Novel Low Solid State Fuel Cells

Chonglin Chen

Department of Physics, University of Texas at San Antonio

and

The Texas Center for Superconductivity & Department of Physics, University of Houston, Texas

Collaborations:

J. Liu, G. Collins, P. Nash, J. Weaver, Z. Yuan, and L. Chen* (UTSA Lab

A. J. Jacobson – Univ. Houston

**J. C. Jiang, and E. I. Meletis -- **University of Texas at Arlington

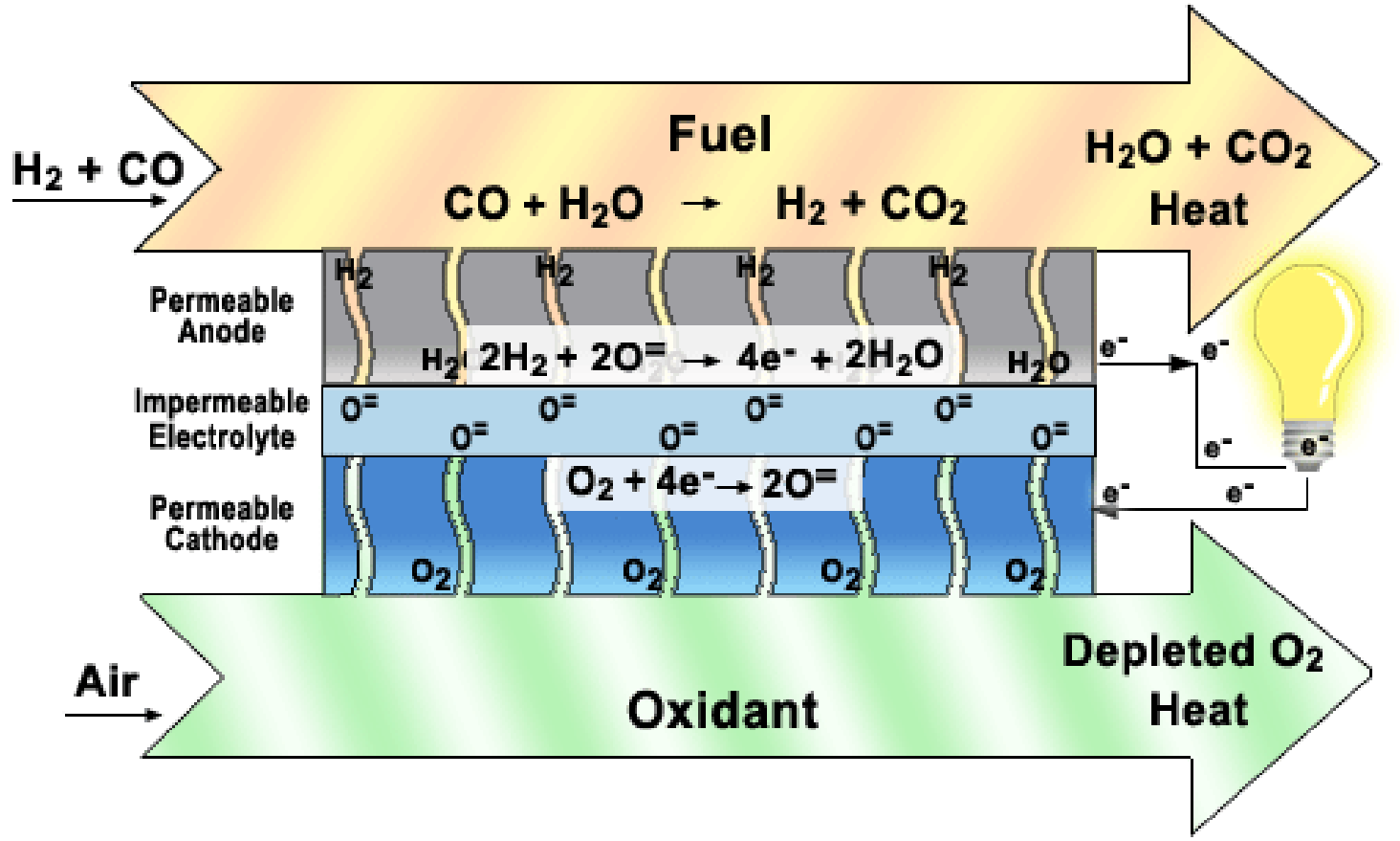
Sponsors:

Department of Energy National Energy Technology Laboratory and partially from the State of Texas

Project Manager:

Dr. Patricia Rawls

Principle of Solid State Fuel Cells



Electrode Reactions:

Anode: $$H_2 + O^= \Rightarrow H_2O + 2e^-$$

Cathode: $$O_2 + 4e^- \Rightarrow 2O^=$$

Overall: $$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$$

DOE report (2001)

Current Difficulties

- High operating temperature:
  - 800 ^{o}C to 1000 ^{o}C
- Low efficiency & low current (power) density
- Difficult in packaging
- High cost for practical market applications;
- Low lifetime

Overall, the operating temperature is too high!

Goal of This Research

- To study the new highly ionic conductive oxides: Electrodes and electrolytes:
  - Electrical Conductivity Relaxation
  - Isotope Exchange and Depth Profiling
  - Impedance Spectroscopy
- To characterize the performance of the half cells and full cells;
- To develop intermediate temperature solid state fuel cells based on new oxide materials.

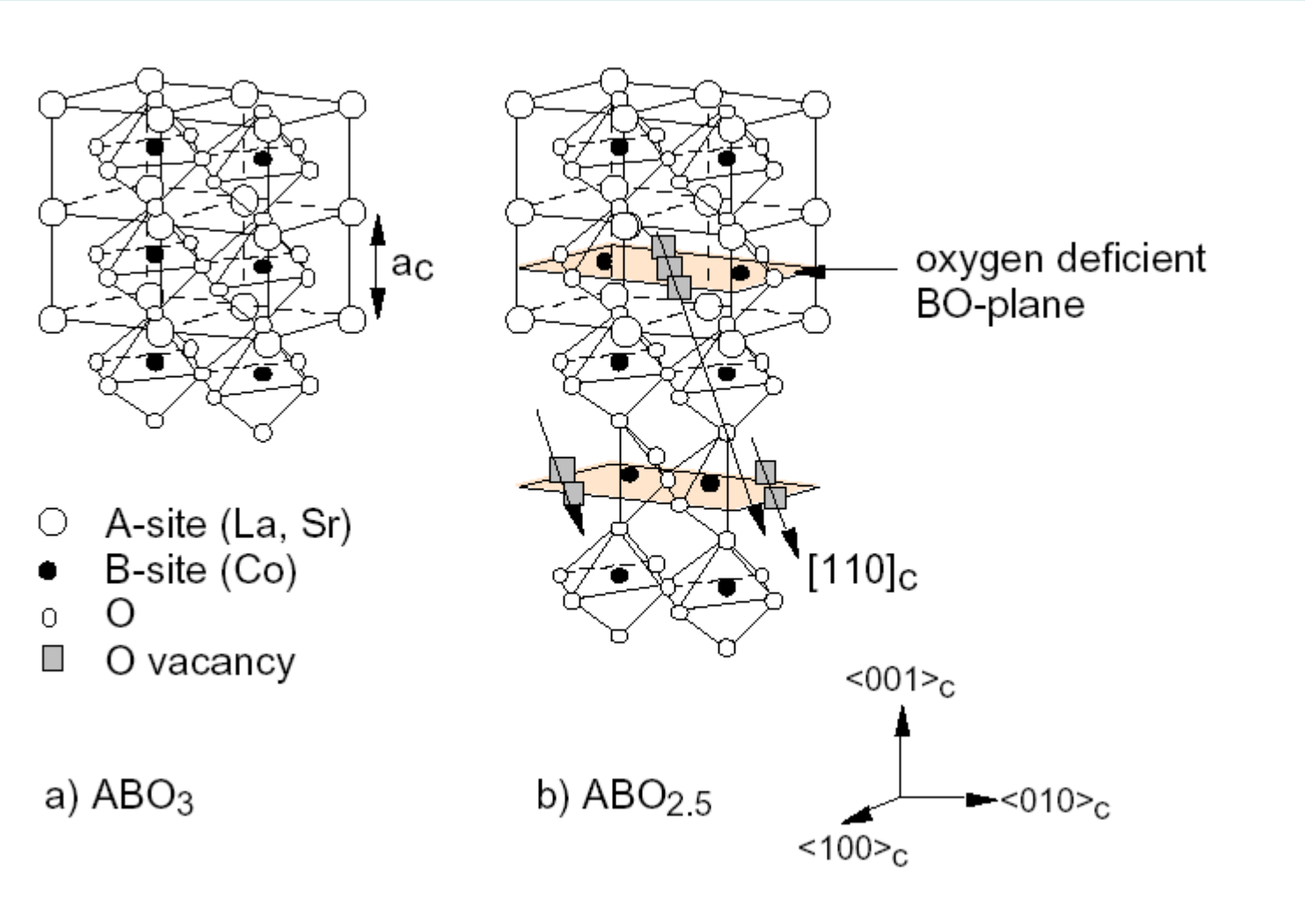
Outline

- New oxide materials:
  - Electrodes and electrolytes
- New technology (existing tech in semiconductor):
  - Thin film structural fuel cells;
- Lower operating temperature

  (550 ^{o}C – 725°C)

Improving operating efficiency and device lifetime, enhancing the power density, and reducing the cost.

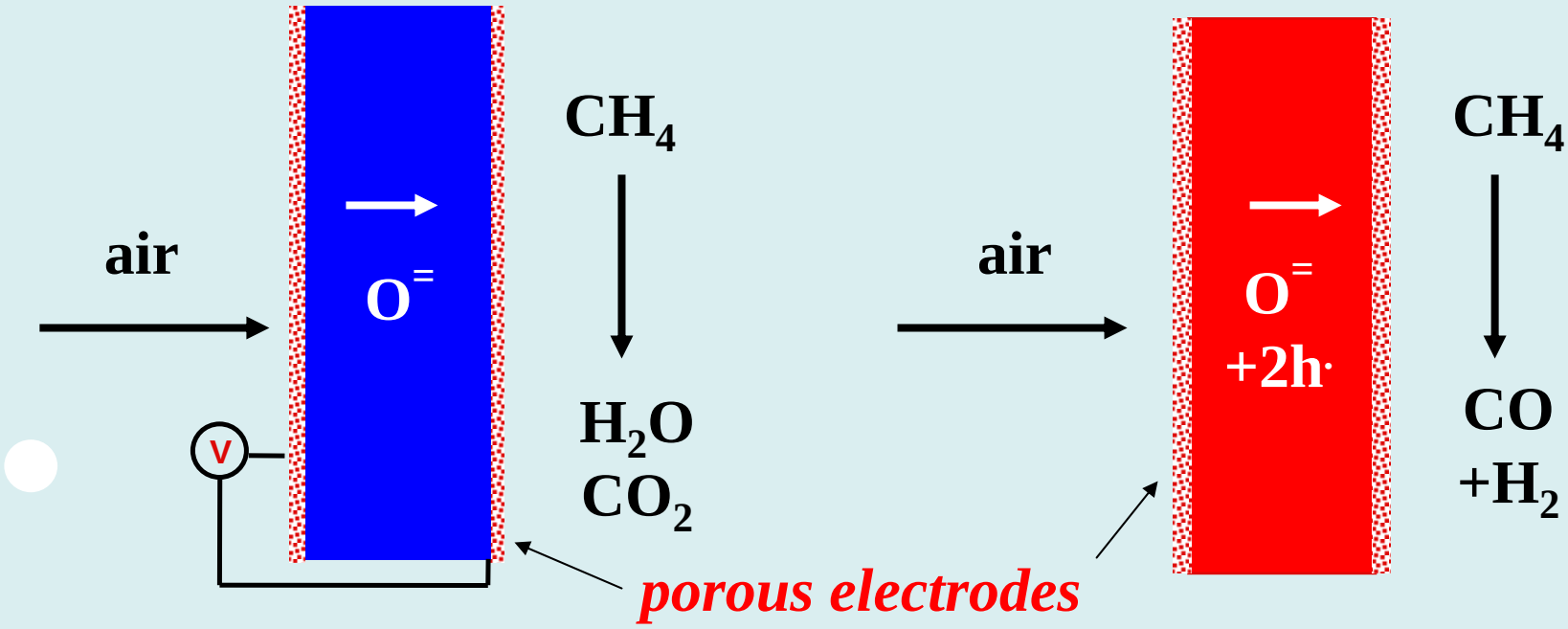
Perovskite Structure Oxides ABO_{3-x}



- actual stoichiometry depends on T and pO_2

Oxygen Transport Membrane Devices

high temperature 700 – 1000 °C



ionic conductor + external circuit

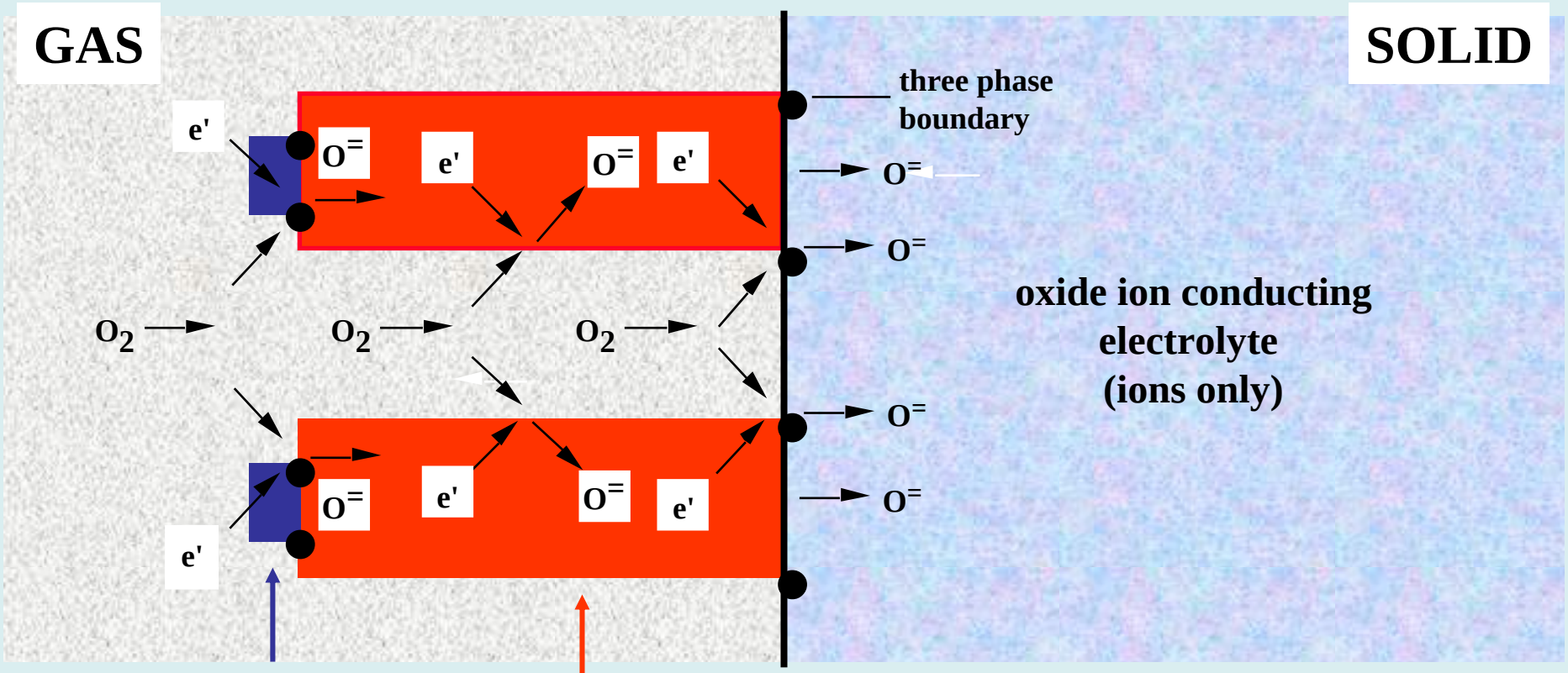
fuel cells,
electrocatalytic reactors

single phase or dual phase
mixed conductors

membrane reactors

related chemical sensors

Schematic Porous Oxygen Electrode



metal current collector (electrons only)

porous oxide electrode (ions and electrons)

good electrodes require high:

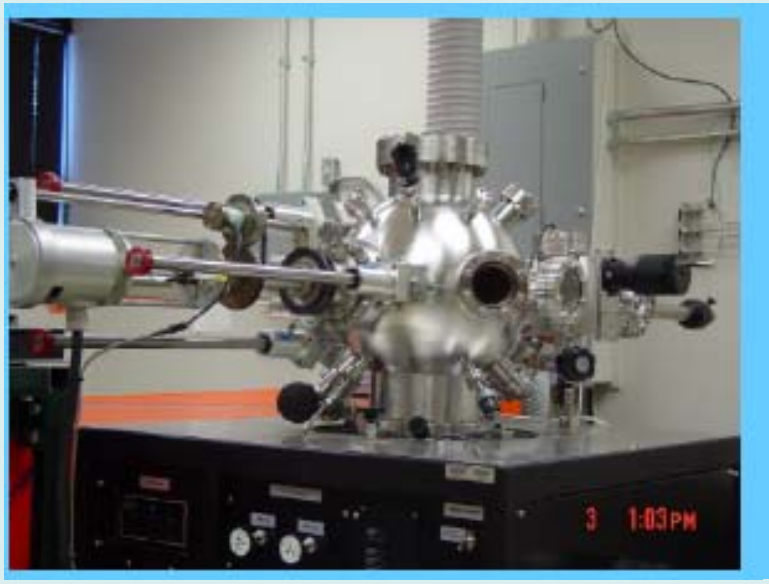
- **surface area and porosity**
- **ionic and electronic conductivity**
- **surface reaction rates**

