NANOMATERIALS FOR BETTER BATTERIES, GAS SENSORS AND FUEL CELLS

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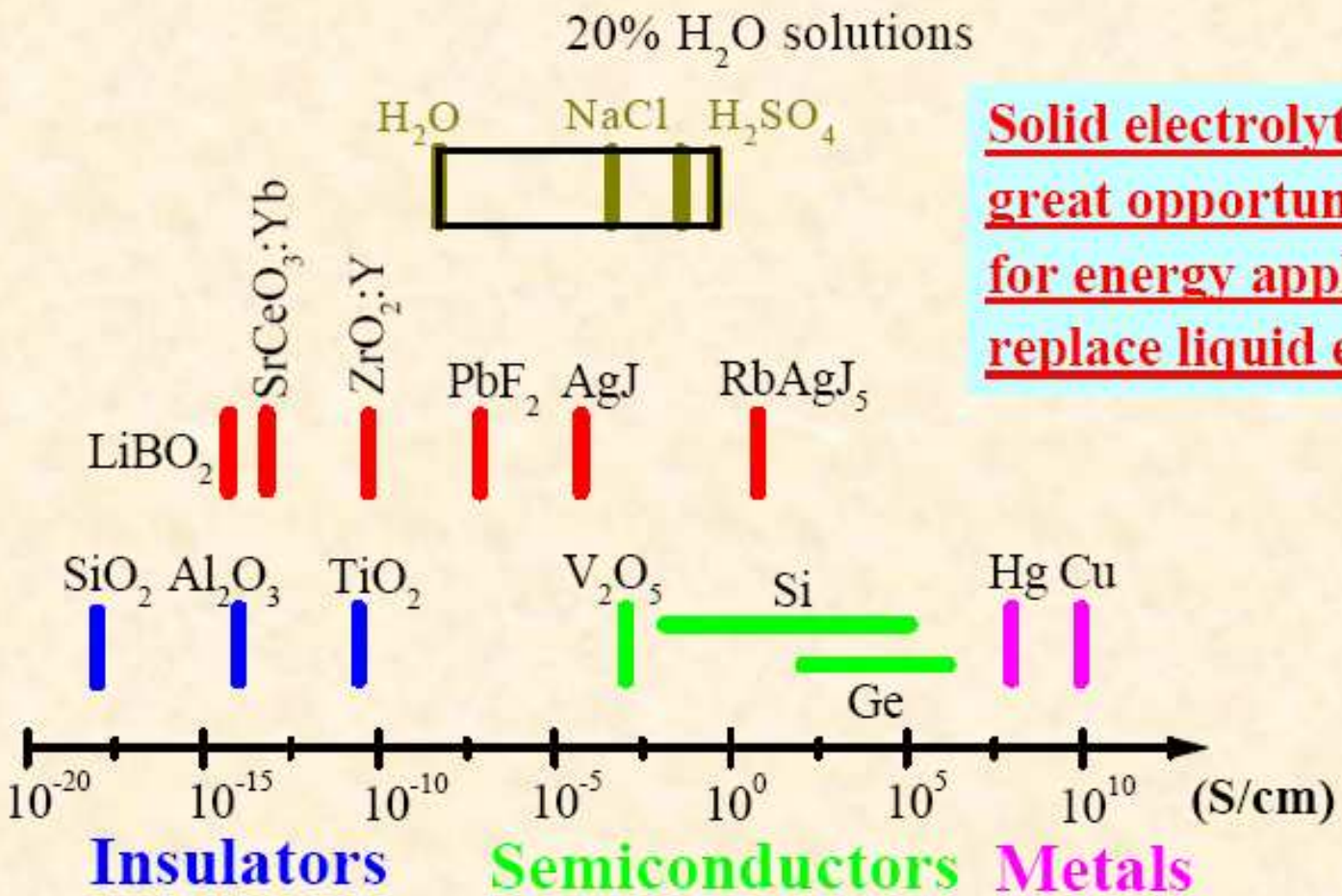
- solid electrolytes for batteries, fuel cells, gas sensors
- what is the limit of ionic conductivity in solids?
- advanced materials – nanoceramics, superlattices, mesoporous
- concept of superlattice electrolyte
- performance of novel devices

Nanotechnology Colloquium
Nanomaterials Application Center, Houston, TX

February 23rd 2009

Electrical Conductivity of Selected Materials



Solid electrolytes - great opportunity for energy application replace liquid electrolytes

Ionic conductivity in solids reported for first time by M. Faraday in 1833

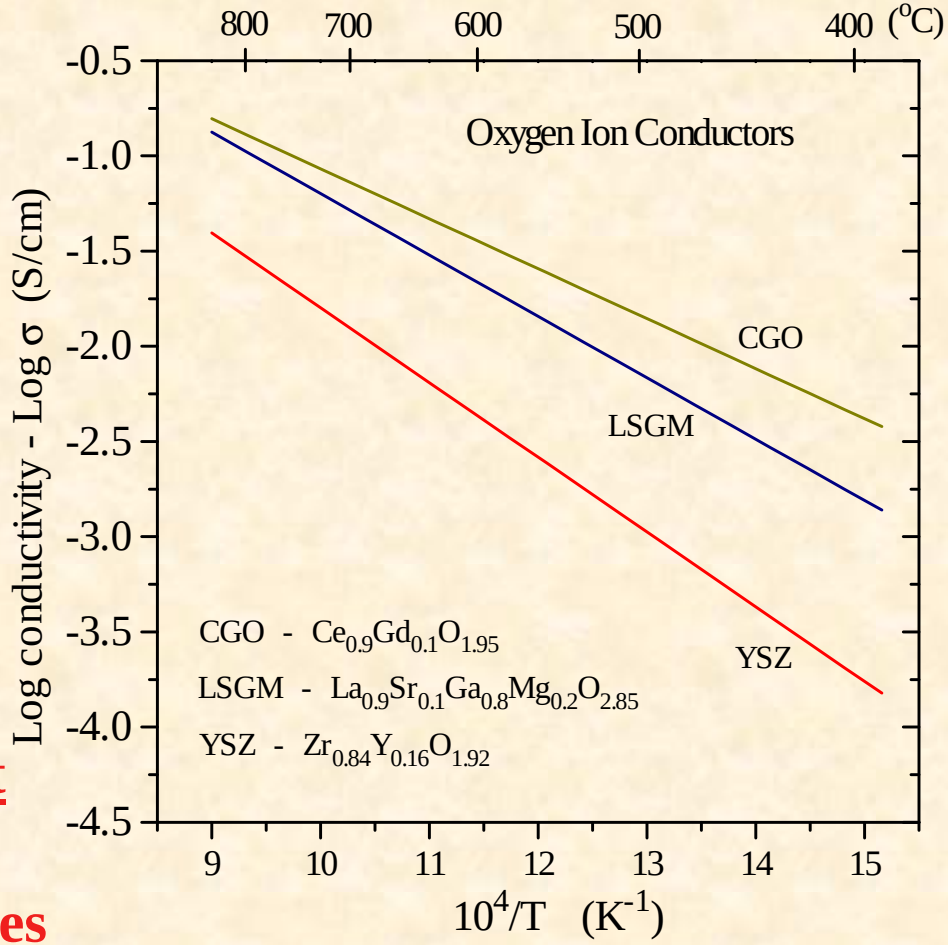
- **the electrical conductivity of AgJ, AgCl and AgBr exhibits extremly high value at temperatures below melting point**
- **the charge carriers are Ag ions**

Important ion conductors for energy application

- **Oxygen conductors** - CeO_2:(Gd, Sm), ZrO_2:(Y, Sc, Ca), $LaSrGaMgO_3$
- **Lithium conductors** – Li_2O , $LiCoO_2$, $LiMn_2O_4$, $LiBO_2$, PEO_6:$LiXF_6$
- **Materials requirements:**

  * enhance the electrical transport
  * control σ_i/σ_e
    $\sigma_i/\sigma_e > 100$ for solid electrolytes
    $\sigma_i \sim \sigma_e$ for electrodes
  * enhance the reaction kinetics
  * chemical and mechanical stability

- **Success in the optimizing the material properties determines the development of electrochemical devices as sensors, batteries, fuel cells and ionic membranes**



First Application of YSZ – Nernst Lamp 1897

1864 - 1941

German Patent D.R.P. No. 104872

$$E = \frac{R \cdot T}{\eta} \cdot \ln \frac{C}{c}$$

Nobel Price in Chemistry 1920

- glover based on $ZrO_2:Y_2O_3$ ceramic

CARL ZEISS, JENA

Nernstlampe

als Mikroskopierlampe

(Mikro-Nernstlampe).

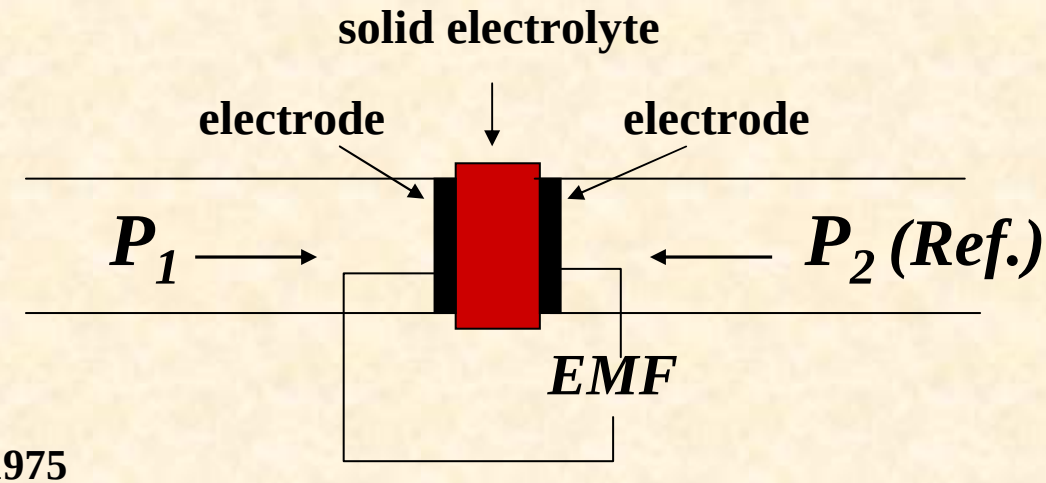
Nernst research and inventions begun the modern electrochemistry

- oxygen sensors

- solid oxide fuel cells

Nernst - type automotive sensor has 30 years

Honda 2002



Bosch 1975

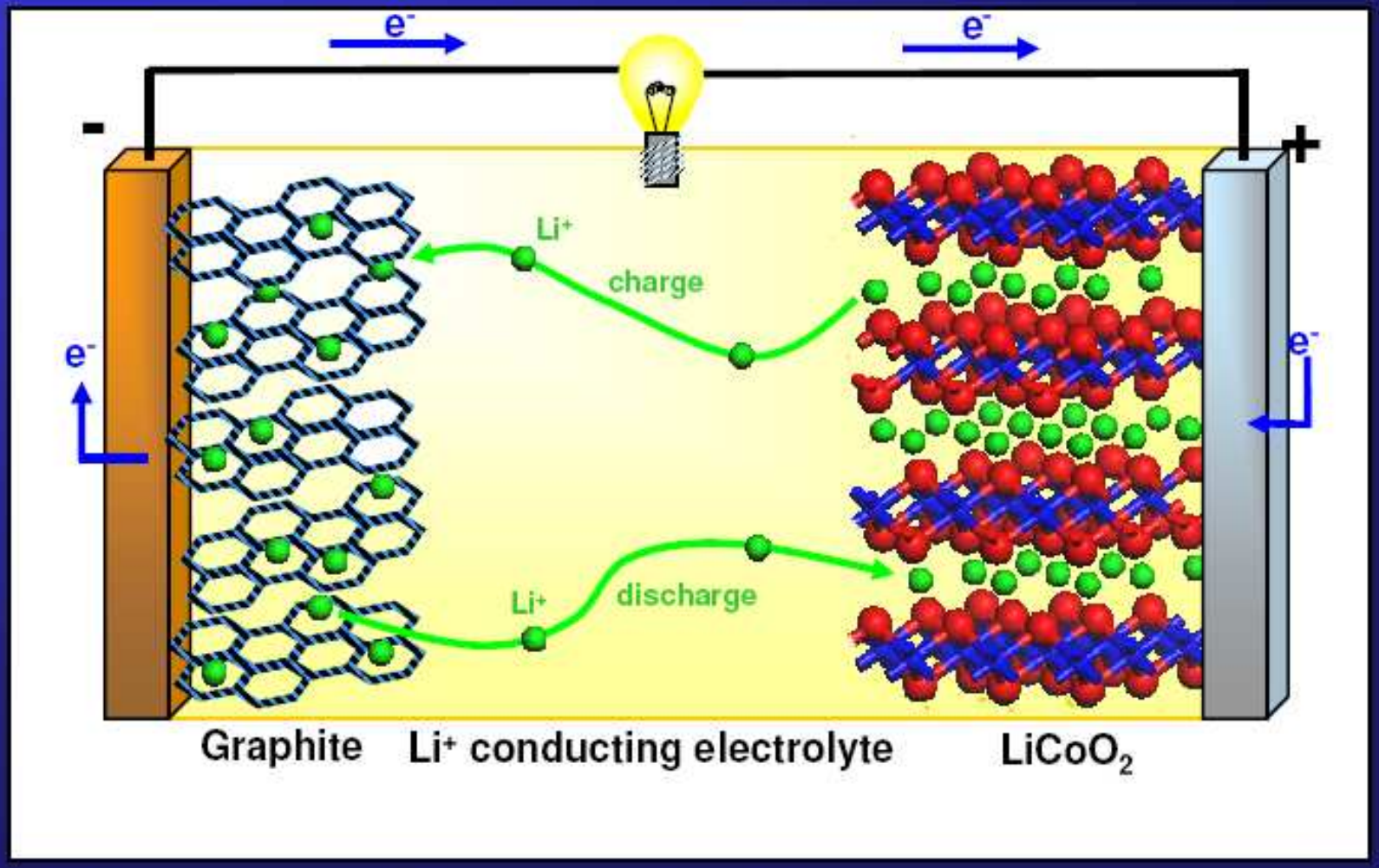
$$EMF = \frac{t_i RT}{nF} \ln \frac{P_1}{P_2}$$

Limitations:

- ionic transport number must be $t_i \sim 1$ – good signal
- pressure and temperature limits of operation, T > 600°C
- material must be > 97% of theoretical density
- gas leakage
- reference gas composition

Rechargeable Lithium Battery

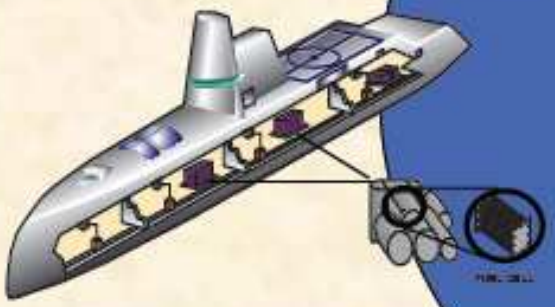
- 2-3× energy density of conventional rechargeable batteries

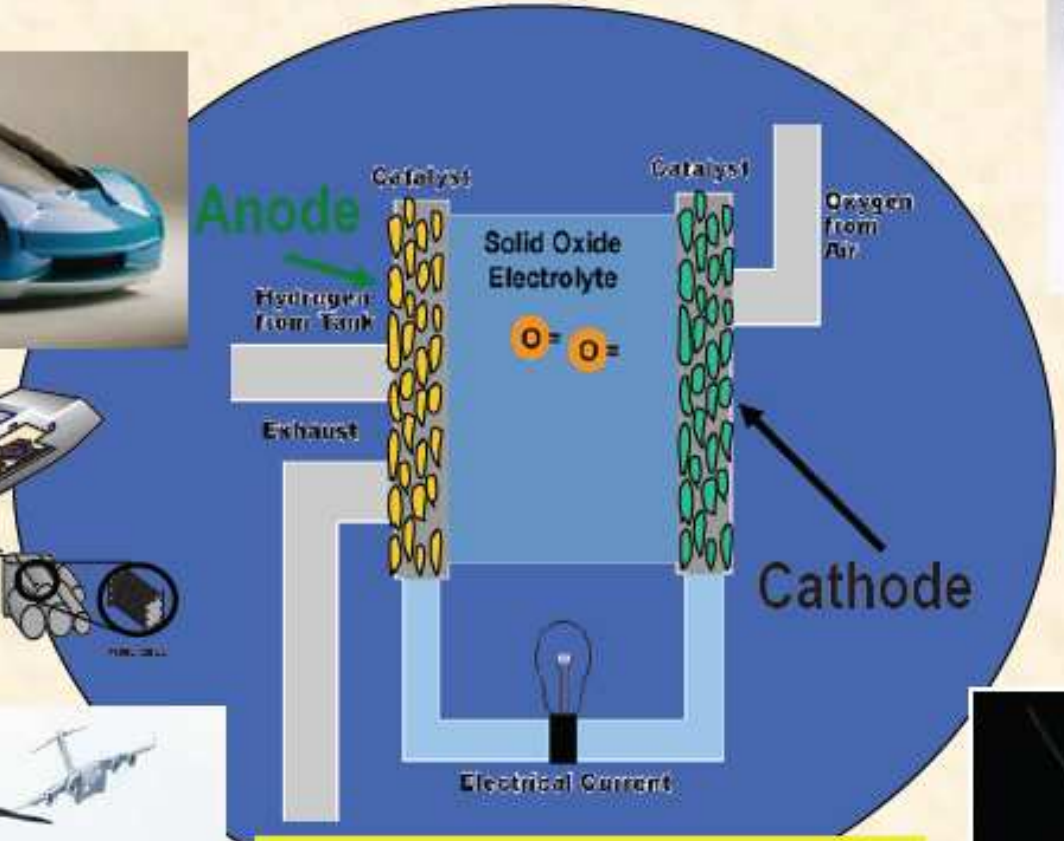


- New generations required for new markets

Higher energy
Higher power
} STEP CHANGE in MATERIALS

SOLID OXIDE FUEL CELLS (SOFC)





Advantages:

- high efficiency, 70 - 80%
- high power density, MW/m^3
- clean power

Problems with existing materials:

- high operation temperature, 900 - 1000°C
- high cost of manufacture

Materials needed:

- electrolyte – $\sigma_i >> \sigma_e$
- anode – $\sigma_i \sim \sigma_e$ at low P_{O2}
- cathode – $\sigma_i \sim \sigma_e$ at high P_{O2}

First Paper on Fuel Cell by W. R. Grove - 1838

.P568

MASS. INSTITUTE OF TECHNOLOGY
JUL 10 1891

THE

LONDON AND EDINBURGH

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

CONDUCTED BY

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RICHARD PHILLIPS, F.R.S. L. & E. F.G.S. &c.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Monit. Polit.* lib. i. cap. 1.

VOL. XIII.

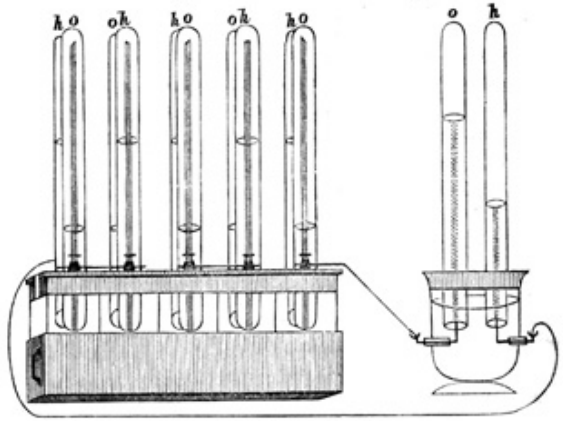
NEW AND UNITED SERIES OF THE PHILOSOPHICAL MAGAZINE, ANNALS OF PHILOSOPHY, AND JOURNAL OF SCIENCE.

JULY—DECEMBER, 1838.

LONDON:

PRINTED BY R. AND J. E. TAYLOR, RED LION COURT, FLEET STREET:
SOLD BY LONGMAN, ORME, BROWN, GREEN, AND LONGMANS; CADELL; BALDWIN AND CRADOCK; SHERWOOD, GILBERT, AND PIPER; SIMPKIN AND MARSHALL; WHITTAKER AND CO.; AND S. HIGHLEY, LONDON: — BY ADAM AND CHARLES BLACK, AND THOMAS CLARK, EDINBURGH; SMITH AND SON, GLASGOW; HODGES AND SMITH, DUBLIN: AND G. W. M. REYNOLDS, PARIS.

Fig. 6. Fig. 7.



