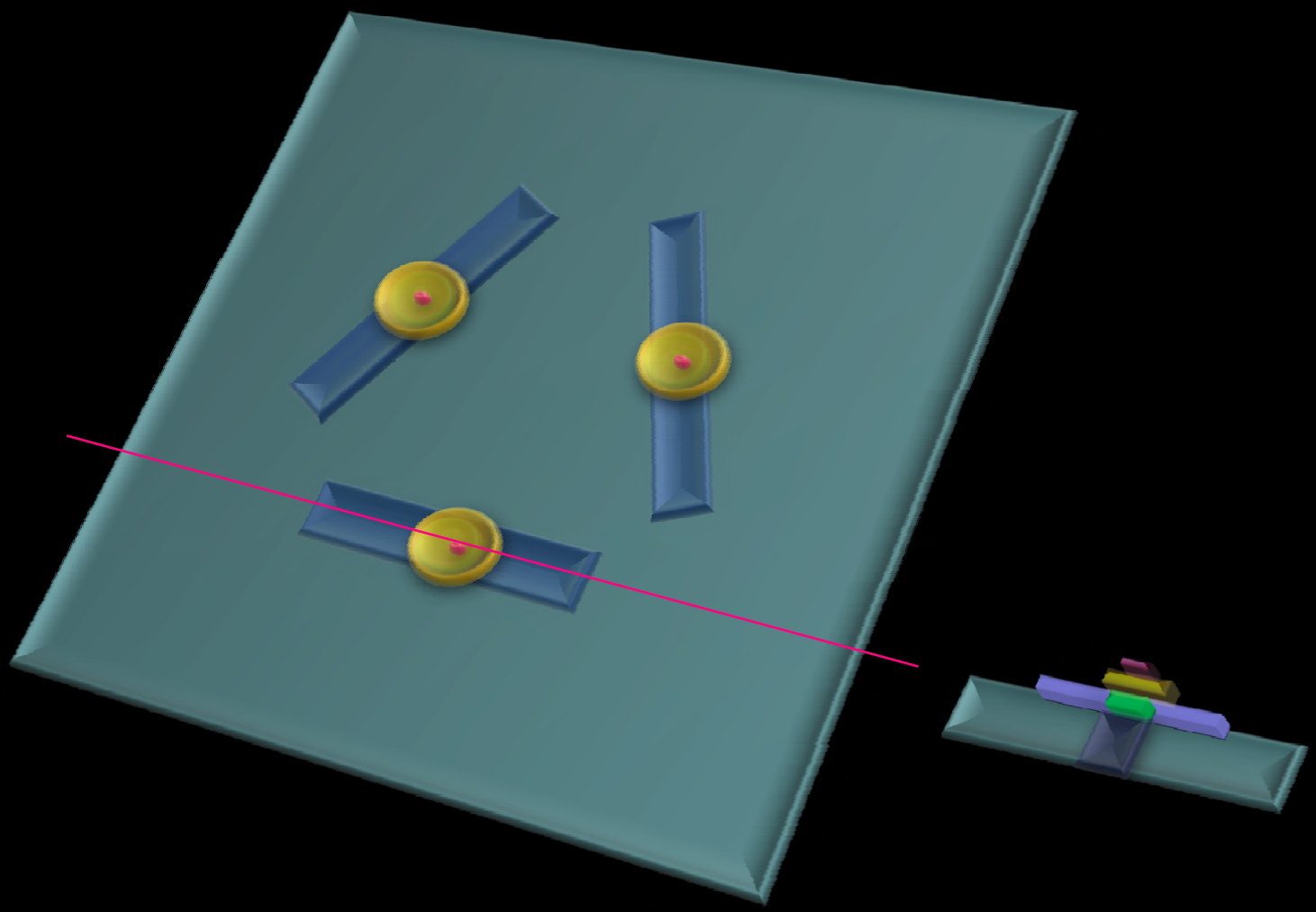
L.J. Gauckler, D. Beckel, U. Mücke, P. Müller and J.L.M. Rupp, PCT patents: PCT /CH 2006/000573, PCT /CH 2006/000575, PCT /CH 2006/000605, 2006