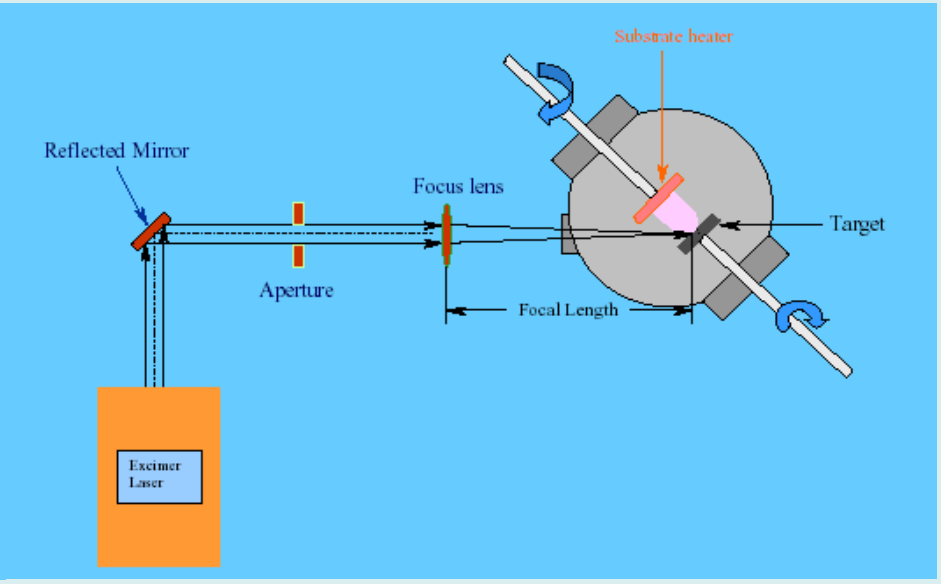
Advantages in new thin film oxide structures

- much simpler than porous structures – isolate aspects of the kinetics
- $PrBaCo_2O_{5+\delta}$ has high ionic and electronic conductivity
- new multilayered $Gd:CeO_2/YSZ$ has high ionic conductivity and low electronic conduction.
- for films <5000 Å bulk diffusion very fast
- gas - solid and solid – solid interfaces dominate
- direct application in membrane devices for oxygen separation (thick dense films)

Thin film deposition technique

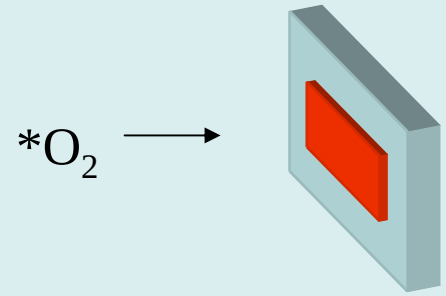
- Pulsed Laser Deposition (PLD) was employed to fabricate various oxide thin films and multilayered structures with controllable microstructures.
- KrF excimer laser with pulse frequency of 5 Hz.
- Deposition times of 60 min gave 300 nm thick films



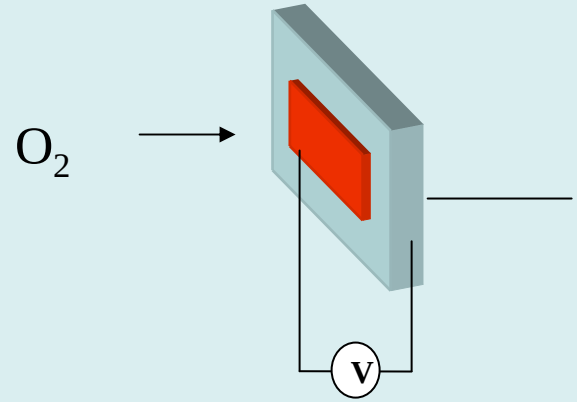


Characterization Technique:
Surface reaction rates & interface resistances

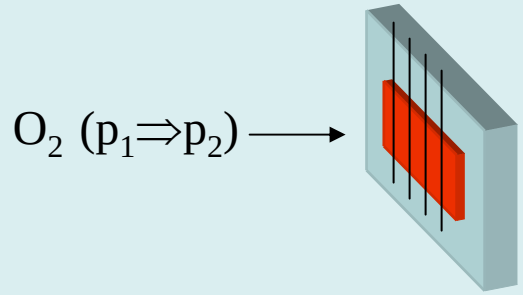
- equilibrium
  - isotope exchange
    - — $^*O_2 \Leftrightarrow O_2$



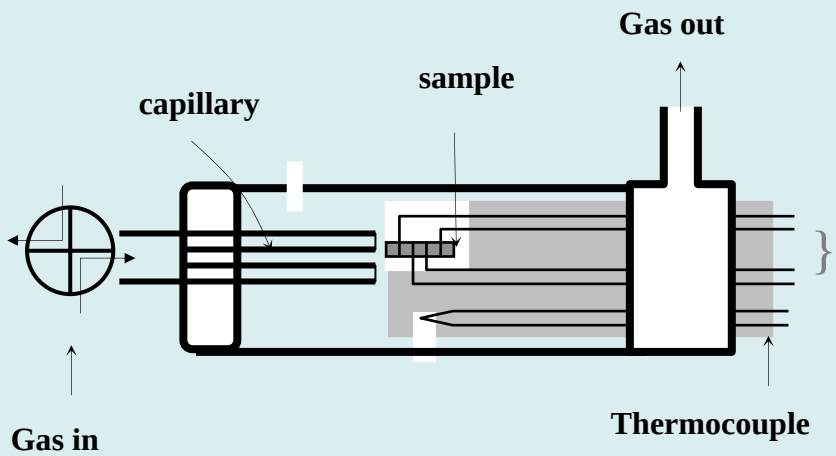
- close to equilibrium
  - ac impedance
  - response to a small ac change on a dc bias



- non-equilibrium
  - conductivity relaxation
    - — dc response to an abrupt change in pO_2



Electrical Conductivity Relaxation



Measure change with time of dc conductivity after $p_1 \Rightarrow p_2$

ECR measures only the surface reaction rate because bulk diffusion very fast

Film oxidation

$$\tfrac{1}{2}O_2 + V_O^{\bullet\bullet} \leftrightarrow O_O^{\times} + 2h^{\bullet}$$

O flux into the film

$$j_O(t) = k_{chem}(c_O(t) - c_{O,e})$$

Vacancy concentration

$$\partial c_v / \partial t = -(A/V)k_{chem}\Delta c_v$$

Conductivity

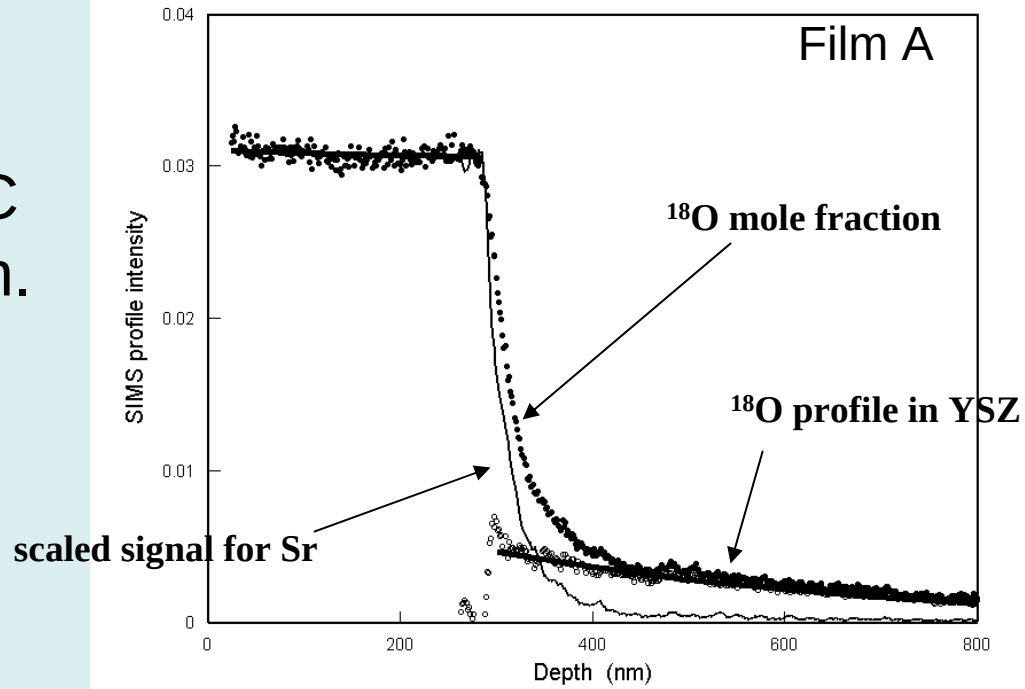
$$g(t) = \frac{\sigma(t) - \sigma_1}{\sigma_2 - \sigma_1} = \frac{c_v(t) - c_{v1}}{c_{v2} - c_{v1}}$$

$$g(t) = 1 - exp(-k_{chem}t/l)$$

^{18}O profile on $La_{0.5}Sr_{0.5}CoO_{3-x}$ on YSZ

film exposed at 300 °C to 20% $^{18}O_2$ for 30 min.

analyzed by SIMS



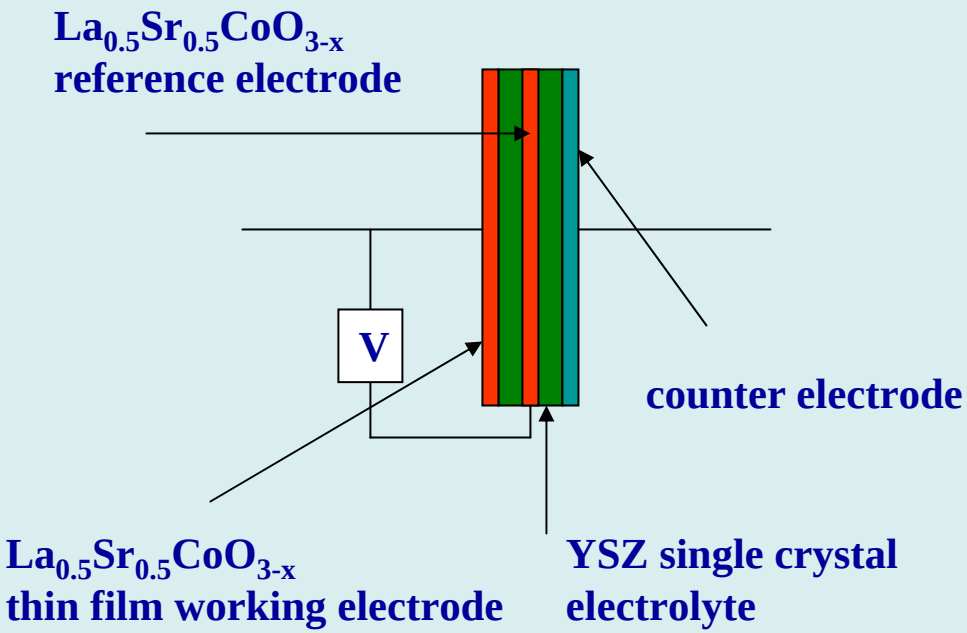
Heavy solid lines are simulated fit of the ^{18}O profile with the parameters:

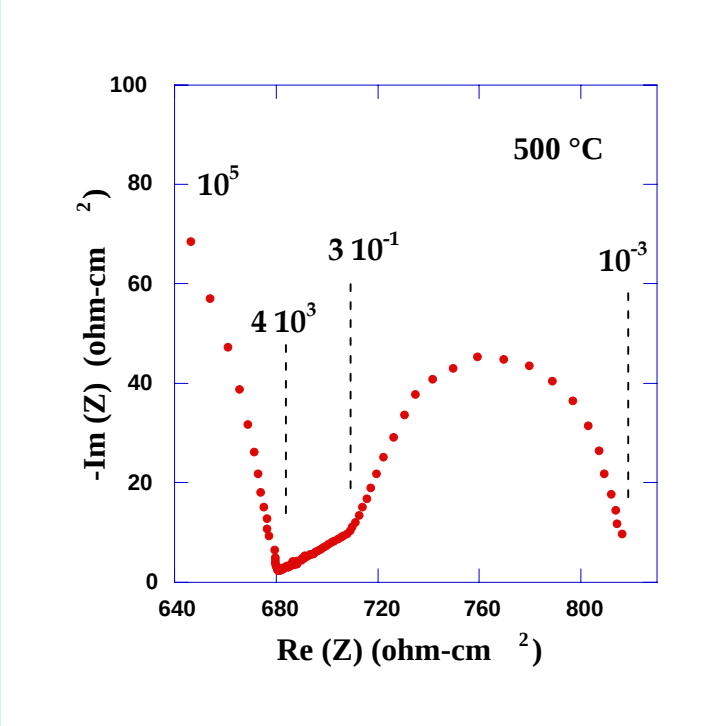
k_{fg} = 7.6 x 10^{-10} cm s^{-1} ; D_f = 3.0 x 10^{-11} cm^2 s^{-1};

k_{fb} = 7.5 x 10^{-9} cm s^{-1} ; D_b = 1.6 x 10^{-12} cm^2 s^{-1}.