LVI. *On a new Voltaic Combination.* *By* W. R. Grove, *Esq., M.A.*

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

On first hearing of porous porcelain being employed as a diaphragm for preventing the mutual precipitation of the metals on each other in voltaic combinations, it struck me that one of the plates of metals usually employed might be dispensed with by precipitation upon the other from a metallic solution. After some unsuccessful trials, I constructed a trough as following: a piece of common stout millboard of the length required, and of breadth sufficient to form the bottom and sides, is separated lengthwise into three parallel divisions by cuts one-third through; it is then covered with a thin layer of cement and bent up into the form of a trough; four-inch squares of common sheet iron and unglazed porcelain plates of the same dimensions are then warmed and slid alternately into the trough, as in Cruickshank's form, at about three tenths inch distance *. A solution of sulphate of copper and dilute acid being poured into the alternate cells, a very active series is formed by the precipitation of the copper on one surface of the iron; that which I formed was of twenty plates: the shock, without coils or condenser of any description, was so powerful as to be scarcely tolerable. When a wire was scraped along the edge of the plate at one extremity, the other hand touching the opposite end, the decomposition of water was also rapid, though I have not yet accurately measured its powers: its action continued unabated for nearly three hours without the addition of any acid or sulphate. If greater constancy be required, the alternate cells can be filled up with coarsely powdered sulphate, and some added as required. I was fearful that upon a second trial the intensity would have much abated, in consequence of the oxidated surface of the plates preventing so uniform a deposition of the precipitate, but was gratified to find that, after having been suffered to dry and remain at rest for several days, its action was as intense and constant as upon the first trial. The advantage of this form, where series and sustained power are required, I consider to be its extreme œconomy, a single cheap metal being employed instead of two expensive ones; the greater durability of iron as compared with zinc; the cutting in squares, so that none is wasted; and the tiresome process of soldering being altogether dispensed with. The diaphragms and solutions are common to every form of constant battery: possibly very thin plates of deal might do as well as porcelain; the durability of the latter material, however, makes its expense unimportant. My object in this communication is not so much to vaunt this particular form of battery as to direct increased attention to the porous filter as likely to form an important element in the analysis of the voltaic trough: it may possibly throw some light upon the organization of the torpedo.

Hoping you will consider this letter of sufficient importance to merit insertion in the Philosophical Magazine,

I remain, Gentlemen, yours, &c.

Swansea, Oct. 26, 1838. W. R. Grove.

* Pasteboard is preferable to wood for the formation of these troughs: it has not strength sufficient by its warping to crack the cement, is much more easily constructed, and a better insulator; it should be thinly coated with varnish on the outside to prevent capillary absorption by accidentally touching liquids. The plates of porous ware here mentioned may be conveniently employed for rendering constant the common Cruickshank trough, being warmed sufficiently to melt the cement and slid into the cells.

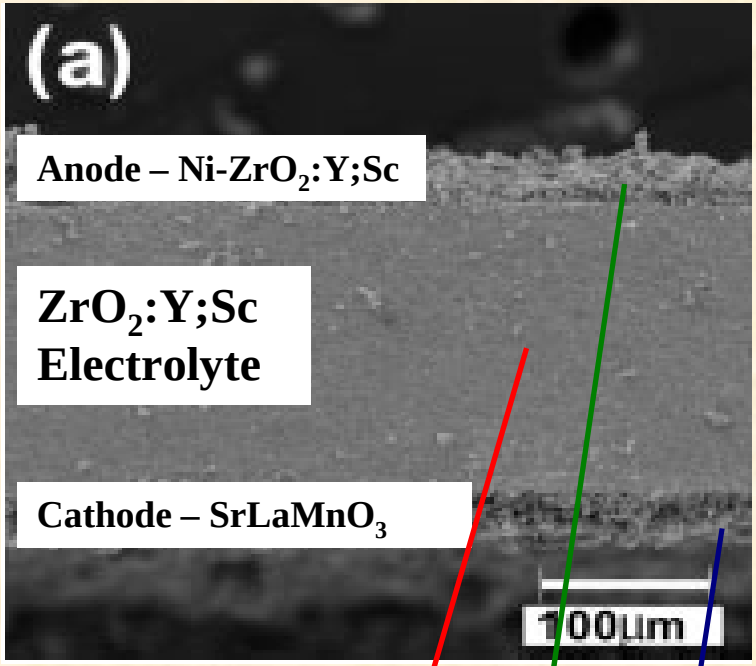
LVII. *On the Reduction of the Chlorides of Mercury when mixed with Organic Substances.* *By* John B. Nevins, Esq.

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

A short time since Mr. West, Lecturer on Chemistry at the Medical School in this town, mentioned to me the fact, that if a mixture of Hg Cl with some vegetable substances be heated, metallic Hg is sublimed; and recommended that the circumstances upon which this depended should be ex-

Electrical Resistance of Solid Oxide Fuel Cells



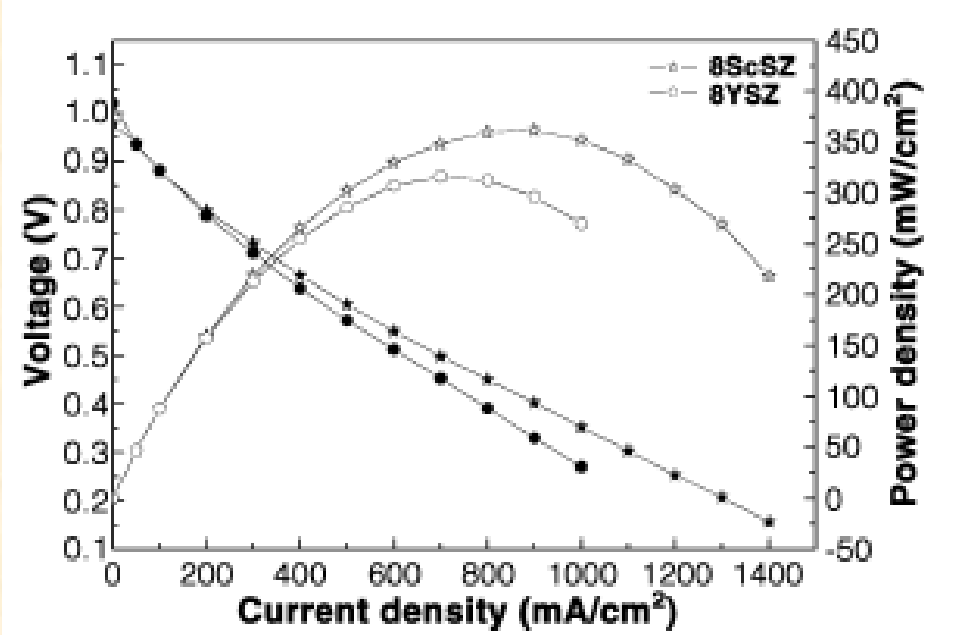


Fig. 8. Performance of a single cell with 8YSZ or 8ScSZ electrolyte at 750 °C.

$$V = EMF - IR - \eta_A - \eta_C$$

$$U = E - IR_{\text{int}}$$

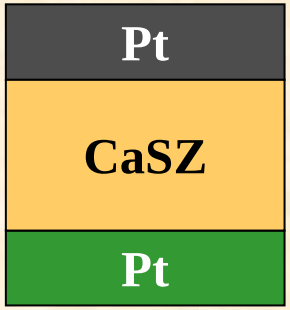
$$P = IE - I^2 R_{\text{int}}$$

$$P_{\max} = \frac{E^2}{4 \cdot R_{\text{int}}}$$

Reducing the electrolyte resistance, the electrode polarization effects have to be considered and minimized

Solid Progress in SOFC Performance

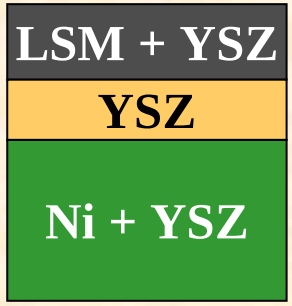
Bulk Materials Technology 1962 - 1995



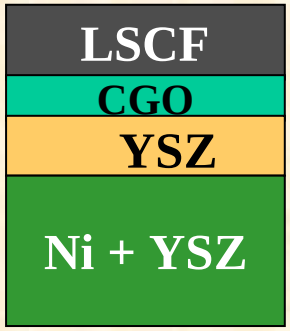
P = 36mW/cm²

1962

Thin Film Technology – 1995 => present

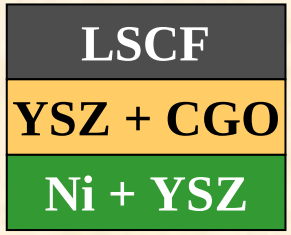


P = 700mW/cm²



P = 2000mW/cm²

2002



Next challenge: advanced materials design based on interface engineering

Nanotechnology

1000°C 850°C 700°C < 600°C

Operation Temperature

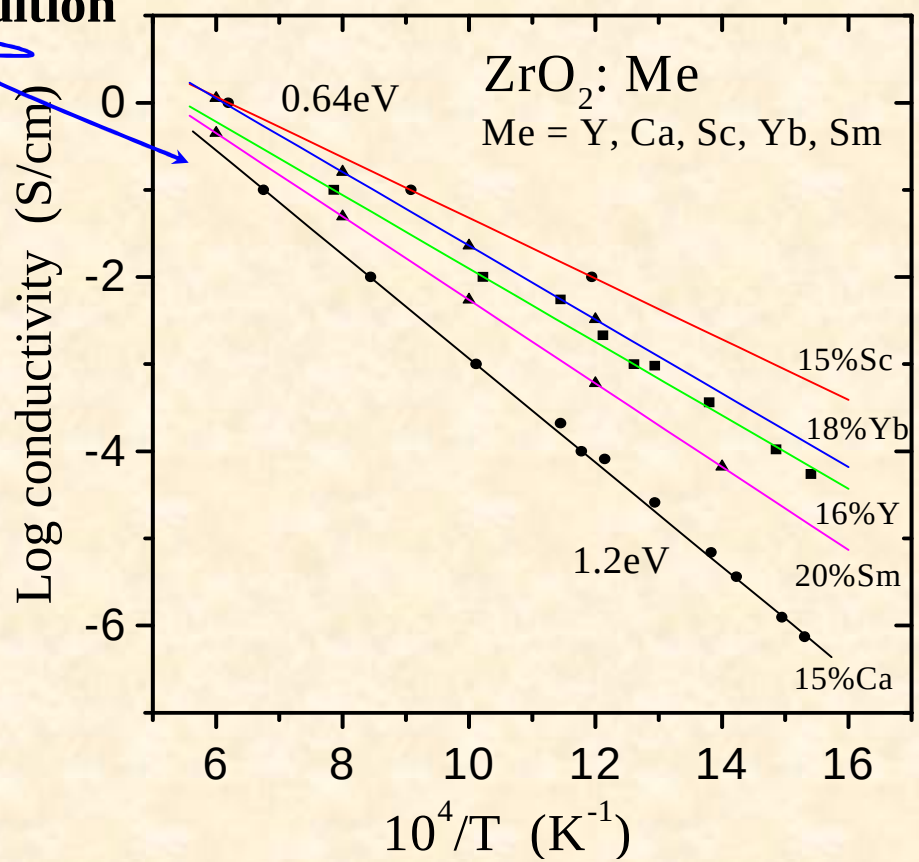
LSM = $LaSrMnO_3$; CaSZ = $Ca:ZrO_2$; YSZ = $Y:ZrO_2$; CGO = $Gd:CeO_2$; LSCF = $LaSrCoFeO_3$

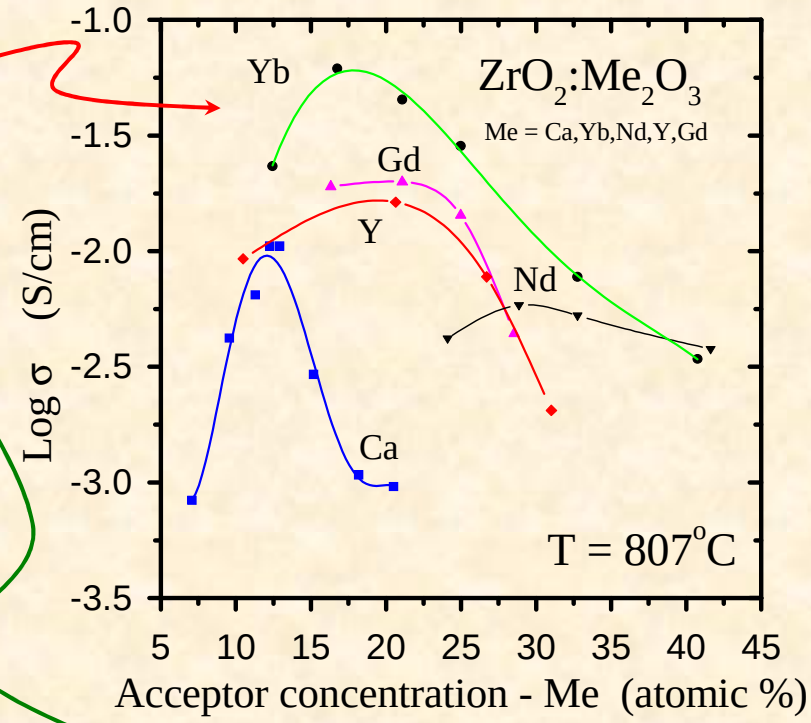
To enhance the SOFC performance at reduced temperatures we need

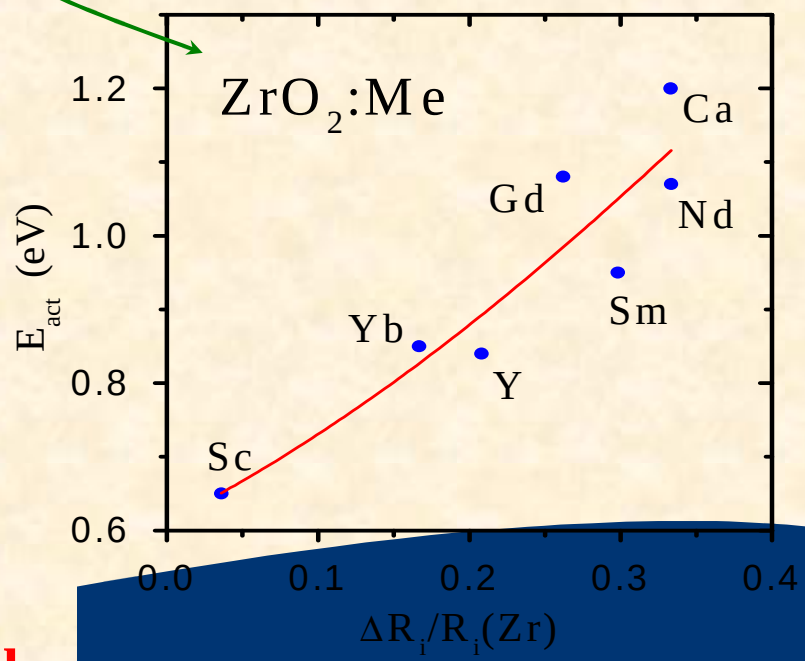
- **reduce the cell internal resistance**
- **develop the catalytic electrodes**

Conventional materials have reached a limit !!!

- ionic conductivity reaches maximum for dopants levels [A'] ~14 - 20% =>[A'] = 2 [$V_o^{\cdot\cdot}$]
- the activation energy, E_{act} decreases as acceptor ion radius approaches to Zr^{4+}
- highest conductivity observed with Sc addition







New materials with enhanced ionic conductivity and catalytic activity are needed

Ionic conductivity in conventional solid electrolytes limited by lattice diffusion

$$\sigma = 2 \cdot e \cdot \left[V_o^{\cdot\cdot}\right] \cdot \mu_{Vo}$$

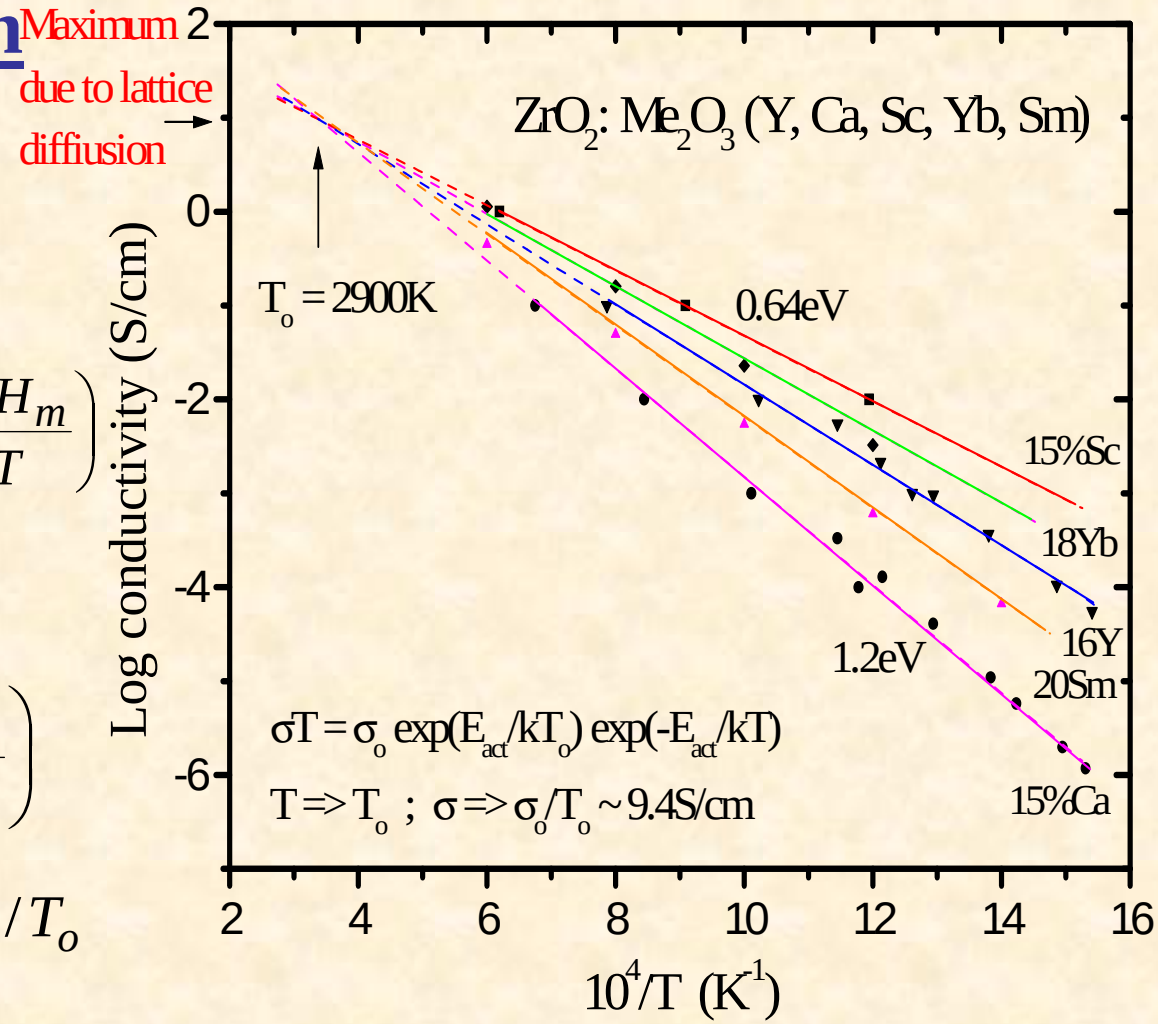
ion mobility in hopping model:

$$\mu_{Vo} = \frac{a \cdot e \cdot \nu \cdot r^2}{kT} \cdot \exp\left(\frac{\Delta S_m}{k}\right) \cdot \exp\left(\frac{-\Delta H_m}{kT}\right)$$

extrinsic region: $[V_o^{\cdot\cdot}] = 1/2[A'_{eff}]$

$$\sigma T = \sigma_o \cdot \exp\left(\frac{E_{act}}{kT_o}\right) \cdot \exp\left(\frac{-E_{act}}{kT}\right)$$

$$T \Rightarrow T_o \quad ; \quad \sigma_{\max} \Rightarrow \sigma_o / T_o$$



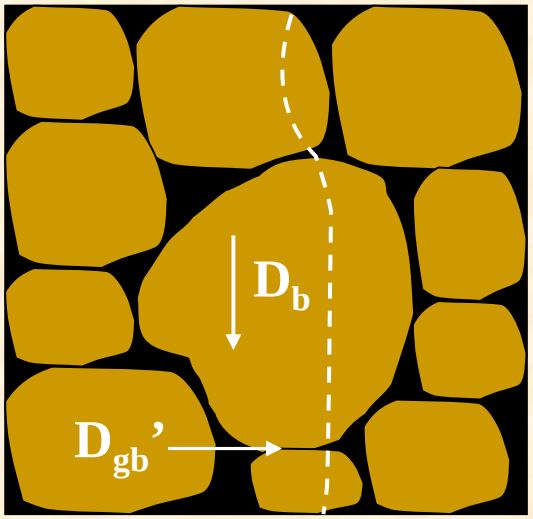
In conventional ceramics:

- ionic conductivity in solids is limited by low ion mobilities – Faraday, 1833

- maximum possible value of the ionic conductivity is ca. 10 S/cm at melting point

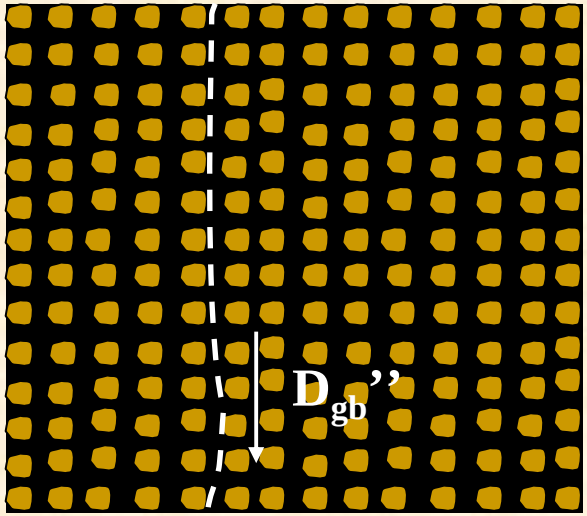
What is the solution? - change the diffusion mechanism to increase the ionic mobility - Nanoscale Materials

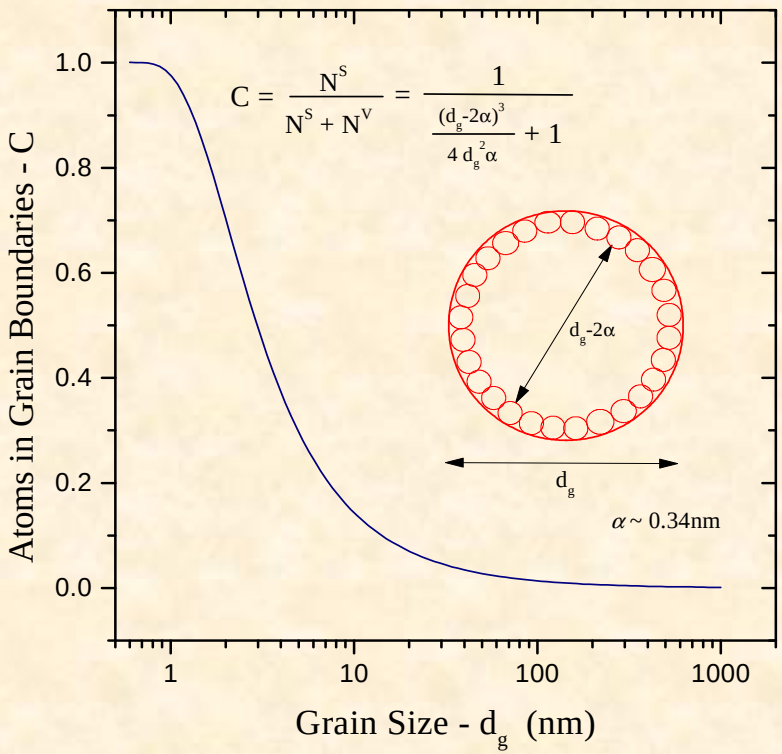
What is unique about nanocrystalline materials?



Conventional - material
0.1% gb fracture

Nano-material
10% gb fracture at
20nm grain size





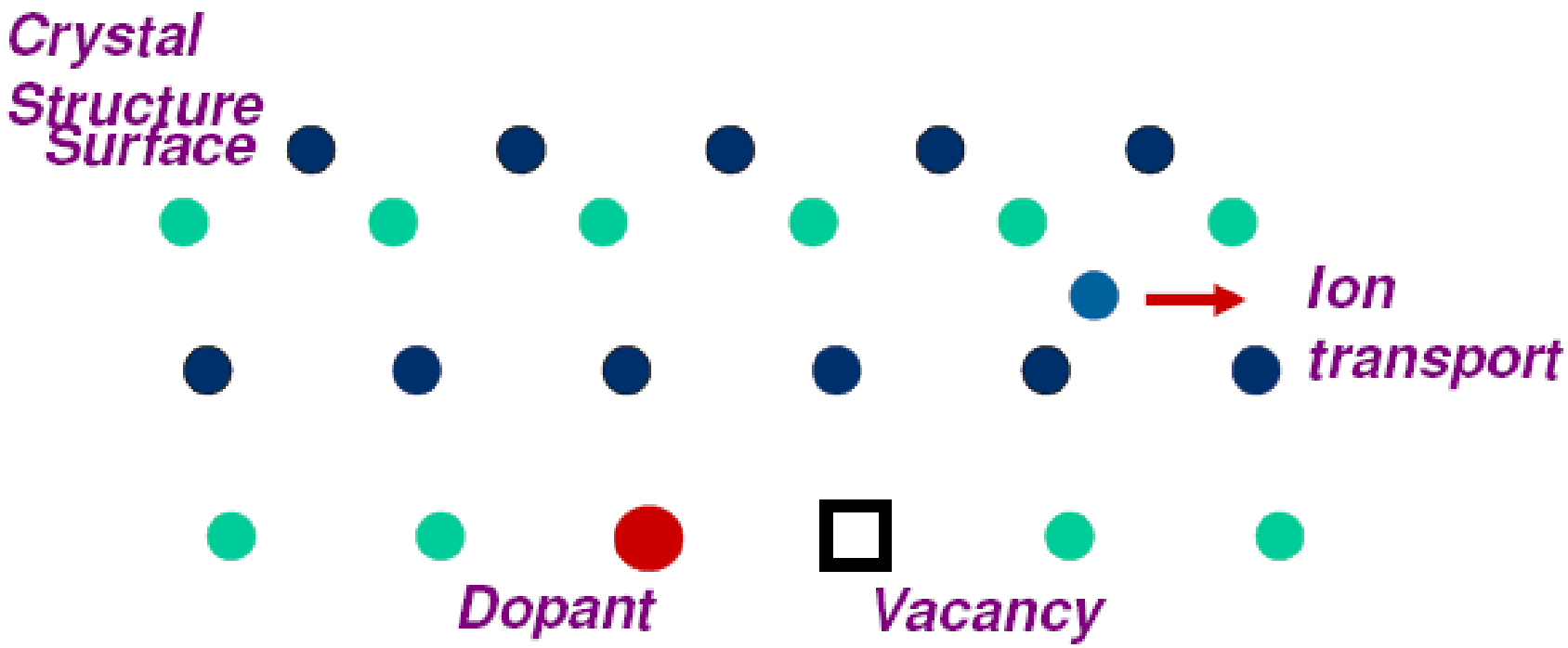
* large number of grain boundaries ~ 10^{19}cm^{-3}
* large ratio of particles in interfacial to volume area ca. 30-60%
* grain boundary impurity segregation
* space charge effects
* surface dependent defect thermodynamics

ADVANTAGES:

* D_{gb}'' >> D_b => hence higher conductivity
* faster reaction kinetics due to extended surface area

Materials Issues

- Structure-property→ electrochemistry
- Basic science: underpins applied work



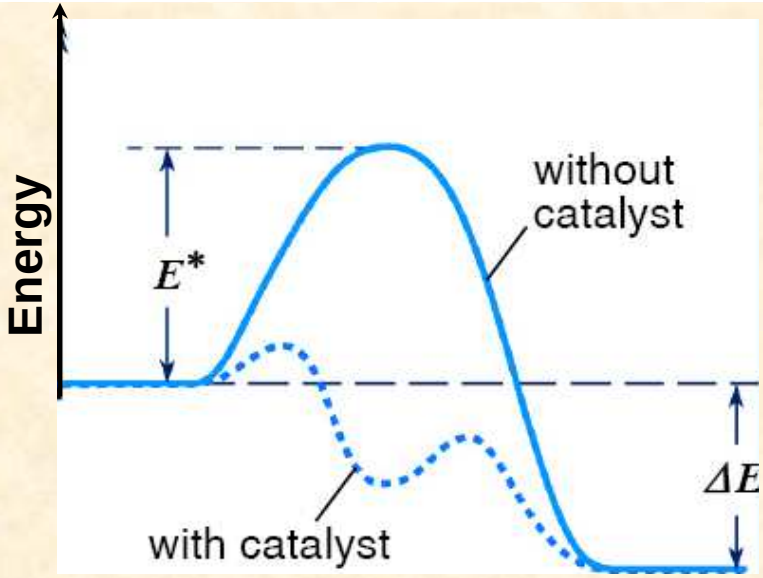
surface has a different structure than bulk due to "broken"chemical bounding between ions

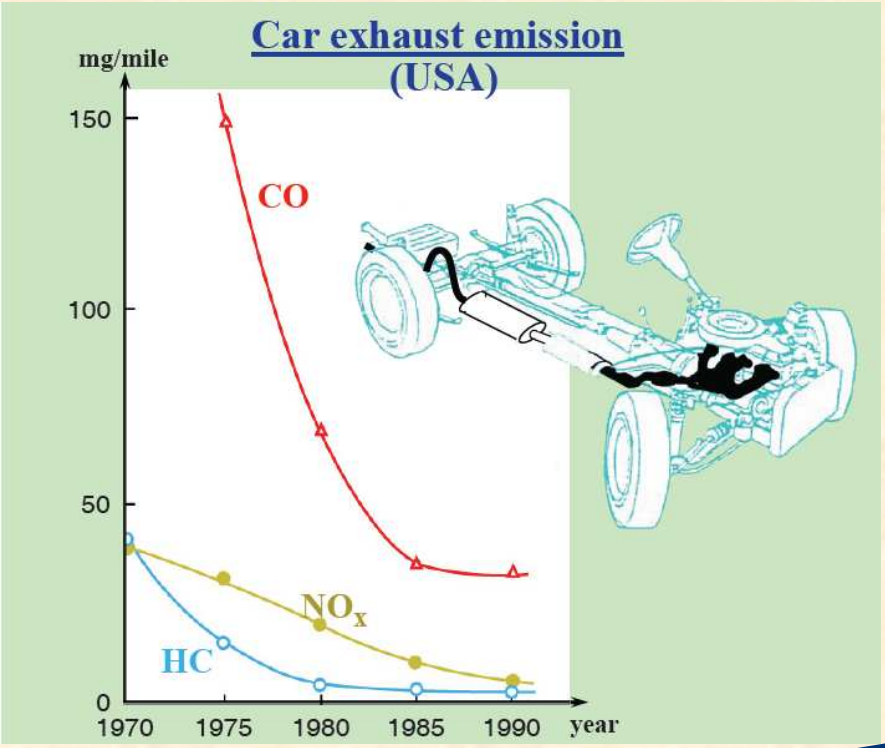
The Nobel Prize in Chemistry 2007

"for his studies of chemical processes on solid surfaces"

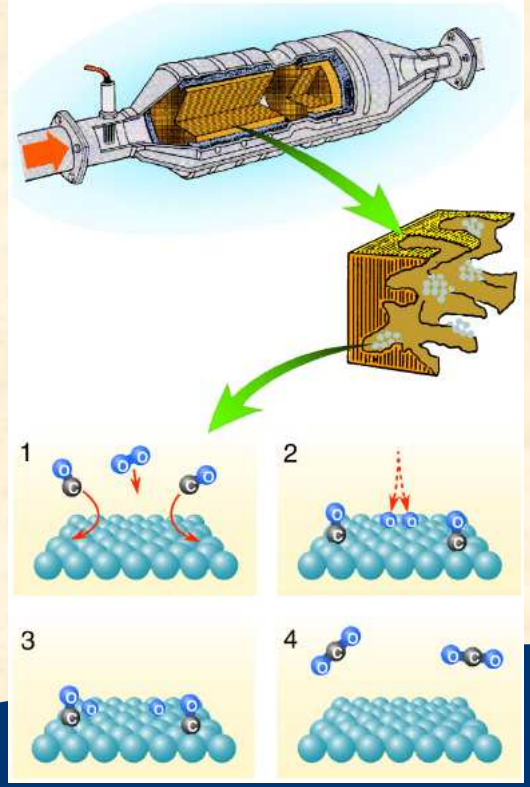
Gerhard Ertl; b.1936

Fritz-Haber-Institut der Max-Planck-Gesellschaft
Berlin, Germany





Catalytic oxidation of CO



Objectives:

- The research has focused on nanocrystalline YSZ, ScSZ, CeO_2 and Sm:CeO_2 films and CeO_2:Sm/CeO_2 heterostructures

- Preparation of thin films with controlled grain size, texture and thickness

- The unique role of length scale on the electrical properties of ion conducting oxides – grain size or film thickness

  * effect of grain size on electrical transport and lattice dynamics
  * effect of film thickness and texture on the electrical conductivity
  * transition from lattice - to interface-controlled conductivity

- Can be separated interfacial related conductivity?

- What is the interface thickness?

- Exceptional potential of nanocrystalline ceramics for developing advanced electrochemical devices – fuel cells, gas sensors and ionic membranes what is the limit of ionic conductivity in solids?

Polymeric precursor spin coating process

Zirconium Dichloride Oxide
Cerium Nitrate
Yttrium Nitrate

↓

Gravimetric Analysis

↓

Homogeneous Solution
Add Ethylene Glycol

↓

Viscous precursor
Stirring at 80°C

↓

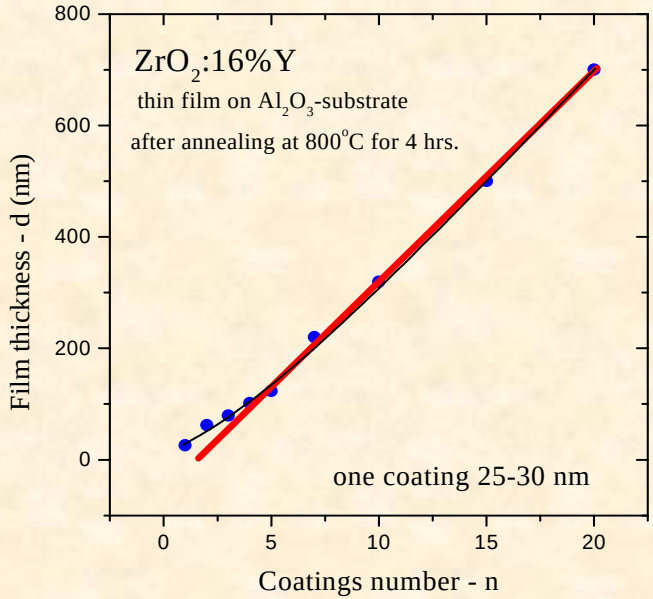
Deposit on Substrate
Spin Coating

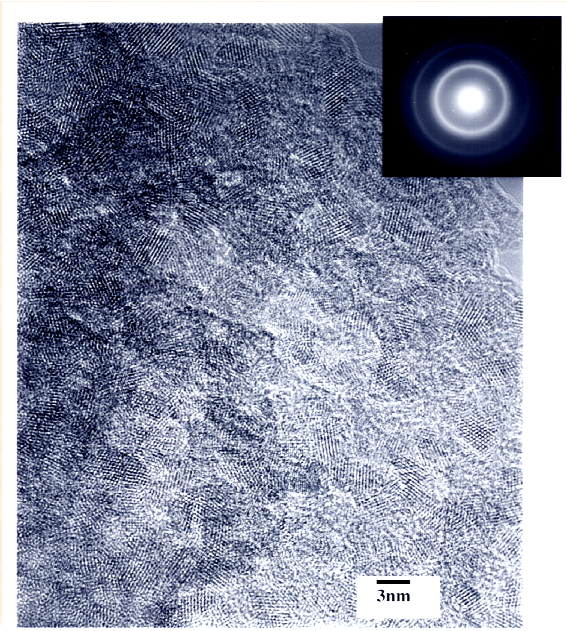
↓

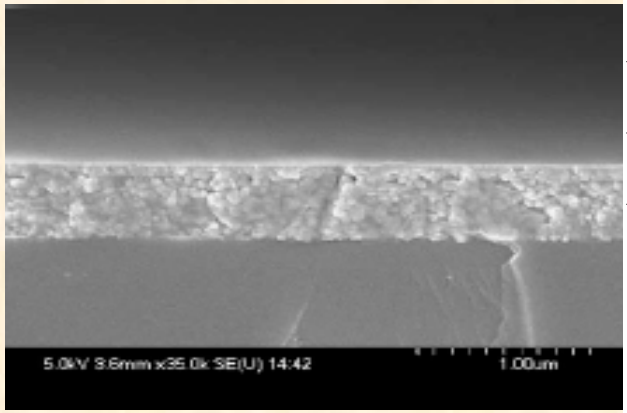
Drying at 320°C

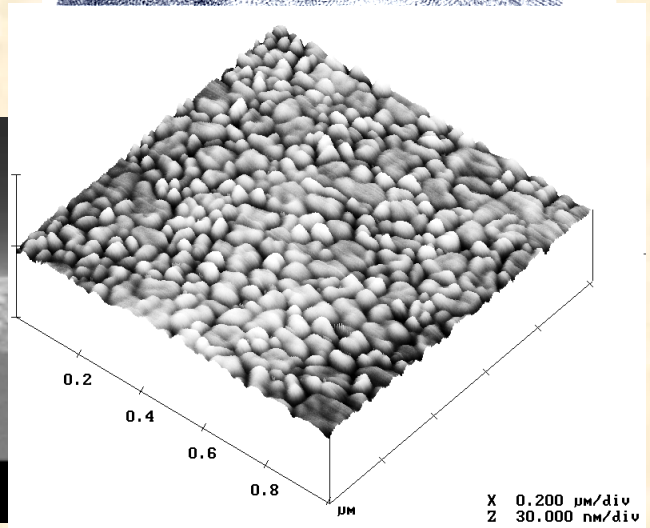
↓

Final annealing at 400-1200°C









- **low processing temperature, 300 - 1000°C**
- **control the grain size, 2 - 400nm**
- **dense, cracks free material**
- **good thickness control 20 - 30nm/deposition**

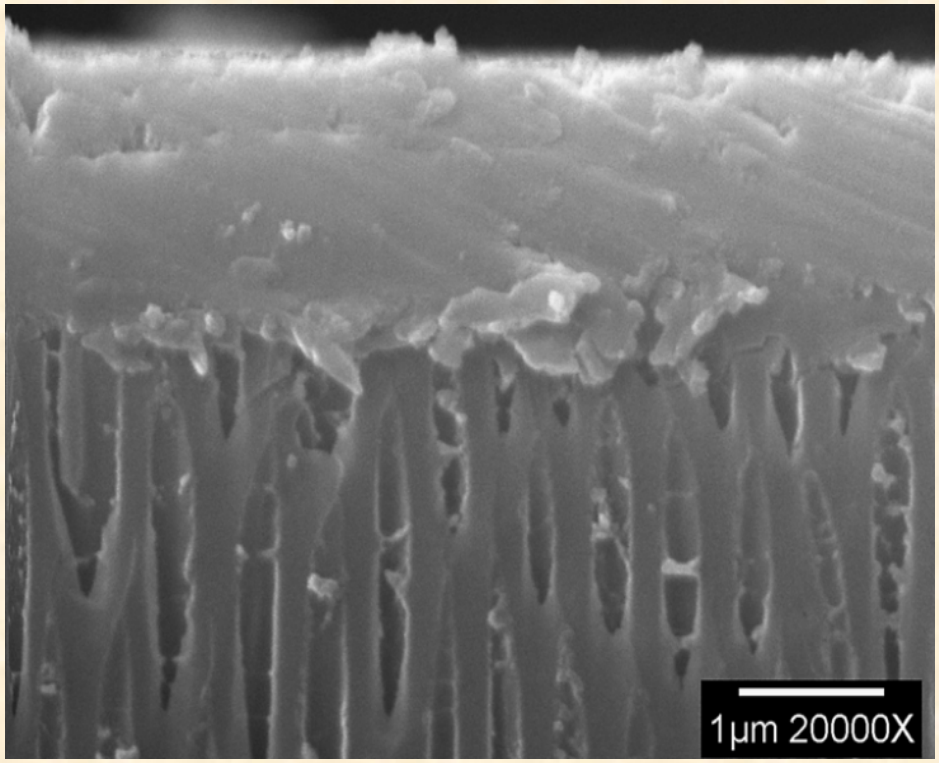
I.Kosacki and H.U.Anderson,
Encyclopedia of Materials 2001, 4, p.3609

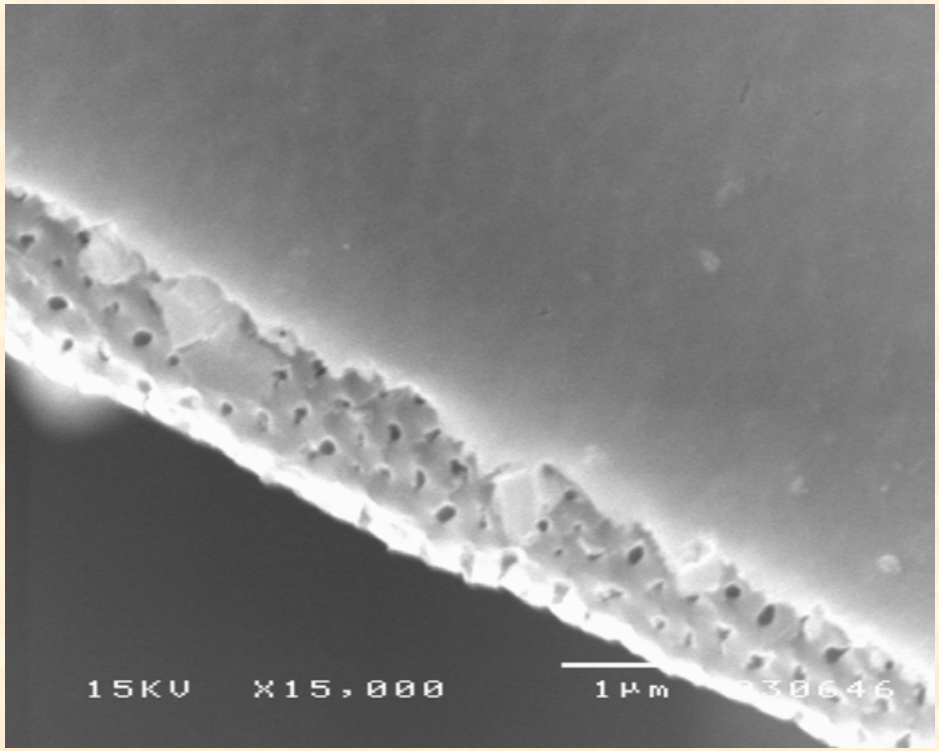
Pioneer work of spin coating technique, bring life to science

The cake obtained by spin coating technique

- Unique ability to fabricate specimens on cylindrical substrate
- Can we do this for ion conducting thin films??