cathode thin film depositions



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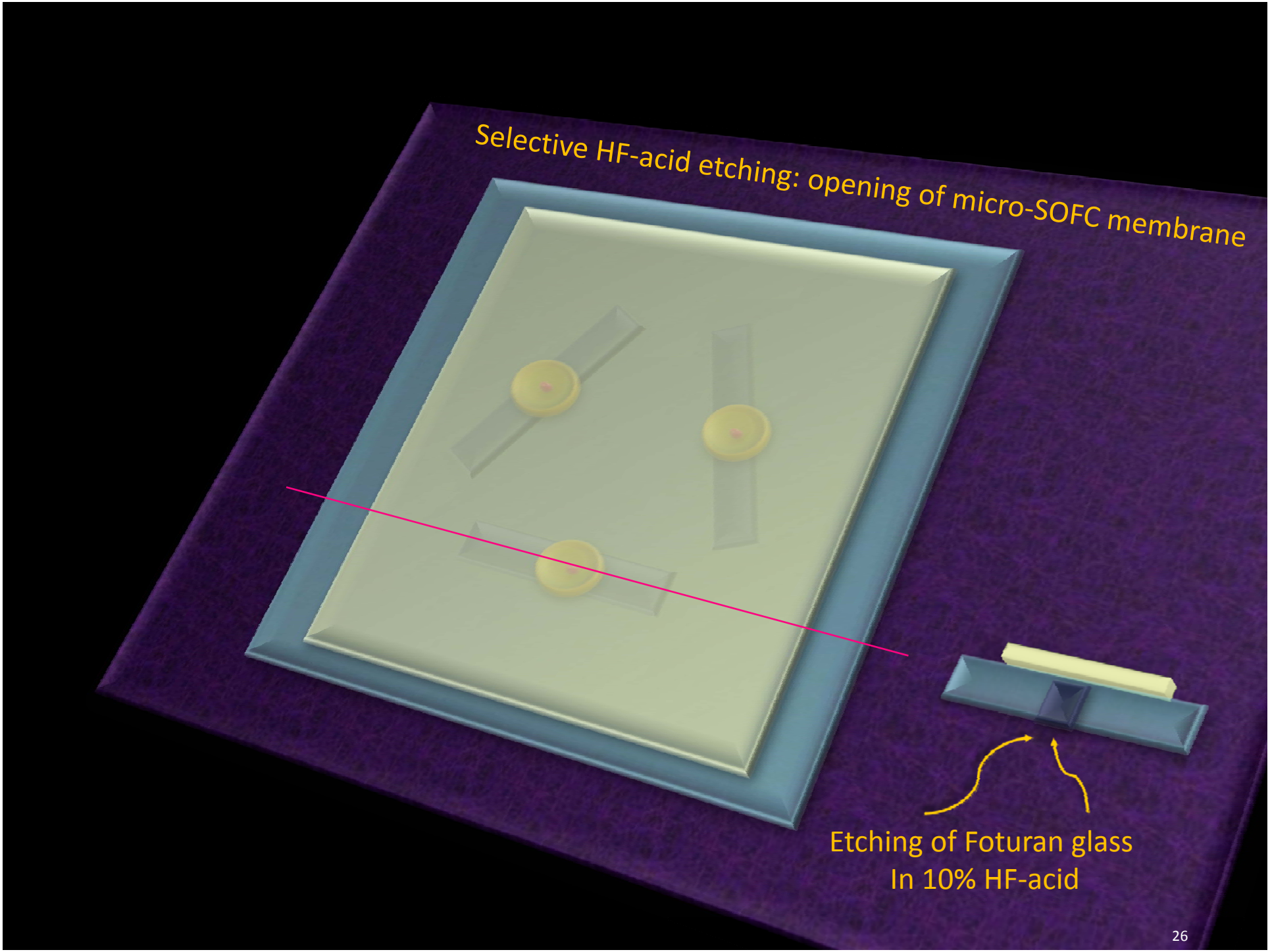
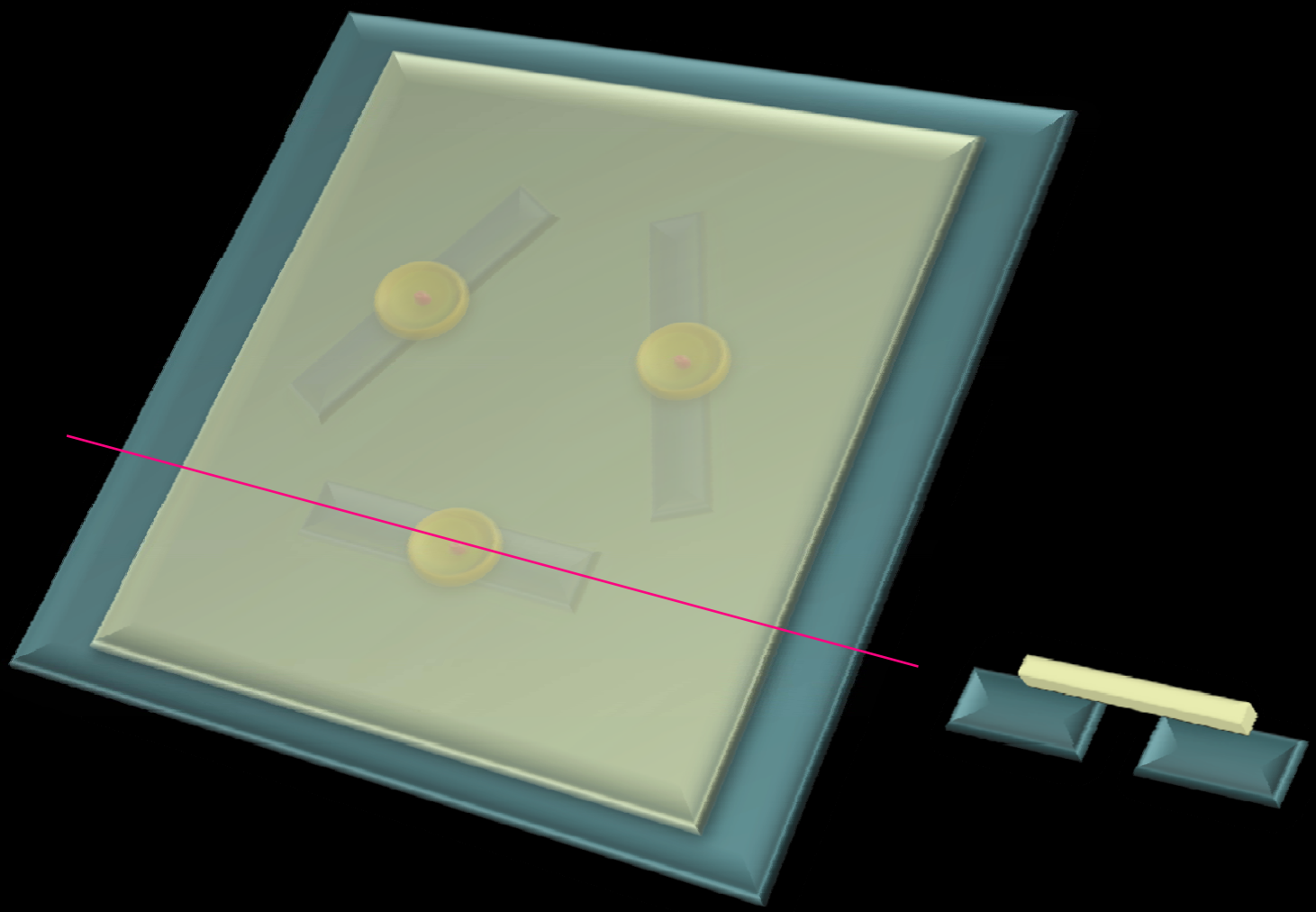

Selective HF-acid etching: opening of micro-SOFC membrane
Etching of Foturan glass
In 10% HF-acid

