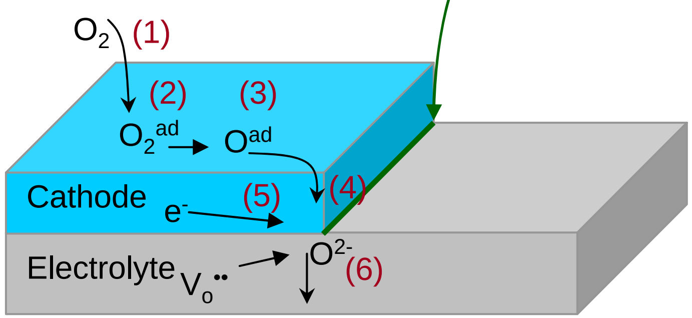
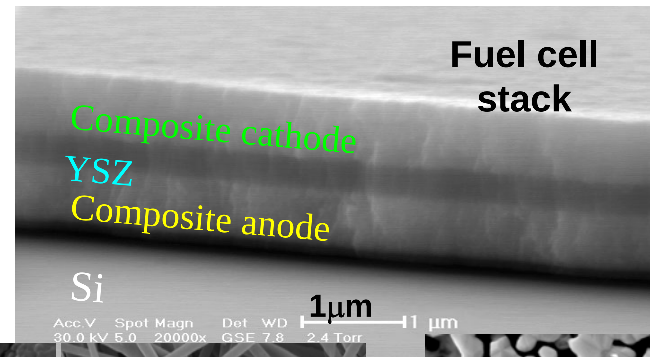
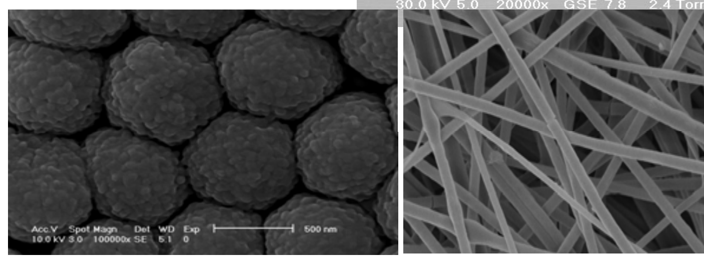
Harry L. Tuller, Department of Materials Science and Engineering
Massachusetts Institute of Technology

Micro-ionics: Next Generation Power Sources and Sensors

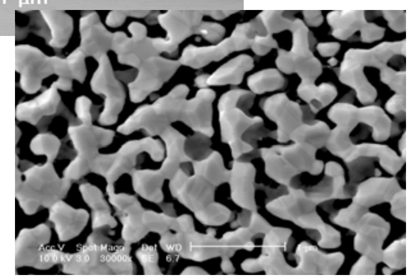
Advances in Ceramic Science and Engineering
"Congratulations to Ludwig Gauckler and Group"
Nonmetallic Inorganic Materials, ETH Zürich
September 5, 2008







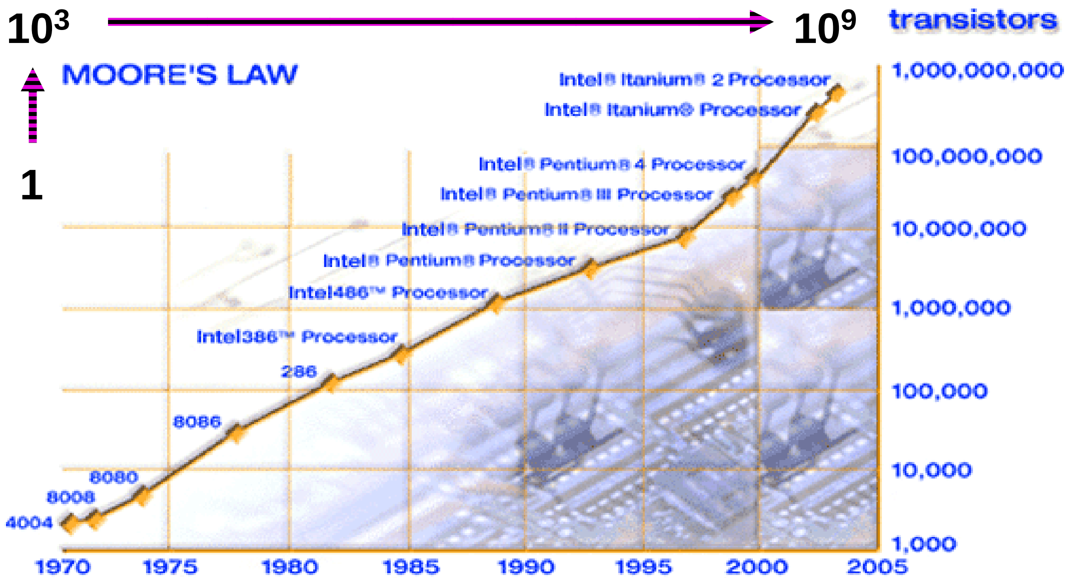
Nanostructured sensors

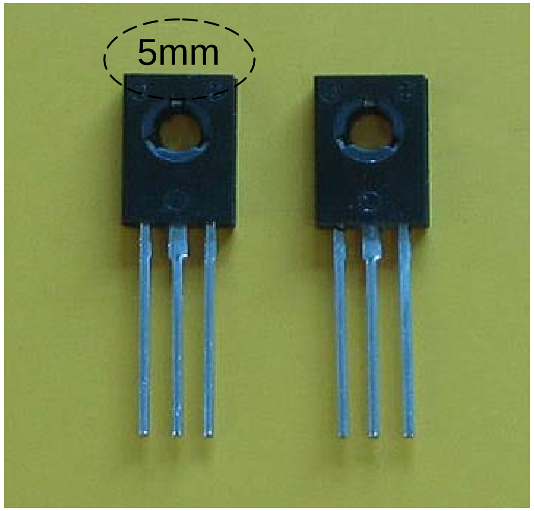


Composite electrode

Research supported by: National Science Foundation and Department of Energy

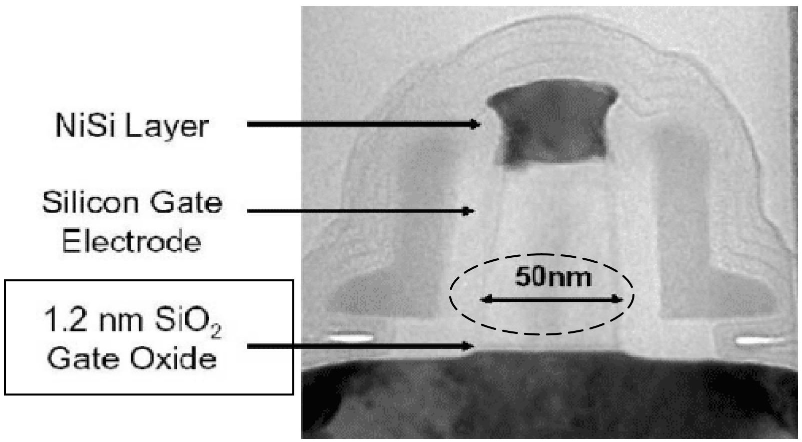
Silicon Age: *Solid State Electronics*





www.germes

Discrete transistors



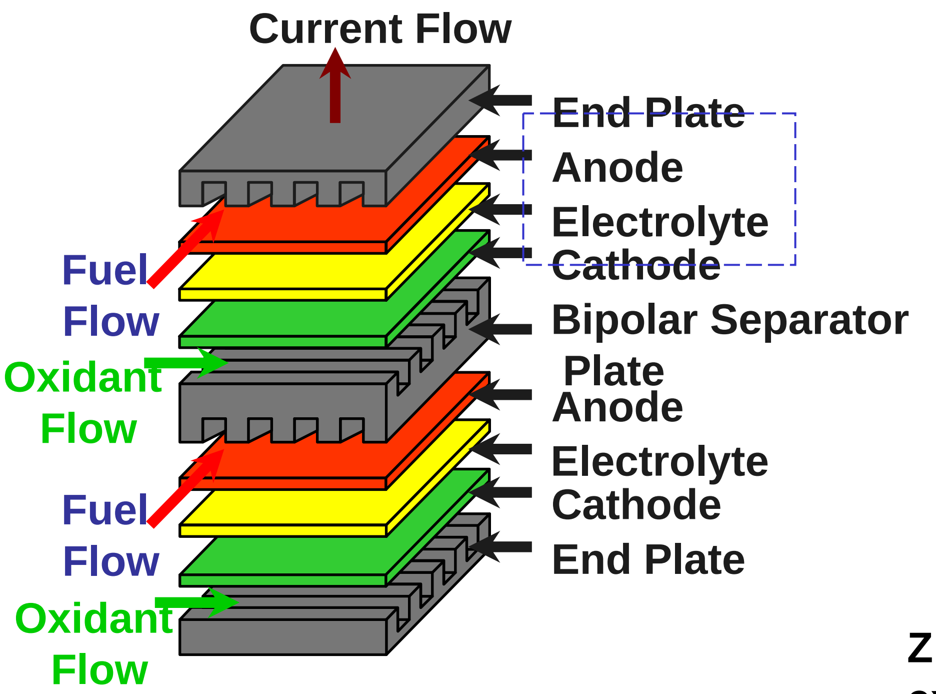
2000 times smaller than human hair

- **Miniaturization**
- **Increase device density by 10^9**
- **Complex functionality**
- **Low power; long life; robust**
- **Highly reproducible**
- **Low cost**

Drives scaling

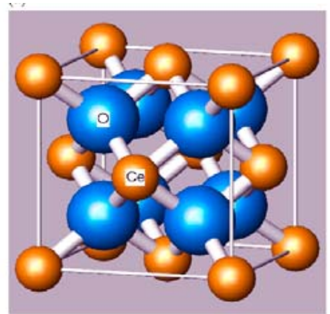
Solid State Ionics – Scalable - Integration