$SrCeO_3$:5%Yb thin film on porous Al_2O_3 substrate obtained from polymeric precursor



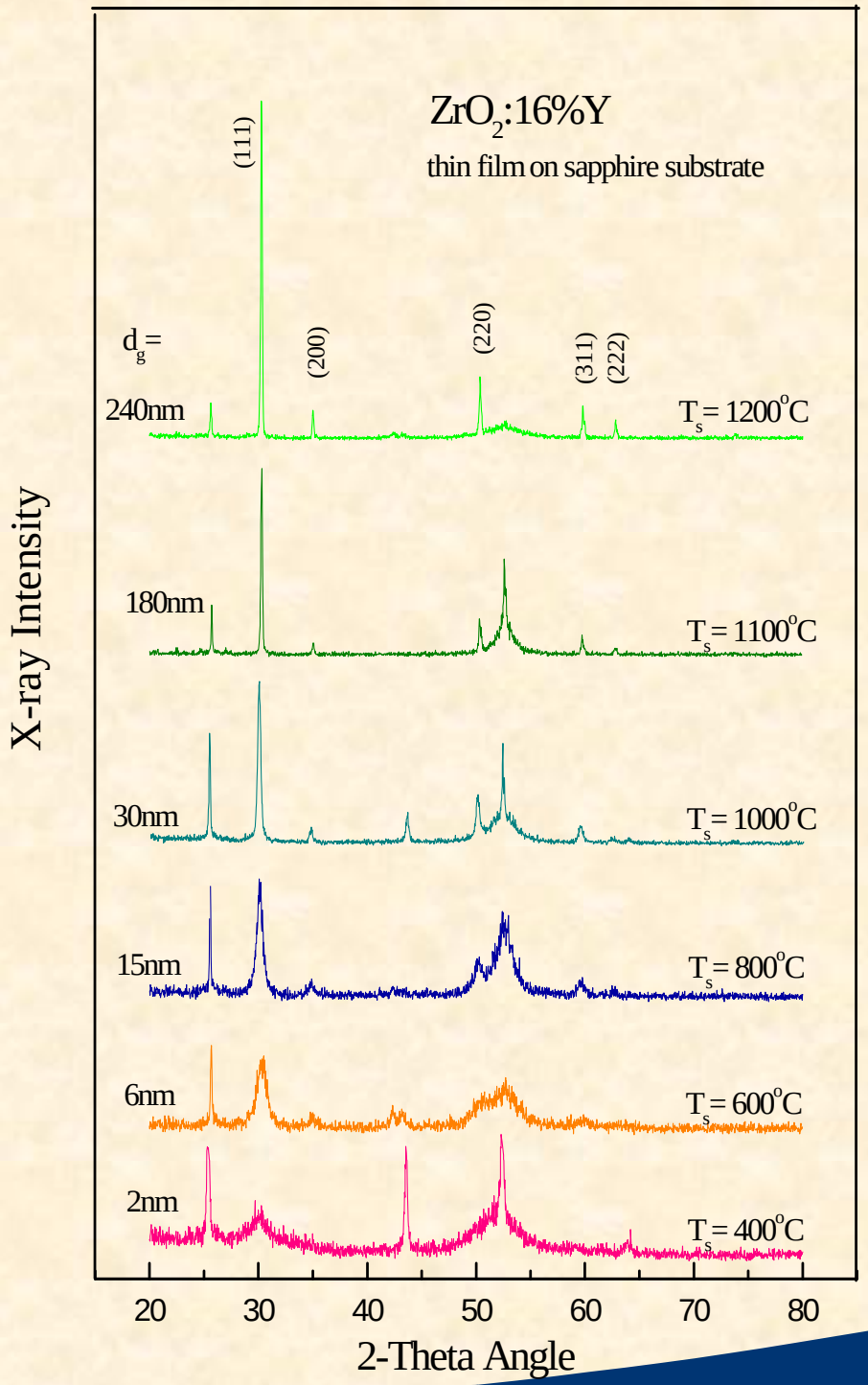


SEM images of cross-section and top view of thin film

Unique opportunity for ionic membranes and electrode-supported thin films technology

X-ray study of YSZ thin films

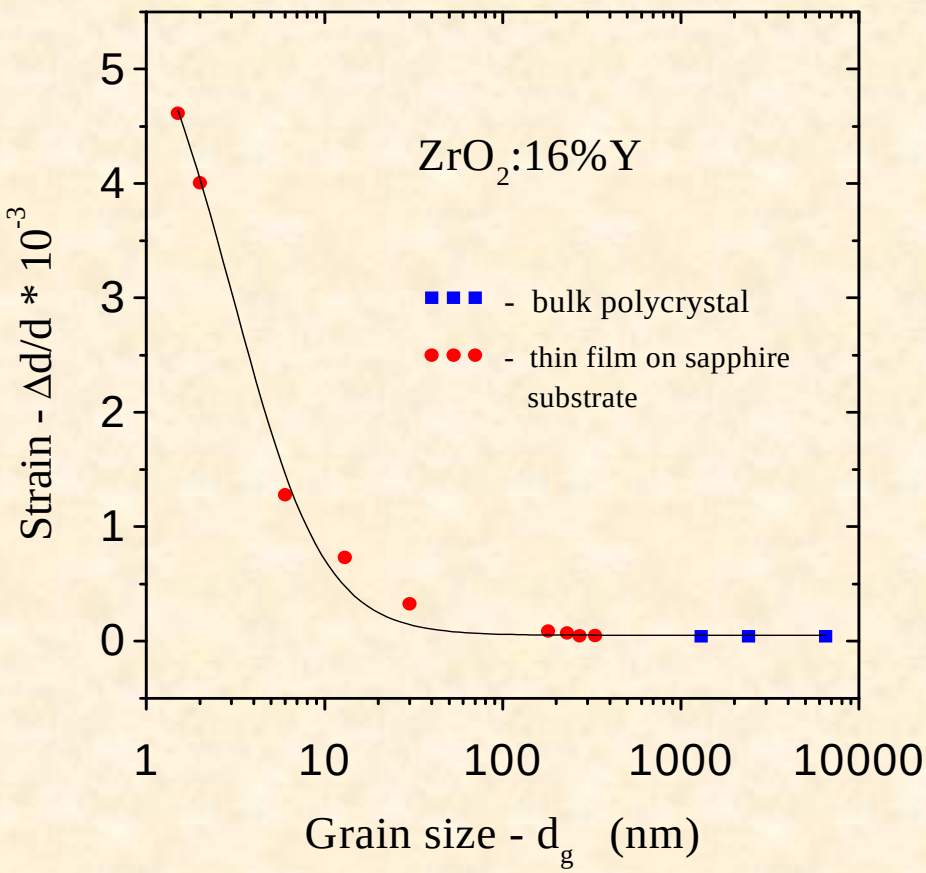
I.Kosacki at al.
Appl. Phys. Letters 74 (1999) 341-343



$$\beta = \beta' + \beta''$$

$$\beta' = 1/d_g \cos\theta \quad ; \quad \beta'' = 4\,\varepsilon\, \mathrm{tg}\theta$$

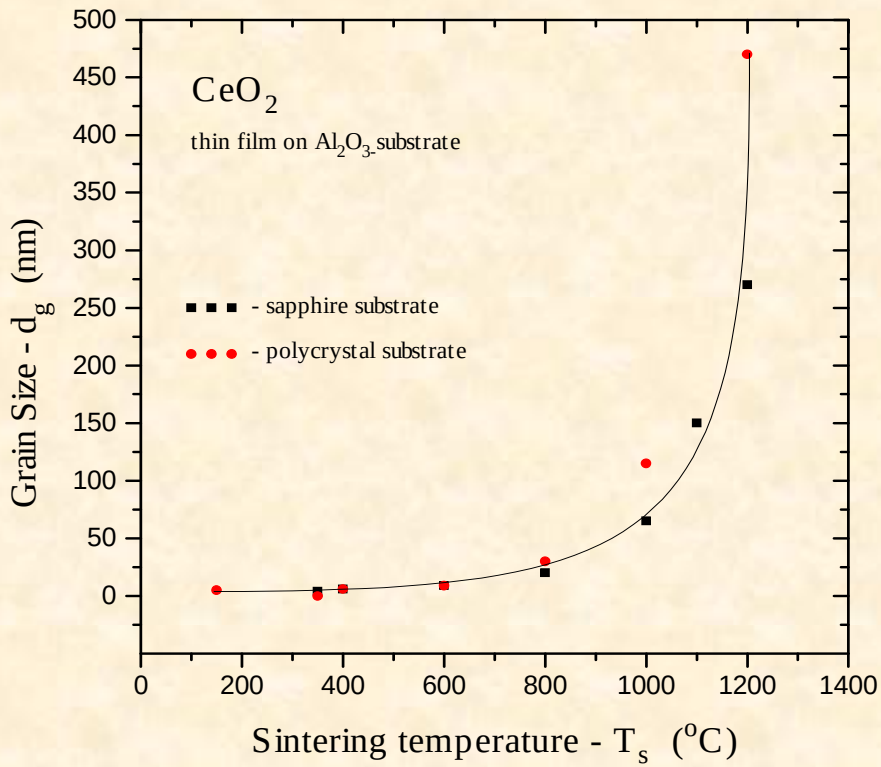
X-ray line broadening can be described as a effect of strain (ε) and grain size (d_g)

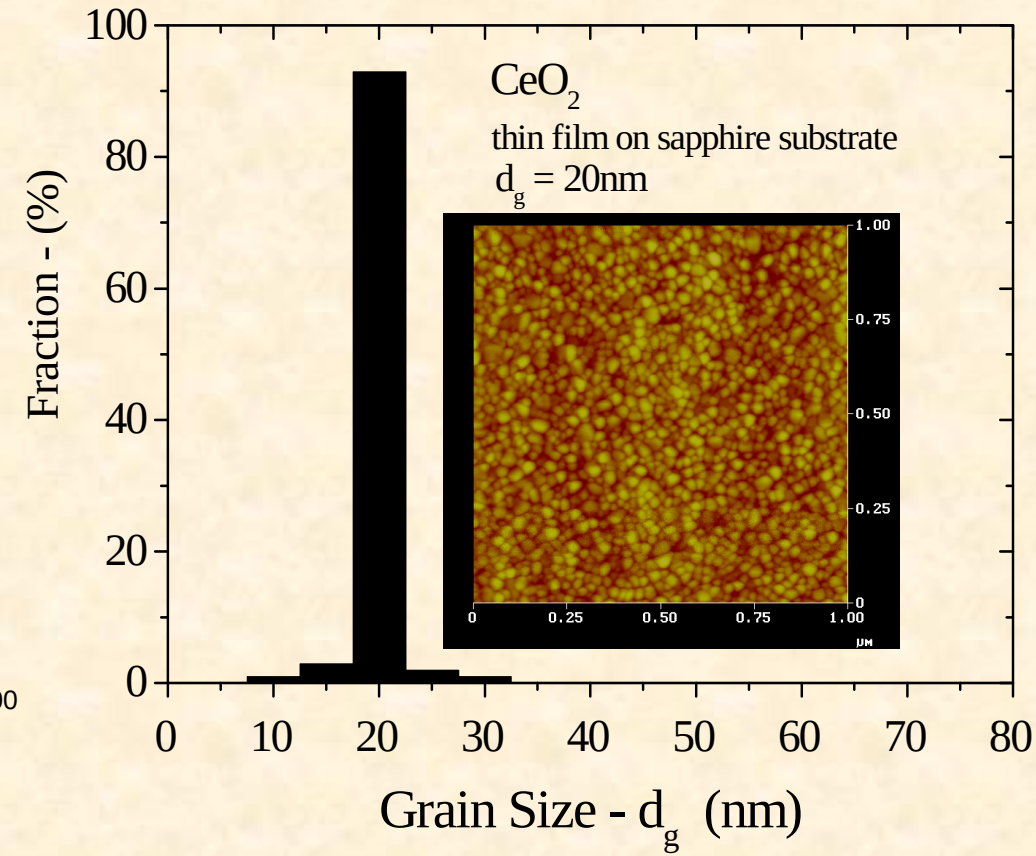


G.E.Rush, A.V.Chadwick, I.Kosacki and H.U.Anderson
J.Phys.Chem. B 104 (2000) 9597 - 9606

Processing is the key to controlling nanocrystalline materials

Polymeric precursor spin coating ideal method for obtaining nanocrystalline and multilayer films with desired compositions.

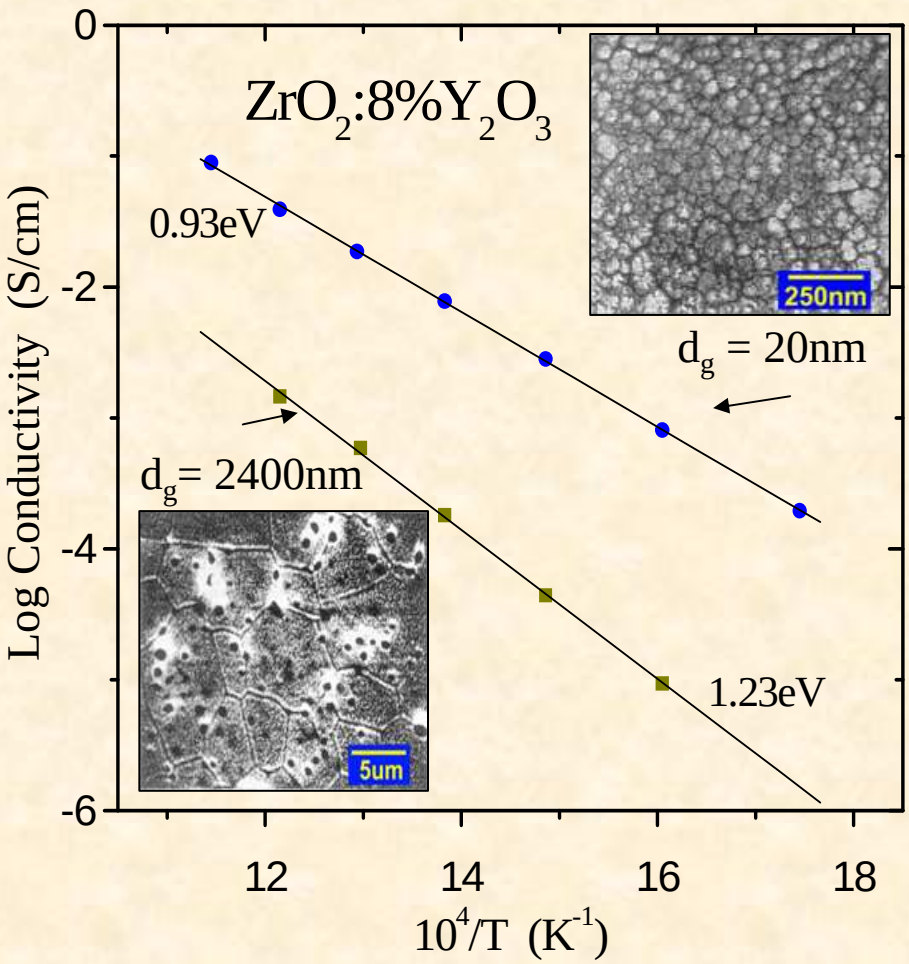


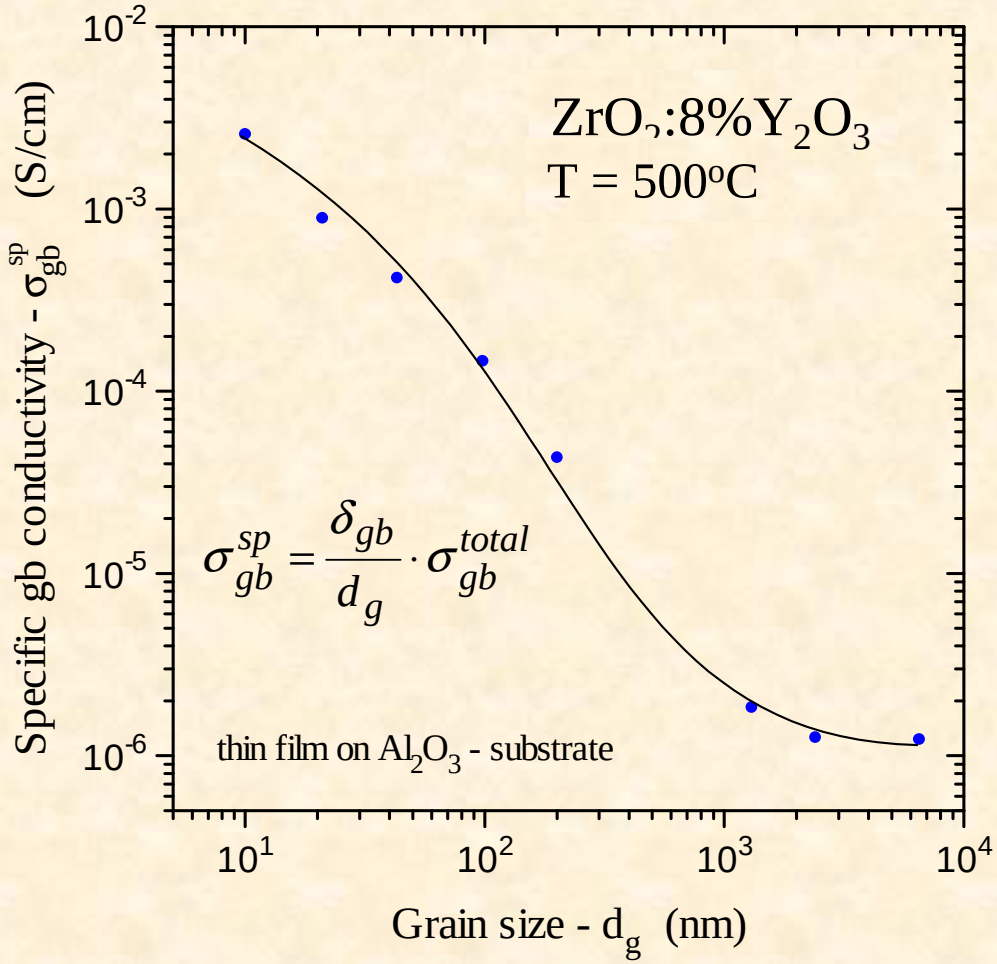


- exceptional control of the grain size
- very narrow grain size distribution
- dense, cracks free material