free standing membranes covered with photoresist



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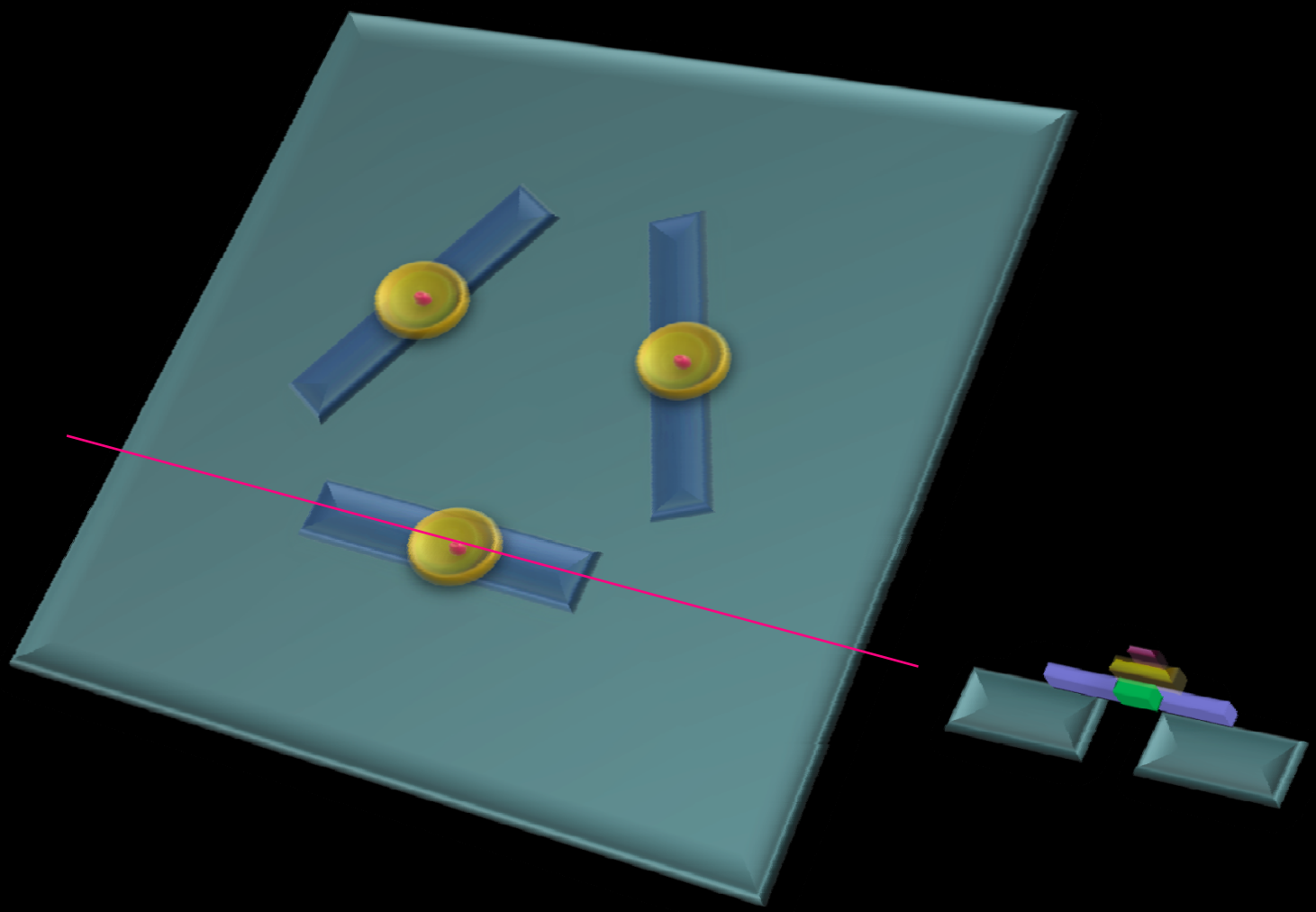
free standing SOFC membranes