- Solid state membranes: Ready separation of reactants; High chemical and thermal stability; High power density
- Thin film microelectronics/MEMS compatible
- Electrochemical devices **scale** w/o loss of efficiency



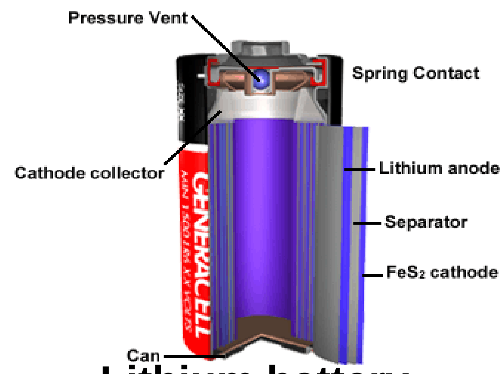
Planar SOFC; T_{op}~800-1000C

S. Singhal, PNNL



Haile / Acta Materialia 03

Zirconia-based auto exhaust sensor



Lithium battery

www. Micro.magnet.fsu.edu/

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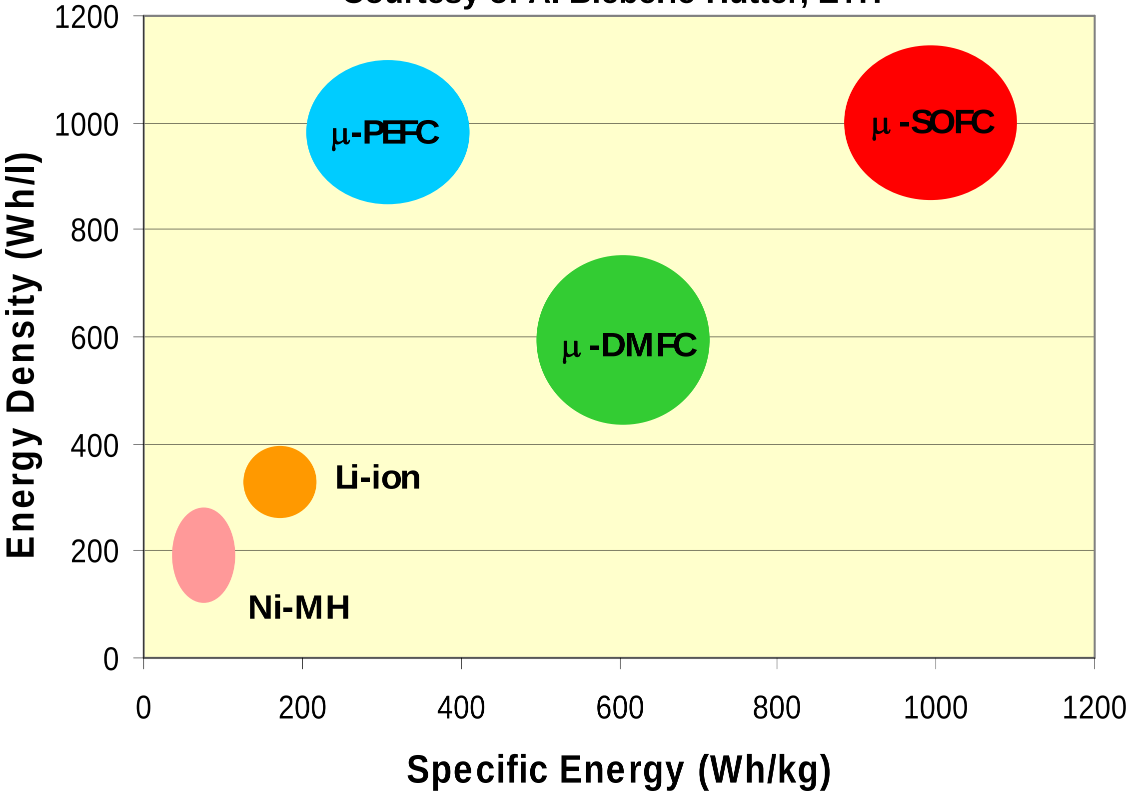
Micro Solid Oxide Fuel Cells

Courtesy of A. Bieberle-Hütter, ETH

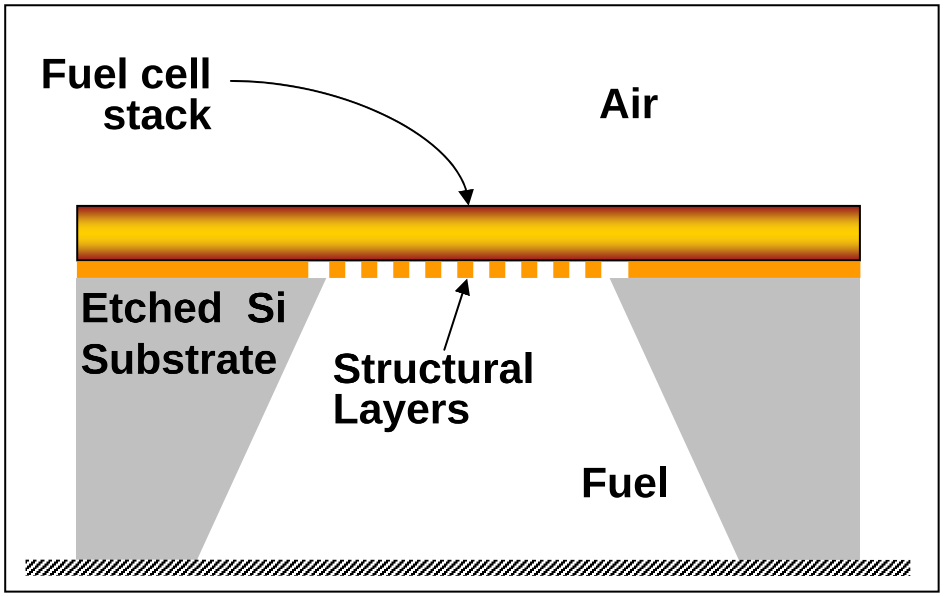


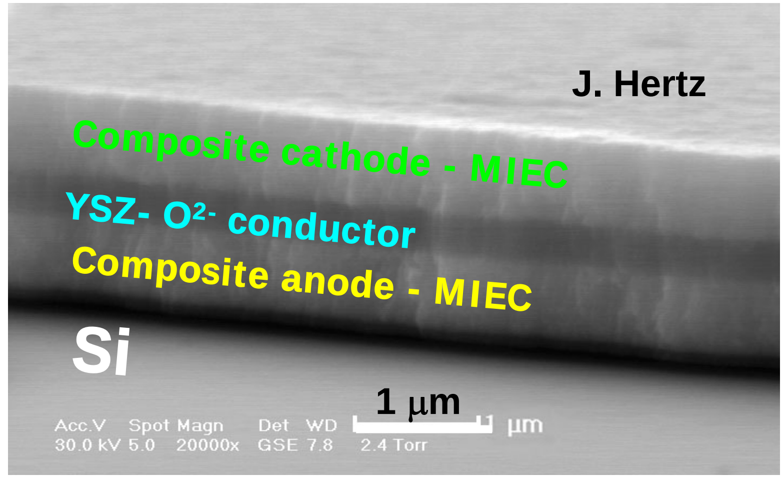
μ-SOFC promise ~5 times higher energy densities than Li ion batteries!

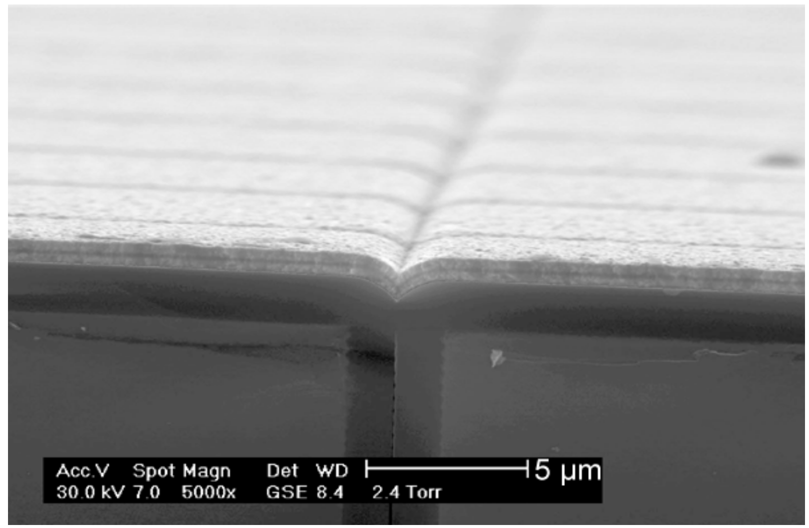
Micro-SOFCs: Portable Power

- High energy density
  - Extended operation
  - Quick *recharge*
- Rapid turn on