T.Suzuki, I.Kosacki and H.U.Anderson
Solid State Ionics 151 (2002) 111-121

Nanocrystalline oxides offer tremendous potential



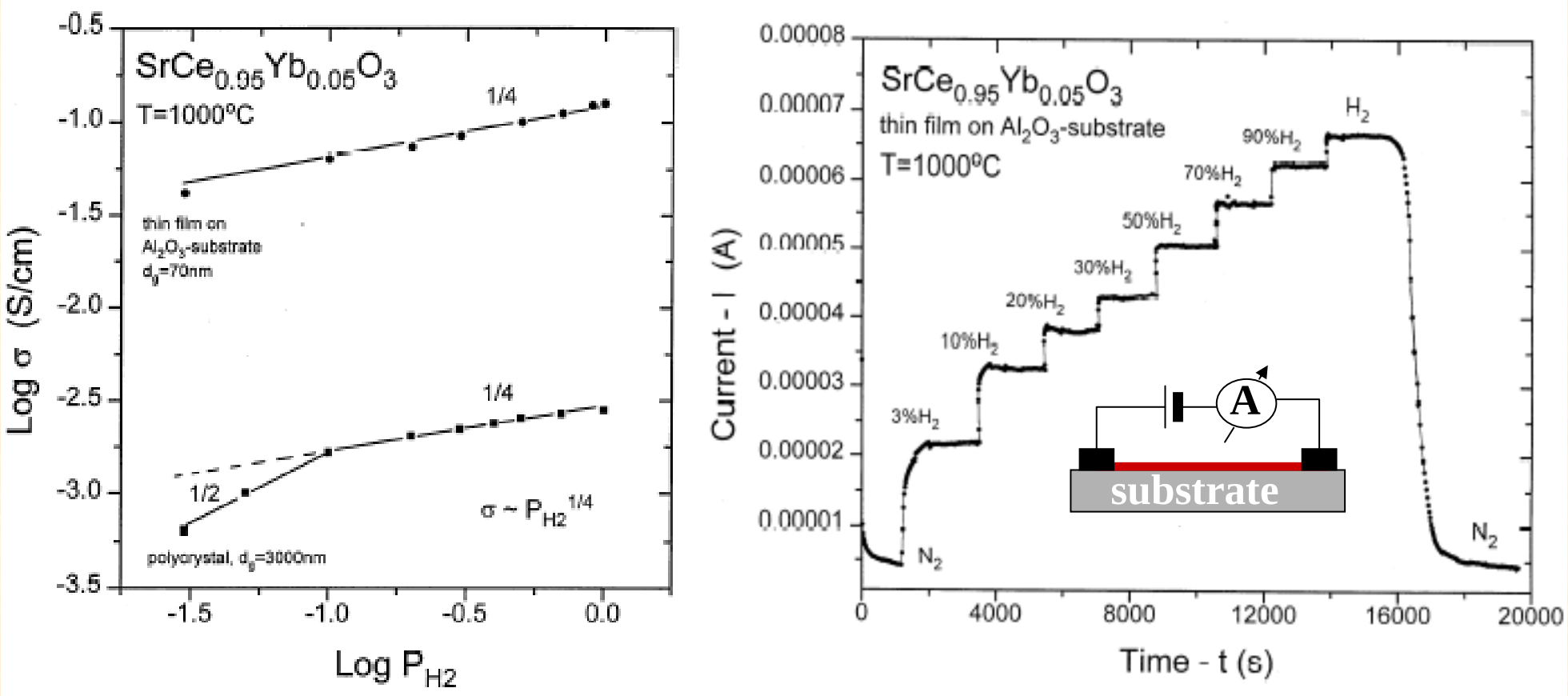


$$\sigma_{gb}^{sp} = \frac{\delta_{gb}}{d_g} \cdot \sigma_{gb}^{total}$$

I.Kosacki and H.U.Anderson in Encyclopedia of Materials 2001, 4, p.3609

- **10^2 enhancement in electrical conductivity observed**
- **this effect is attributed to grain boundary controlled electrical transport**

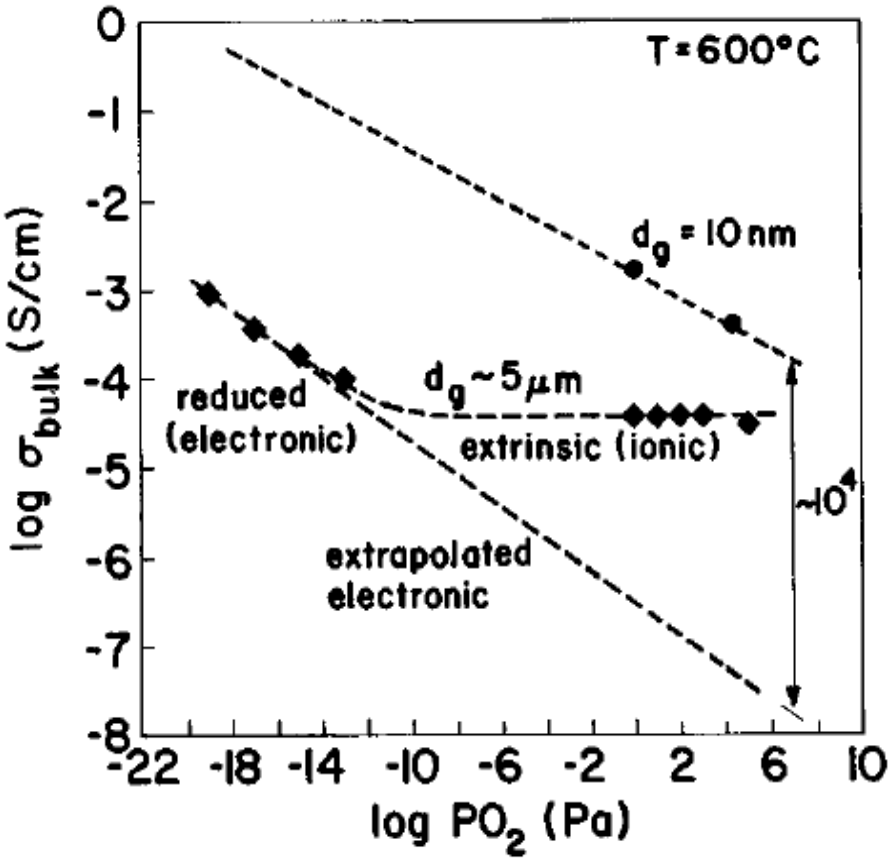
NANO-CRYSTALLINE CERAMICS FOR GAS SENSORS

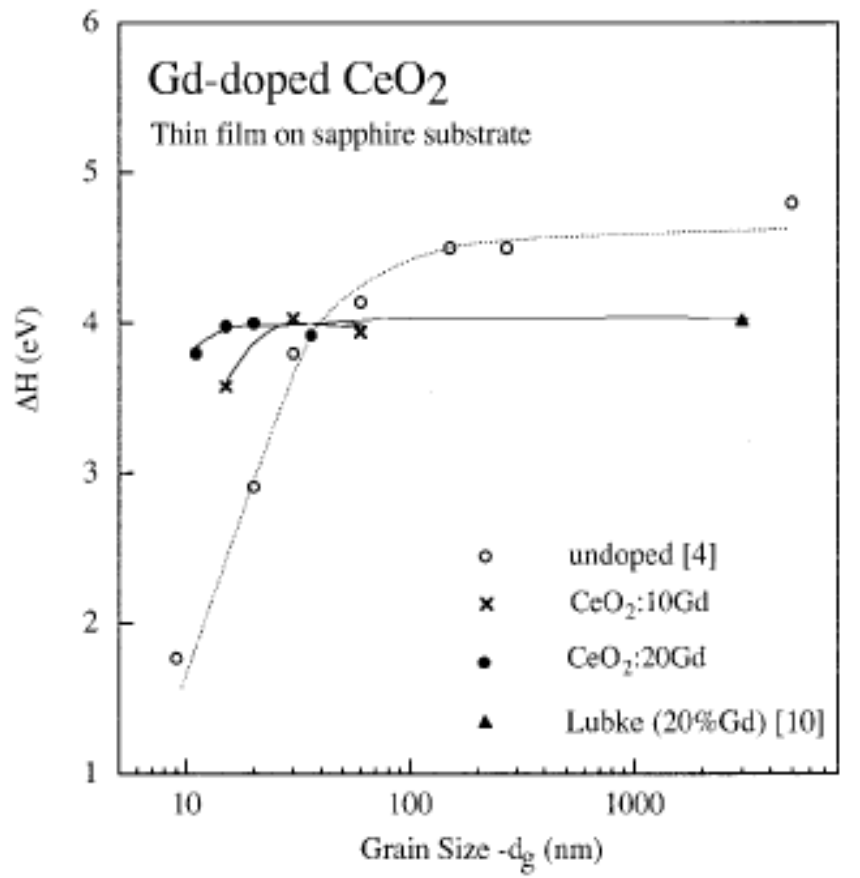


I.Kosacki and H.U.Anderson, Sensors and Actuators, B48 (1998) 263-269

* **enhanced protonic conductivity**
* **rapid response - the kinetics of the electrical conductivity is 10^3 faster than bulk**
* **simpler construction**

Enhanced electronic conductivity in nanocrystalline CeO_2



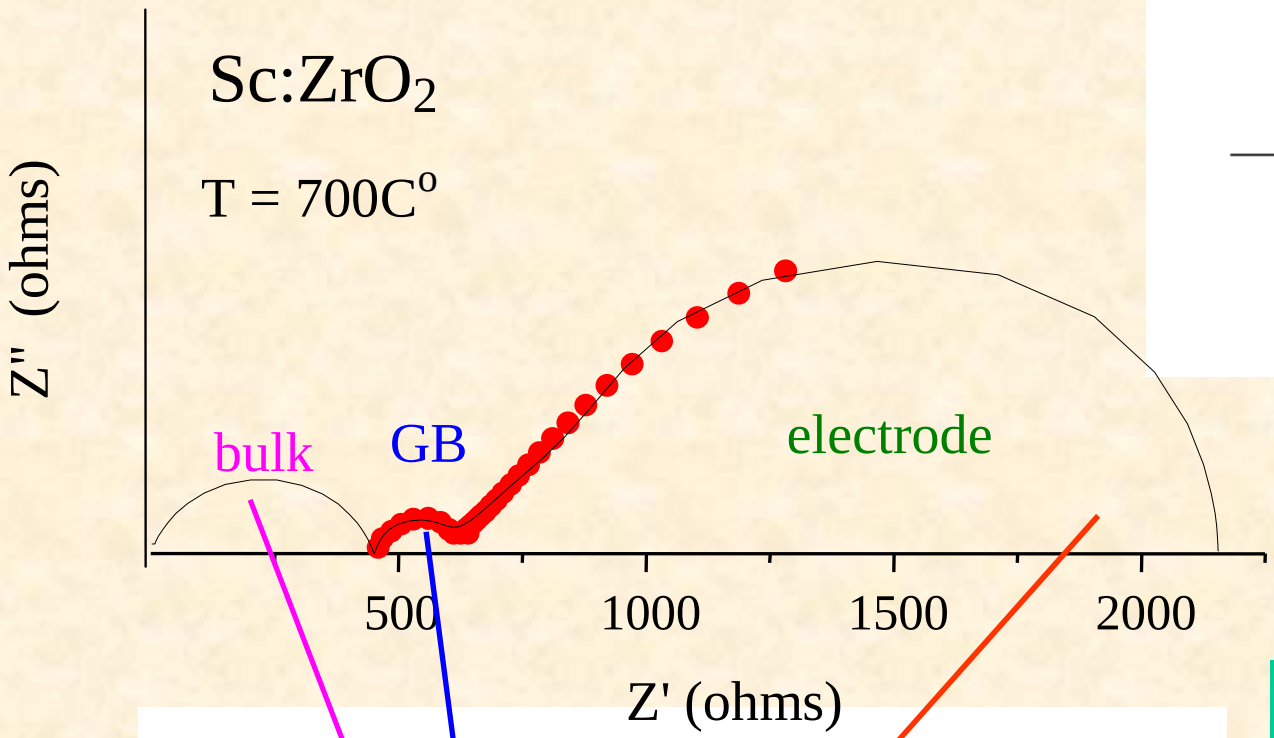


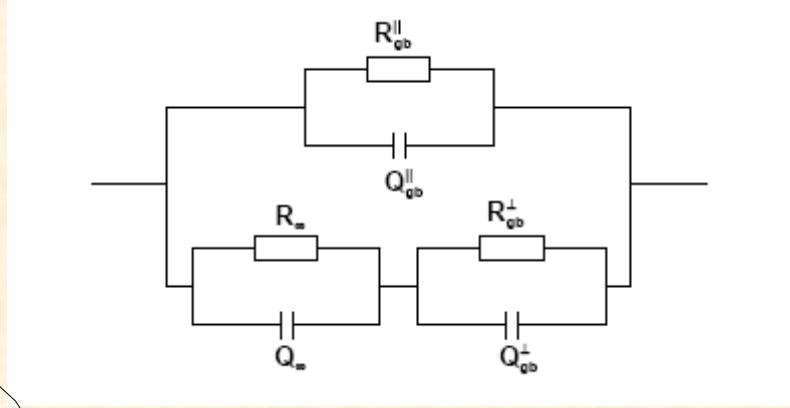
I.Kosacki at al.Appl. Phys. Lett. 69 (1996) 185

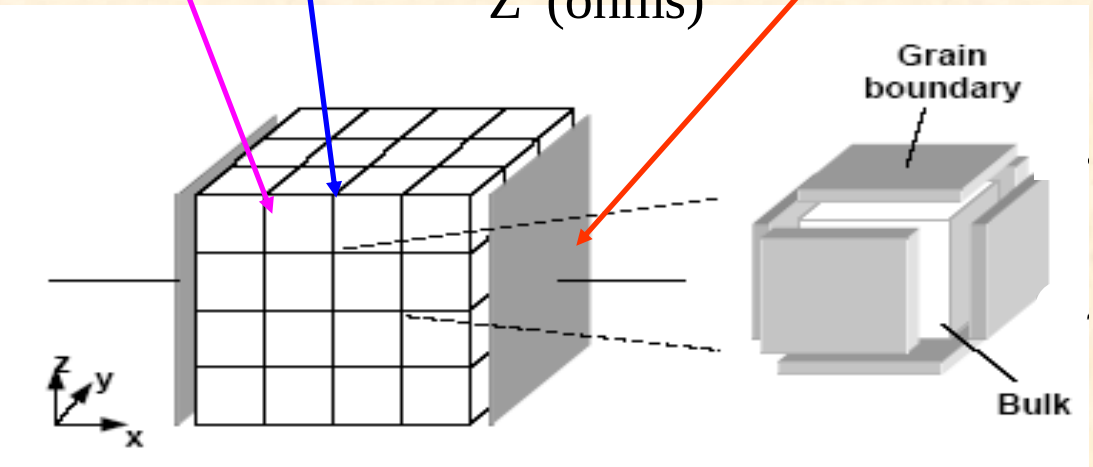
T.Suzuki, I.Kosacki and H.U.Anderson
J. Am. Ceram. Soc. 85 (2002) 1492

- 10^4 enhancement in electronic conductivity observed in nanocrystalline CeO_2
- this effect is related to a decrease in the enthalpy of oxygen vacancy formation

Grain Boundary and Electrical Conductivity in Ceramics

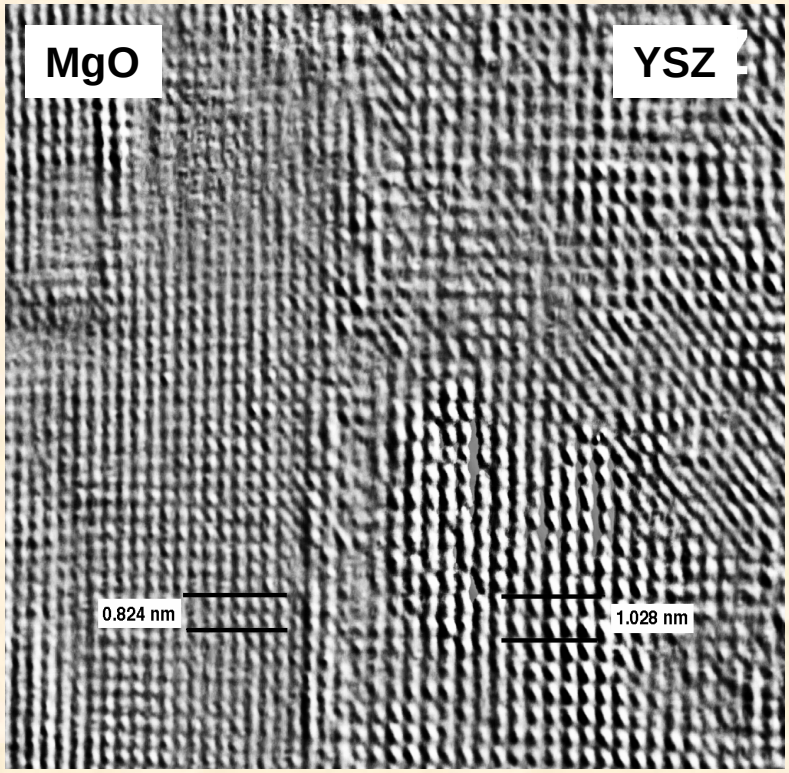


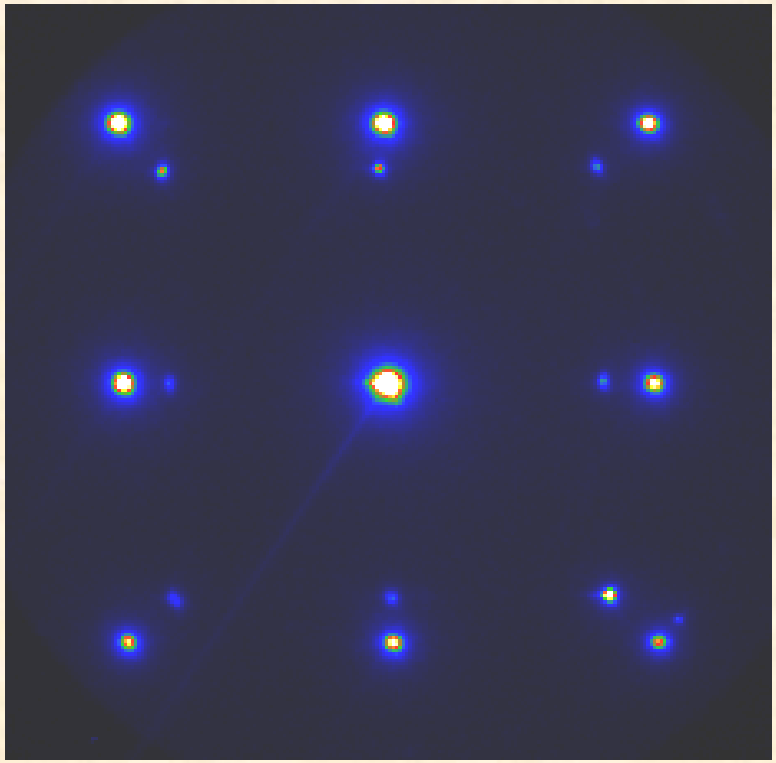




Unblocking gb can play important role in electrical transport in nanoscale ceramics

Exceptional quality of pulsed laser deposited nanometer scale, oriented YSZ films on (001) MgO