***J. Electrochemical Society*, 147 (2000) 4001**

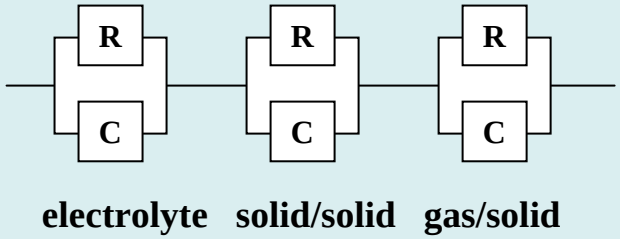
ac impedance of thin films





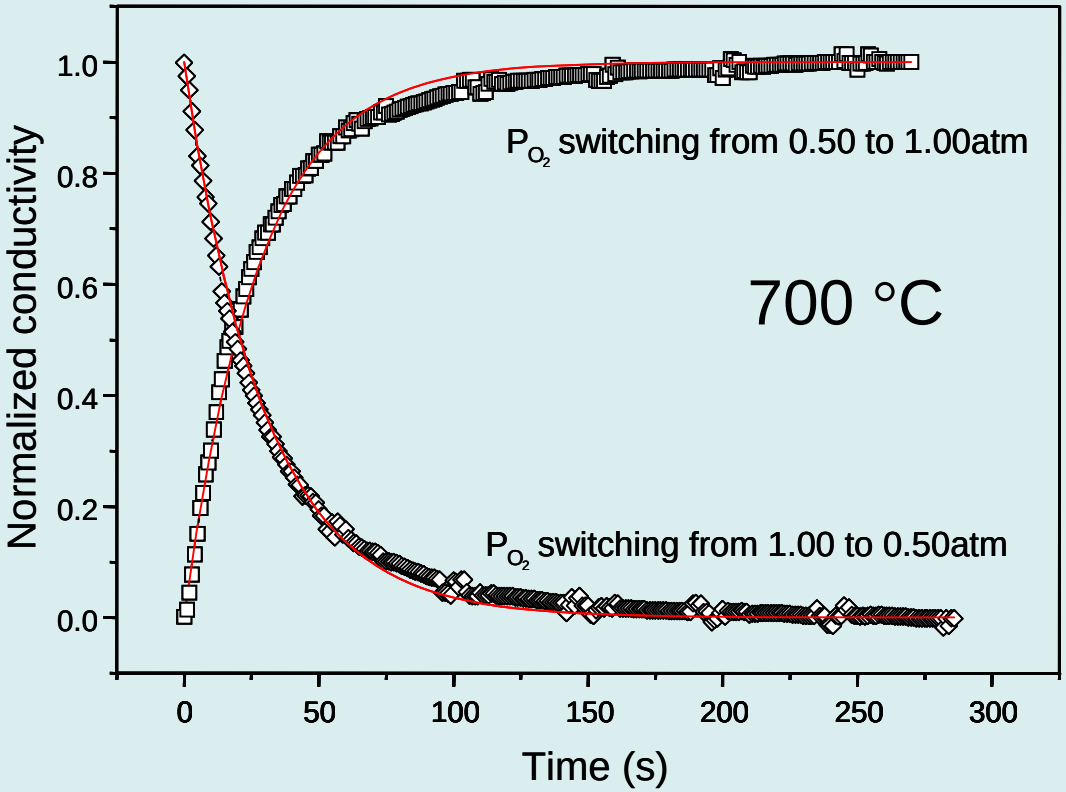
YSZ blocks the electron current

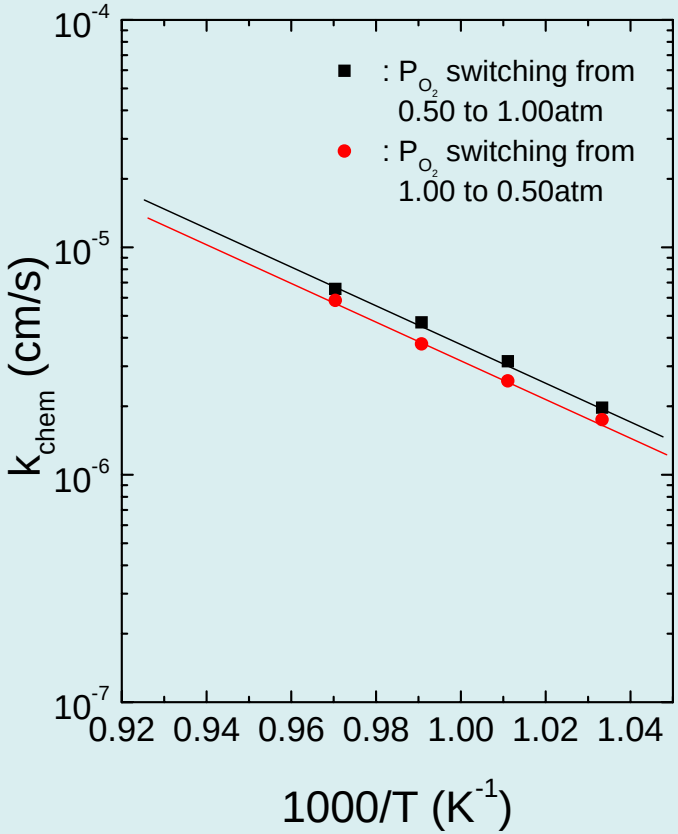
RC time constants give the rates



Electrical Conductivity Relaxation

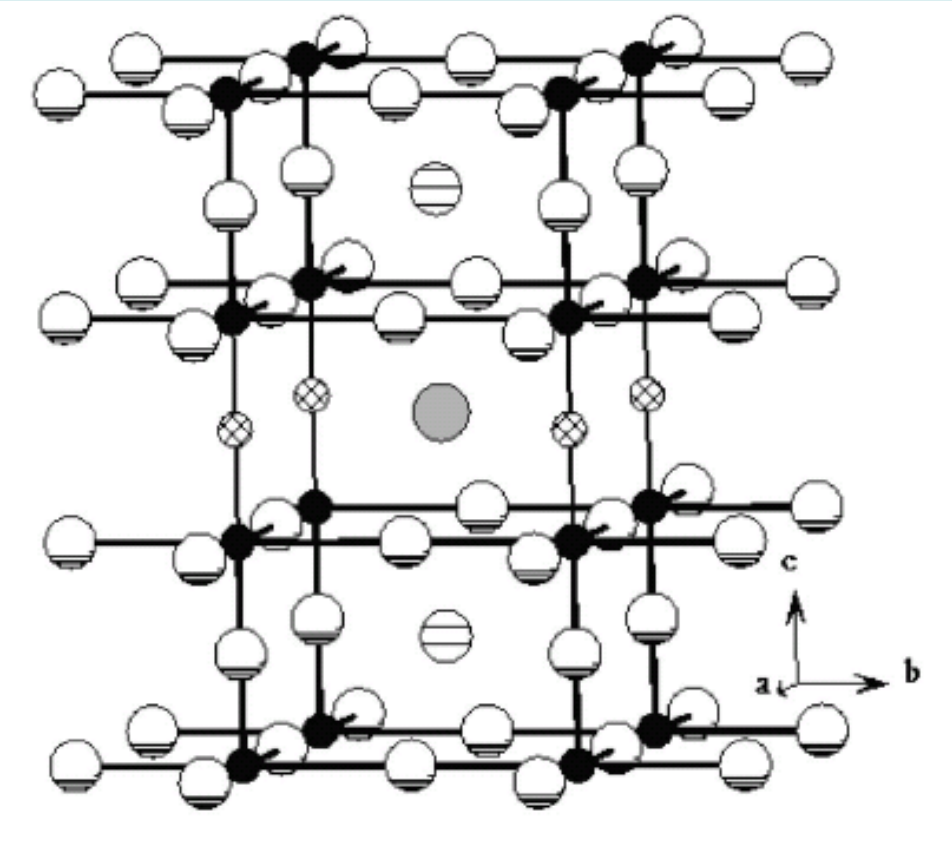
LSCO film on (100) LAO by PLD at 550 °C





***Appl. Phys. Lett.*, 79 (2001) 776**

PBCO as New Cathode Materials

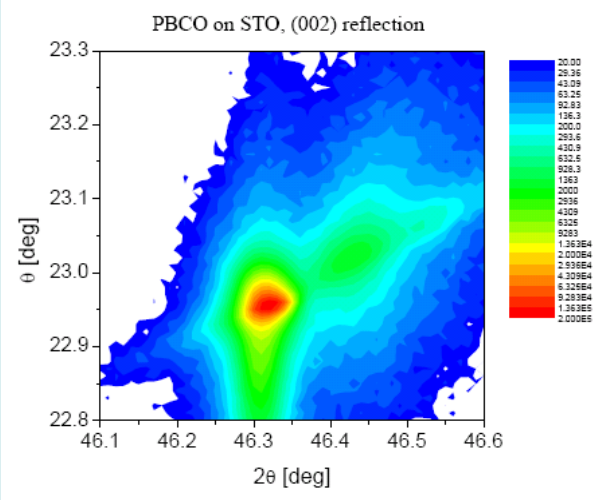


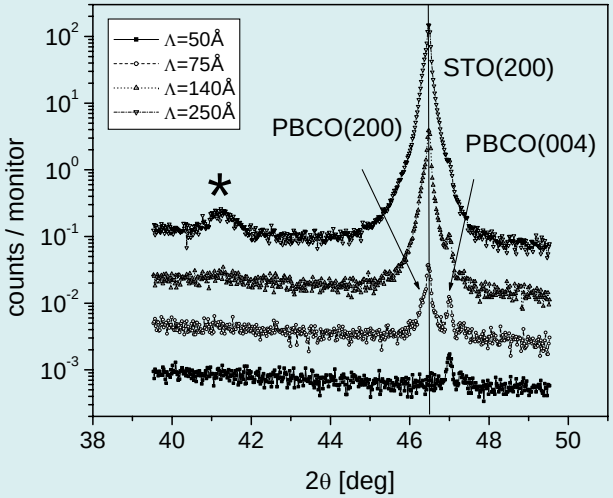
a = 3.90841 Å
b = 3.90521 Å
c = 7.63431 Å

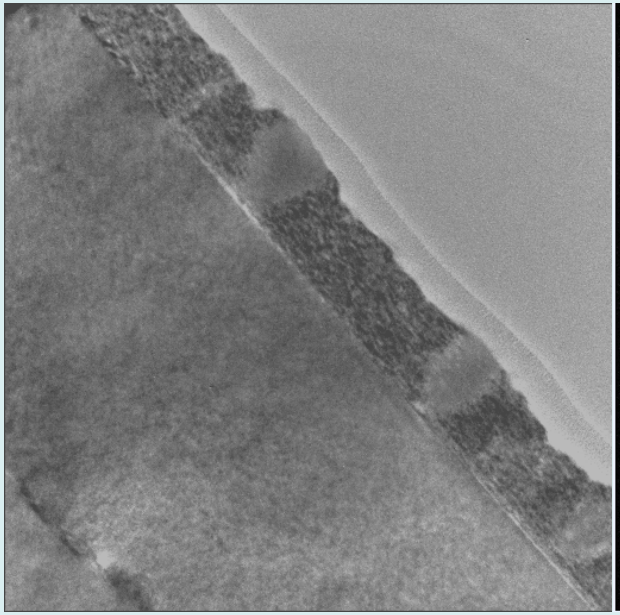
The structure of $PrBaCo_2O_{5+x}$: oxygen, barium, cobalt, and praseodymium atoms are shown as partially shaded, shaded, filled, and gray circles, respectively. The partially occupied oxygen atom sites are shown as cross-hatched circles.

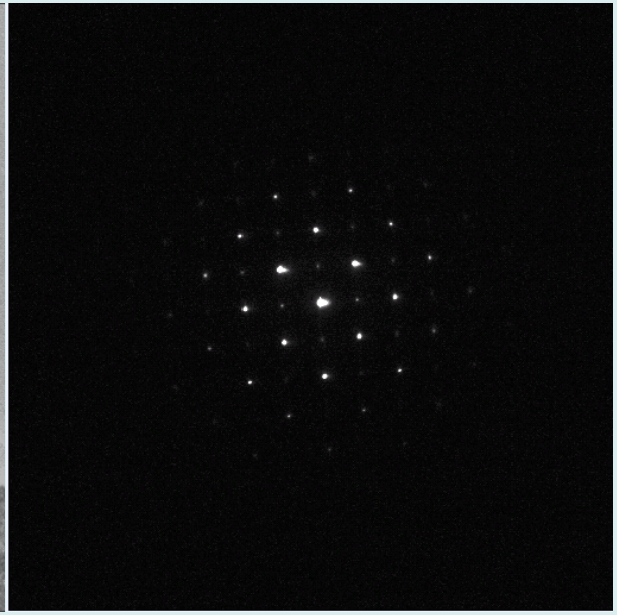
***Appl. Phys. Lett.*, 88 (2006) 024103**

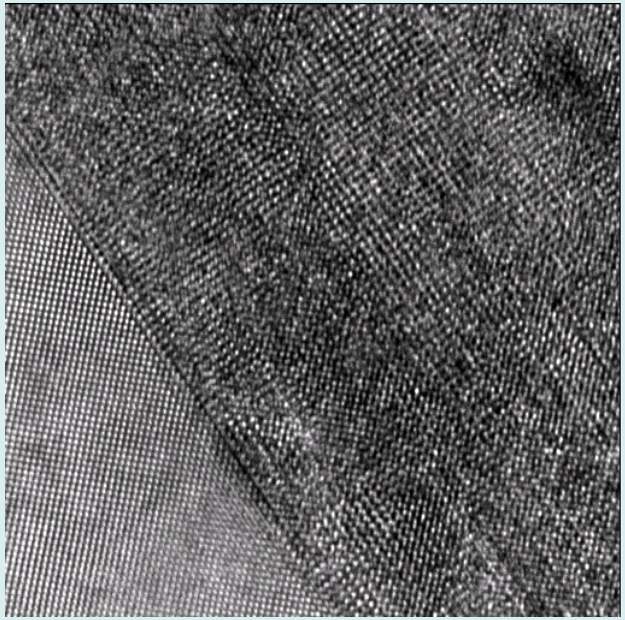
Microstructure and Epitaxial Nature of PBCO





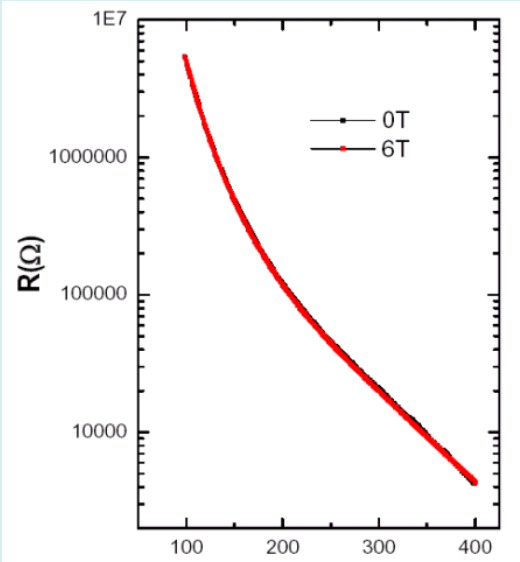


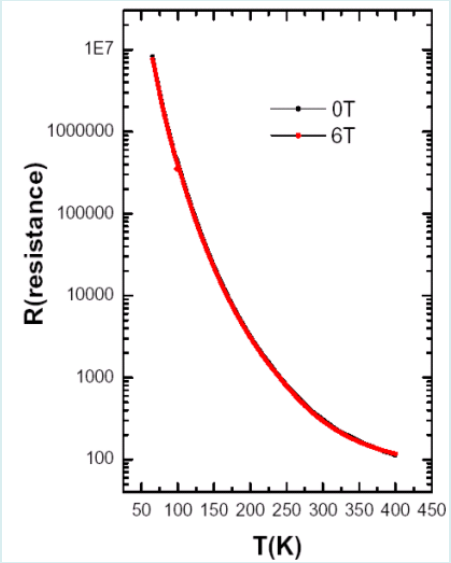


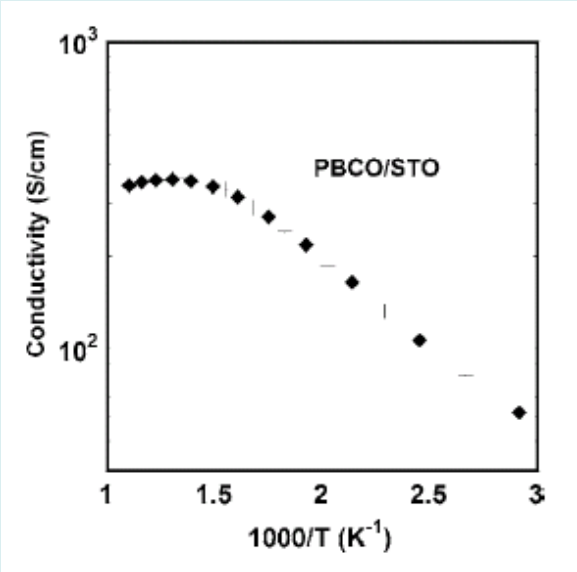


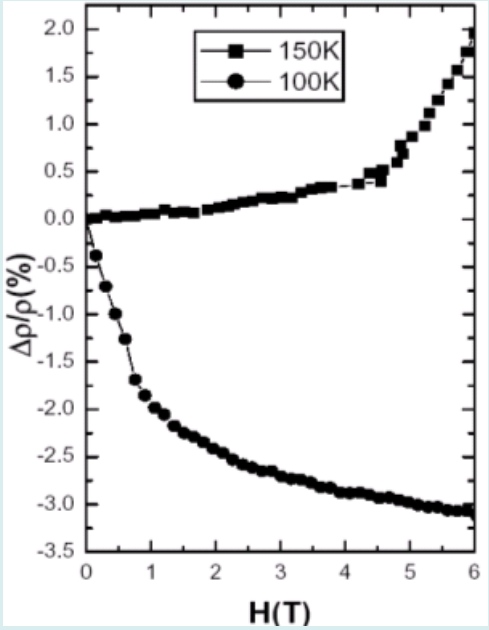
Appl. Phys. Lett., 88 (2006) 024103

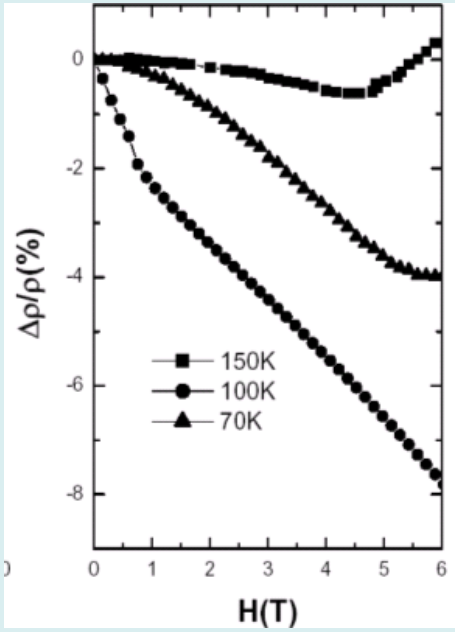
Physical Properties of PBCO Thin Films on STO