➔ ***Require lower operating Temp.***



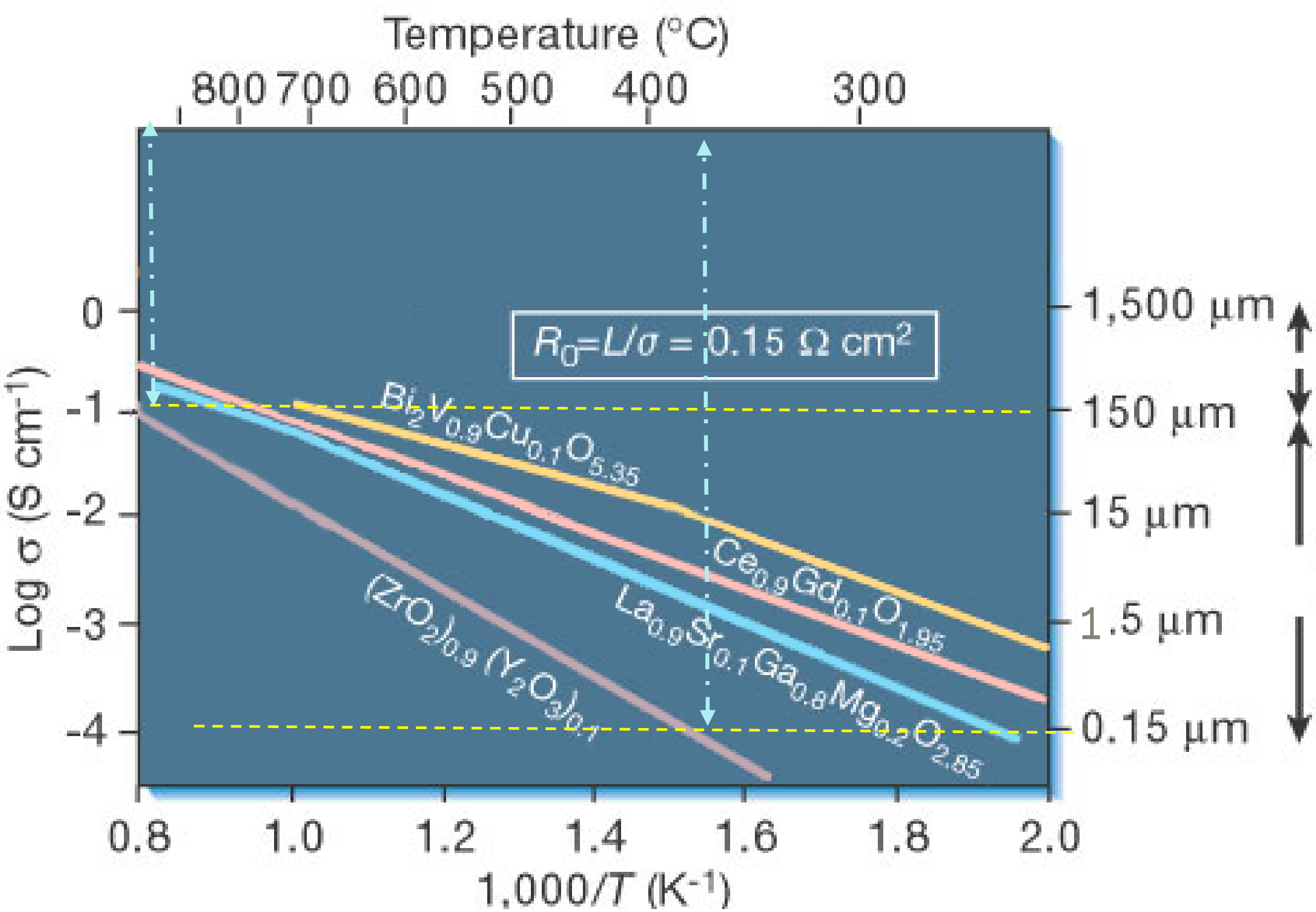


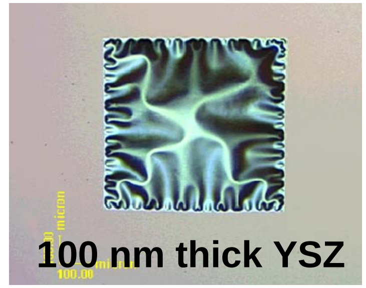


Baertsch, Jensen, Hertz, Tuller, Vengallatore, Spearing, and Schmidt, *J. Mater. Res.* 19 2604 (2004)

I. Electrolyte – Resistance, R_{SE}: *Scaling*

Thin films offer **low ohmic resistance**, and potential operation <400C.

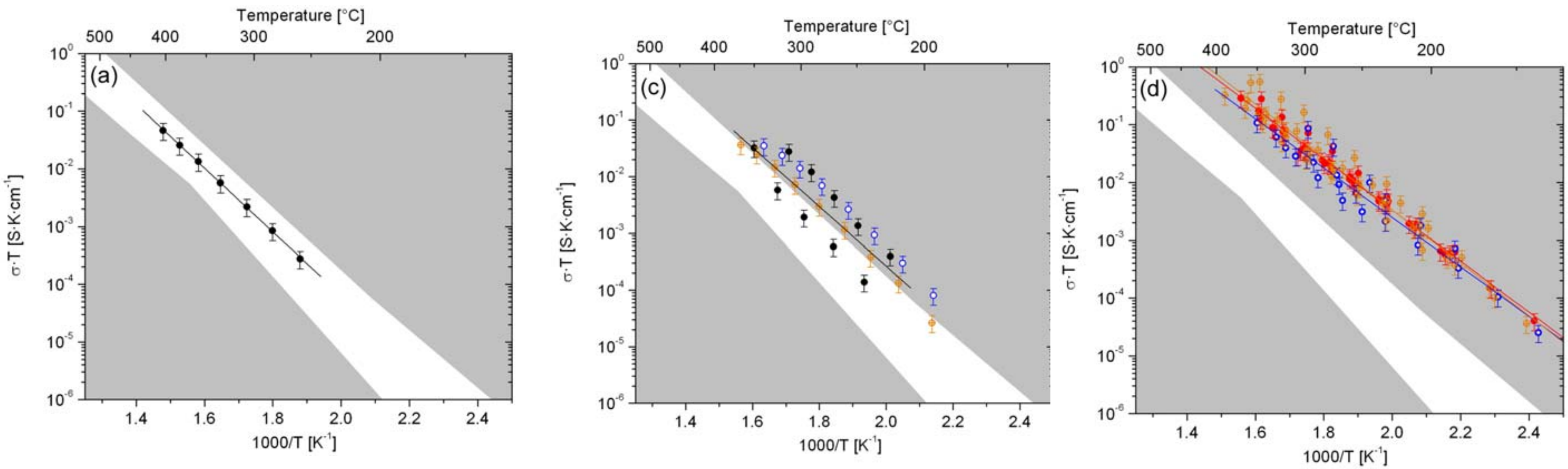




$$R_j = \frac{1}{\sigma_j}\frac{l}{A}$$

B.C.H. Steele and A. Heinzel, *Nature*, **414,** 345-352 (2001).

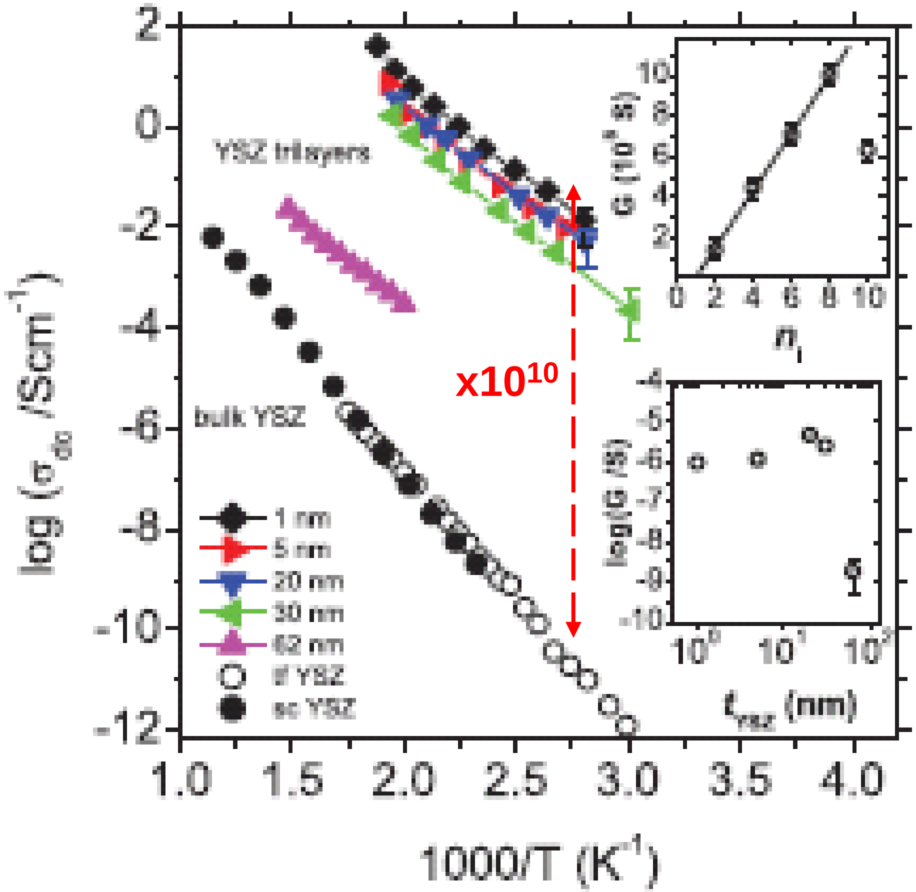
Ionic Conductivity – YSZ: R_{SE}, *Beyond Scaling*



Ionic conductivity 9YSZ (a) tapecast YSZ; (b) (111) oriented YSZ single crystal;
(c) YSZ films (200-500nm) deposited on silica substrates – reactive sputtering;
• White stripe in background approximates range of literature values

Josh Hertz, PhD thesis, MIT, 2006

Colossal Ionic Conductivity @ *Interfaces*!!??



•**Ionic conductivity of STO/YSZ/STO trilayers:** Thickness range of the YSZ layer is 1 to 62 nm.

•Top inset: 400 K conductance of [YSZ1nm/STO10nm] superlattices as a function of the number of interfaces, n_i.