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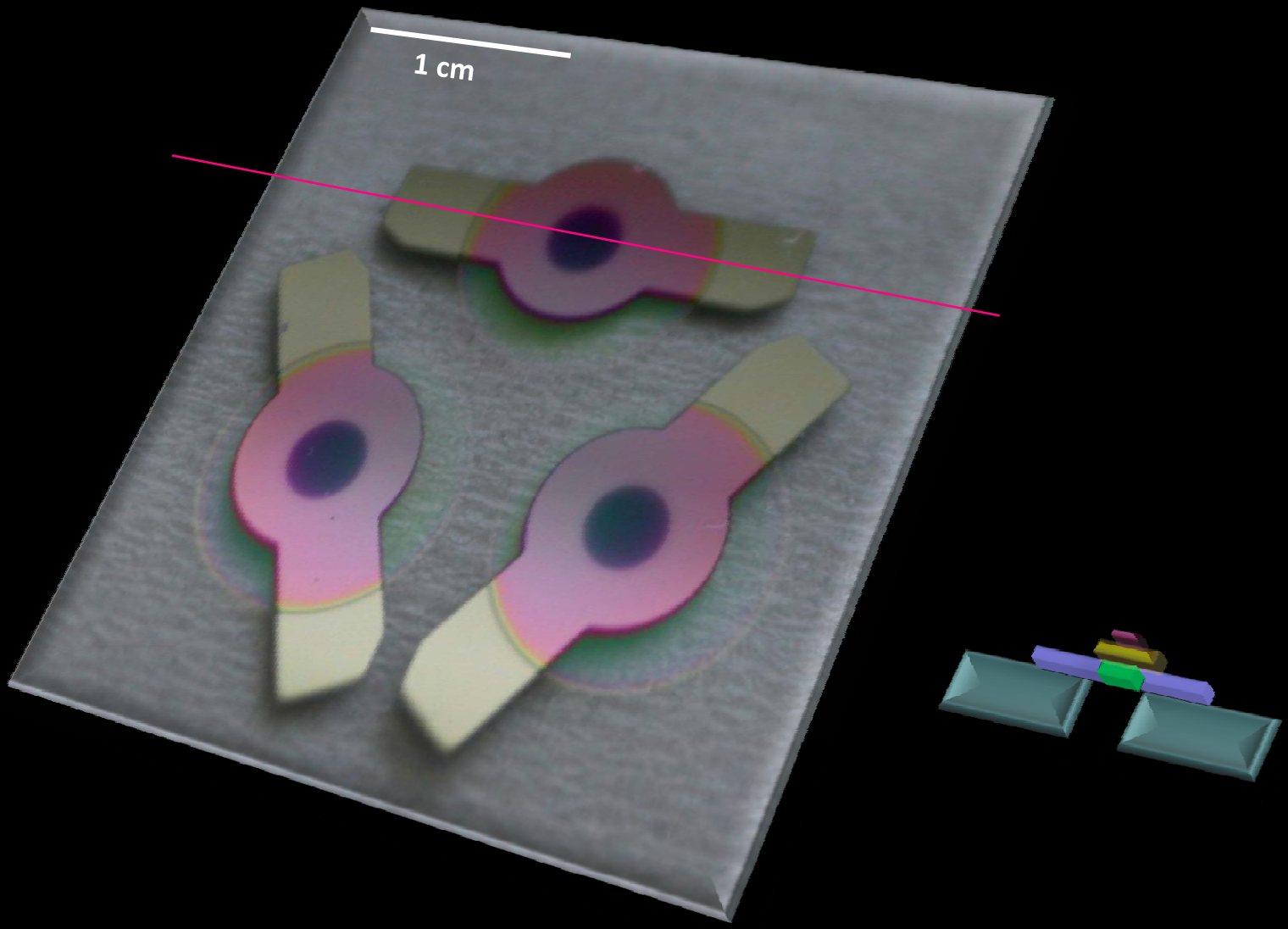
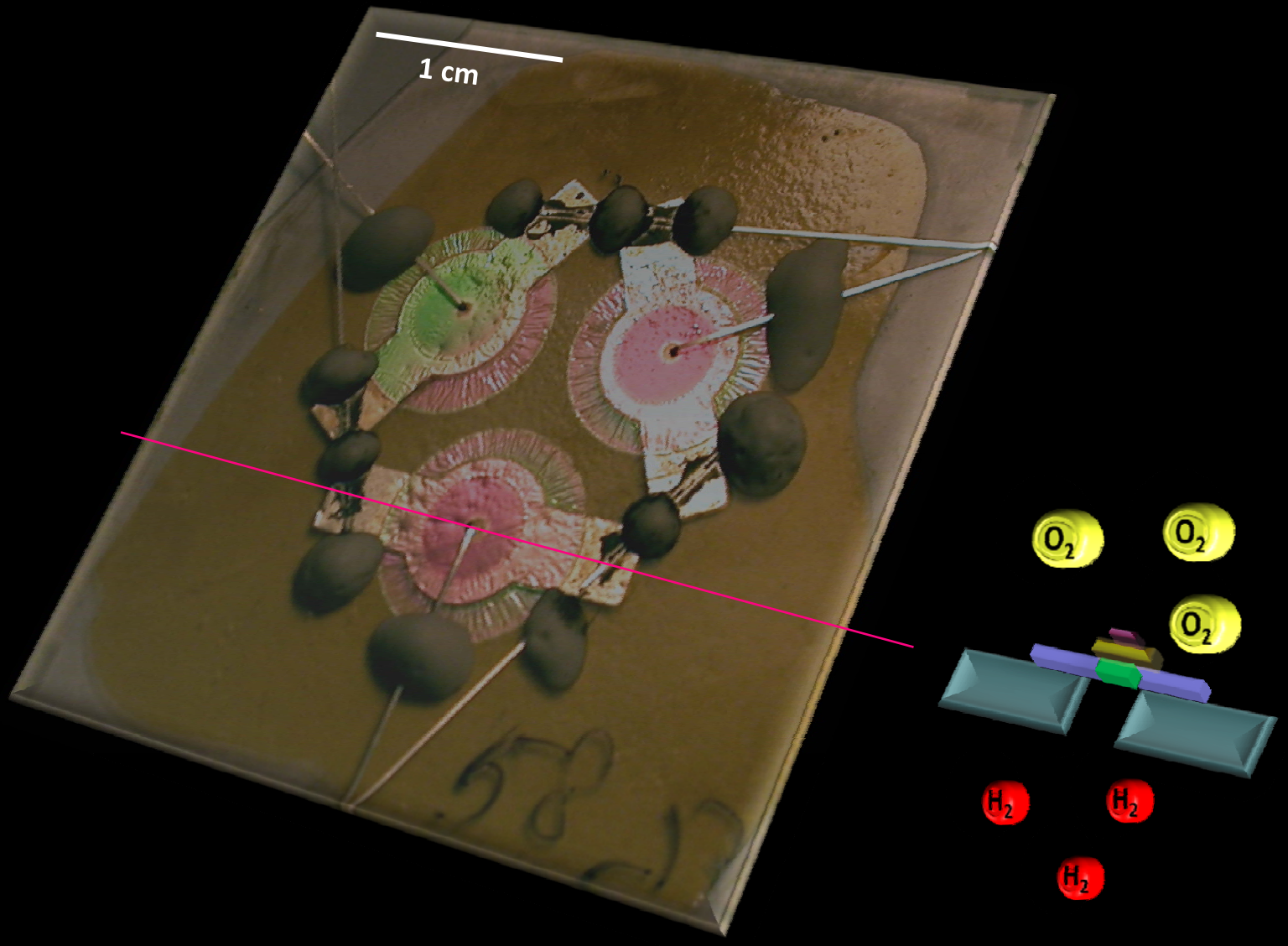
L.J. Gauckler, D. Beckel, U. Mücke, P. Müller and J.L.M. Rupp, PCT patents: PCT /CH 2006/000573, PCT /CH 2006/000575, PCT /CH 2006/000605, 2006

free standing SOFC membranes before cell testing



U.P. Muecke, D. Beckel, A. Bernard, A. Bieberle-Hütter, S. Graf, A. Infortuna, P. Müller, J.L.M. Rupp, J. Schneider and L. J. Gauckler, Advanced Functional Materials, accepted 2008
L.J. Gauckler, D. Beckel, U. Mücke, P. Müller and J.L.M. Rupp, PCT patents: PCT /CH 2006/000573, PCT /CH 2006/000575, PCT /CH 2006/000605, 2006

free standing SOFC membranes after cell testing at 550 °C



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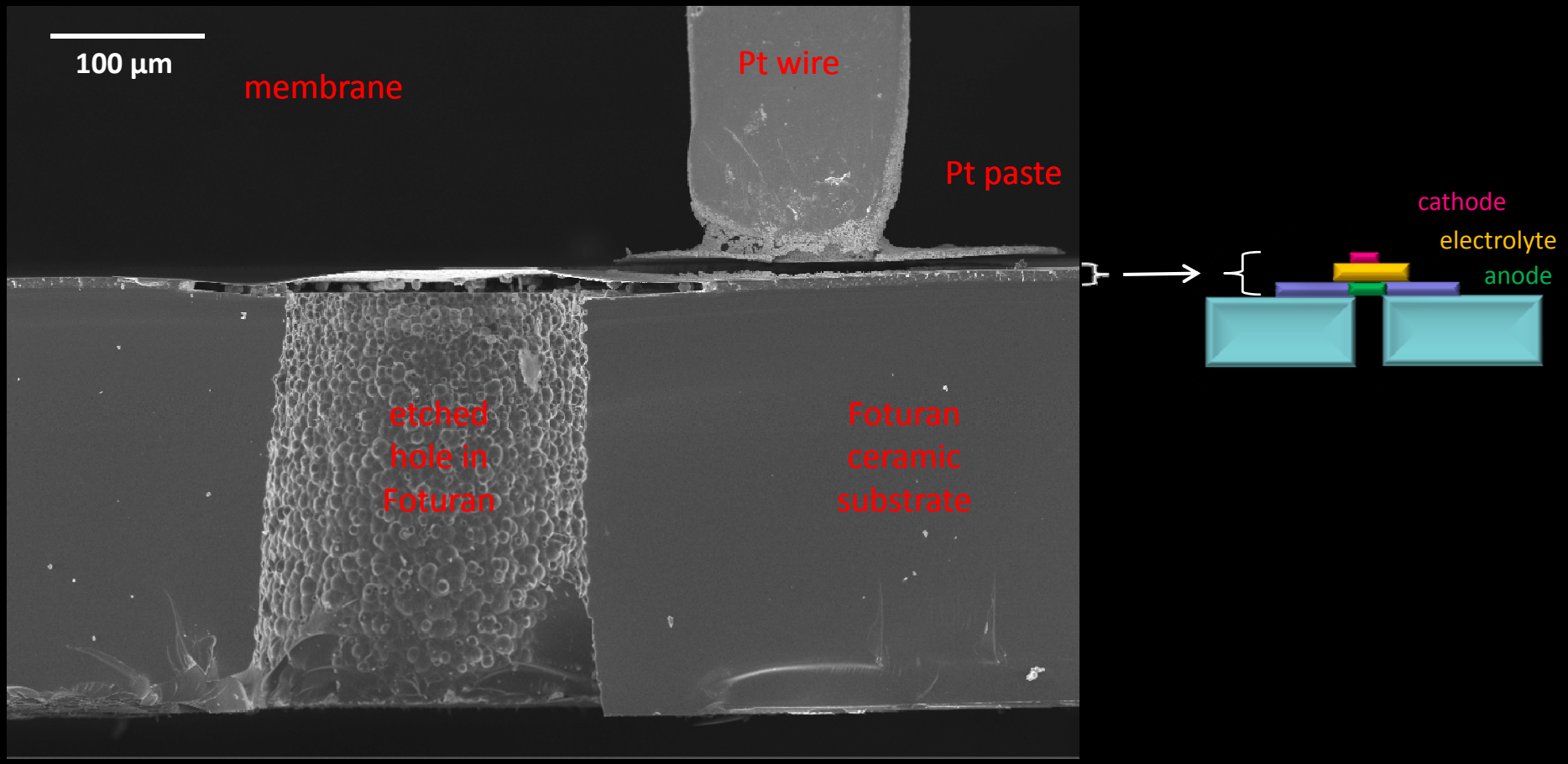