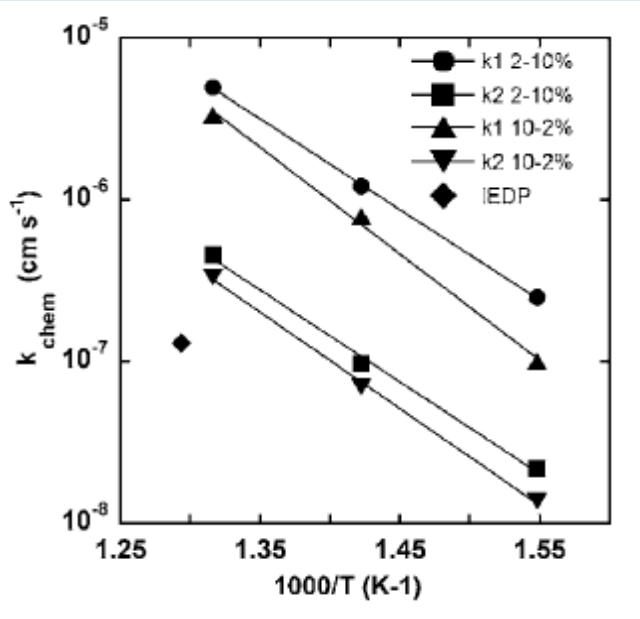






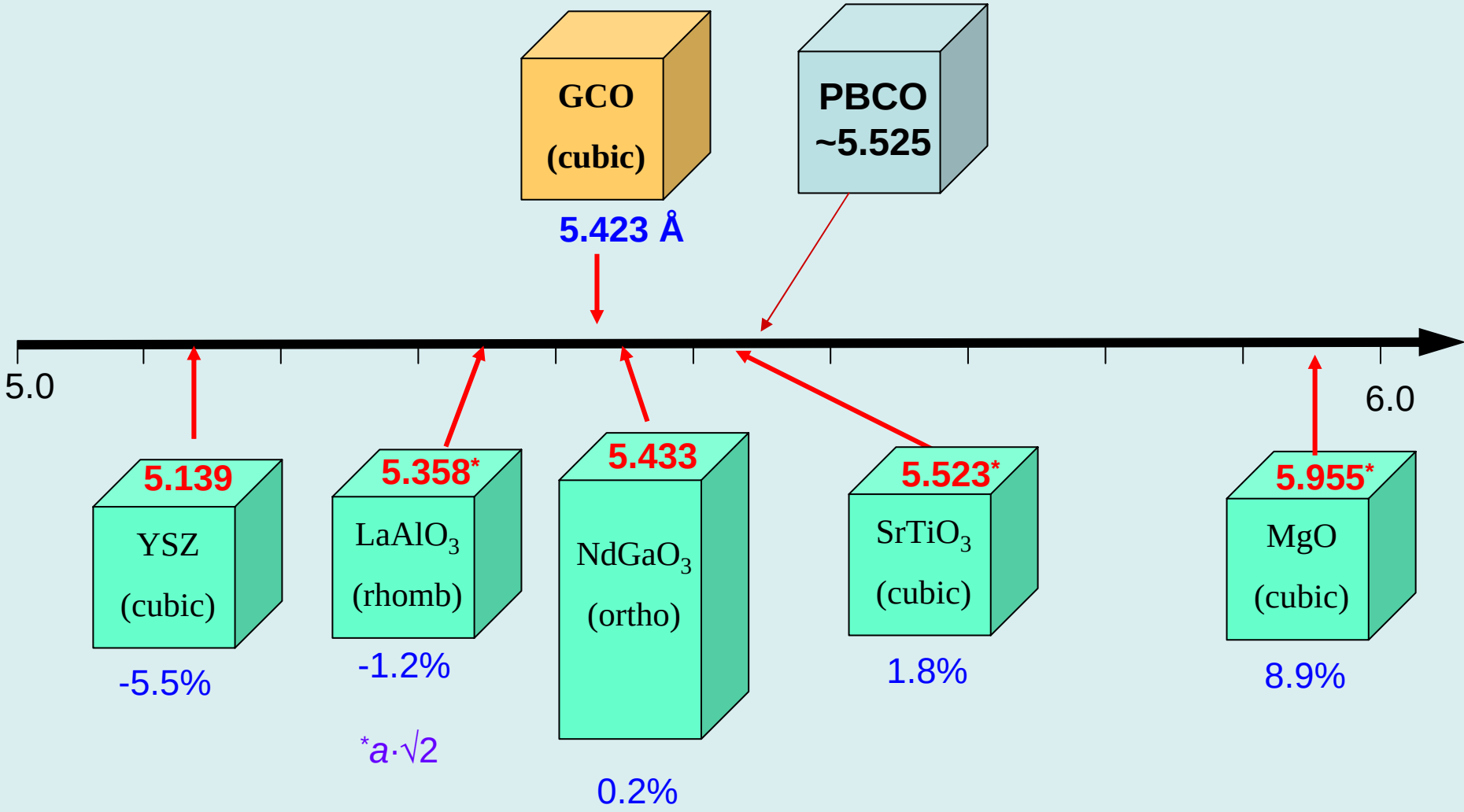




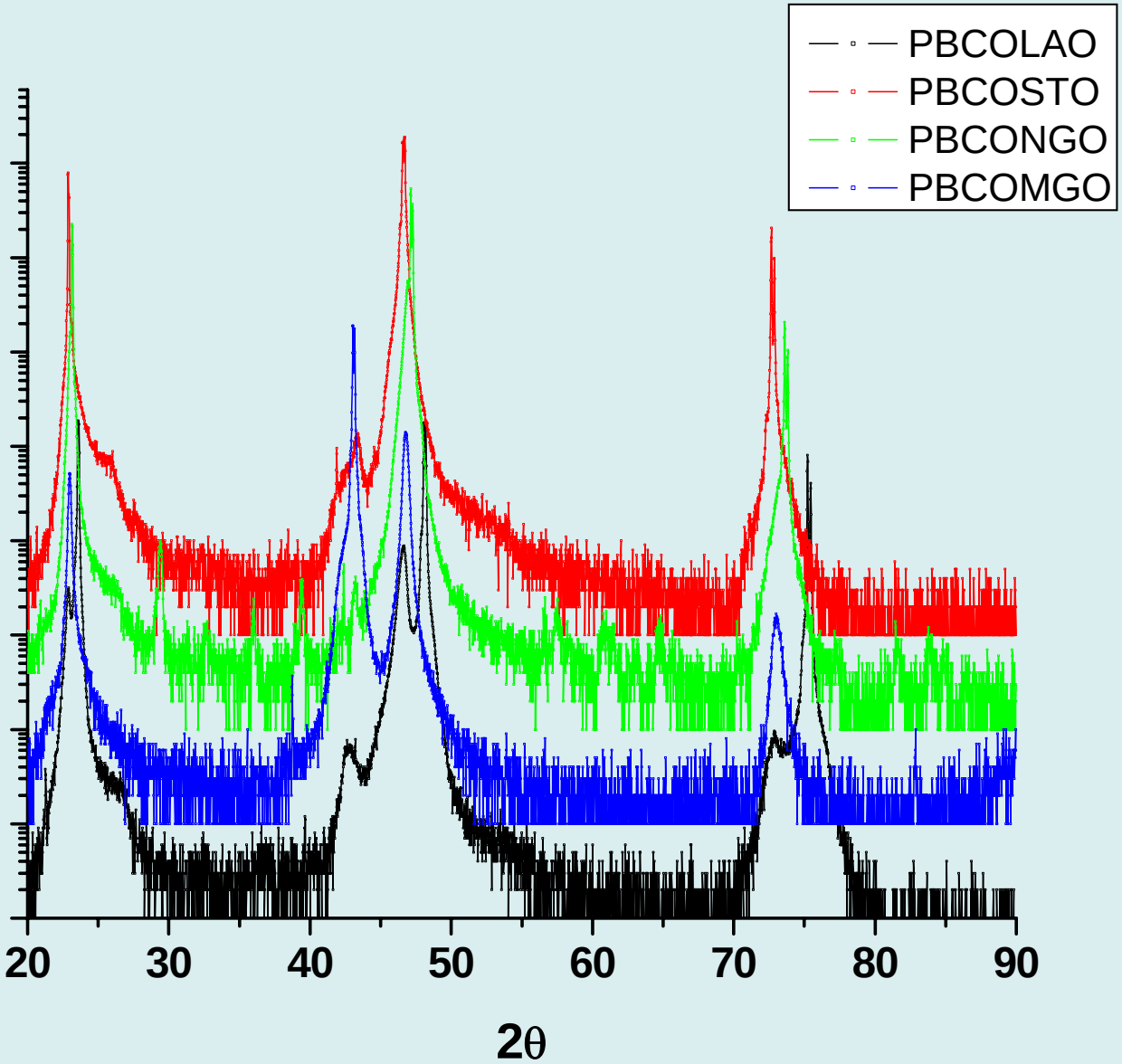


Appl. Phys. Lett., **88** (2006) 024103
Appl. Phys. Lett., **90** (2007) 212111

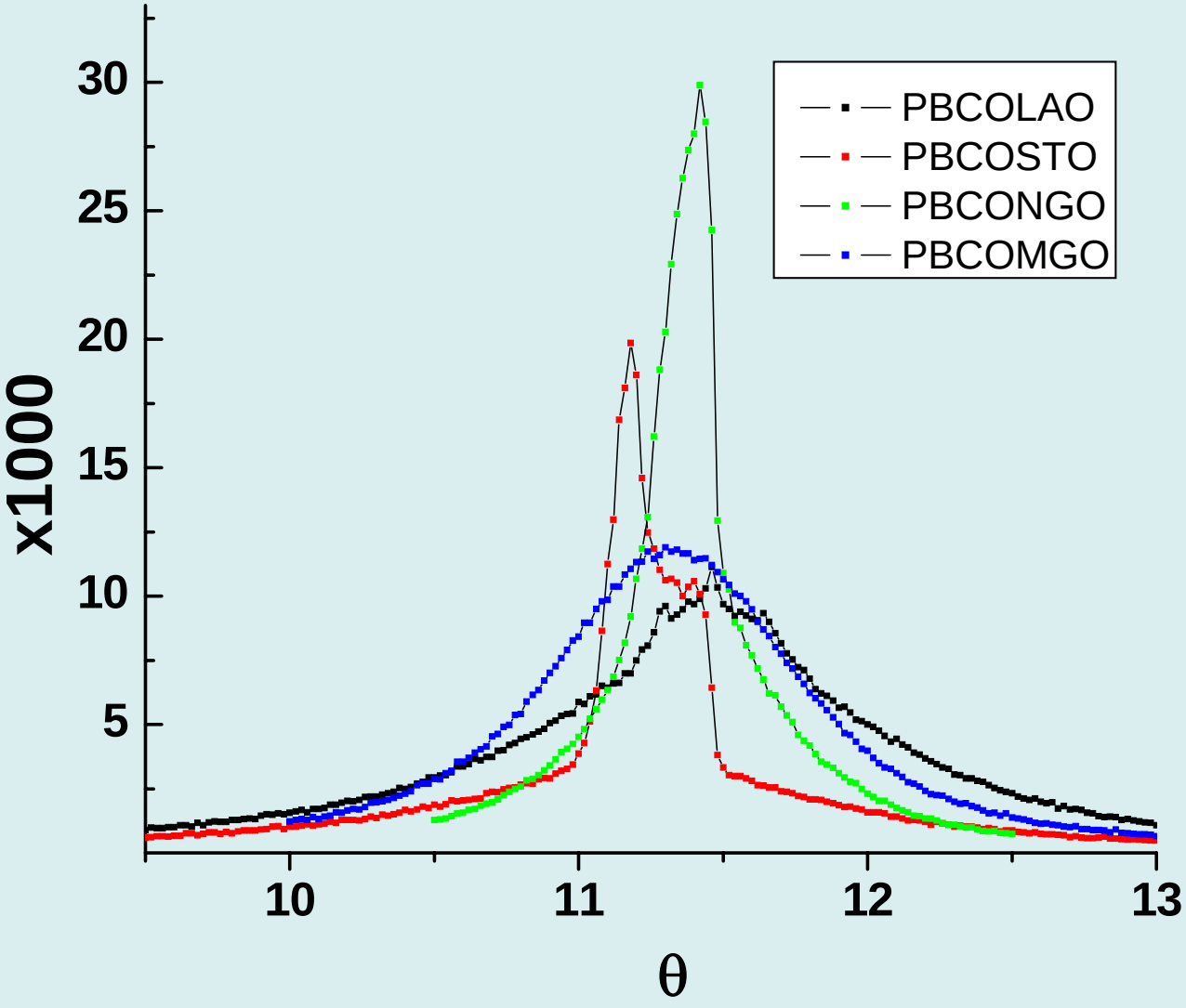
Comparison of Lattice Parameters



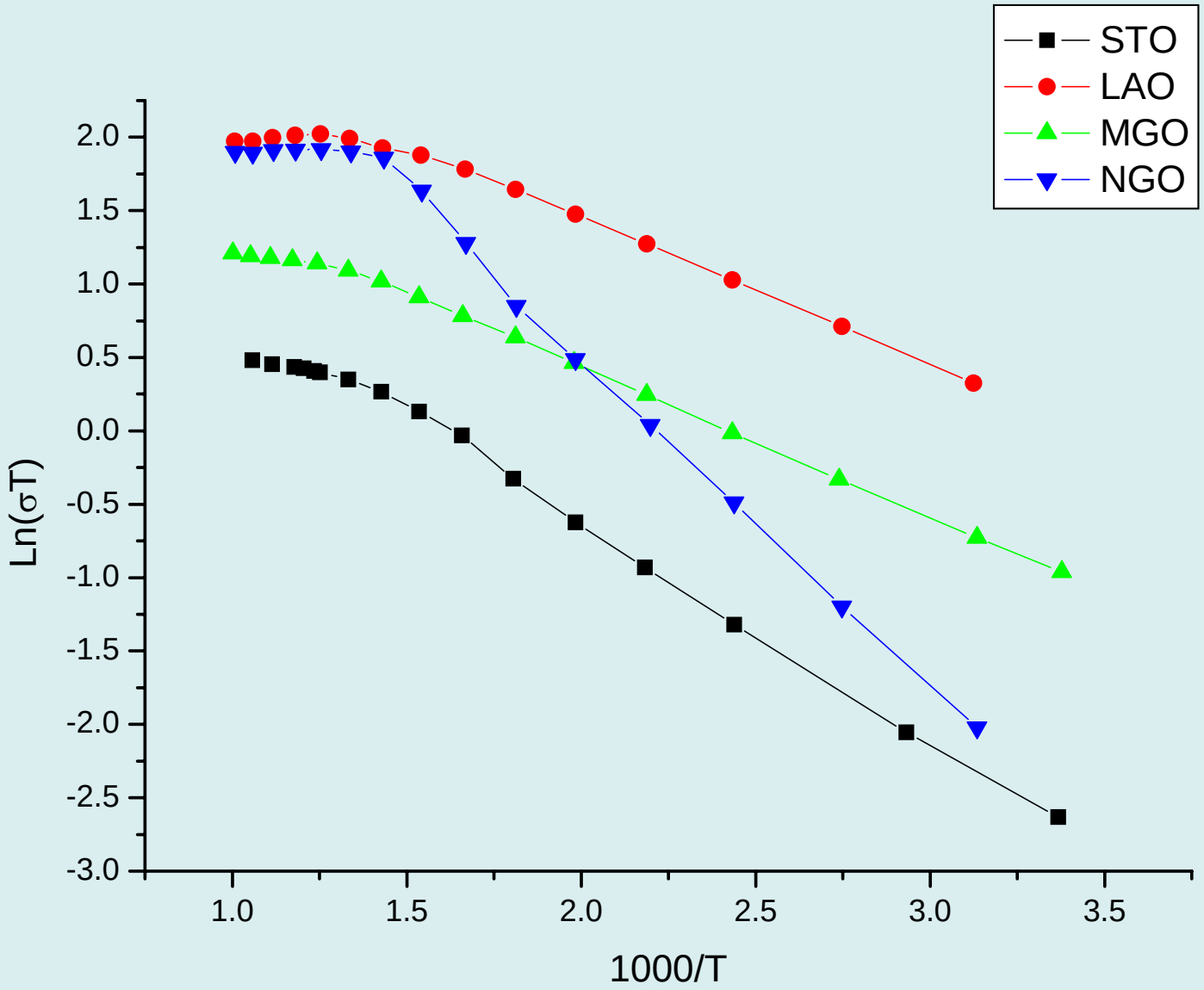
Strain effects on PBCO growth



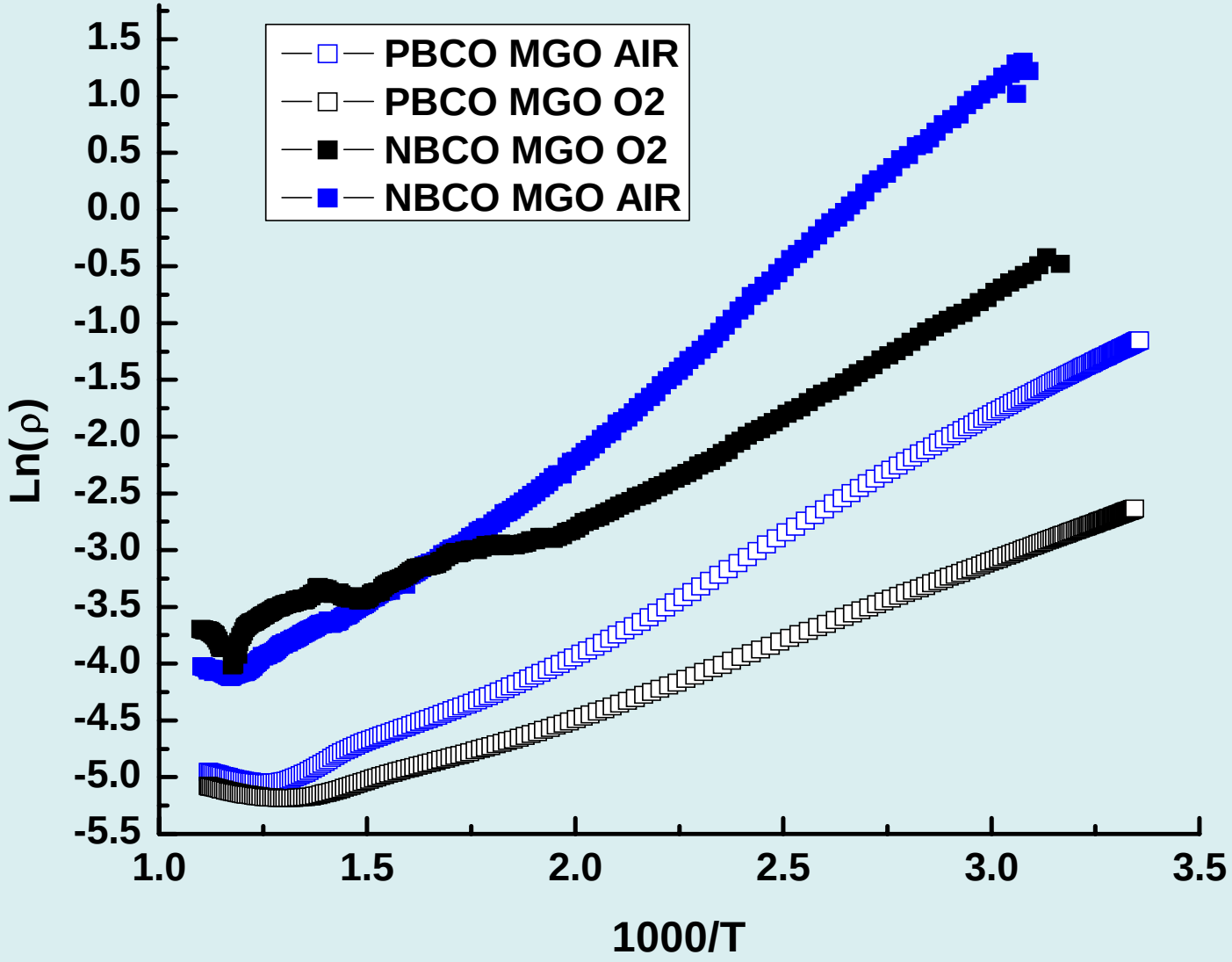
Strain effects on PBCO crystallinity



Strain Effect in PBCO Thin Films



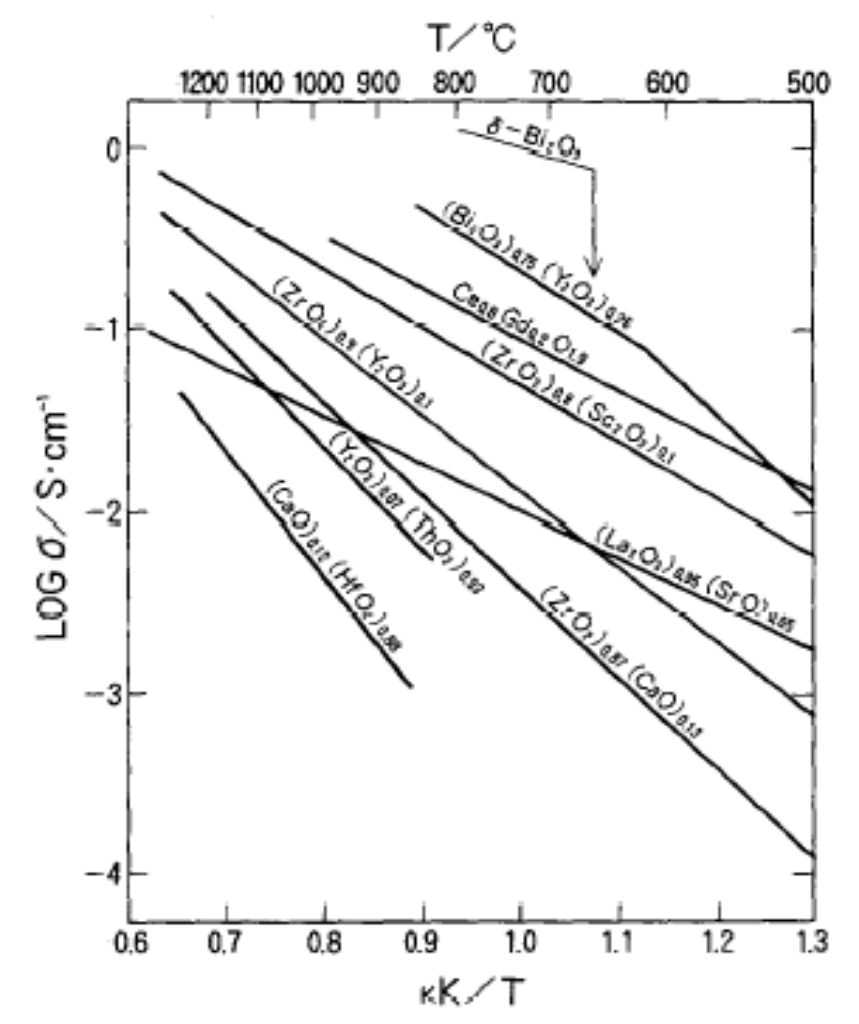
PBCO vs. NBCO on MGO



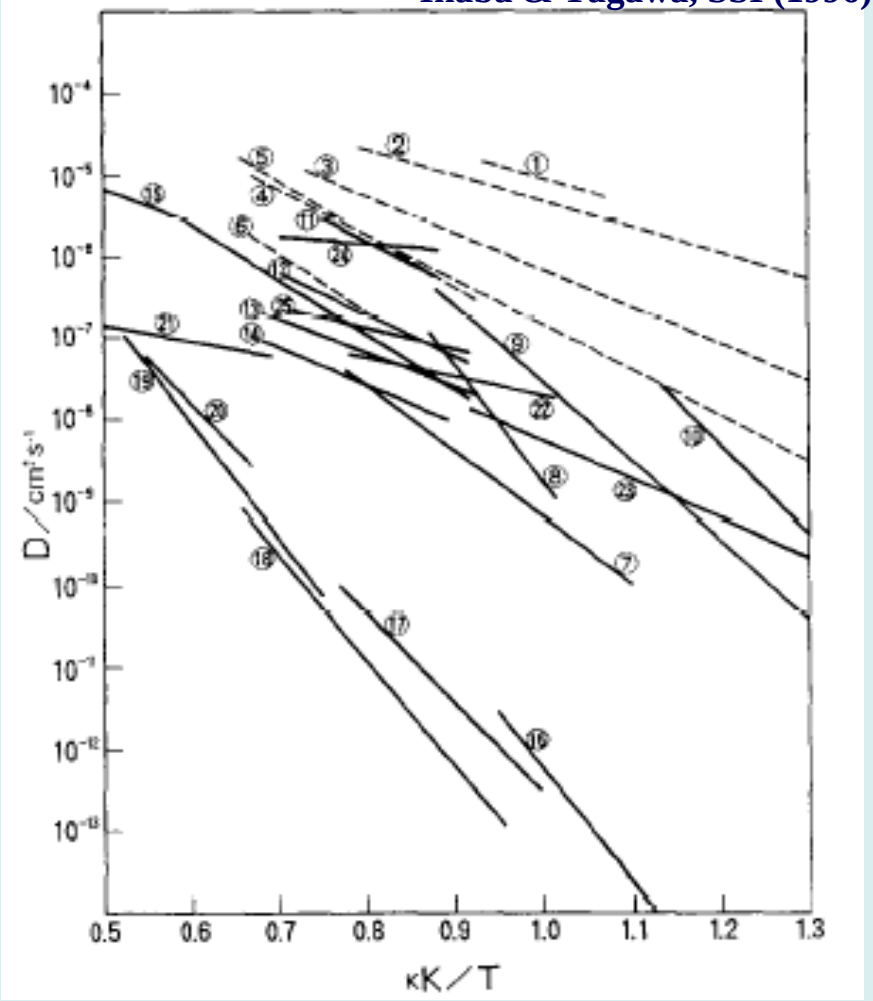
Summary of Cathode Electrodes

- PBCO Oxide thin films provide new important information about gas - solid and solid – solid interfaces for new cathode application
- Strong strain effect has been observed in the PBCO system
  - depend on annealing conditions and dc bias
  - evidence for multiple paths
- In the future, more detailed relations with microstructure, surface structure and composition need to be developed

Properties of Oxide Electrolyte



Inaba & Tagawa, SSI (1996)



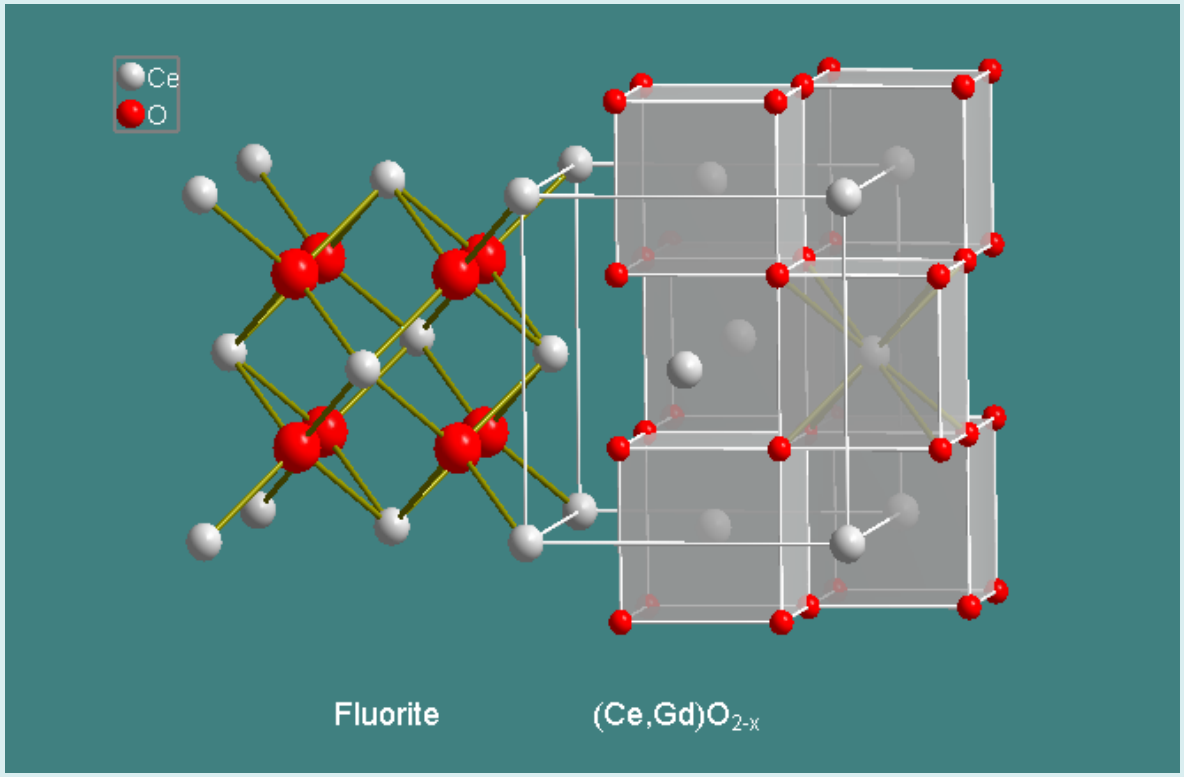