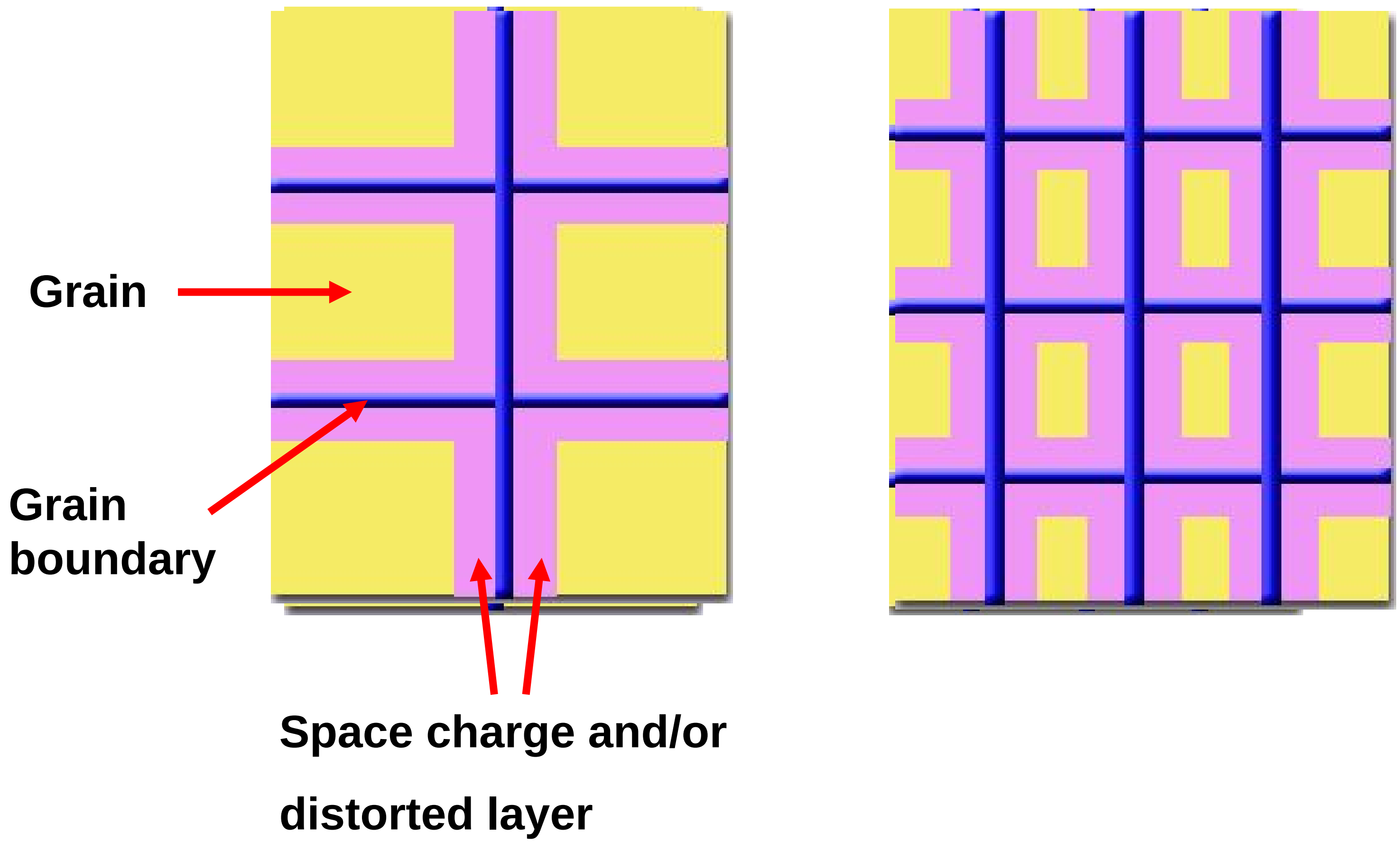
•Bottom inset: Dependence of conductance of [STO10nm/YSZXnm/STO10nm] trilayers at 500 K on YSZ layer thickness.

Increase by factor of ~10^{10}
Is that feasible?

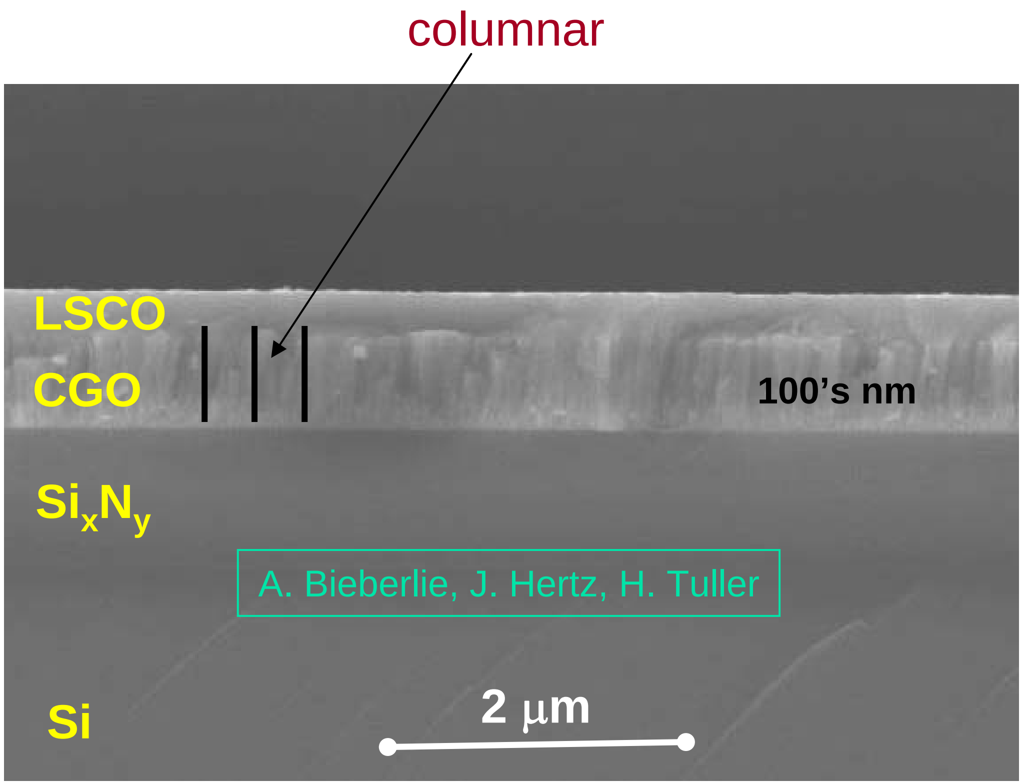
Colossal Ionic Conductivity at Interfaces of Epitaxial ZrO_2:Y_2O_3/$SrTiO_3$ Heterostructures
J. Garcia-Barriocanal et. al., *Science* 321, 676 (2008)

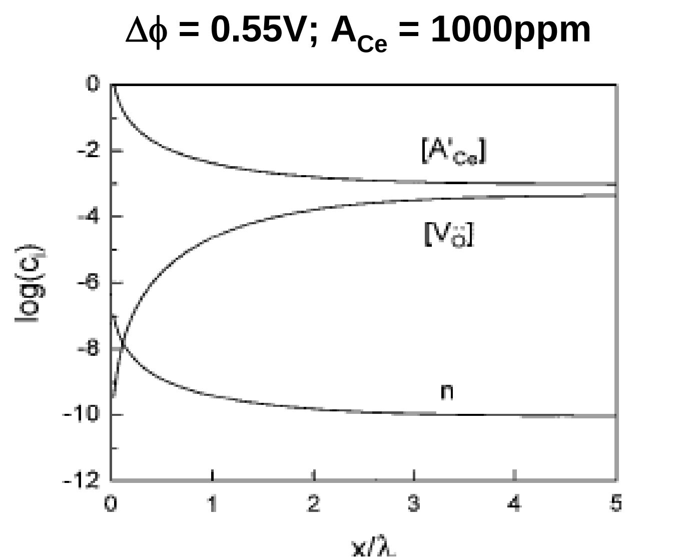
Nanocrystalline *Ionic* Solids

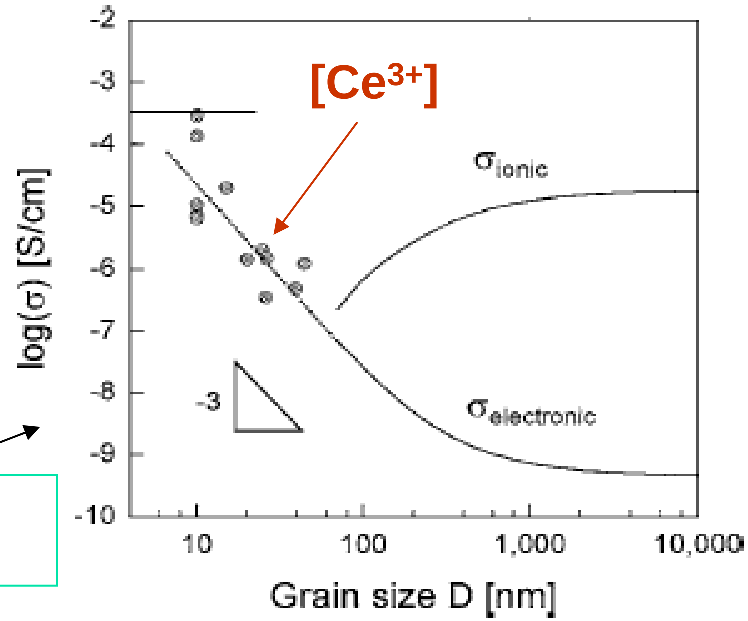
- What happens as grain boundaries come closer together?



Nanoscale in *Microionics*







Nanoionic effect in ceria:

Y.M. Chiang, E.B. Lavik, I. Kosacki, H.L. Tuller and J.Y. Ying , J. Electroceram. 1, 7-14 (1997).