Micro-SOFC membranes on Foturan substrates are feasible: 200 µm wide & < 1 µm thin

U.P. Muecke, D. Beckel, A. Bernard, A. Bieberle-Hütter, S. Graf, A. Infortuna, P. Müller, J.L.M. Rupp, J. Schneider and L. J. Gauckler, Advanced Functional Materials, accepted 2008
L.J. Gauckler, D. Beckel, U. Mücke, P. Müller and J.L.M. Rupp, PCT patents: PCT /CH 2006/000573, PCT /CH 2006/000575, PCT /CH 2006/000605, 2006

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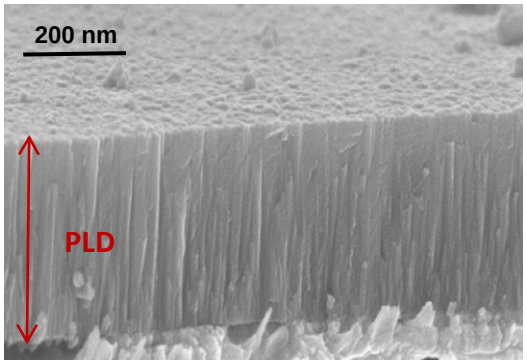
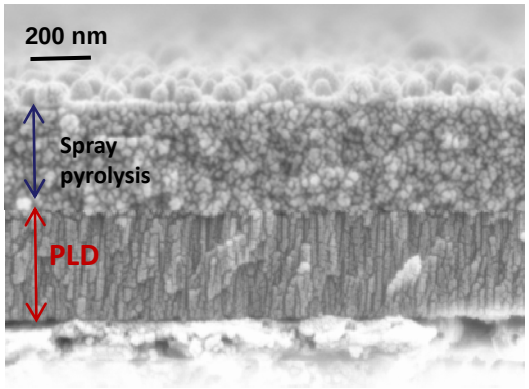
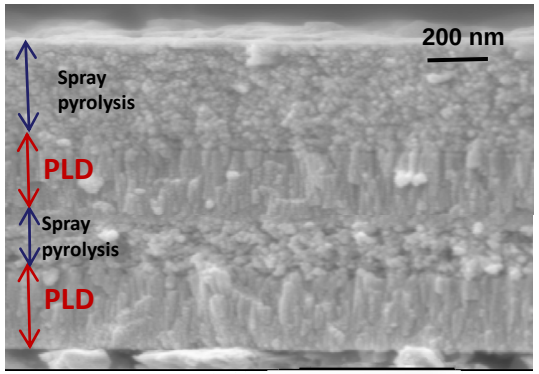
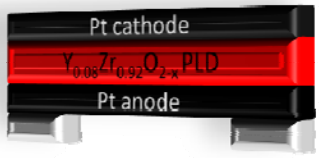
Impact of µSOFC electrolyte-microstructure on cell performance

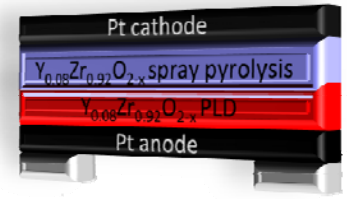
SEM: $Y_{0.08}Zr_{0.92}O_{2-x}$ thin films