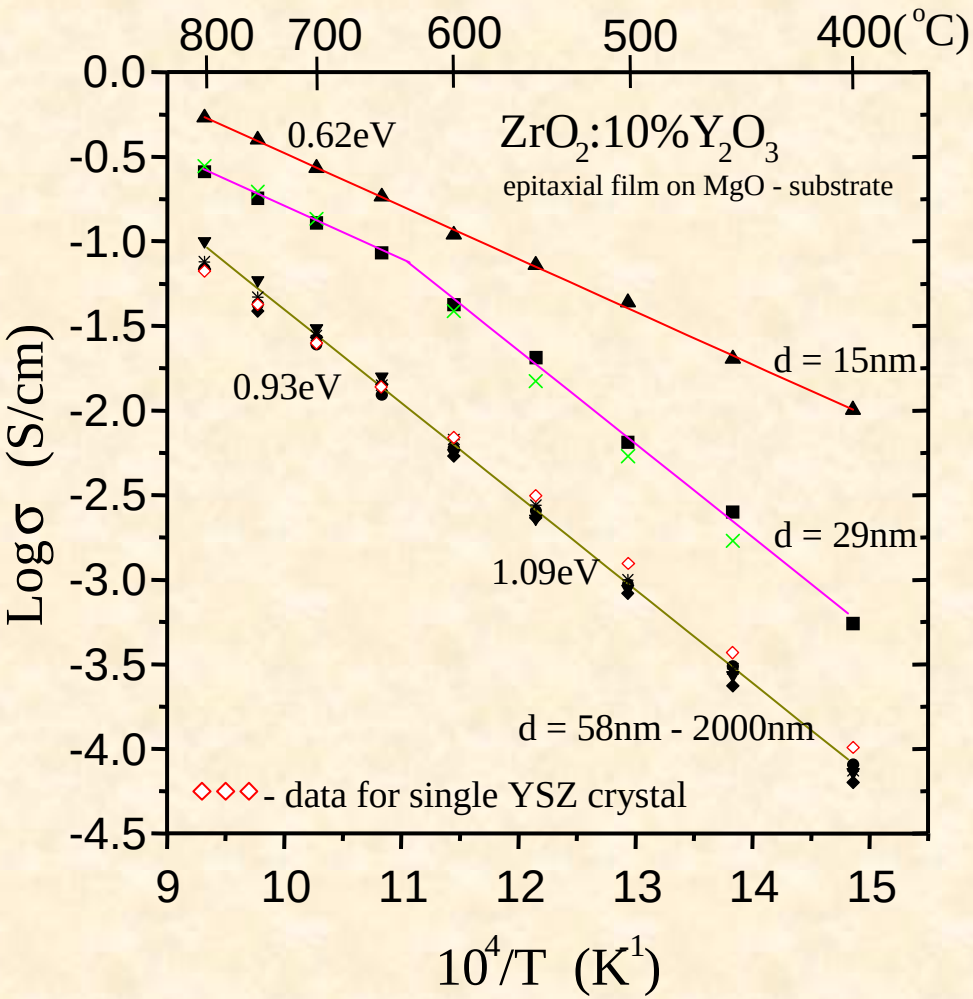


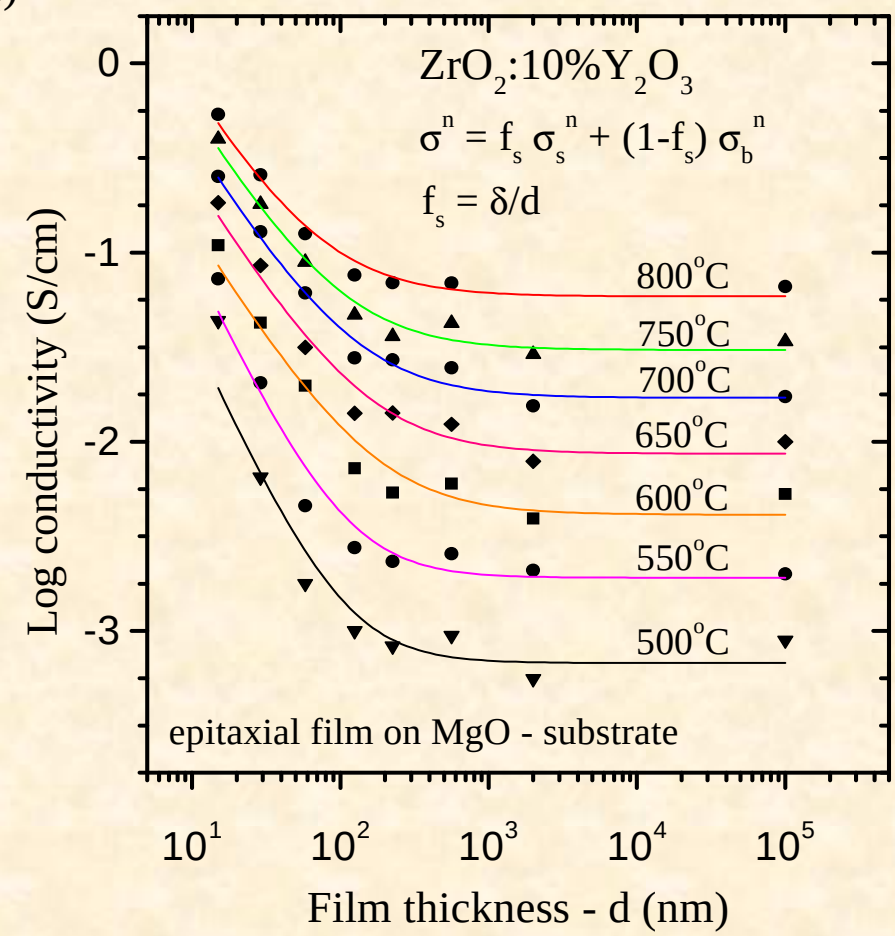


I.Kosacki, C.Rouleu, P.F.Becher and D.Lownes, Electrochem. Solid State Letters 2004, 7, A459 – A461

- cube-on-cube orientation and absence of dislocation arrays
- EDS analysis confirms composition is ZrO_2 – 9.5 mol % Y_2O_3
- lattice imaging reveals YSZ films high degree of crystalline perfection
- YSZ epitaxial film on MgO can be consider as a model of single grain boundary

Superionic conductivity observed in nanoscale YSZ thin films

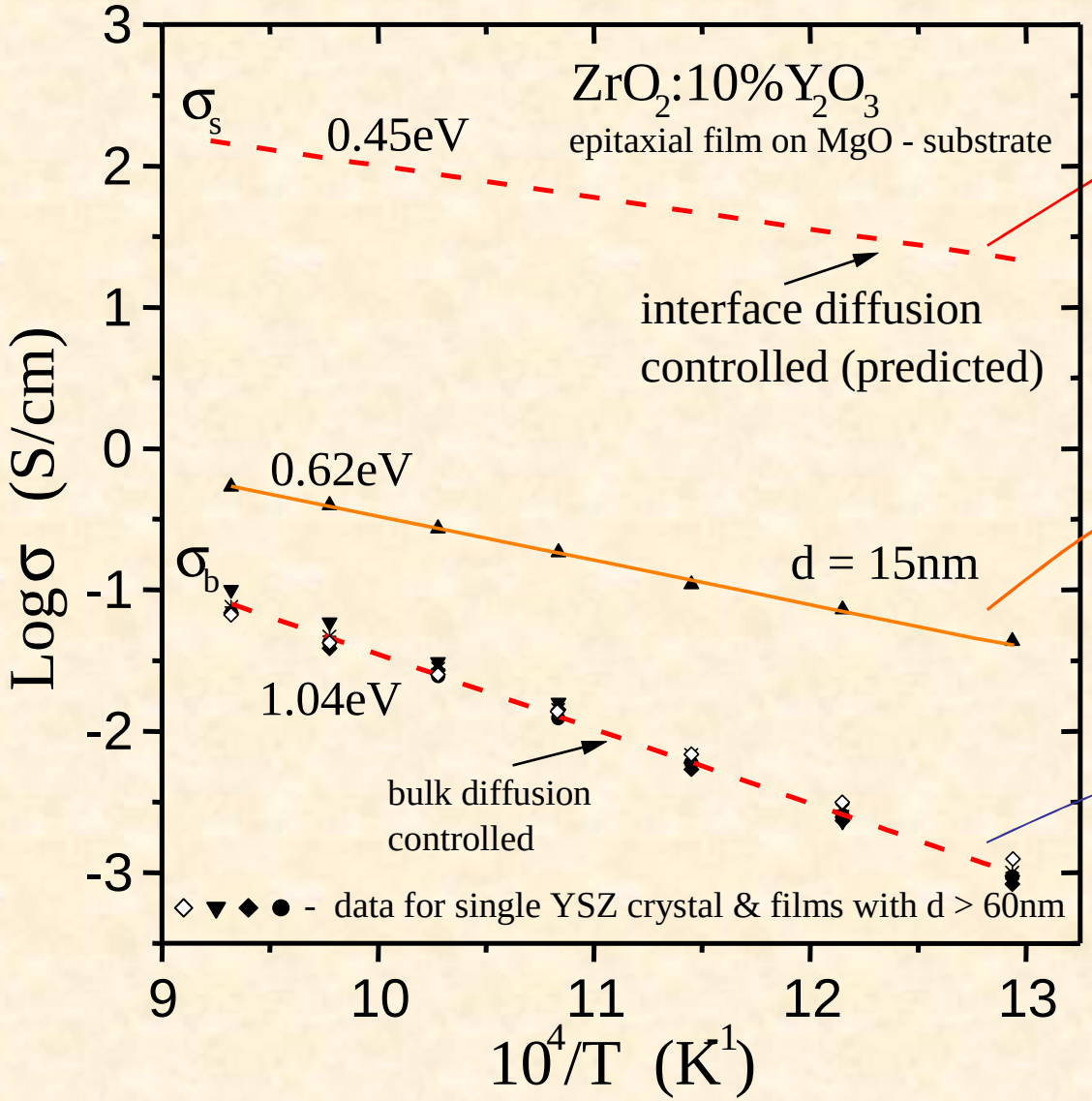




I.Kosacki, C.Rouleu, P.F.Becher and D.Lownes, Solid State Ionics 176 (2005) 1319-1326

- **15nm thick YSZ film exhibits highest ionic conductivity ever reported**
- **electrical conductivity of YSZ films is the superposition of grain boundary/surface and bulk contributions and can be described in mixing rule model with n = 0.31 => δ ~ 1.6nm**

Exceptionally high ionic conductivity in nano-scale YSZ films



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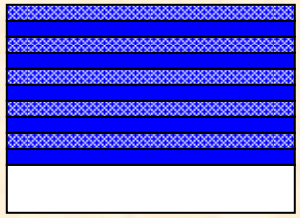
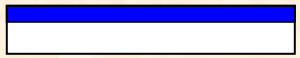
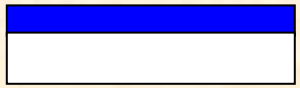


design heterostructures based on high interfacial conductivity



< 60 nm thick film interface contributes to conductivity

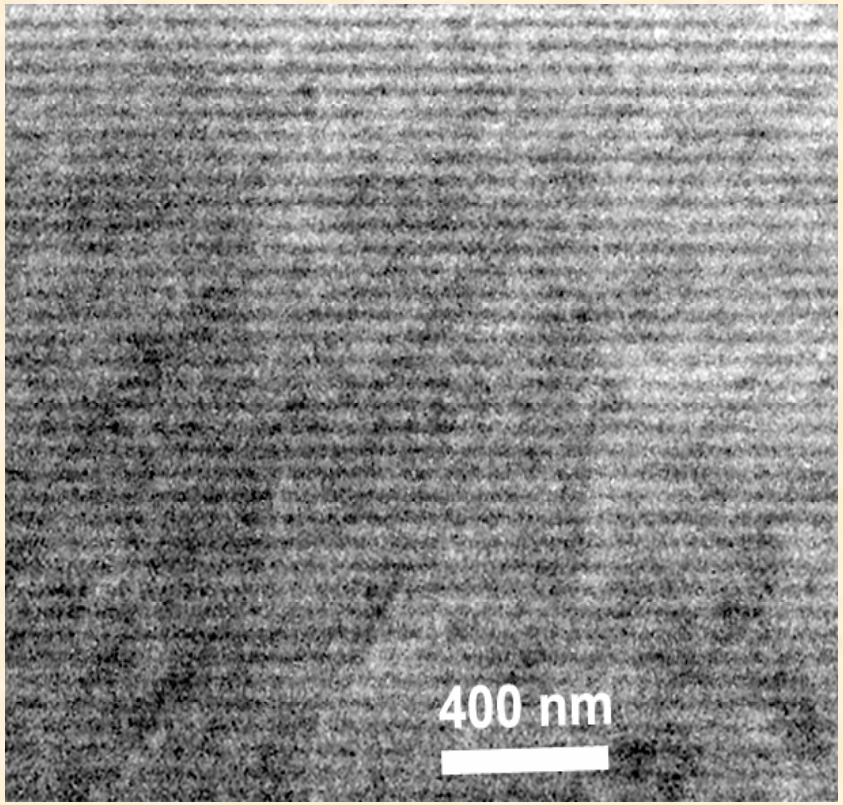


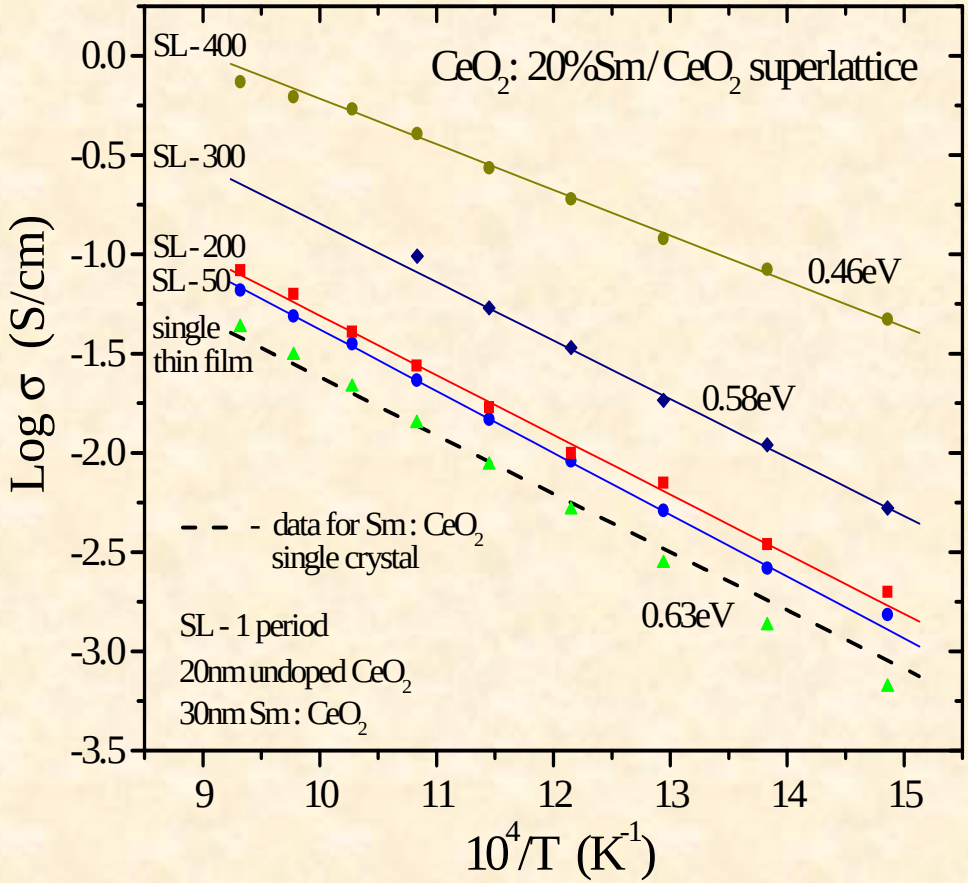
> 60 thick film conductivity controlled by lattice transport

interface + surface conductivities ~ 10^3 greater than that of bulk

I.Kosacki, C.Rouleu, P.F.Becher and D.Lownes
Solid State Ionics 176 (2005) 1319-1326

Can we make bulk material with ionic conductivity determined by surface/interface effects??



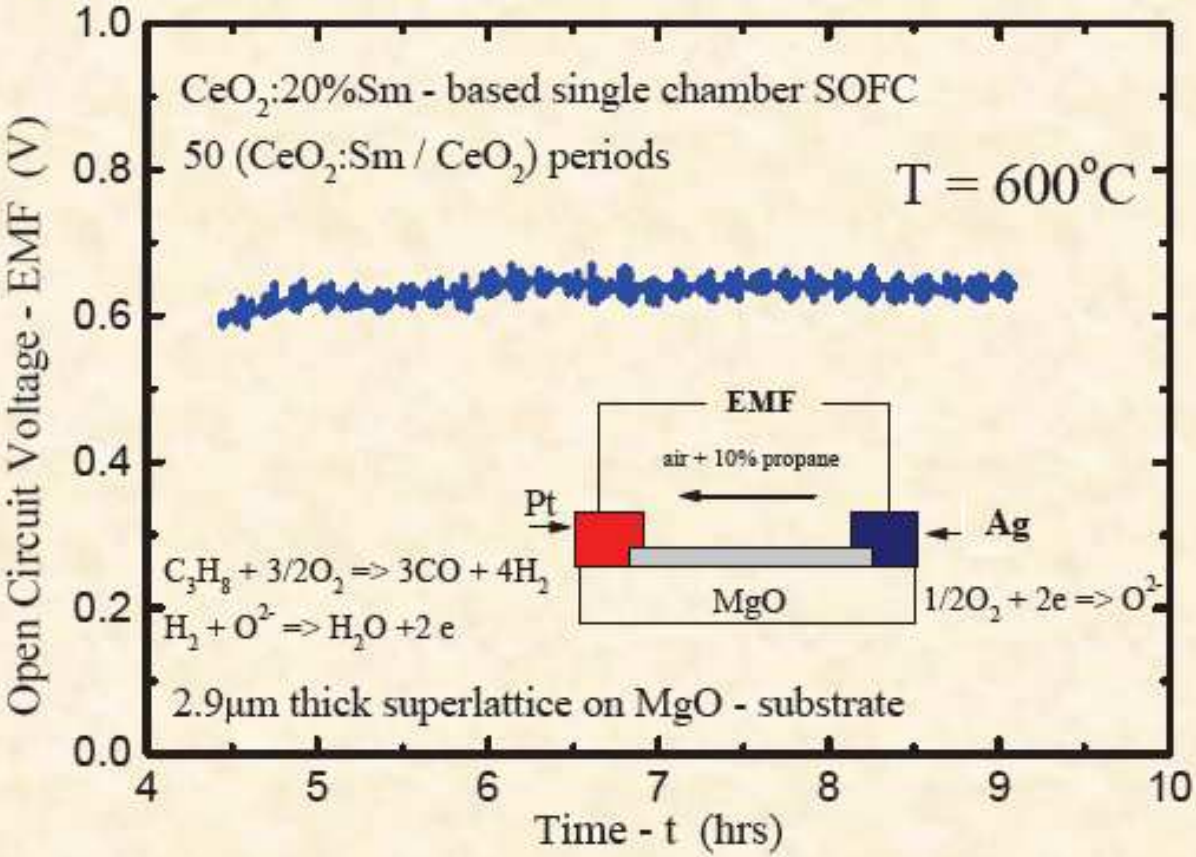


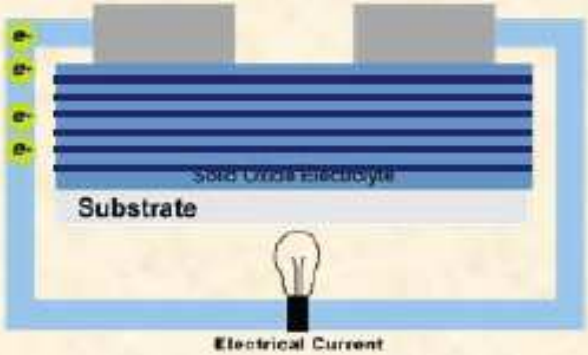
"Superlattice Electrolyte for Energy Application", invention disclosure #5-153.1685, February 2006

Increased conductivity was observed in superlattice structures with alternating 20nm CeO_2:20%Sm and 30nm CeO_2 layers

High texture is critical to enhance electrical conductivity in CeO_2:Sm/CeO_2 superlattice

Performance of single chamber cells with superlattice electrolytes and metallic electrodes





$$EMF = \frac{t_i RT}{nF} \ln \frac{P_{O2}}{P_{H2}} \sim 1V$$

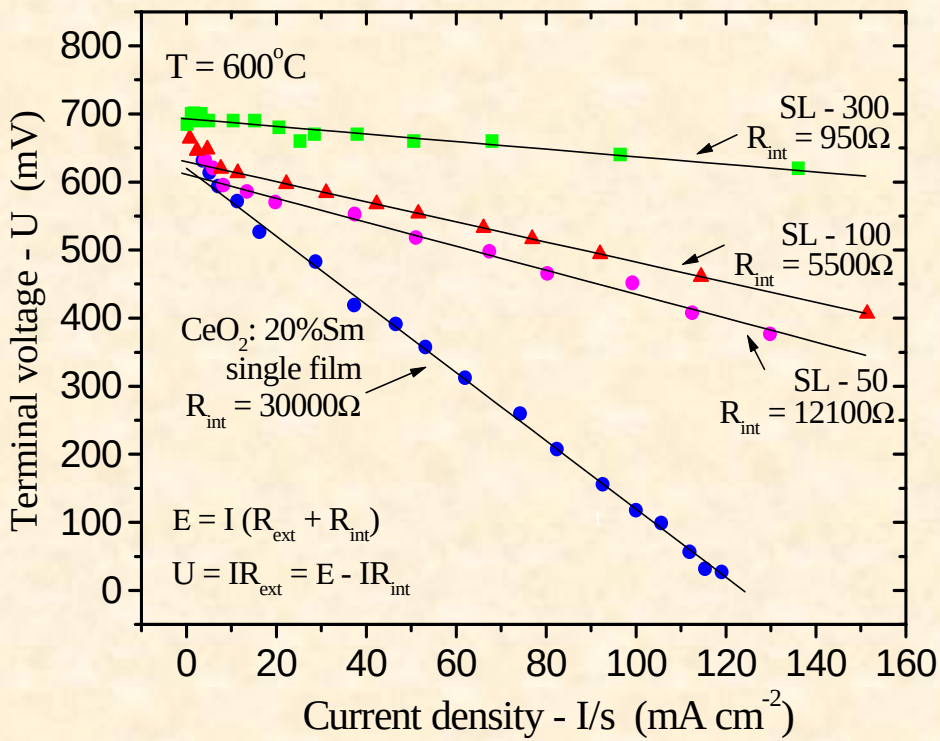
EMF is controlled by gas flow and system geometry