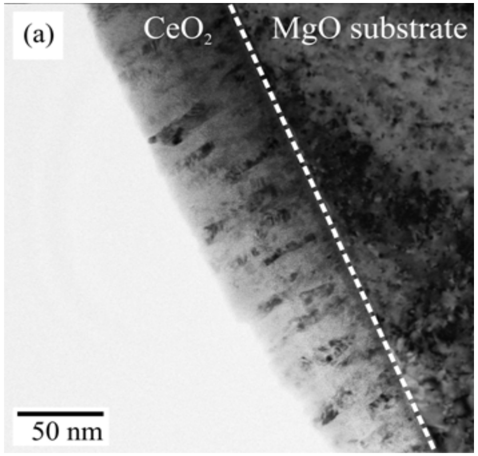
S. Kim, J. Maier, *J. Electrochem. Soc*. 149 (2002) J73

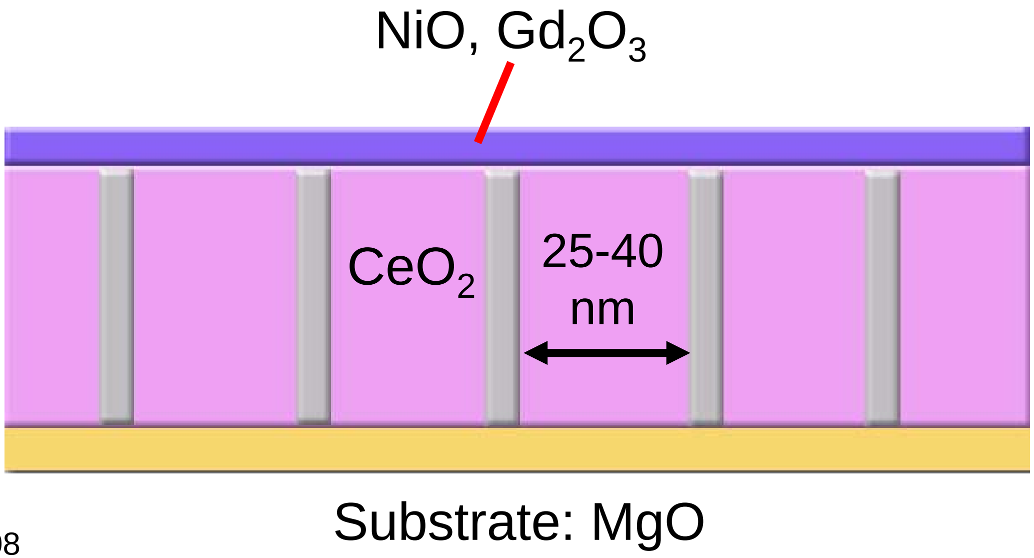
A. Tschope, R. Birringer, J. Electroceram. 7 (2001) 169

Grain Boundary Engineering

Study grain boundary cation diffusion in nanocrystalline ceria thin films

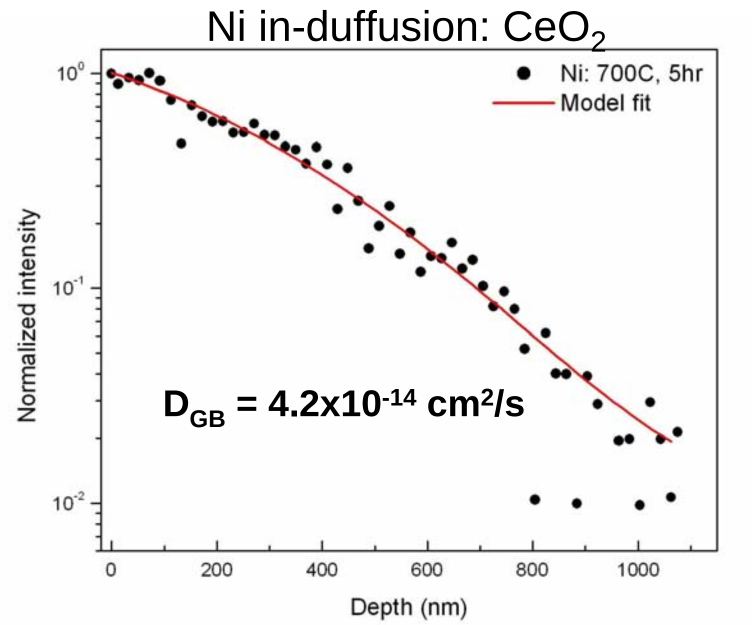
1. **Quantify cation diffusion**
2. **Describe effects of changing chemistry on electronic/ionic conductivity**

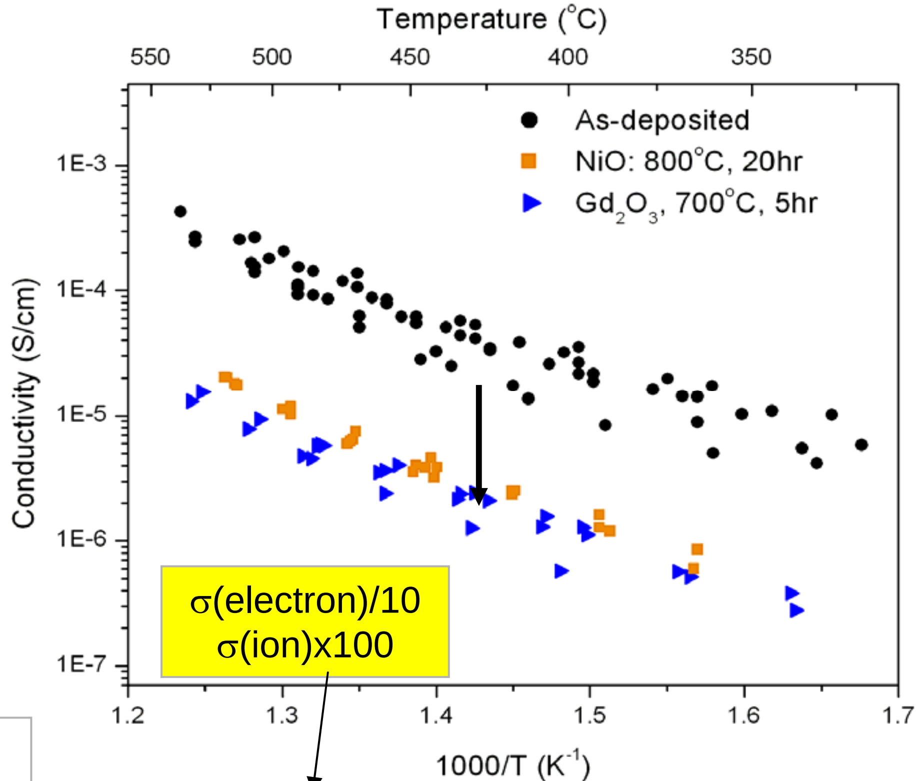




- Ceria deposition: PLD
- Diffusion source deposition
- In-diffusion: 600-800^{o}C
- SIMS/Electrical measurements

Heterogeneous Doping: Nano-CeO_2





Performed in RWTH Aachen University under NSF World Materials Network & Charlemagne scholarship

→ electron blocking experiments

- Heterogenous doping feasible at intermediate temperatures
- Space charge barrier control investigated
- Lifetime implications identified.

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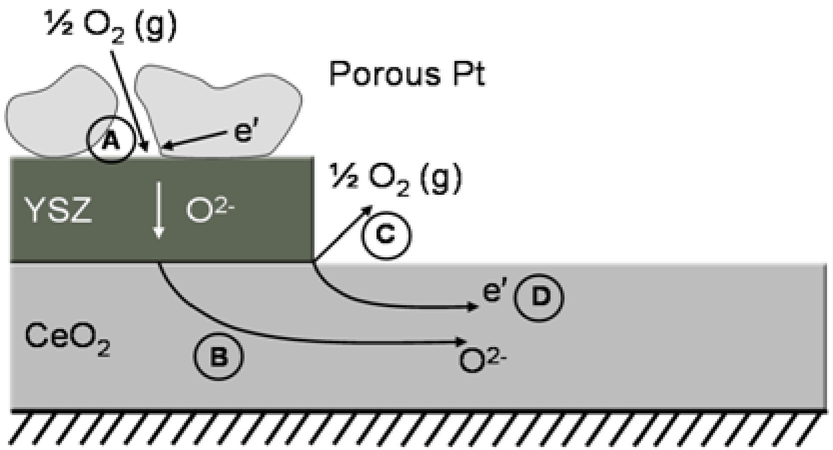
S.J. Litzelman, et al., *J. Electroceramics*, – DOI: 10.1007/s10832-008-9445-y (2008)

Dopant Redistributions

- The decrease in both partial conductivities (by electron blocking) cannot be described solely by a change in ΔΦ
- In addition to grain growth, what other physical changes are occurring?
- Must consider redistribution of dopant cations



See e.g. I. Riess, *Solid State Ionics* 44, (1991)199.

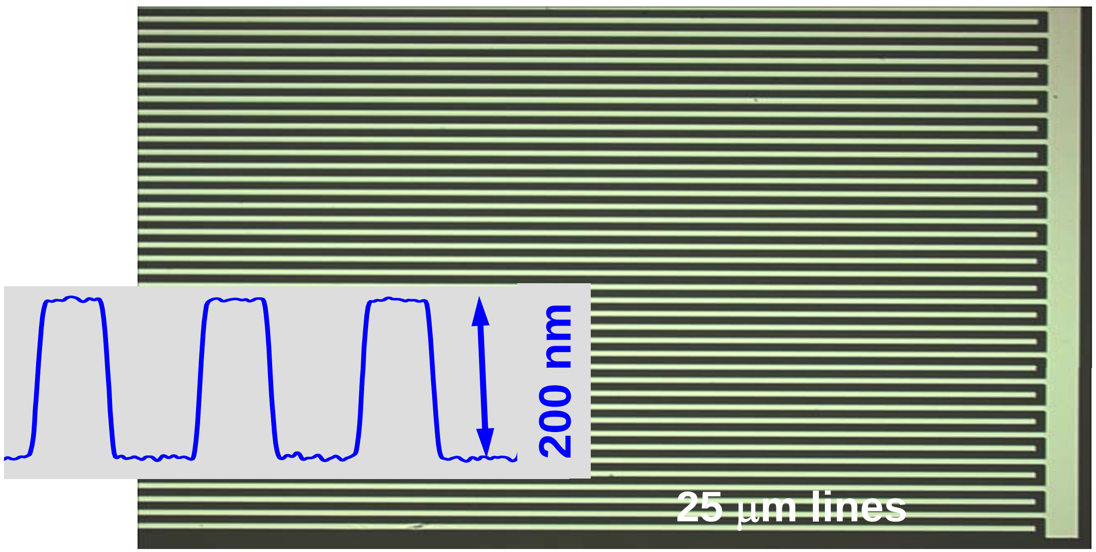
II. Electrodes, R_C: Scaling Effects?