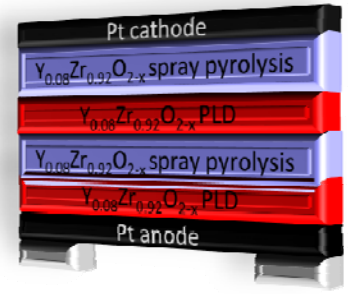












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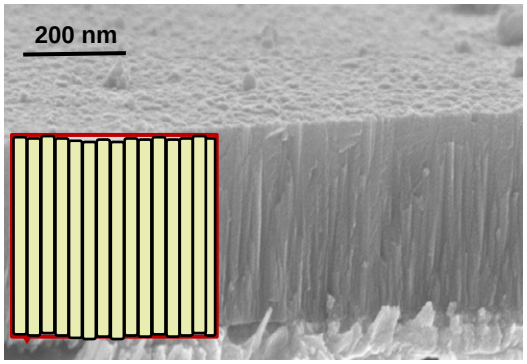
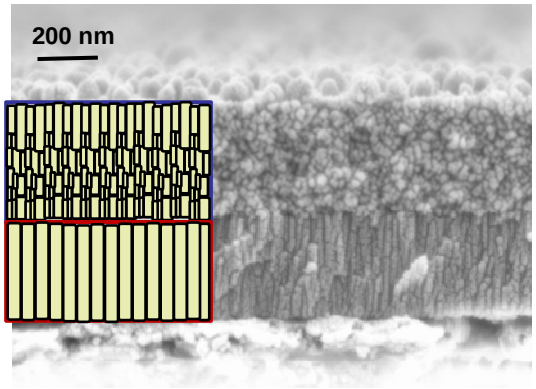
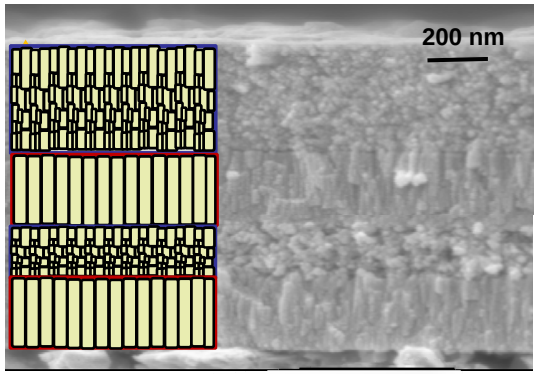
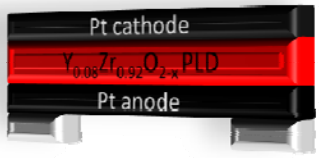
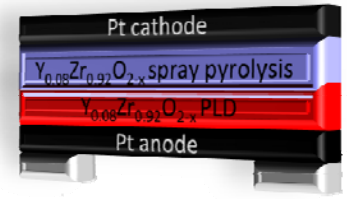
SEM: $Y_{0.08}Zr_{0.92}O_{2-x}$ thin films

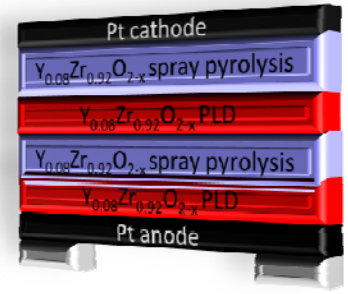












electrolyte thickness

amount of alternating layers (columnar & brick-like)

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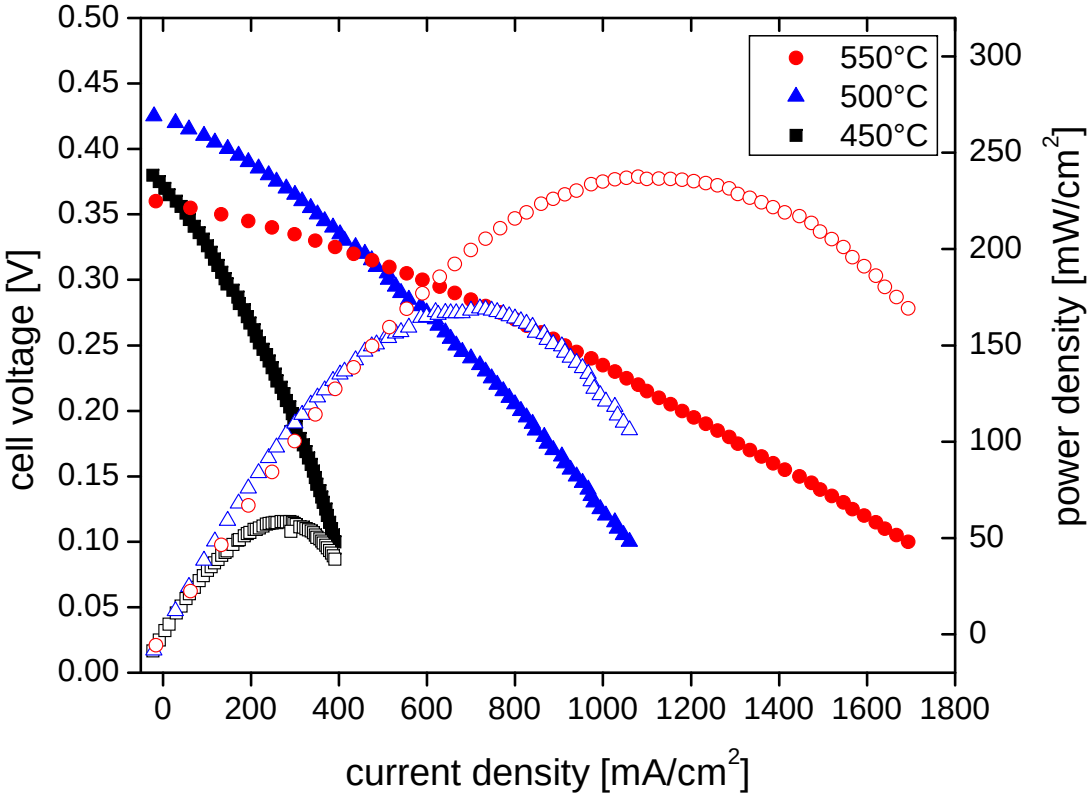
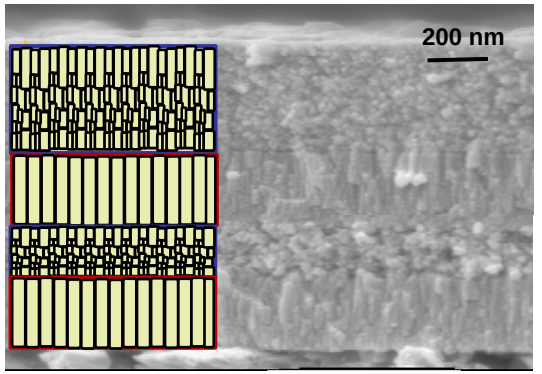
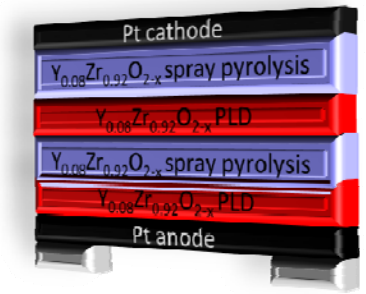
Impact of µSOFC electrolyte-microstructure on cell performance