1: δ-Bi_2O_3; 2: $Ce_{1.8}Gd_{0.2}O_{1.9}$; 3: $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$; 4: $(CaO)_{0.13}(ZrO_2)_{0.87}$; 5: $(ThO_2)_{0.93}(Y_2O_3)_{0.07}$; 6: $(CaO)_{0.12}(HfO_2)_{0.87}$; 7: $Zr_{0.85}Ca_{0.15}O_{1.85}$; 8: CaF_2; 9: BaF_2; 10: $SrCl_2$; 11: $Ce_{0.6}Y_{0.4}O_{1.8}$; 12: $Ce_{0.8}Y_{0.2}O_{1.9}$; 13: $Ce_{0.9}Y_{0.1}O_{1.95}$; 14: CeO_2; 15: $Zr_{0.85}Ca_{0.15}O_{1.85}$; 16: UO_2; 17: PuO_2; 18: UO_2; 19: ThO_2; 20: ThO_2; 21: UO_{2-x}; 22: PuO_{2-x}; 23: UO_{2+x}; 24: CeO_2; 25: $CeO_{1.92}$

Multilayered thin film electrolytes

Oxide Conductors

Fluorites $(M,Zr)O_{2-x}$, M=Ca,Y,Sc and $(M,Ce)O_{2-x}$, M=Sm,Gd

Perovskites $(La,Sr)(Mg,Ga)O_{3-x}$



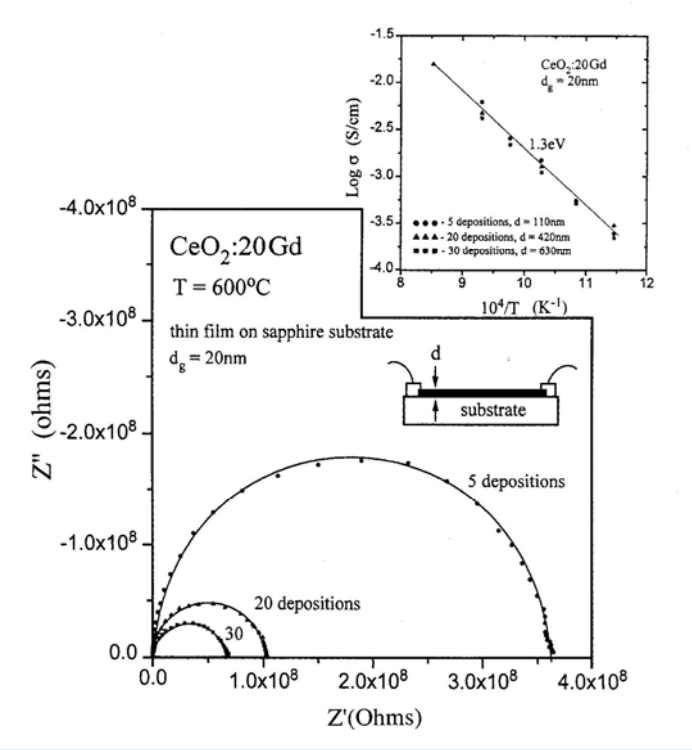
Thin film electrolytes

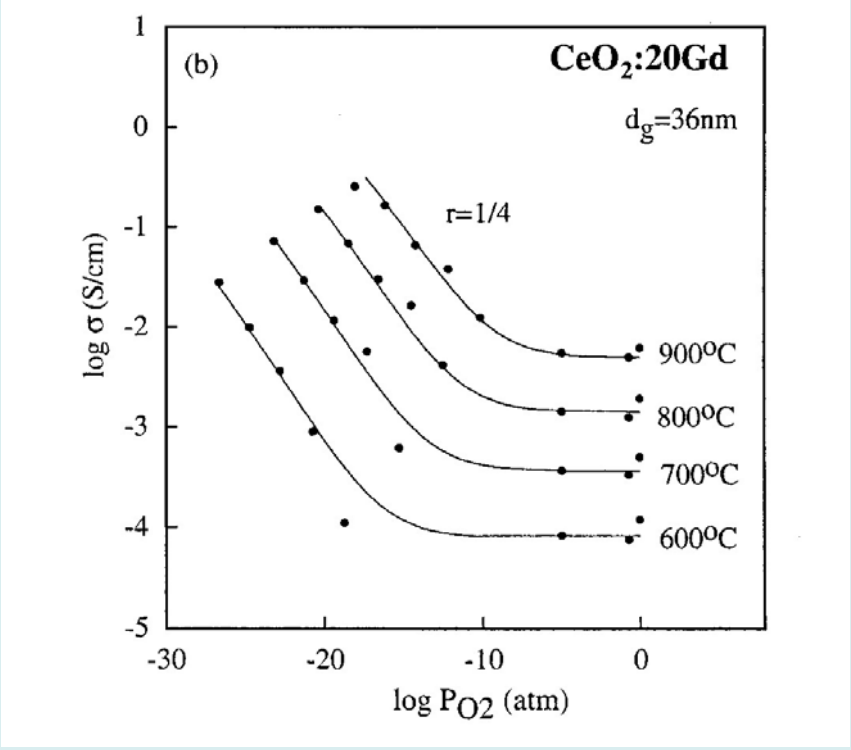
- GCO is candidate electrolyte for intermediate temperature (450 ^{o}C - 650 ^{o}C) SOFCs
- The GCO oxygen-ion conductivity is greater than YSZ:
  - $Gd_{0.2}Ce_{0.9}O_{1.9}$: σ = 35 mS cm^{-1} at 600 ^{o}C, YSZ : σ < 5 mS cm^{-1}
- Thin films reduce ohmic resistance in the electrolyte
- Integrate thin film fuel cells with MEMS
  - (e.g. Jankowski *et al.* US Pat. Appl. 2003/0039874 AI 2003)

Highly Ionic Conductive Gd:CeO_2

📖 GCO is good solid electrolyte at **intermediate** temperature 500ºC-700ºC

📖 The **oxygen-ion conductivity** is better than YSZ (such as $Ce_{0.8}Gd_{0.2}O_{1.9}$ is 35 mS cm^{-1} at 600ºC, YSZ is less than 5 mS cm^{-1})