- Limited SOFC performance by slow cathodic reactions at reduced T
  - Limited degree of understanding
- Majority of Cathode studies
  - Complex electrode morphologies
  - Difficulty in controlling properties

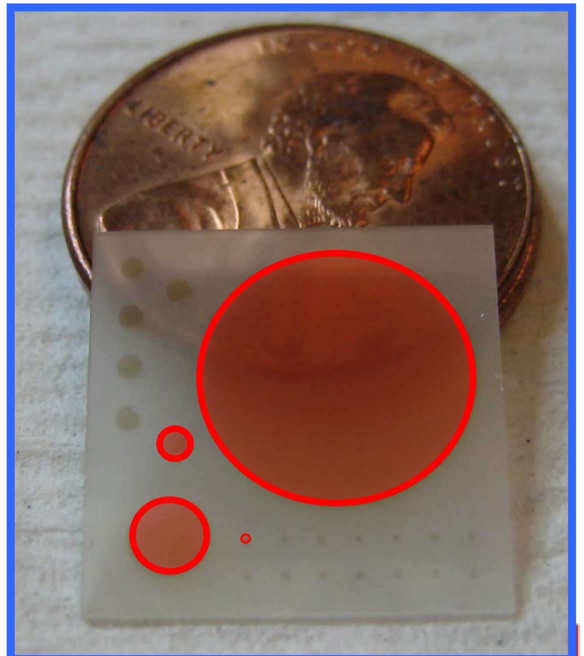
Scalable Geometries/Model Systems

- **Independent control of: TPB length, contact area, conduction path length, thicknes**

Pt on YSZ



$SrTi_{1-x}Fe_xO_3$ (STF) Model *MIEC* Cathode on YSZ



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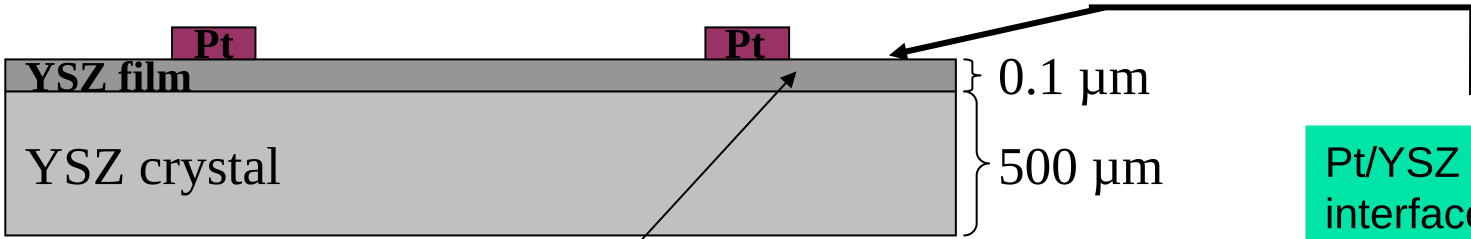
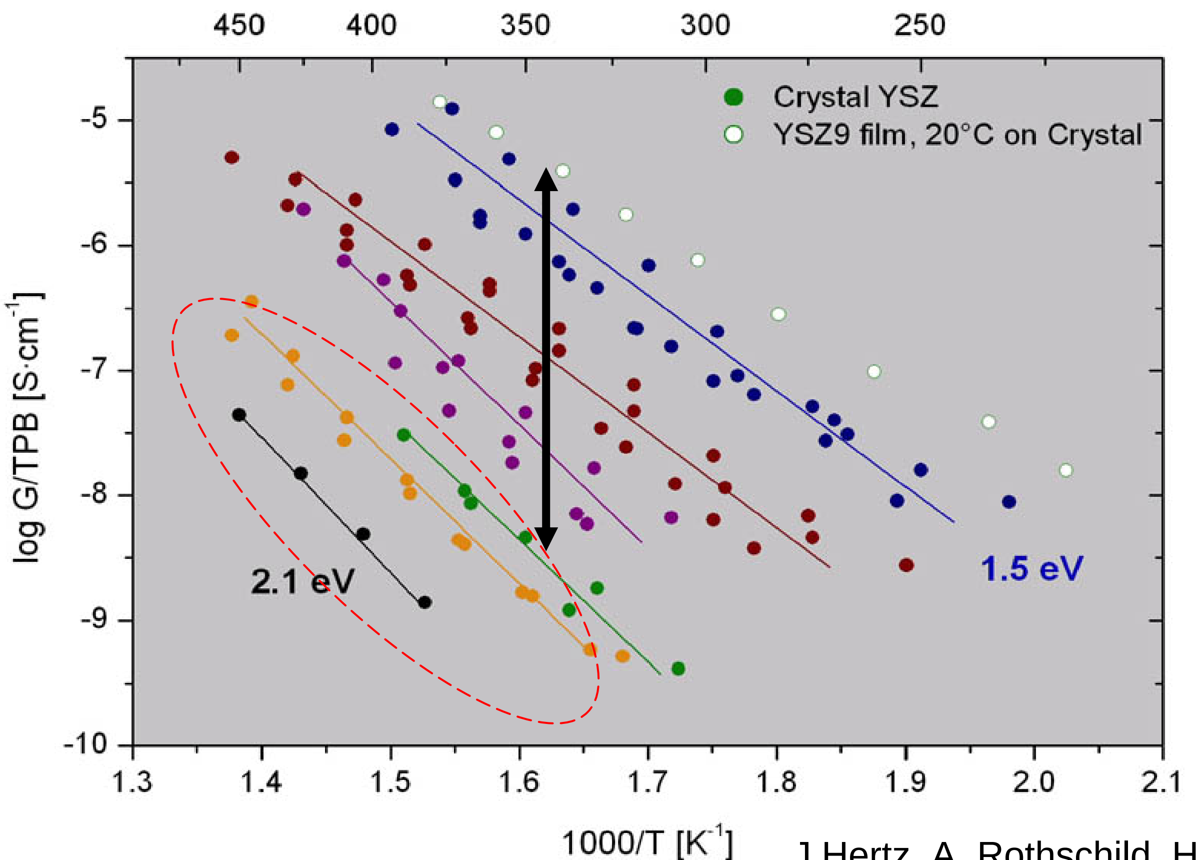
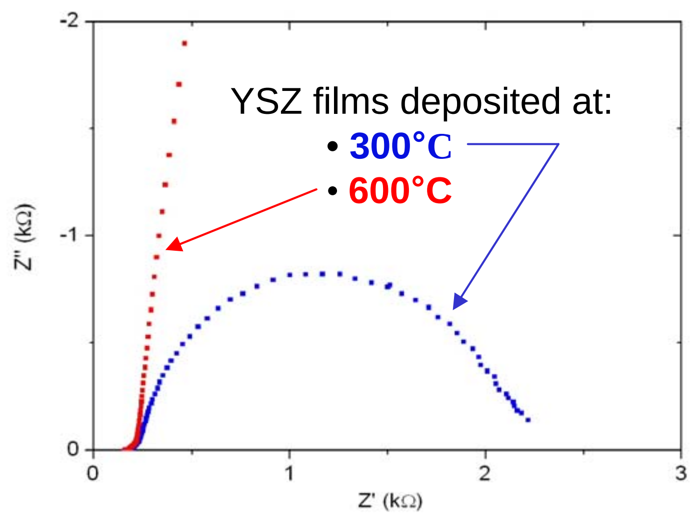
Electrode Performance: *YSZ Dependent!*



Pt/YSZ interface is key. Must be Si free! (XPS)

YSZ film lowers electrode resistance by 3 orders of magnitude!