⇒ Free-standing membrane operates with 237 mW/cm² at 550°C

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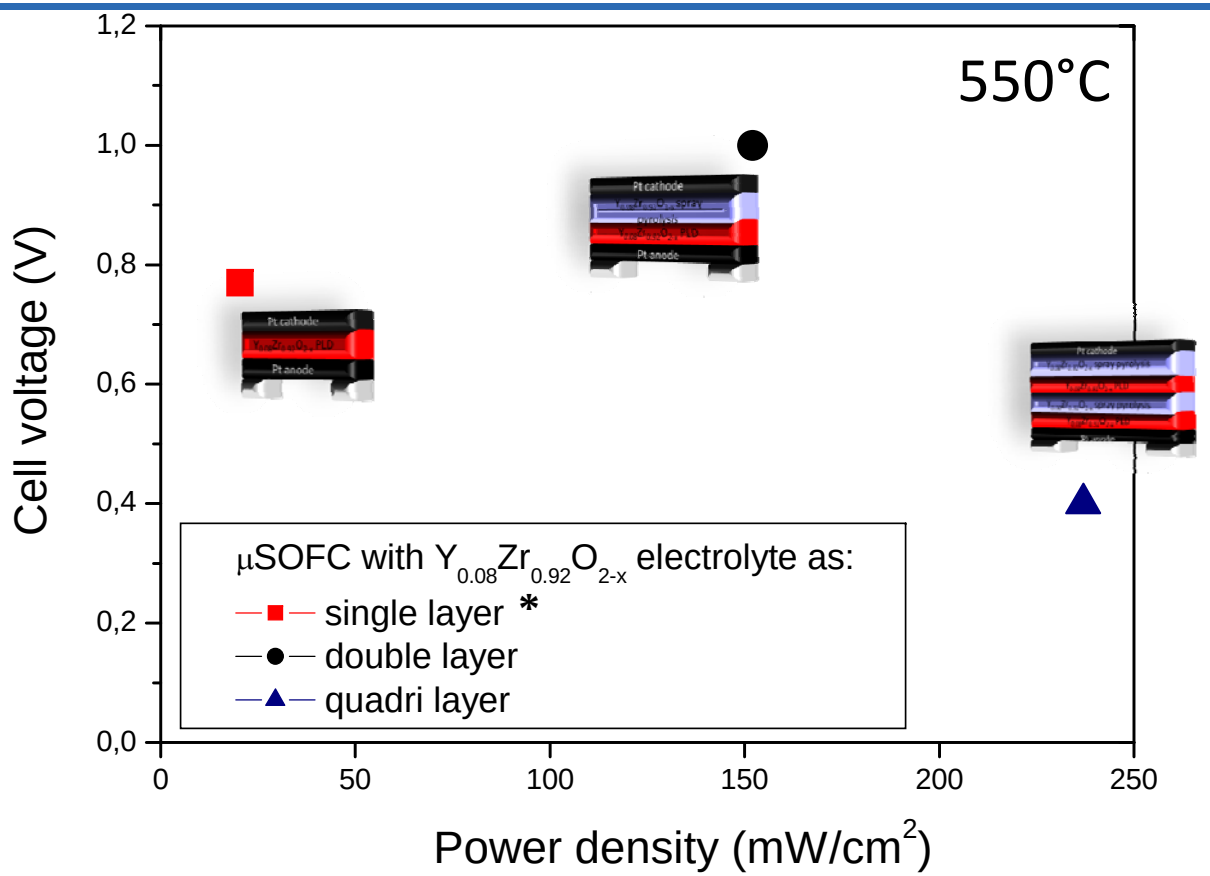
Impact of µSOFC electrolyte-microstructure on cell performance



Ref.: * U.P. Muecke, D. Beckel, A. Bernard, A. Bieberle-Hütter, S. Graf, A. Infortuna, P. Müller, J.L.M. Rupp, J. Schneider and L. J. Gauckler, Advanced Functional Materials, accepted 2008

amount of alternating layers (columnar & brick-like) → cell performance

better sealing, longer annealing steps

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Summary

- Micro-Solid Oxide Fuel Cells are feasible: 210 mW/cm^2 at 550 °C per membrane.

- Performance is highly affected by the choice of SOFC thin film material and its microstructure.

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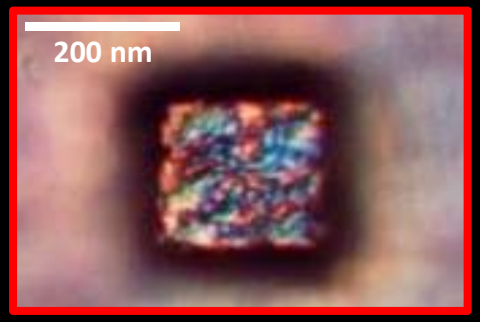
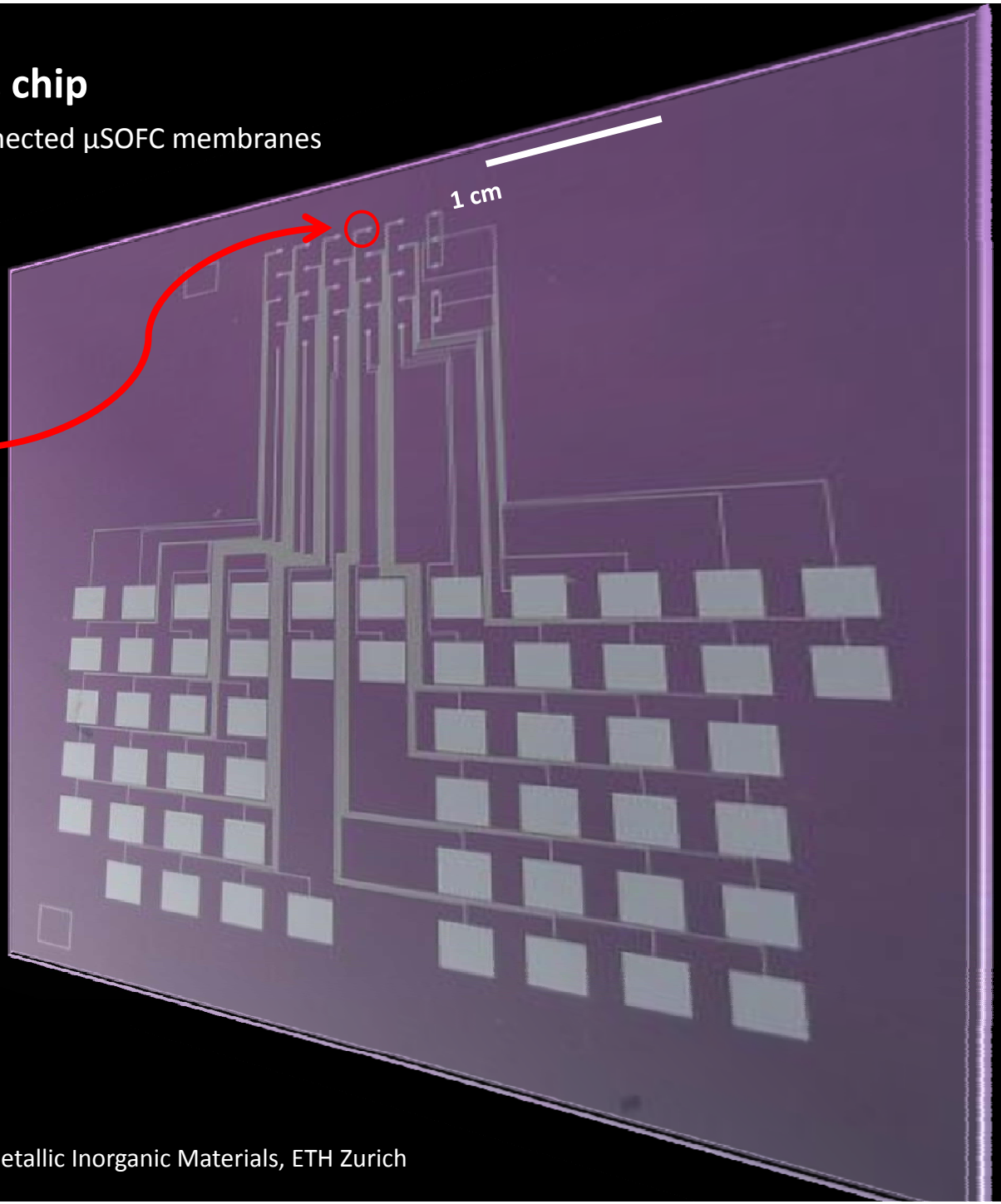
New: Si-based µSOFC chip