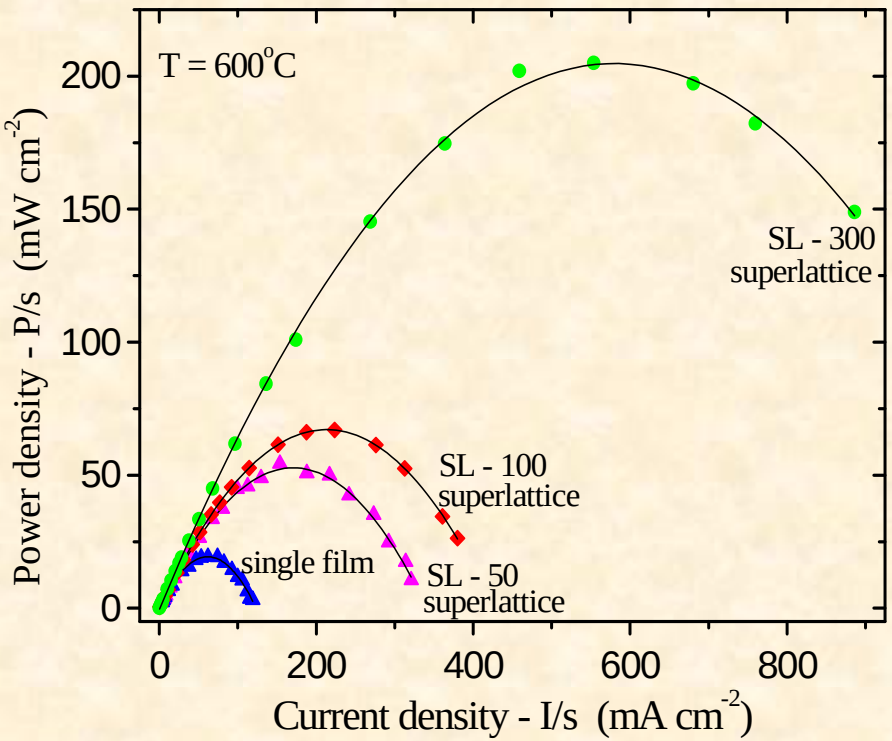
Advantages over 2 chamber SOFC:

- **minimizes gas leakage and seal issues**
- **rapid start-up and cool-down and extended operation time**
- **mass production using microelectronics technology**
- **multiple fuels – H_2, CH_4, C_3H_8, CO**
- **lower operation temperatures --- longer life**

Exceptional potential of nanoscale superlattices for developing advanced solid oxide fuel cells

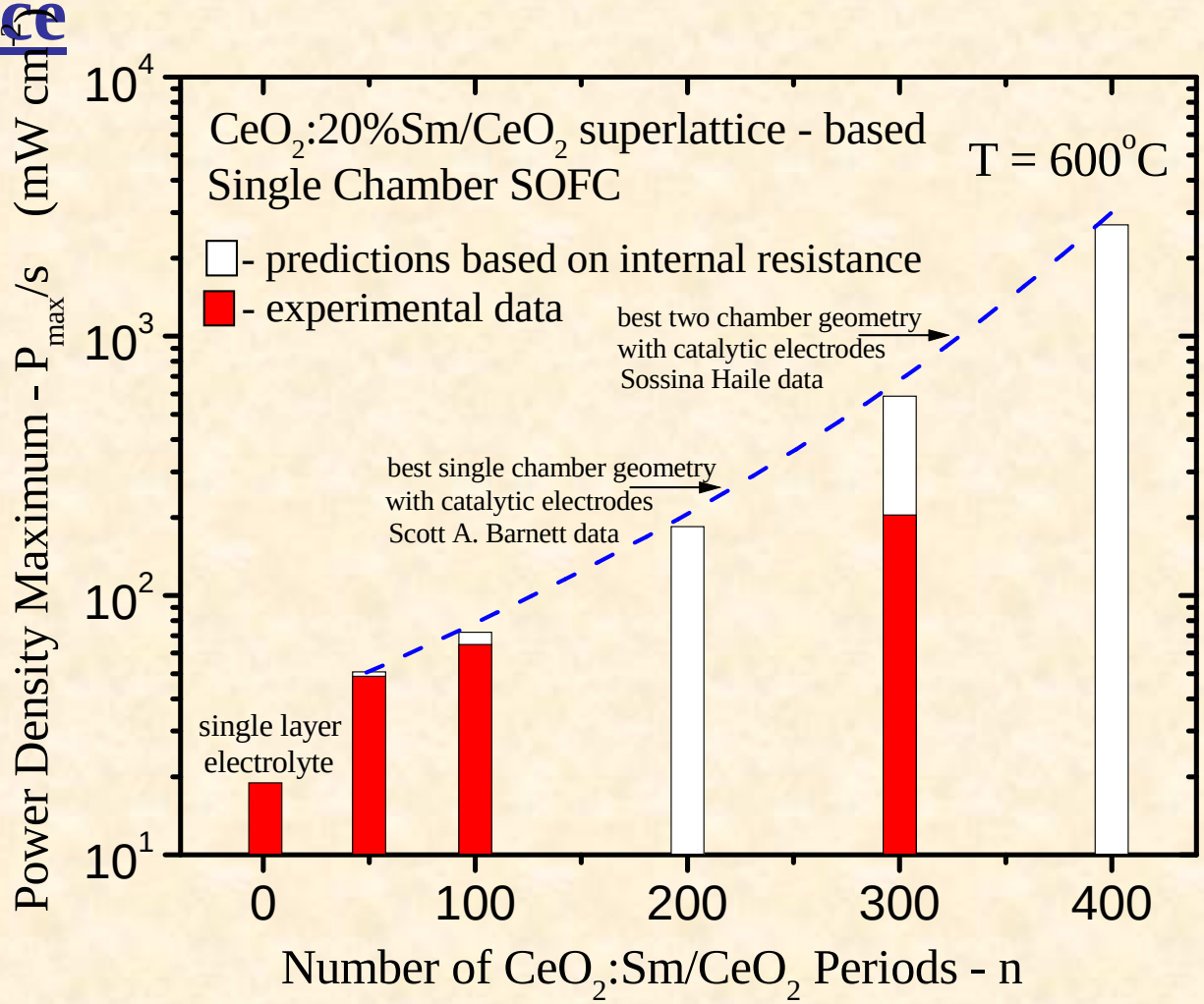
I.Kosacki at al. , 2006





- **CeO_2:Sm / CeO_2 superlattice can be used as solid electrolyte in single chamber fuel cells**
- **internal resistance decreases with increasing number of periods**
- **power density increases with increase in superlattice periods**
- **demonstrated promising performance**

Superlattice electrolyte enhances fuel cell performance



Single chamber fuel cell with 400 period superlattice electrolyte expected to yield 3000 mW/cm^2 or 3 times greater than two chamber SOFC output.

Novel design and approach of nanocomposite materials

US 20060063052A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2006/0063052 A1**

Hu et al. (43) **Pub. Date: Mar. 23, 2006**

(54) **DESIGN AND SYNTHESIS OF GUEST-HOST NANOSTRUCTURES TO ENHANCE IONIC CONDUCTIVITY ACROSS NANOCOMPOSITE MEMBRANES**

(76) Inventors: **Michael Z. Hu**, Knoxville, TN (US); **Igor Kosacki**, Oak Ridge, TN (US)

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(21) Appl. No.: **10/947,836**

(22) Filed: **Sep. 23, 2004**

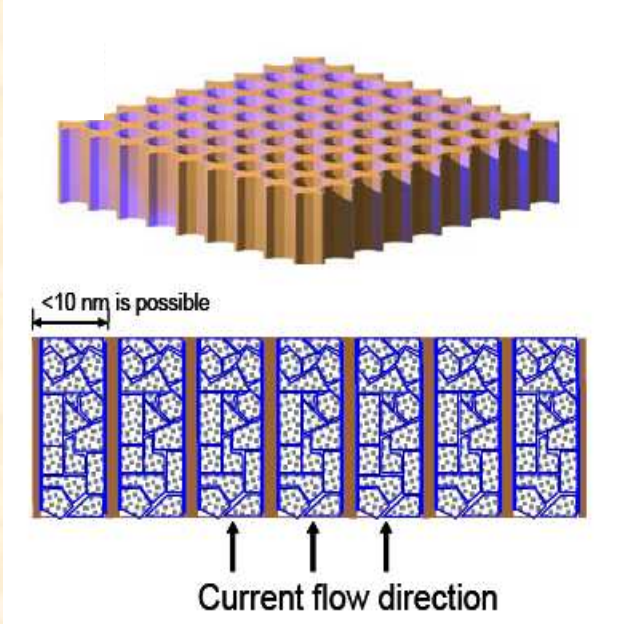
Publication Classification

(51) **Int. Cl.**
H01M 8/10 (2006.01)
G01N 27/26 (2006.01)

(52) **U.S. Cl.** **429/30**; 429/33; 204/424

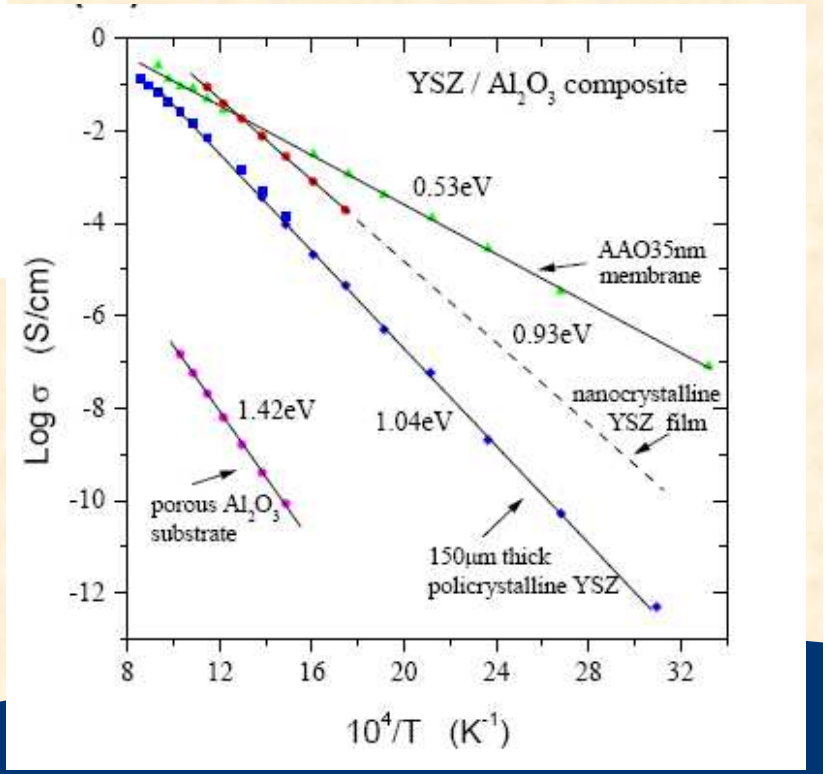
(57) **ABSTRACT**

An ion conducting membrane has a matrix including an ordered array of hollow channels and a nanocrystalline electrolyte contained within at least some or all of the channels. The channels have opposed open ends, and a channel width of 1000 nanometers or less, preferably 60 nanometers or less, and most preferably 10 nanometers or less. The channels may be aligned perpendicular to the matrix surface, and the length of the channels may be 10 nanometers to 1000 micrometers. The electrolyte has grain sizes of 100 nanometers or less, and preferably grain sizes of 1 to 50 nanometers. The electrolyte may include grains with a part of the grain boundaries aligned with inner walls of the channels to form a straight oriented grain-wall interface or the electrolyte may be a single crystal. In one form, the electrolyte conducts oxygen ions, the matrix is silica, and the electrolyte is yttrium doped zirconia.



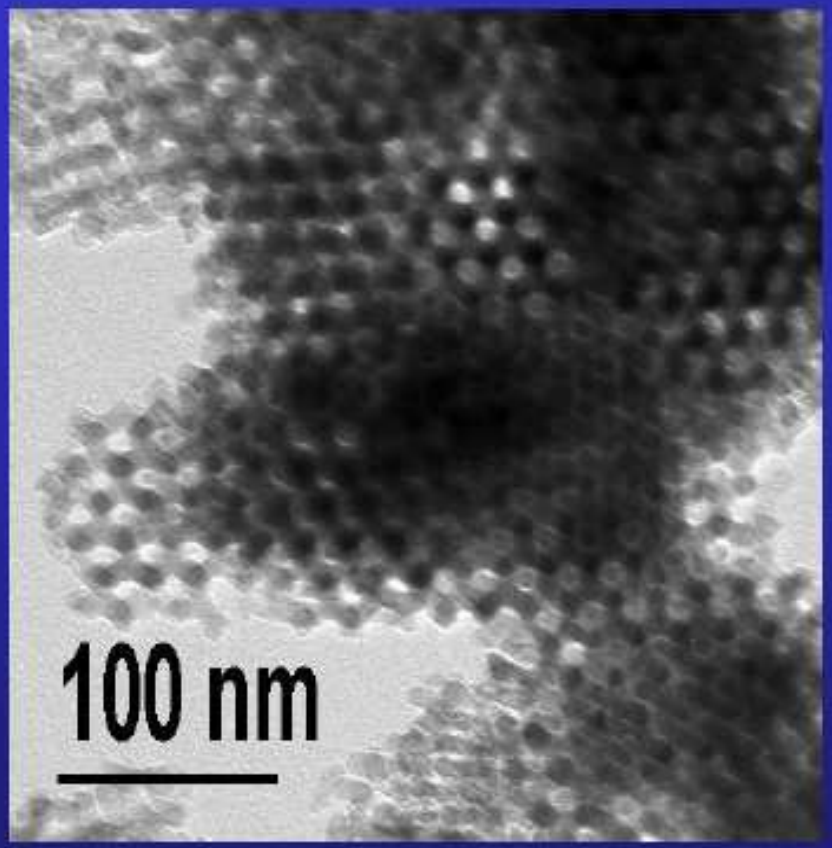
Parallel Mesopore Channels
(dark area, 7.5 nm dia.)

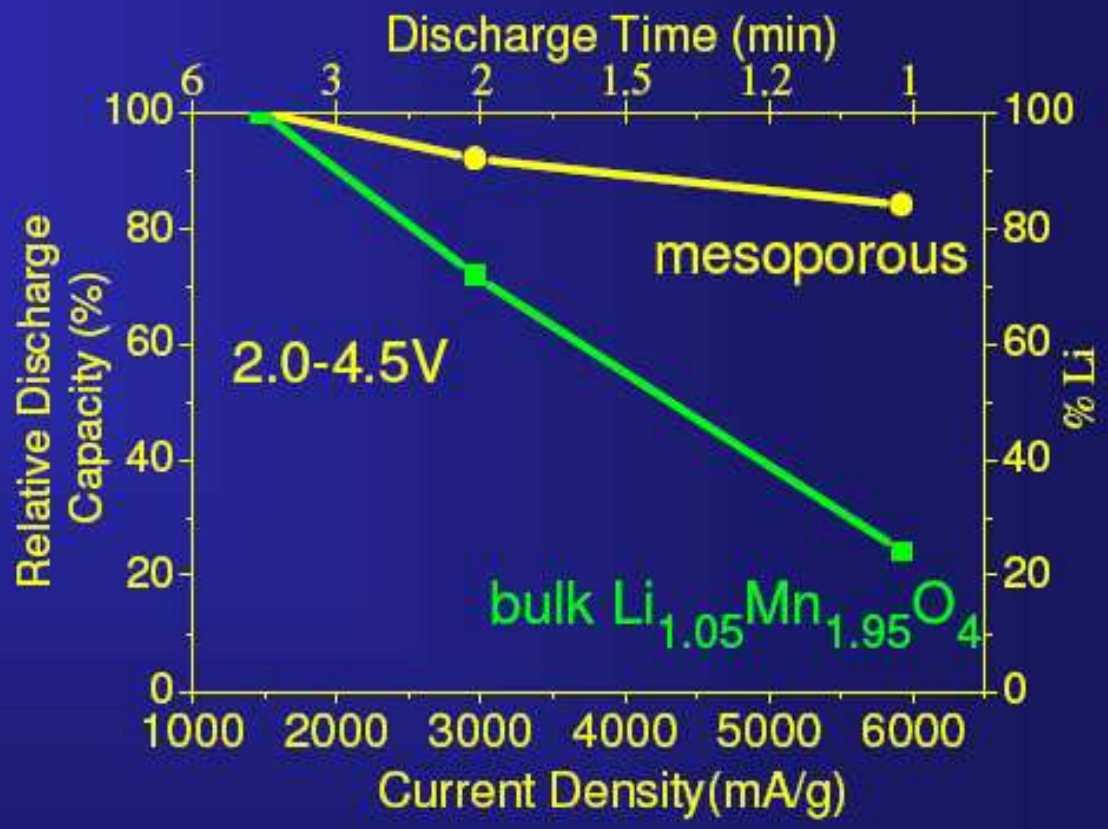
Top Surface View of Hexagonal Order of SiO_2 Layer



Nanostructured $LiMn_2O_4$ as a positive electrode

Mesoporous Materials: pore size 2-50nm => surface area ~500m^2/g !!!!