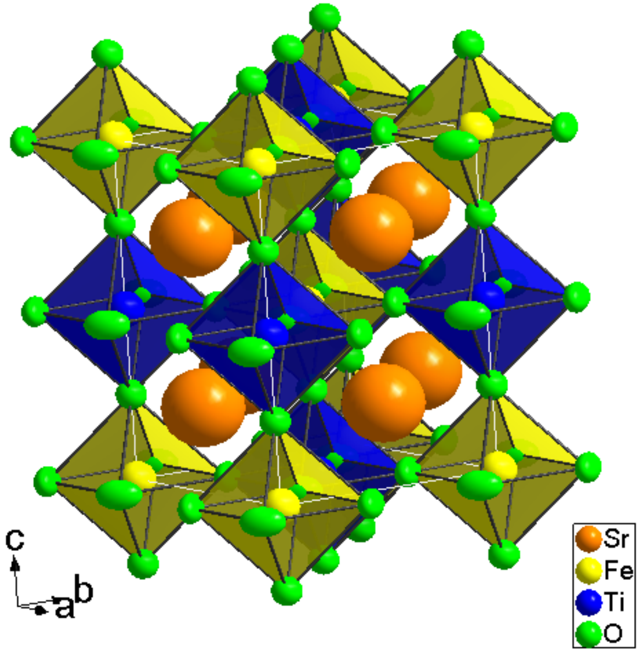




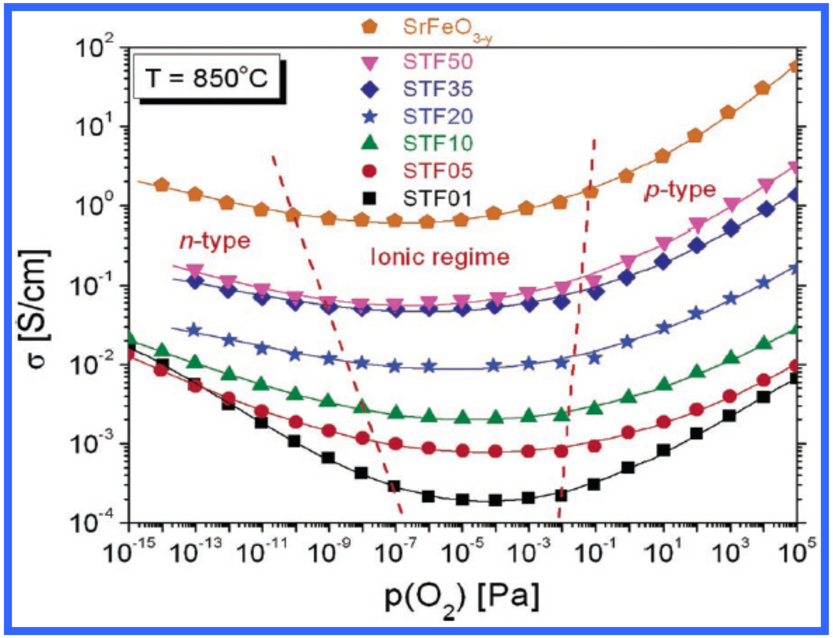
Electrode impedance @ T=405ºC

J.Hertz, A. Rothschild, H. Tuller, J. Electroceram. 08

$SrTi_{1-x}Fe_xO_{3-d}$ (STF) Model MIEC Cathode



$SrTi_{1-x}Fe_xO_{3-y}$ solid solutions:

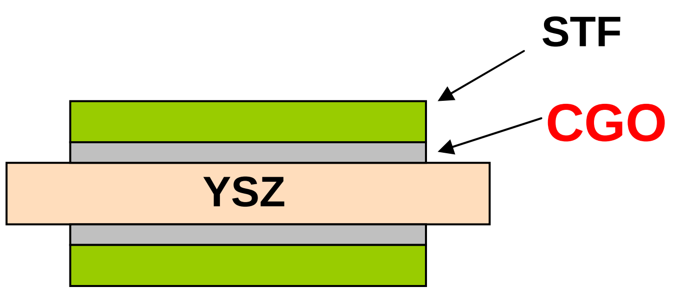


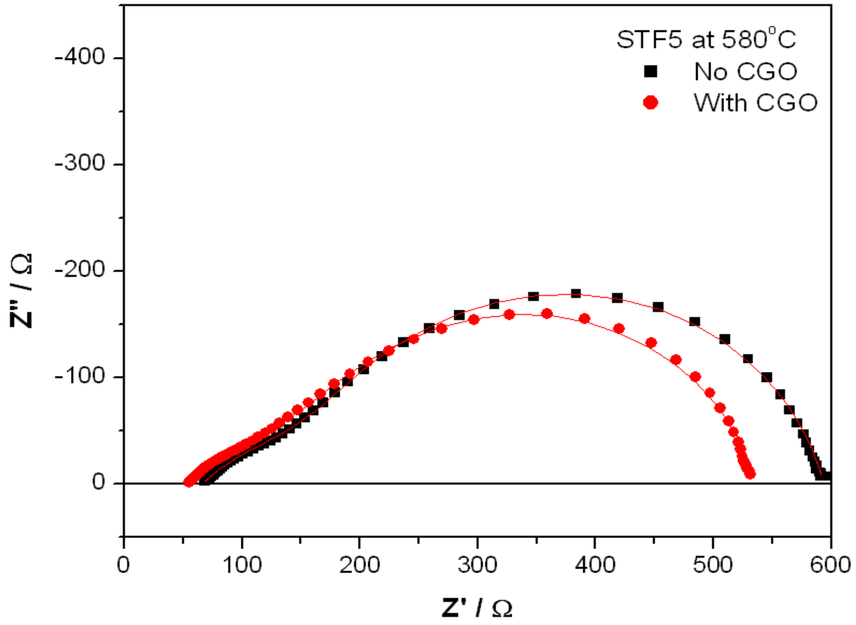
Rothschild, A, Tuller, H.L., et al., Chem. Mater, 18, 3651 (2006)

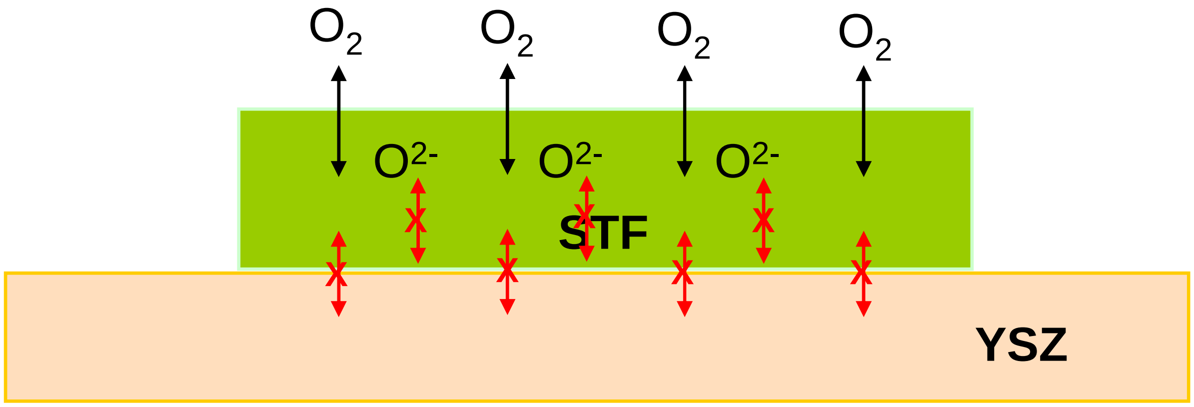
MIEC: Mixed Ionic Electronic Conductor

Rothschild, Litzelman, Tuller, Menesklou, Schneider, and Ivers-Tiffee Sens. Actuators B, **108**, 223 (2005).

Surface Reaction Controlled Rc







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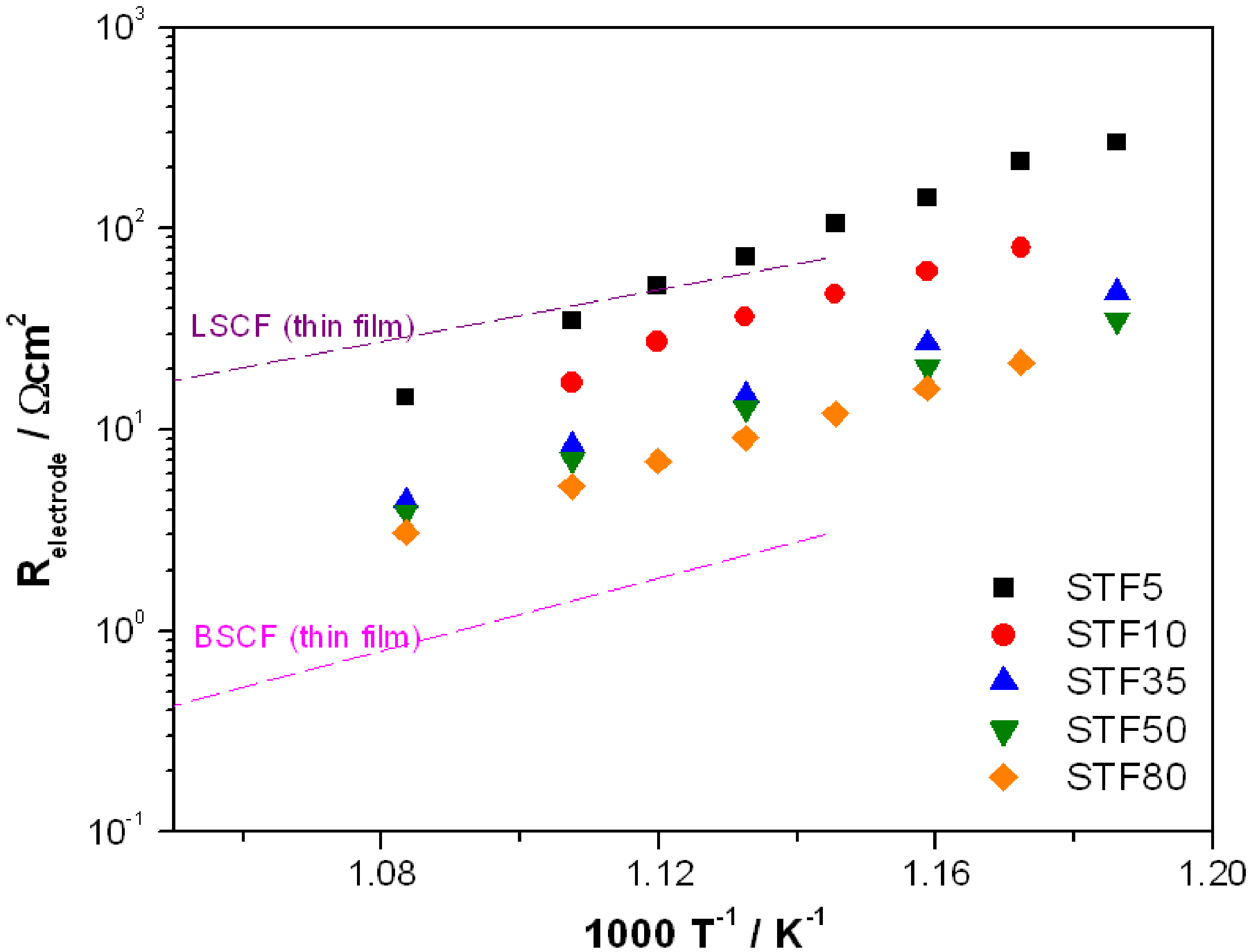
Model STF: Comparable to Best Cathodes!