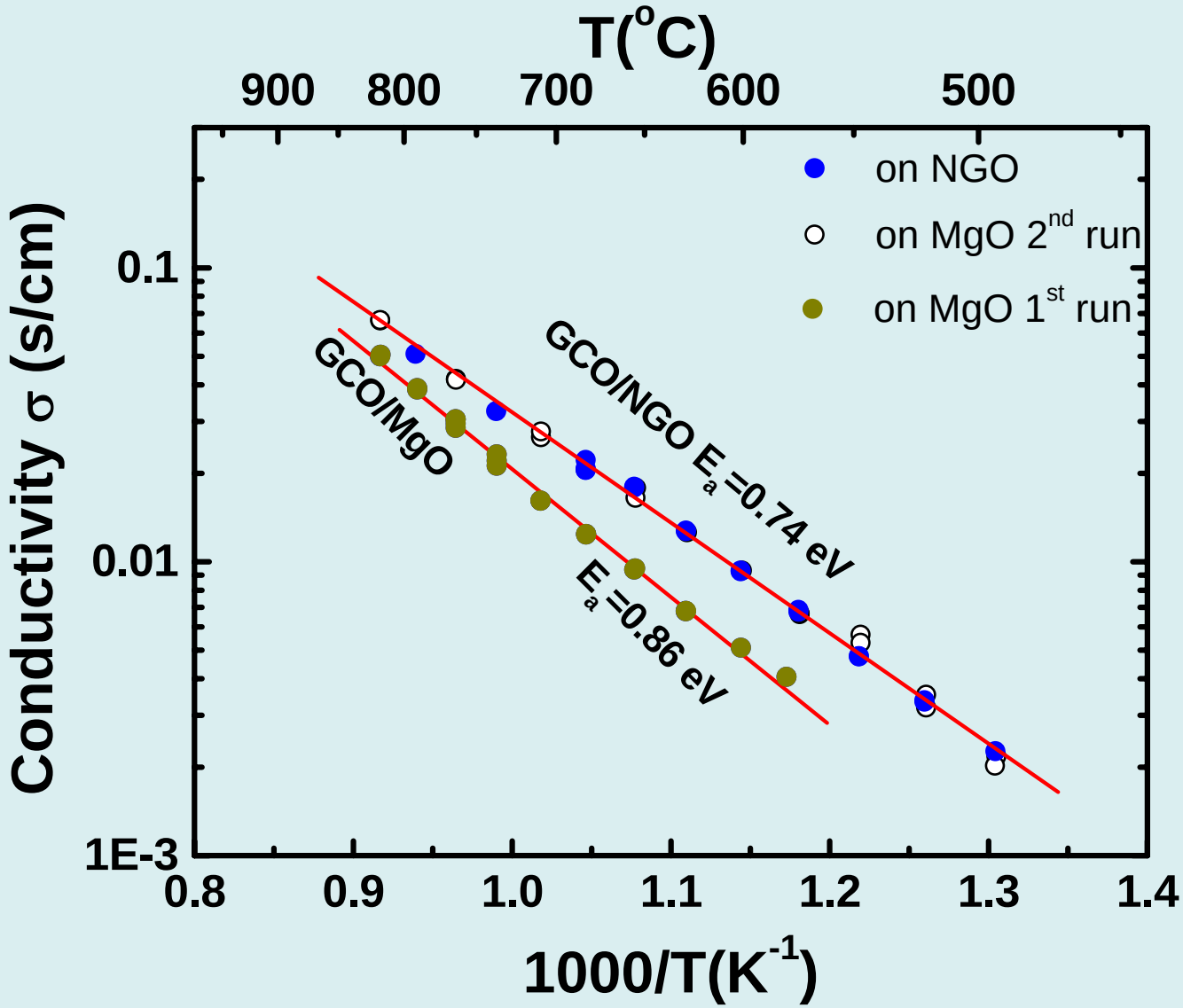


H. Inaba, H. Tagawa, Solid State Ionics 83 (1996) 1-16

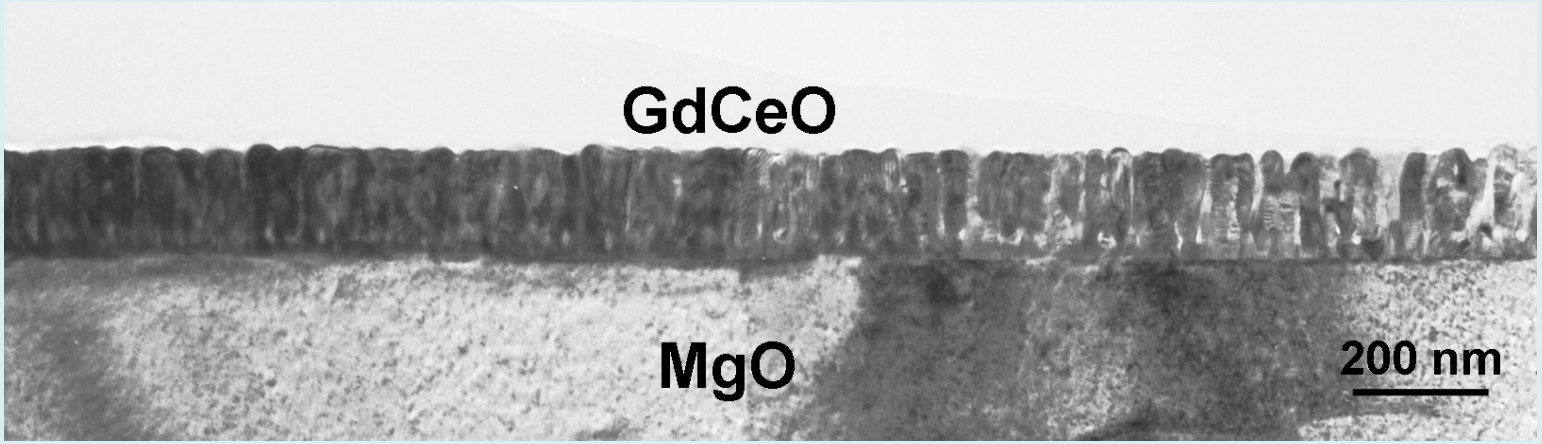
B.C.H. Steele, Solid State Ionics 129 (2000) 95-110

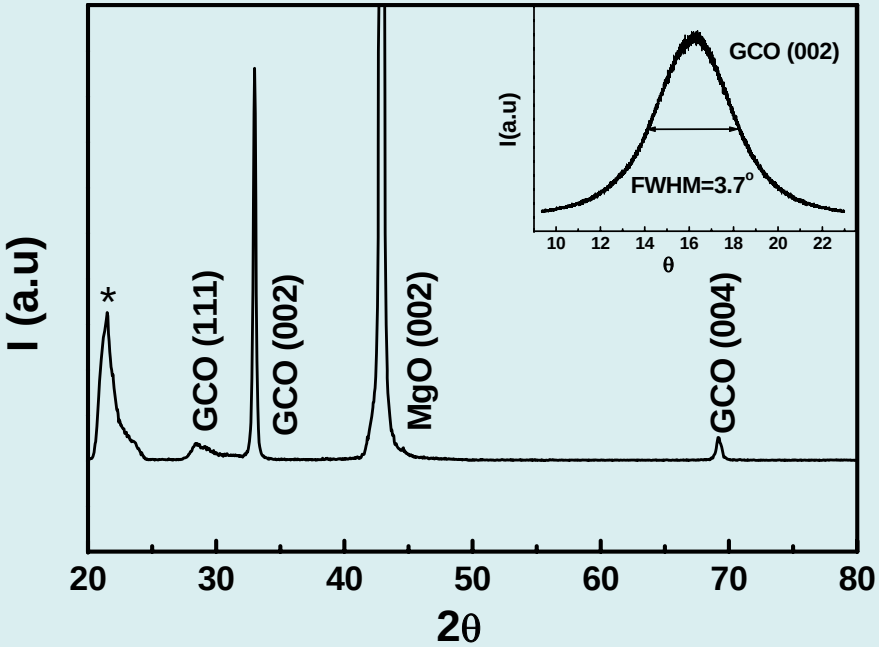
H.U. Anderson, Solid State Ionics 151(2002) 111-121

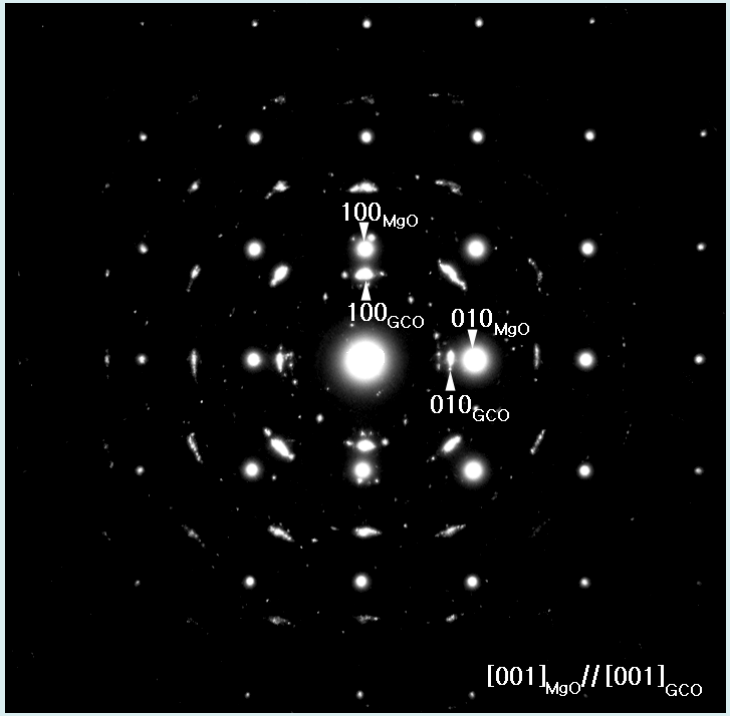
Electrical conductivity of GCO/MgO



Epitaxial Behavior of GCO/NGO (9.1%)