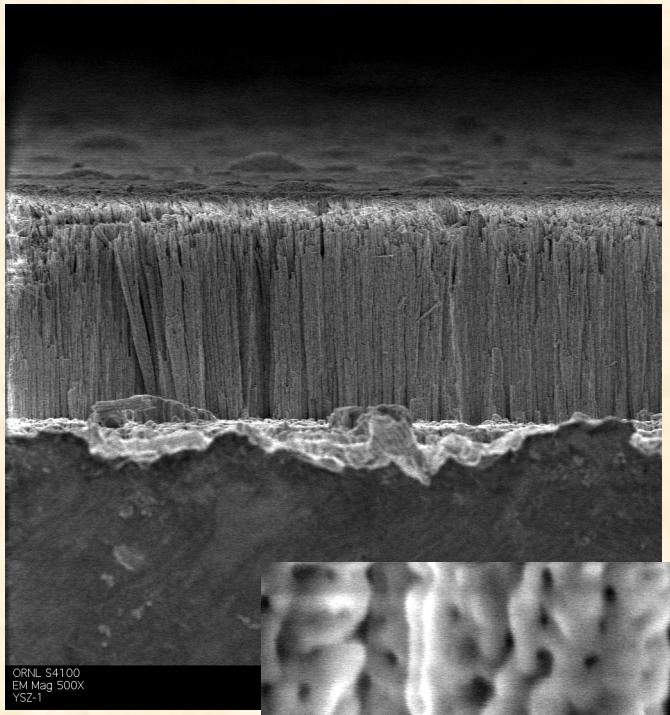
<u>Advantages of Mesoporous Electrodes:</u>

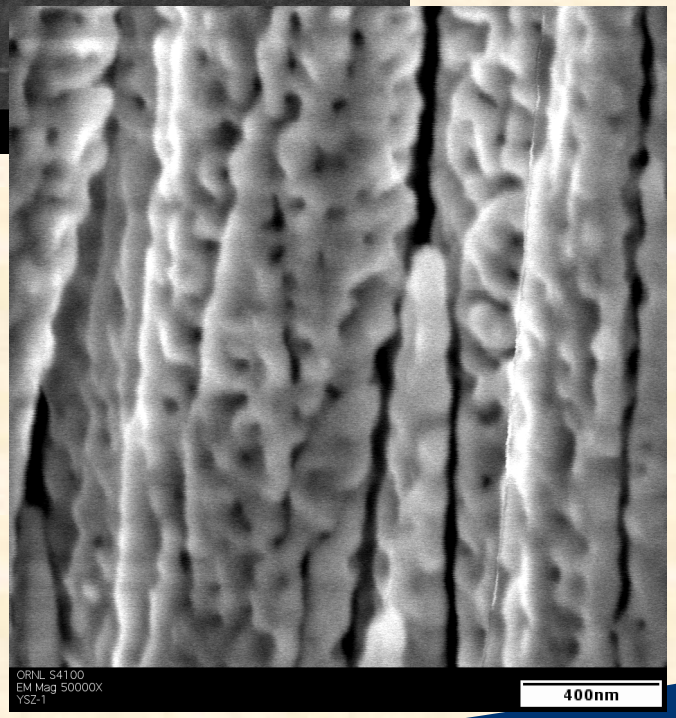
-high surface area in contact with electrolyte

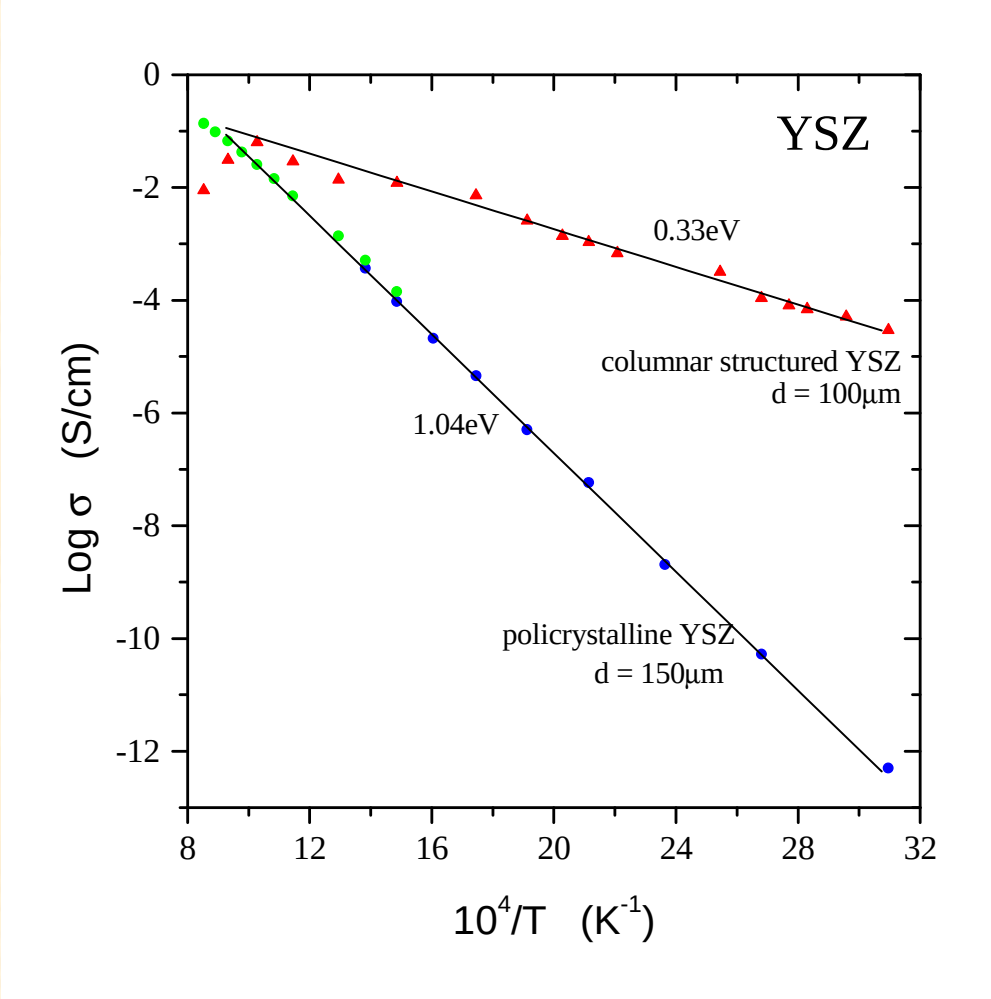
-thin walls – short diffusion distances for Li+ ($t \sim l^2/D$)

-high reversibility – 99.9% per cycle

Enhanced ionic conductivity observed in columnar structured YSZ thin films







I.Kosacki at al. , in preparation

Summary

1. **The interface/surface related phenomena can dominate the bulk properties in nanoscale materials**

   *** the electrical conductivity in oxides can be enhanced by controlling the microstructure (d_g < 100nm) or film thickness (d < 60nm)**

   *** the lattice and interface conductivities were separated – $\sigma_{int}/\sigma_b \sim 10^3$**

2. **Increased conductivity was also observed in superlattice structures with alternating 30nm CeO_2:20%Sm and 20nm CeO_2 layers**

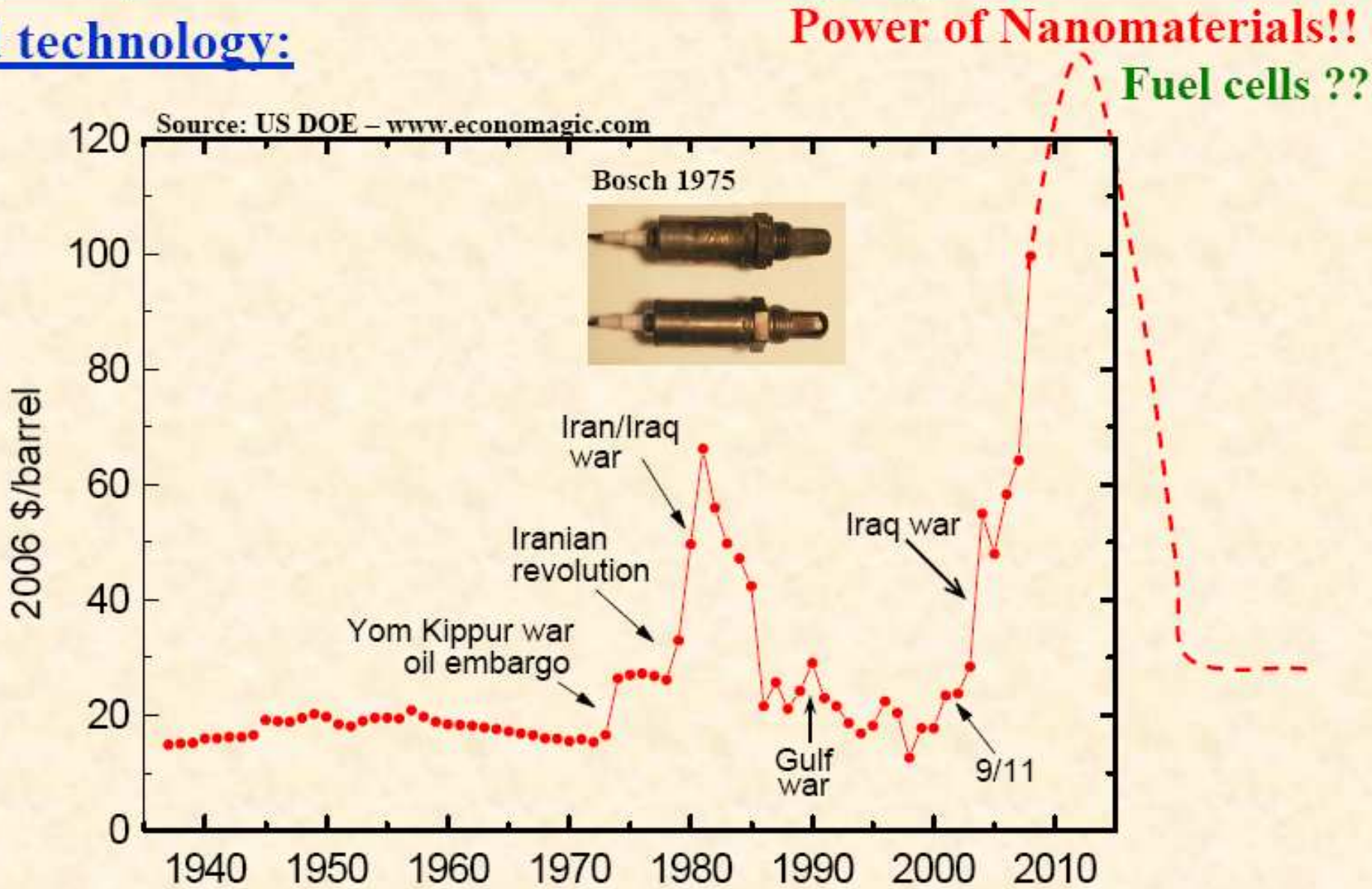
3. **Exceptional potential of nanocrystalline ceramics for developing advanced electrochemical devices**

   *** demonstrated promising performance of prototype single chamber fuel cells using superlattice electrolyte.**

4. **Nanocrystalline materials are more than fancy words!!!**

5. **Materials challenge – new materials are key to major developments in energy conversion - fuel cells and batteries**

High oil price can stimulate the developing of new devices and technology:



1975 - Nernst - type automotive sensor

- what happen in next 10 years??

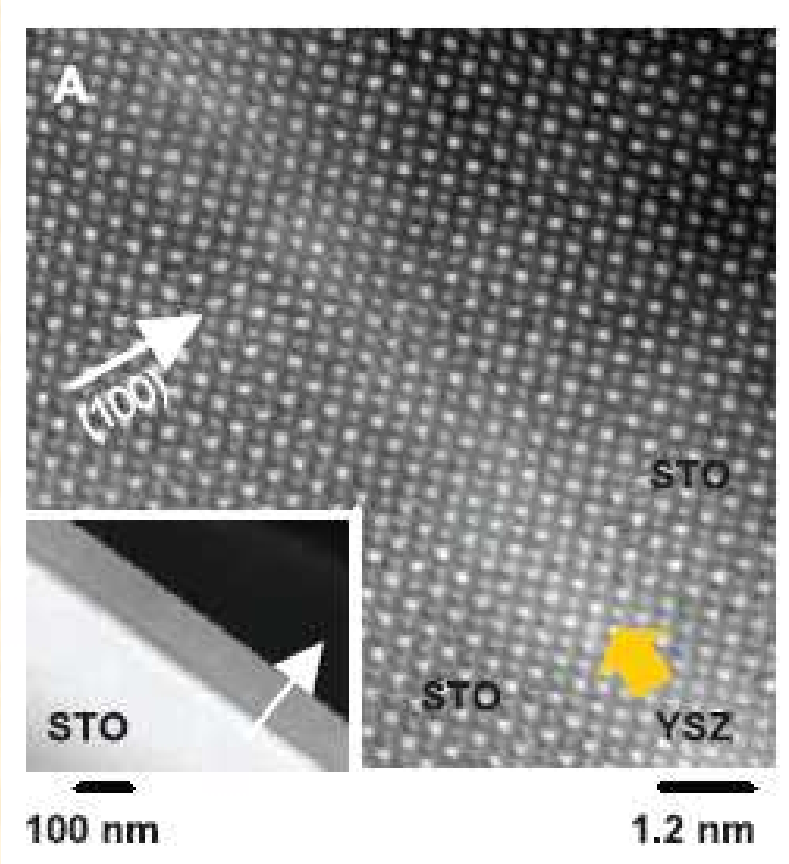
ACKNOWLEDGMENTS:

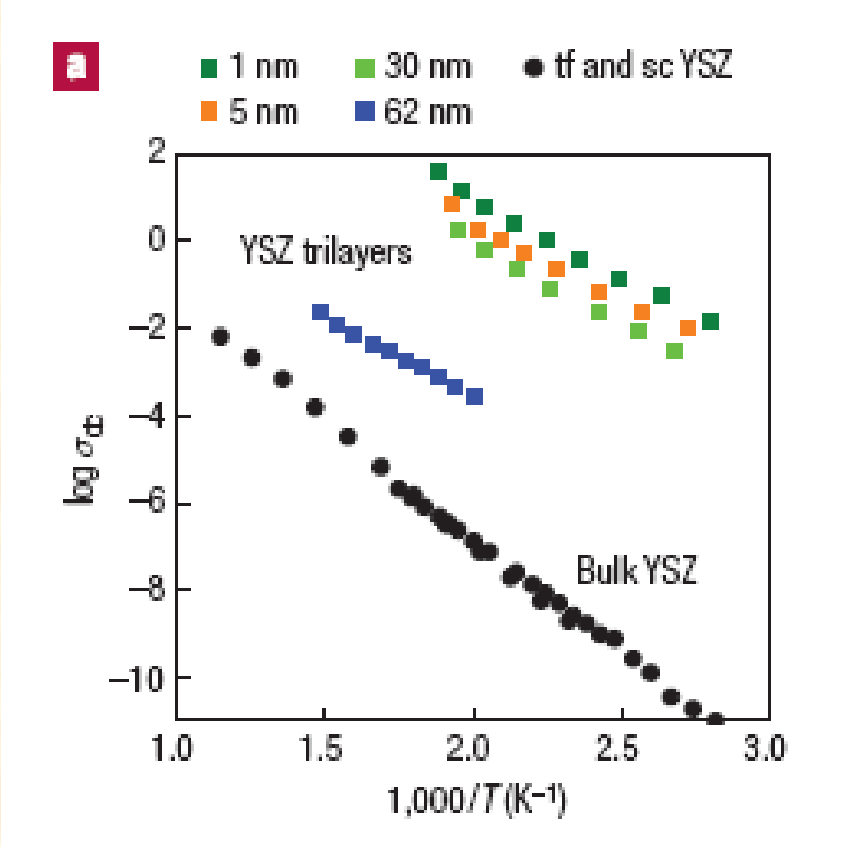
- Harry Tuller, 1992 - 1995
- Yet Ming Chiang, 1994 - 1995

- Harlan Anderson, 1995 – 2001
- Alan Chadwick
- Philippe Colomban
- Piotr Jasinski
- Vladimir Petrovsky
- Toshio Suzuki

- Chris Rouleau
- Jim Bentley
- Takeshi Egami
- Andrew Payzant

Colossal ionic conductivity at interfaces of epitaxial ZrO_2:Y_2O_3/$SrTiO_3$ heterostructures

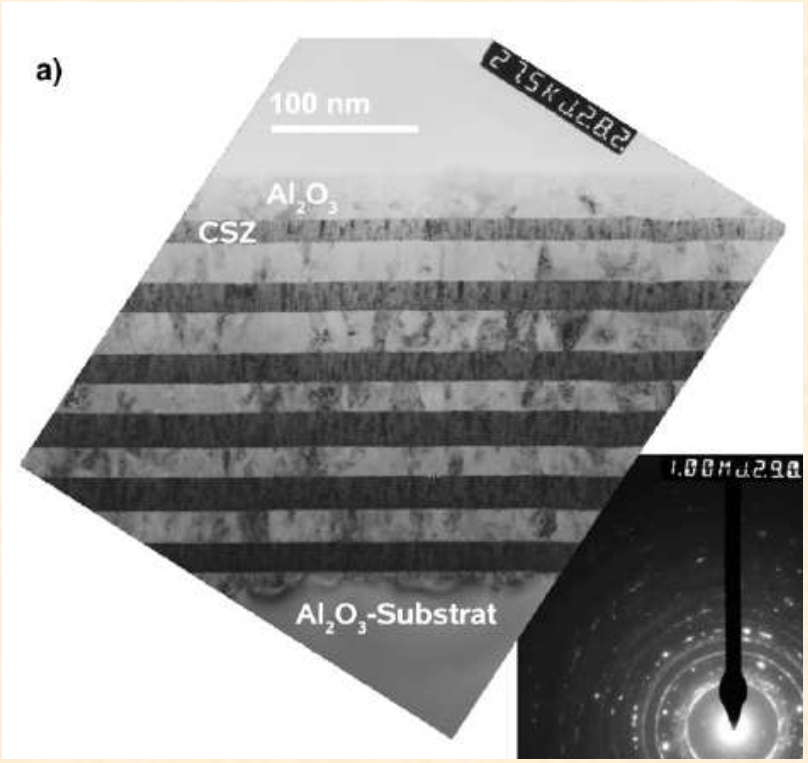


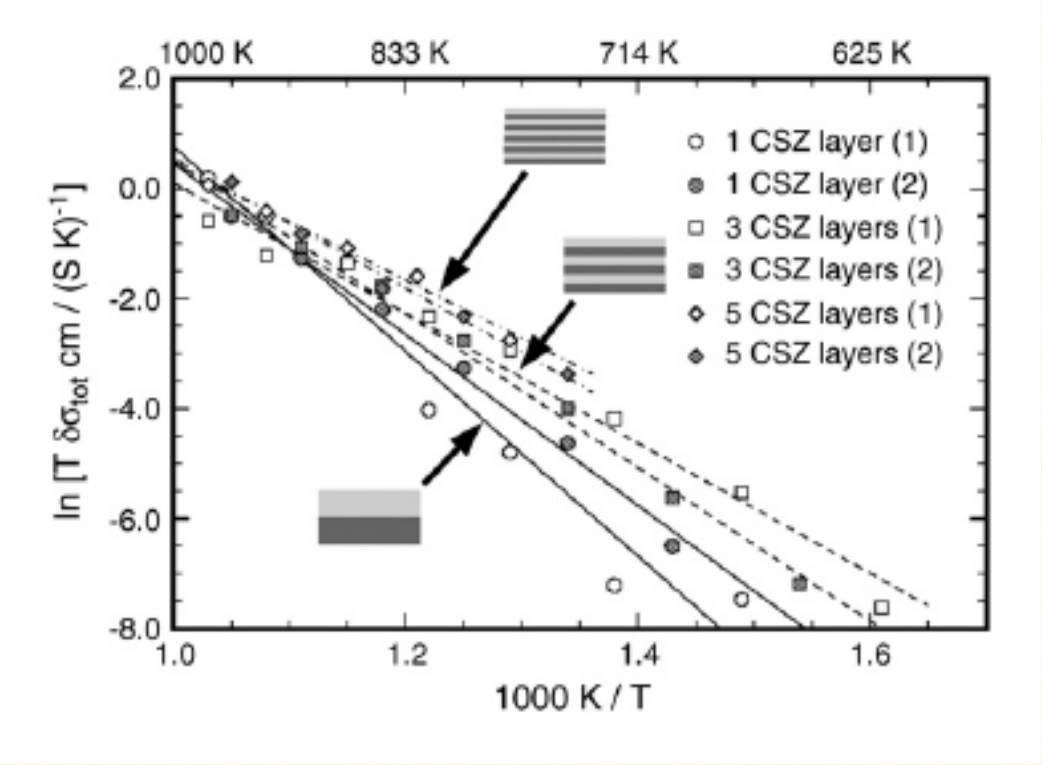


J. Garcia-Barriocanal, A. Rivera-Calzada, M. Varela, Z. Sefrioui, E. Iborra, C. Leon, S. J. Pennycook, J. Santamaria1

Science 321 (2008) 676 - 679

Ionic conductivity in superlattices - multilayer system CSZ (ZrO_2+CaO)/Al_2O_3



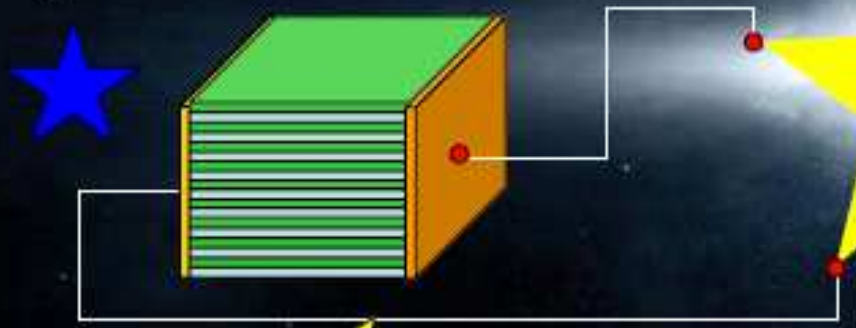


A. Peters, C. Korte, D. Hesse, N. Zakharov, J. Janek

Solid State Ionics 178 (2007) 67–76

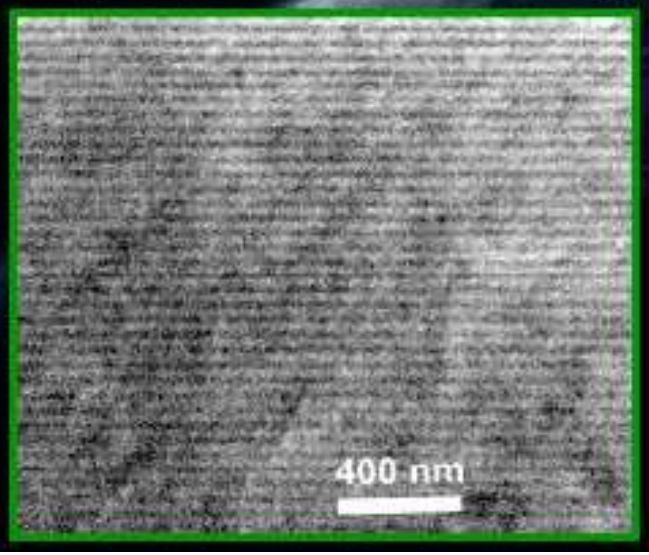
Power of nanomaterials
ORNL developed
superlattice - based SOFC

Merry Christmas - 2005
With Solid Oxide Fuel Cells



1- 5 W/cm^3
power output

Superlattice electrolyte



All of the best for holidays
and Happy New 2006 Year

- Igor Kosacki

Oak Ridge, 2005