up to 30 single & parallel connected µSOFC membranes



single membrane



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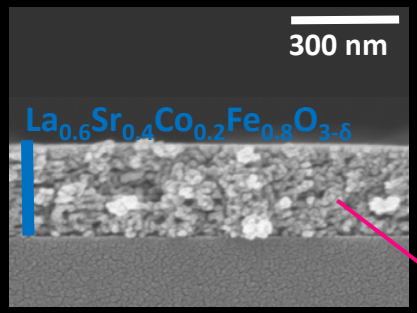
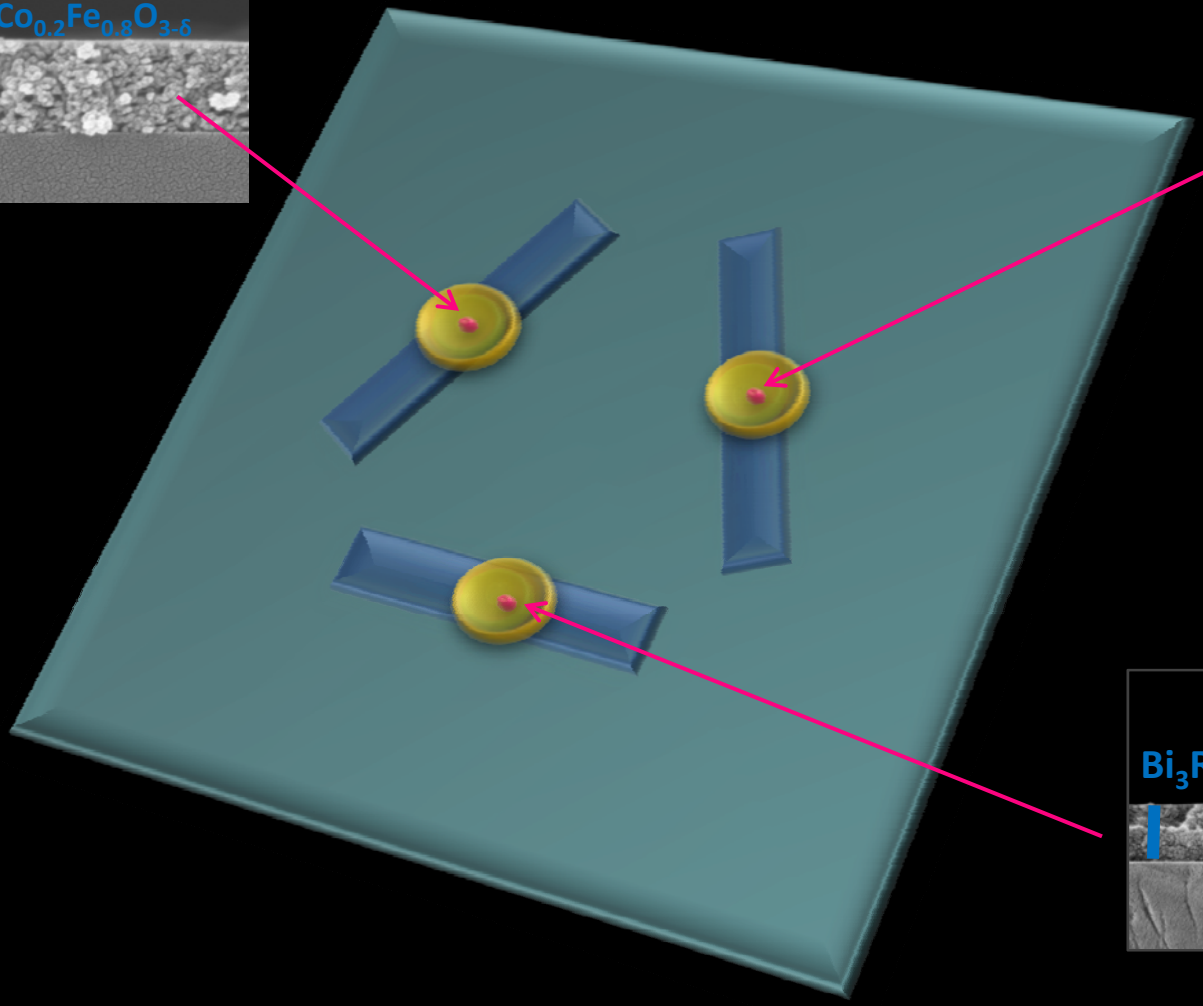
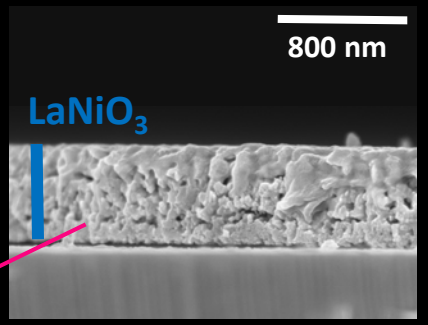
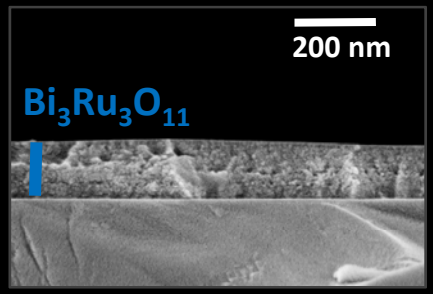
To do next: increasing cell performance by better suited cathodes









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-NANCER partners

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