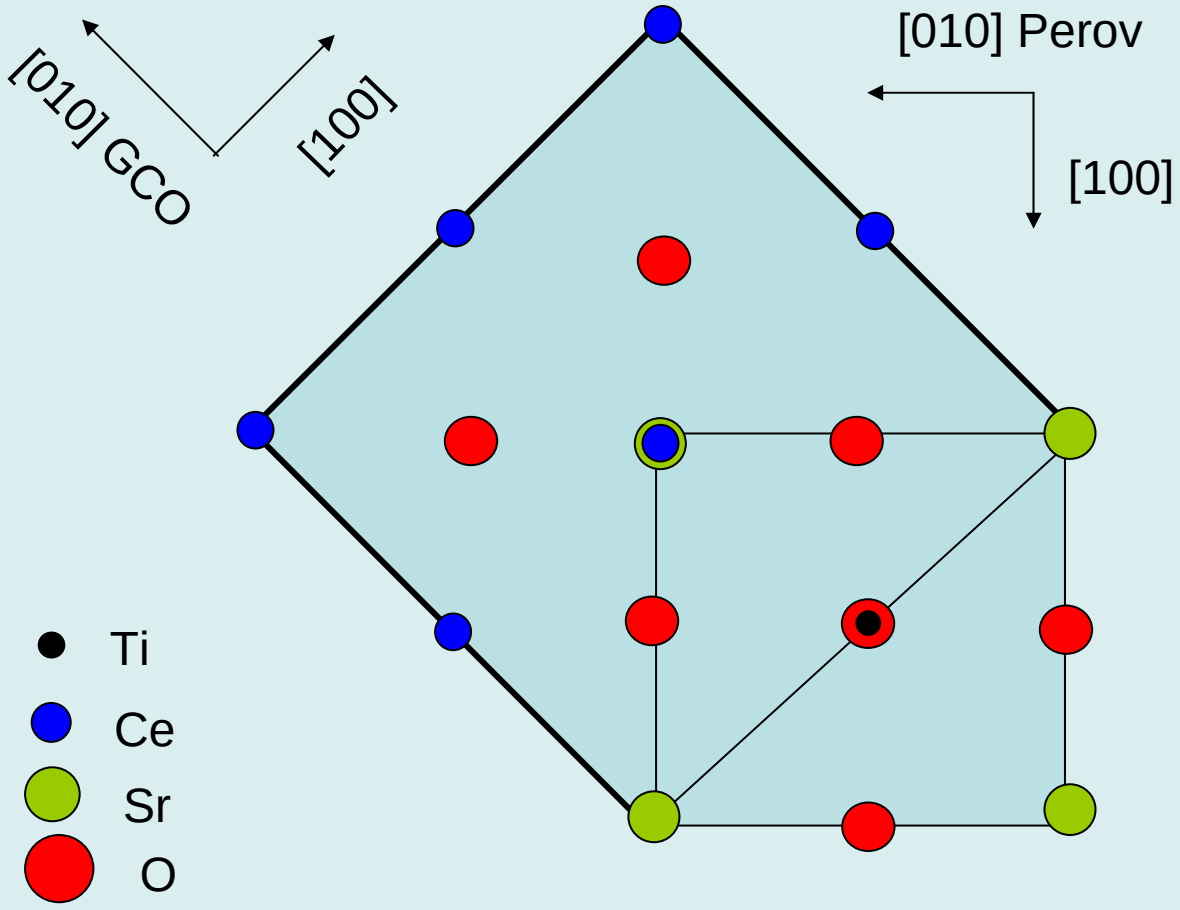




the mismatch are found to be –28.8%

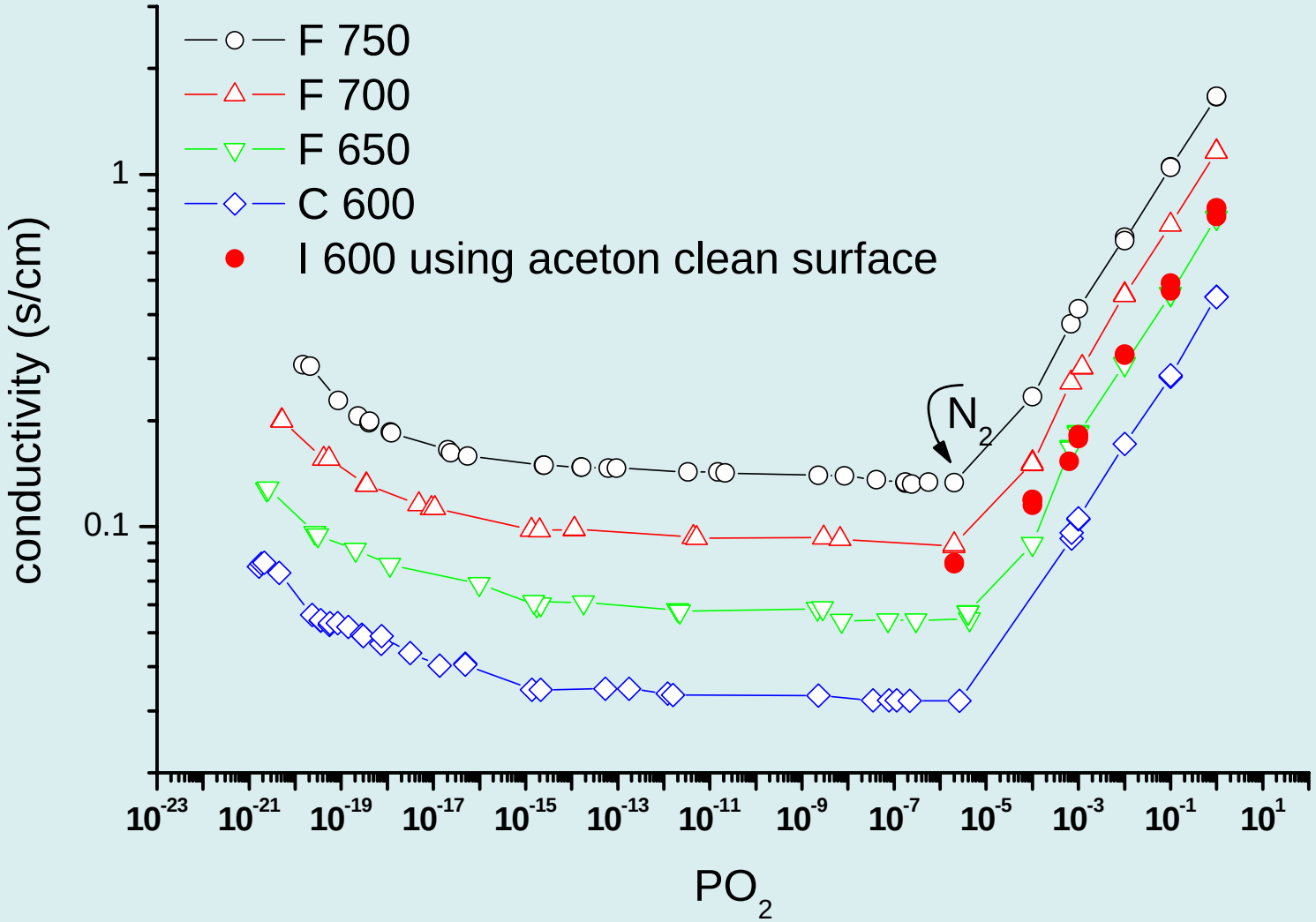
Solid State Ionics, **175** (2004) 103

Epitaxial Relationships of $Gd:CeO_2$



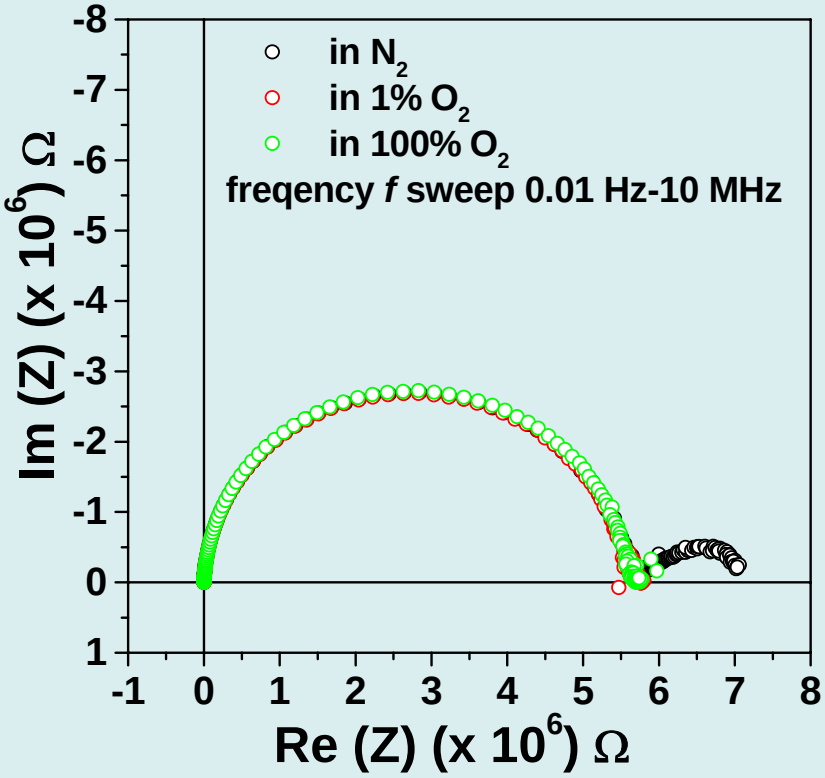
Solid State Ionics, **175** (2004) 103

Oxygen partial pressure dependence of σ for GCO/LAO

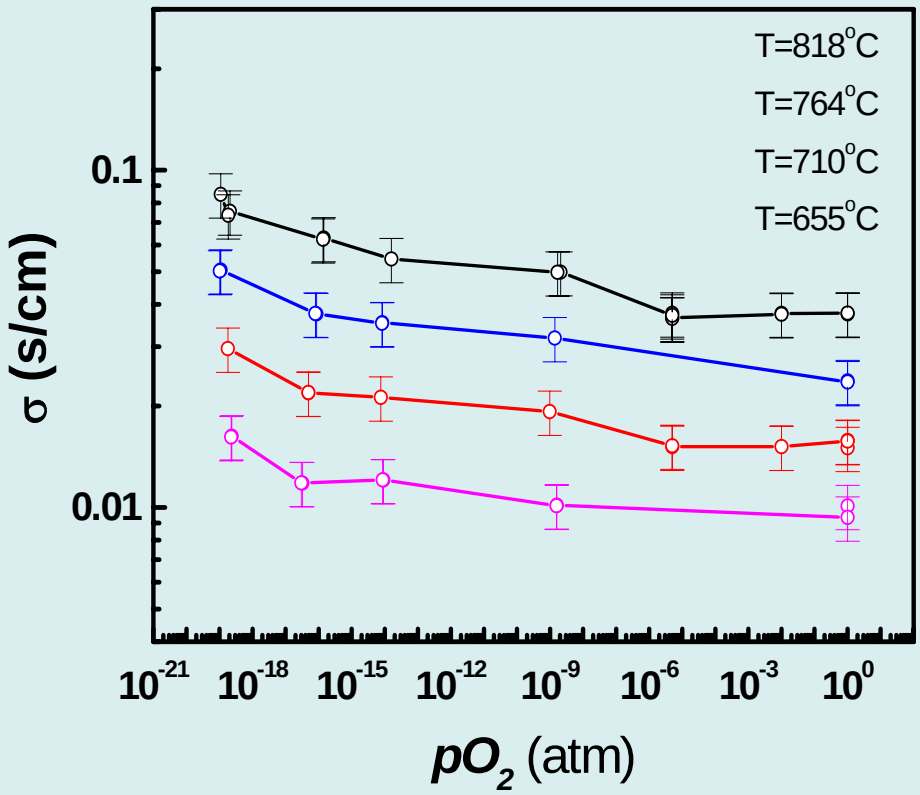


Solid State Ionics, **175** (2004) 103

Impedance Spectrum of GCO on MgO



GCO/MgO IS at T=710°C



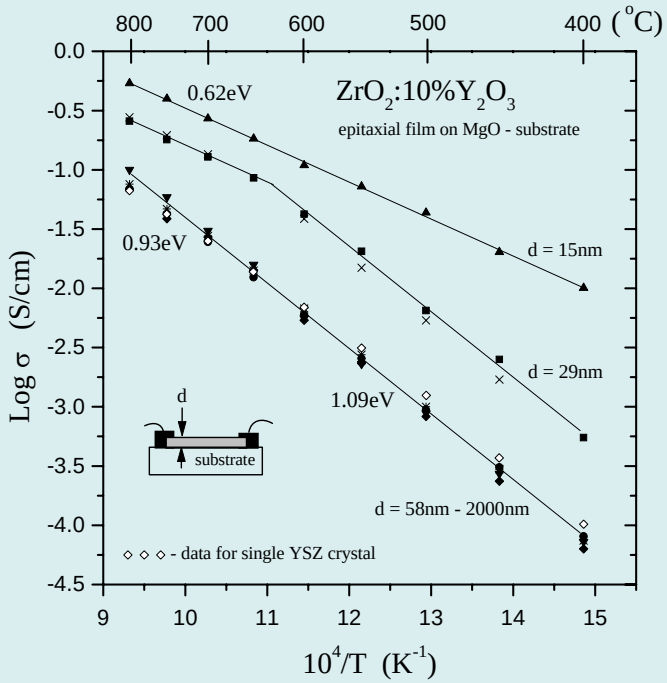
GCO/MgO conductivity oxygen partial pressure dependence

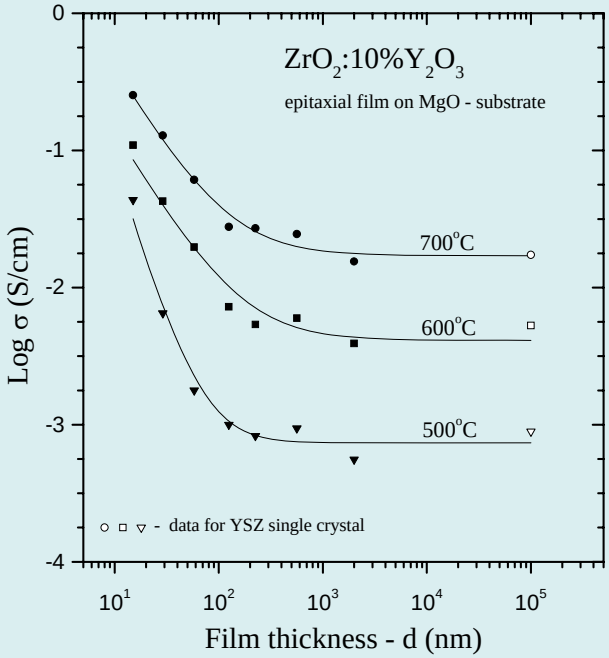
Solid State Ionics, **175** (2004) 103

YSZ on MgO

Enhanced Ionic Conductivity in Nanoscale YSZ Films

Igor Kosacki,* Christopher M. Rouleau,† Paul F. Becher,*James Bentley,* and Douglas H. Lowndes,†
*Metals and Ceramics Division,
†Condensed Matter Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831





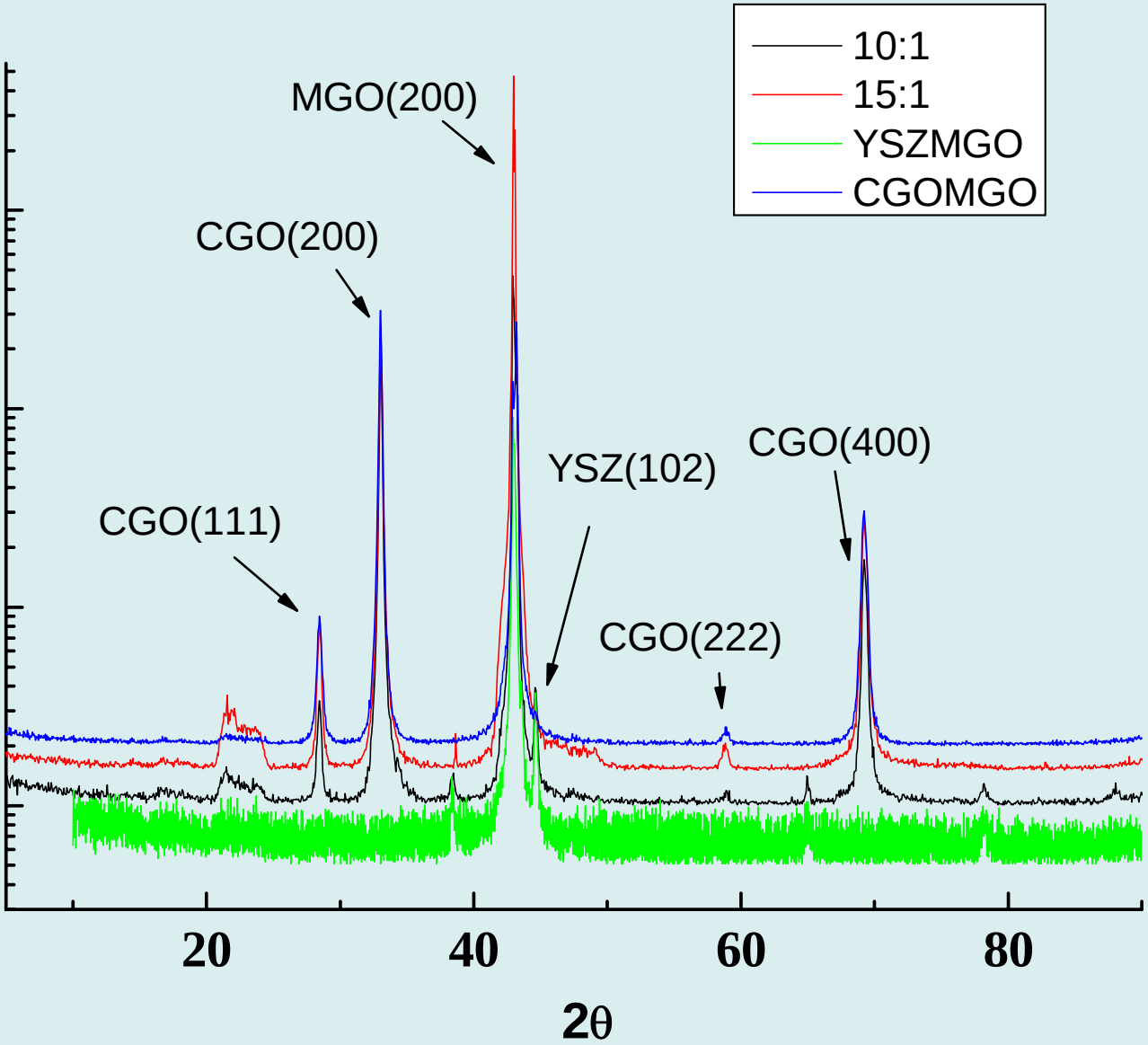
Thickness-dependent conductivity of YSZ films. A dramatic increase in conductivity with decreasing film thickness occurs for films having thicknesses < 100 nm, as shown here for selected temperatures in the range of interest.

Approach for new electrolyte structures

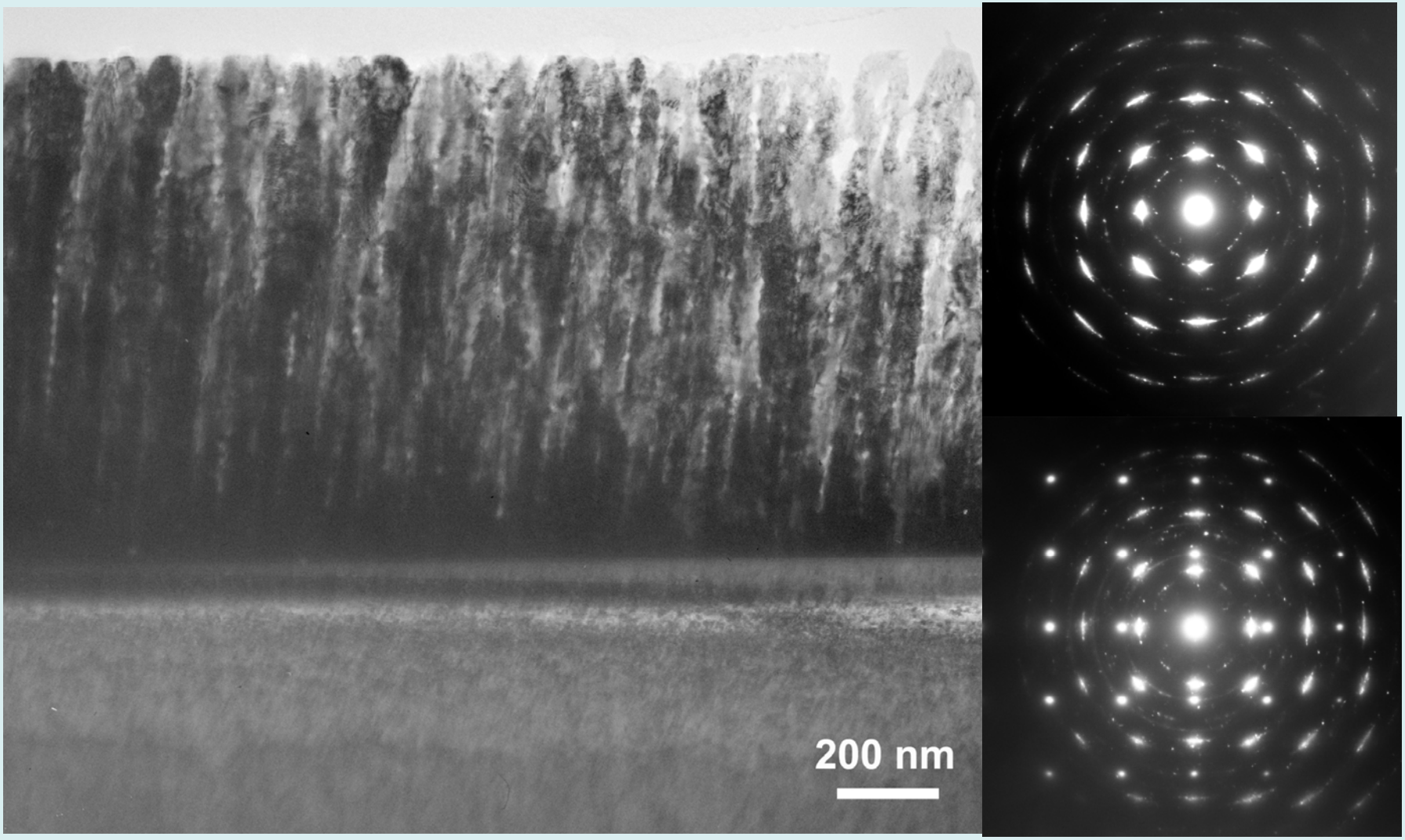
- Prepare GCO/YSZ multilayered thin films with various combinations.
- Investigate the effects of different combination effects on the ionic conductivity
- Optimize the combination conditions and determine the ionic and electronic conductivity in the structures.

Different substrates ⇒ microstructure ⇒ **e**lectrical conductivity

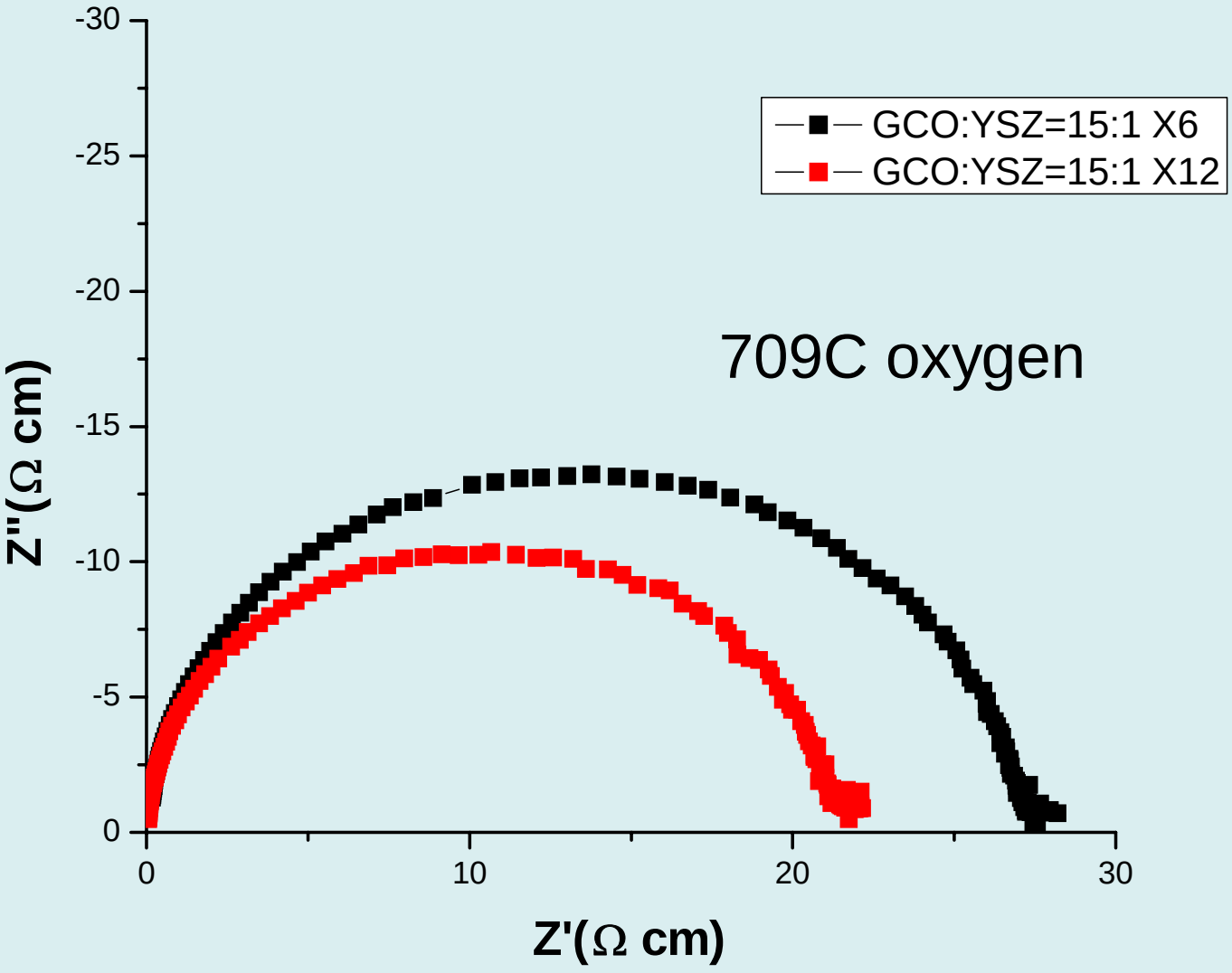
X-ray diffraction of GCO/YSZ Multilayers