Baumann, F.S., et al., *Electrochem. Soc.*, **154**, B931 (2007).

Surface Exchange Coefficient – Control?

$$k^q = \frac{kT}{4e^2 R_S c_O}$$

Maier, J., Physical Chemistry of Ionic Materials, Wiley 2004

T=800°C	k (cm/s)	D (cm²/s)	σ_{el} (S/cm)	σ_{ion} (S/cm)	t_e
STF5	**1.2 × 10^{-5}**	**N/A**	**10^{-3} ~ 10^{-2}**	**10^{-4} ~ 10^{-3}**	**N/A**
STF35	**2.0 × 10^{-5}**	**1.0 × 10^{-7}**	**9.9 × 10^{-1}**	**3.5 × 10^{-2}**	**0.9659**
STF50	**1.7 × 10^{-5}**	**1.1 × 10^{-7}**	**1.8**	**3.6 × 10^{-2}**	**0.9804**
*$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	**5.6 × 10^{-6}**	**2.5 × 10^{-8}**	**302**	**8 × 10^{-3}**	**0.9997**

Electronic conductivity varies by ~ 5 orders of magnitude!

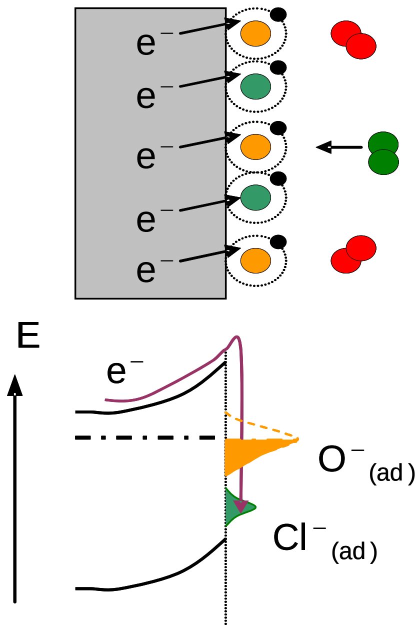
Rothschild, A, Tuller, H.L., et al., Chem. Mater, 18, 3651 (2006)

* Ullmann, H., *Solid State Ionics*, **138**, 79 (2000).

*Benson, S.J., in *Proc. 3rd Int. Symp. Ionic and Mixed Conducting Ceramics*, PV 97-24, p. 596 (1997).

Semiconducing Metal Oxide Sensor Device Physics

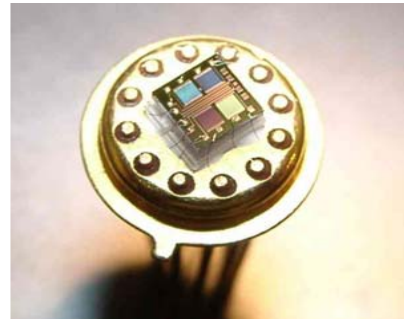
SnO_2, ZnO, TiO_2…

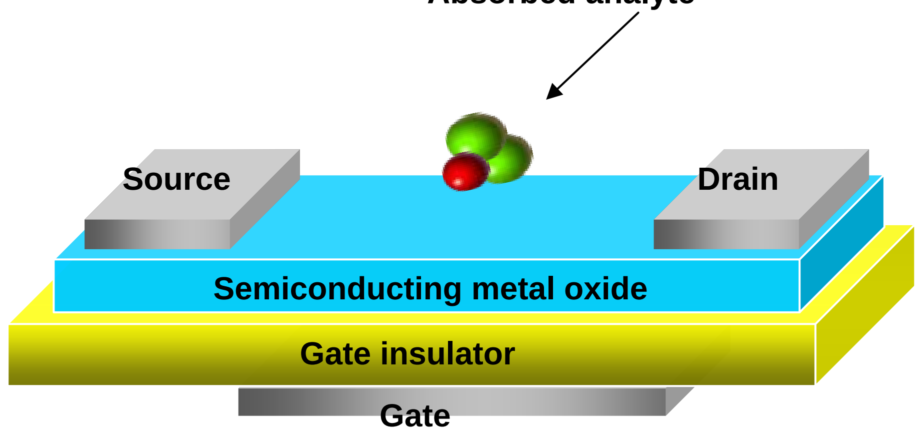


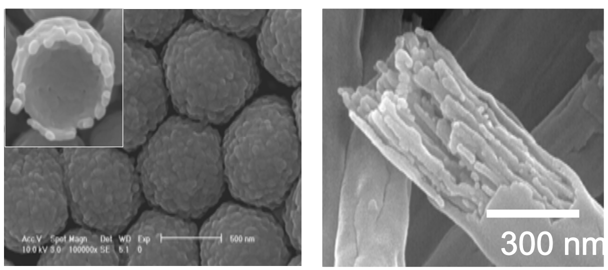
George Whitfield & Yoonsil Jin

- Investigating positions and binding energies of *volatile* surface states

  - photostimulated desorption
  - work function measurements
  - field effect







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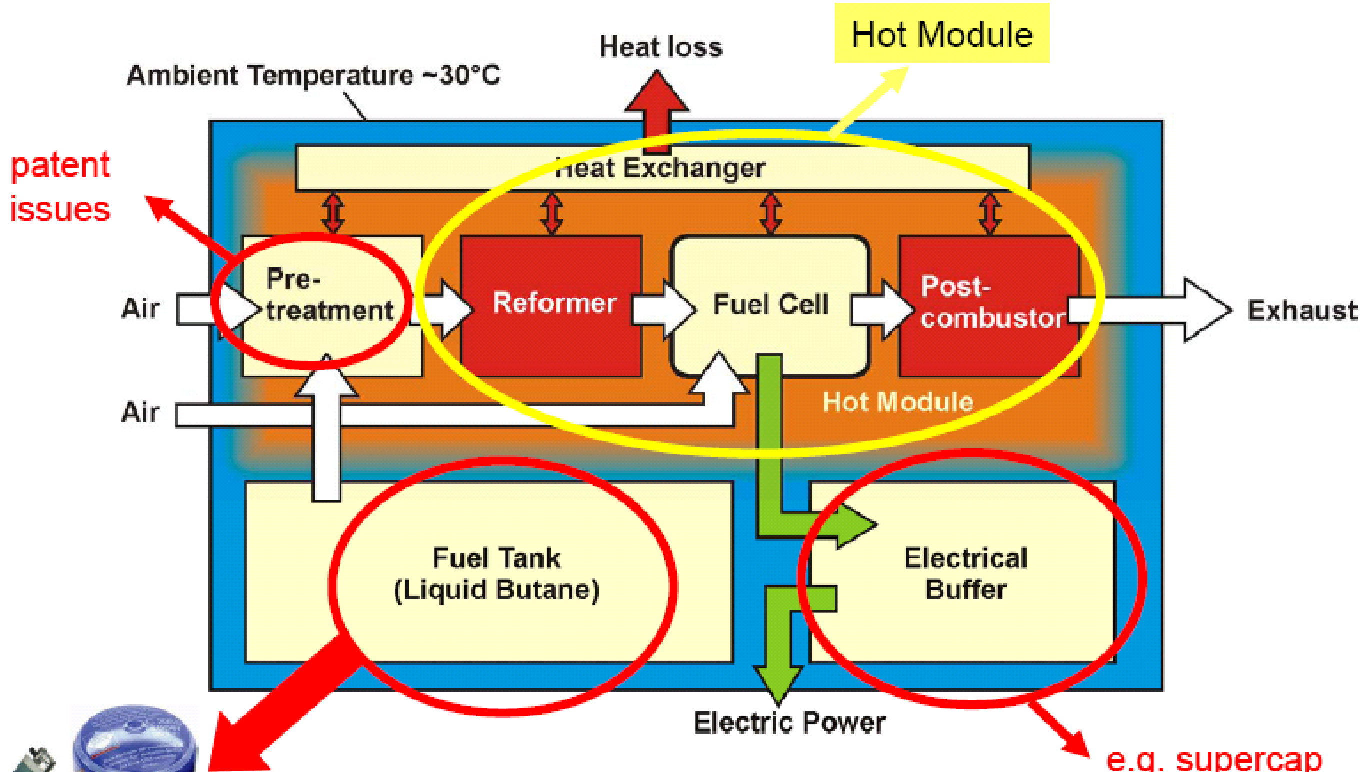
I.D. Kim, A. Rothschild, K. Sahner

Gauckler Group:
Basic Science, Clever Processing; Systems Integration

- Fuel Cell
- Gas Processing
- Thermal Management
- System Development
- Project Management & Industrial Liaison

A. Bieberle-Hütter et al., *J. Power Sources* 177 (2008) 123.



http://www.nonmet.mat.ethz.ch/research/onebat

ONEBAT

Miniaturized fuel cell systems: Challenges and chances, Anja Bieberle-Hütter

Summary

- **Solid state membranes – enable micro ionics:**
  - Micropower – fuel cells, batteries
  - Microsensor arrays

- **Thin film and microelectronic processing**:
  - Nanoscale dimensions; metastable phases
  - Model structures: scalable over orders of magnitude
  - High and controlled purity; reproducible

- **Acknowledgement – Support by National Science Foundation**
- **Josh Hertz, Scott Litzelman, WooChul Jung, Yoonsil Jin**
- **Anja Bieberle-Hűtter, Avner Rothschild, Il-Doo Kim, Kathy Sahner**