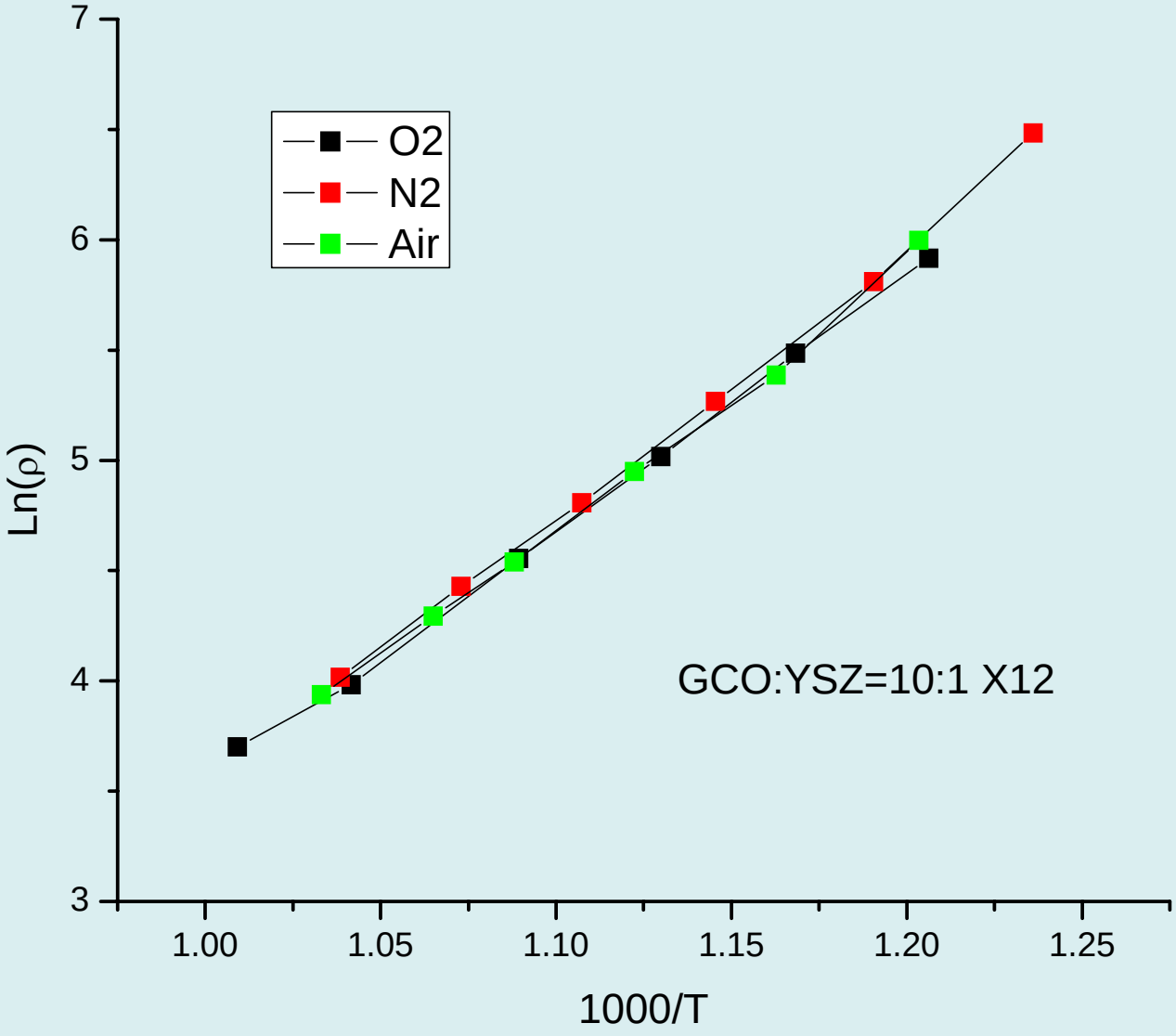
TEM study of multilayered films



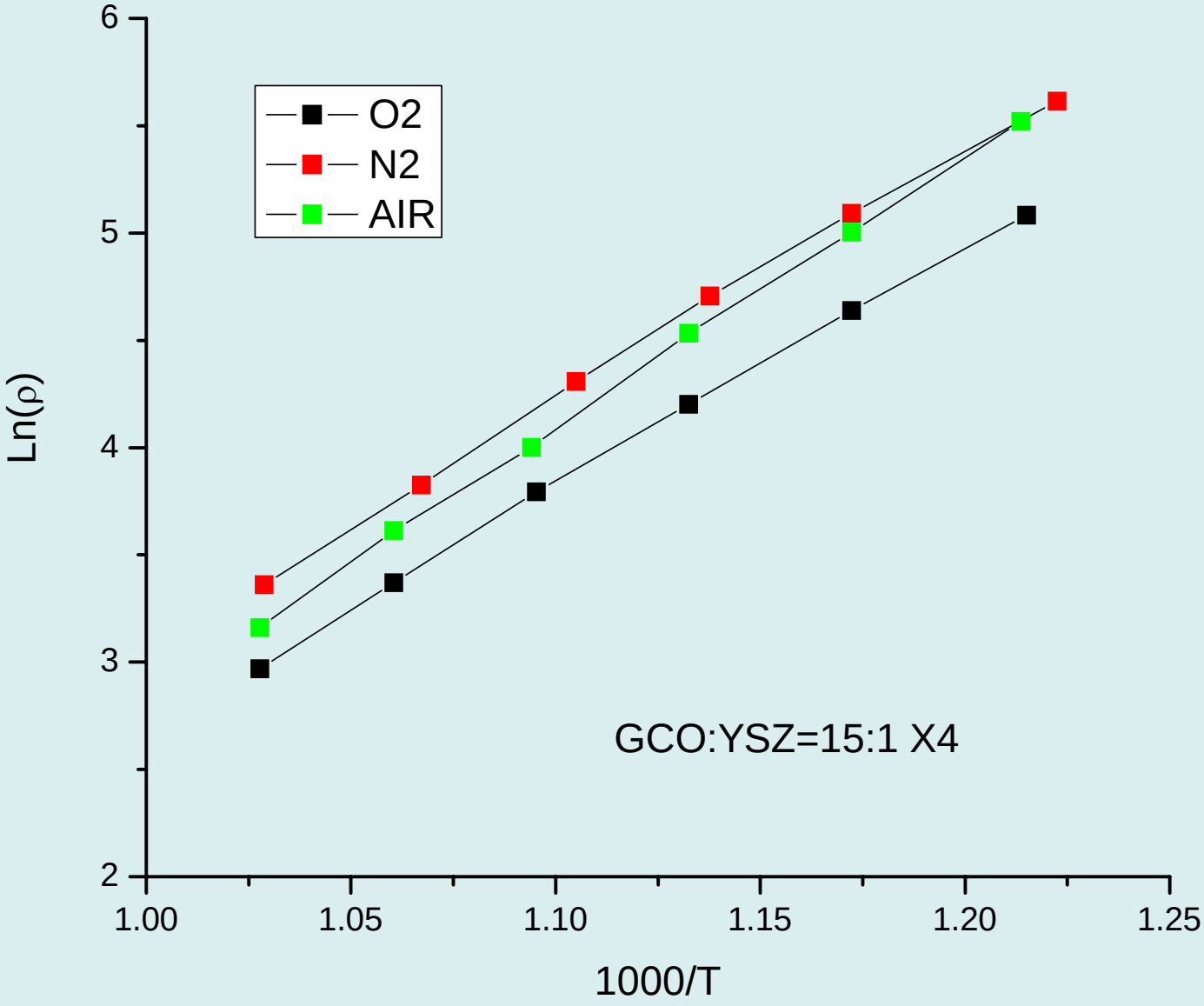
Impedance study of multilayered films



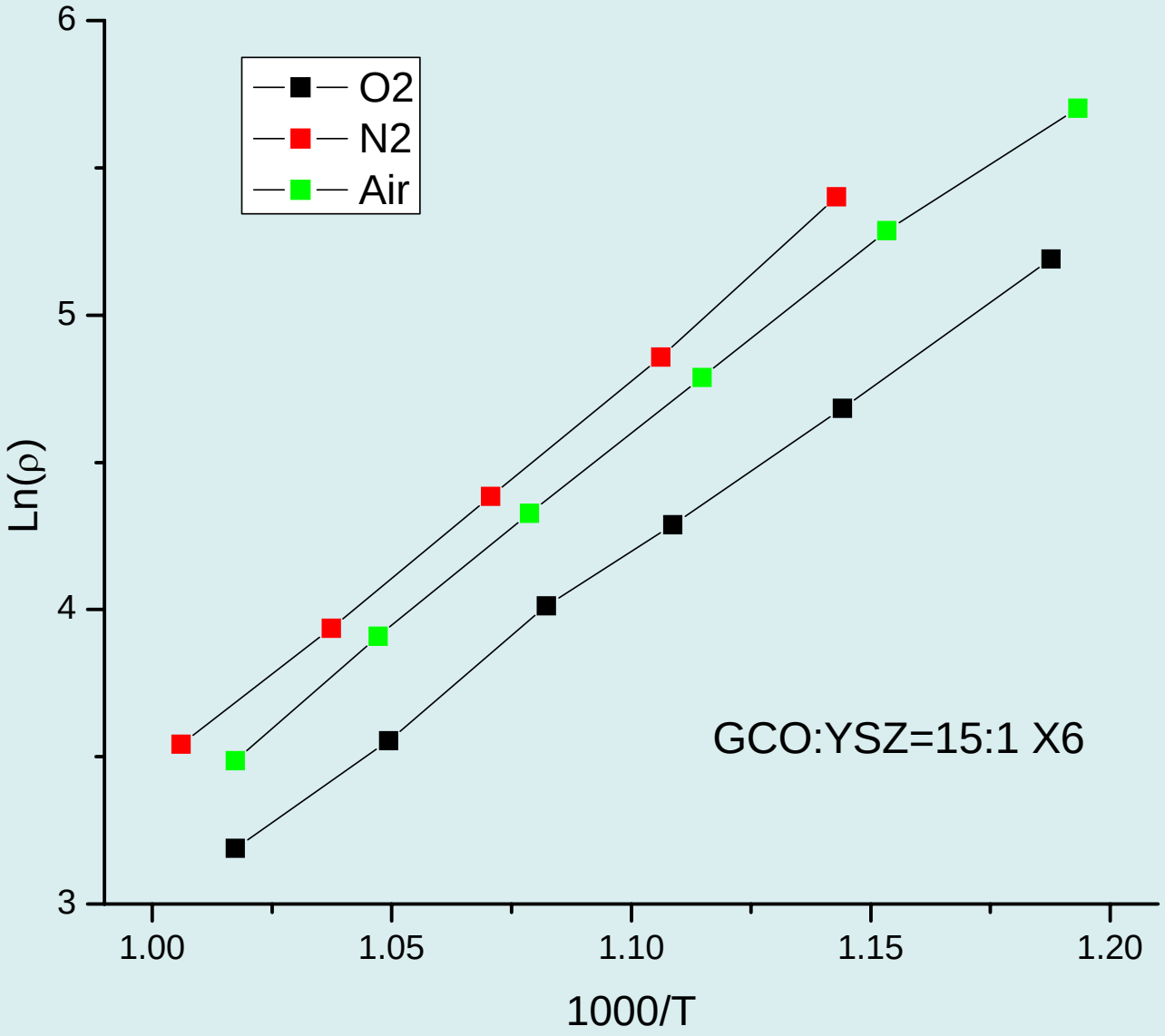
Conductivity study of multilayered films



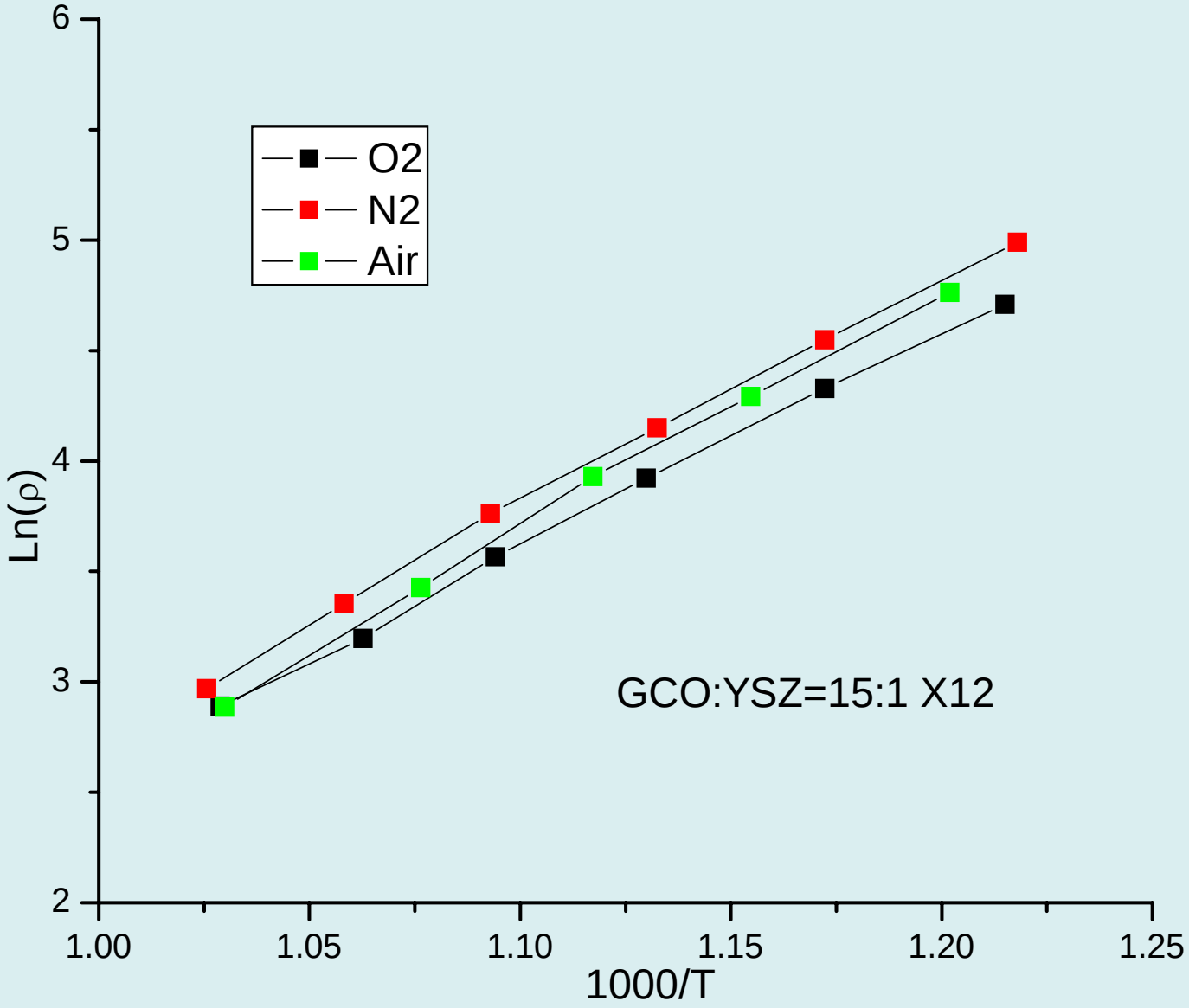
Conductivity study of multilayered films



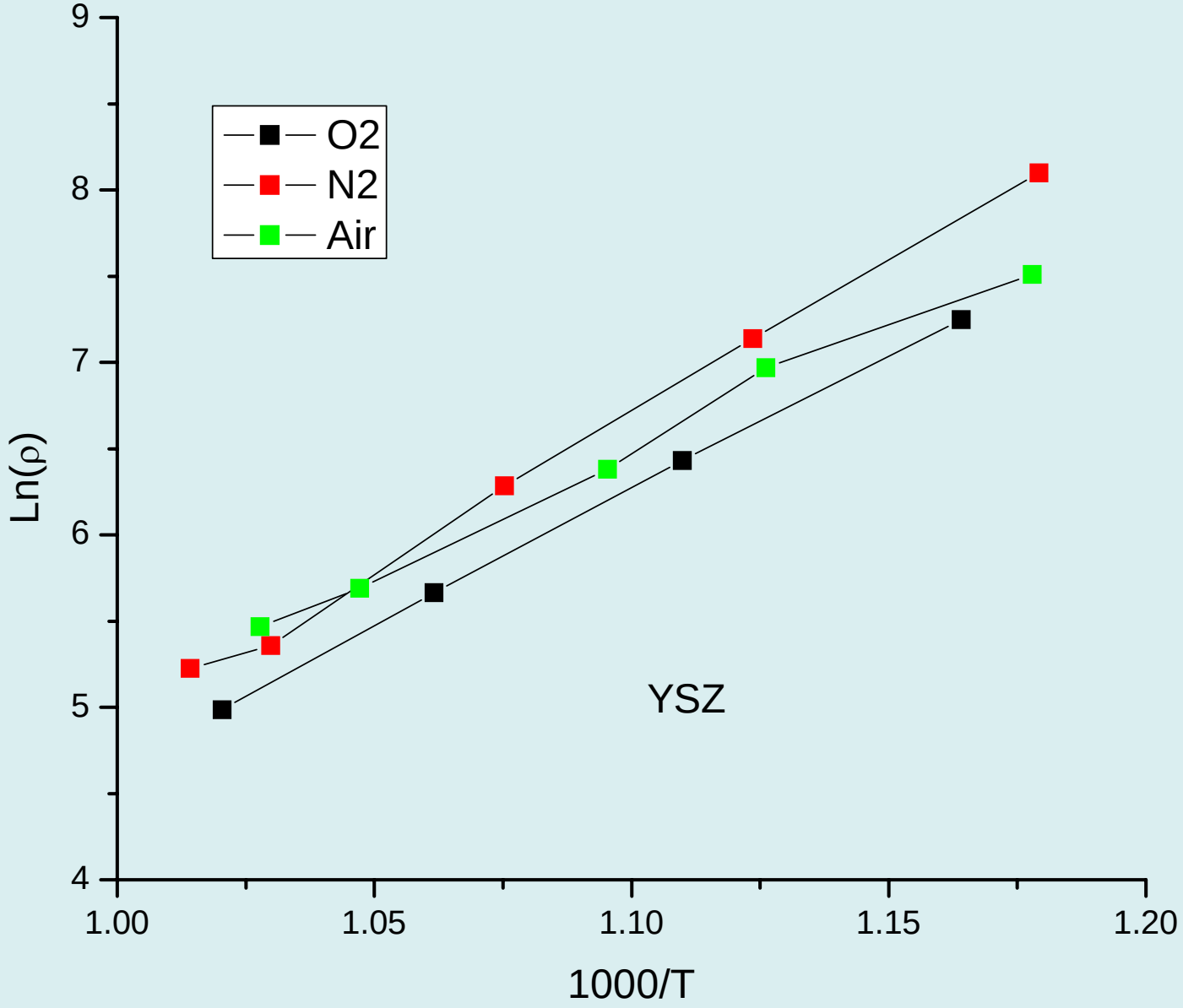
Conductivity study of multilayered films



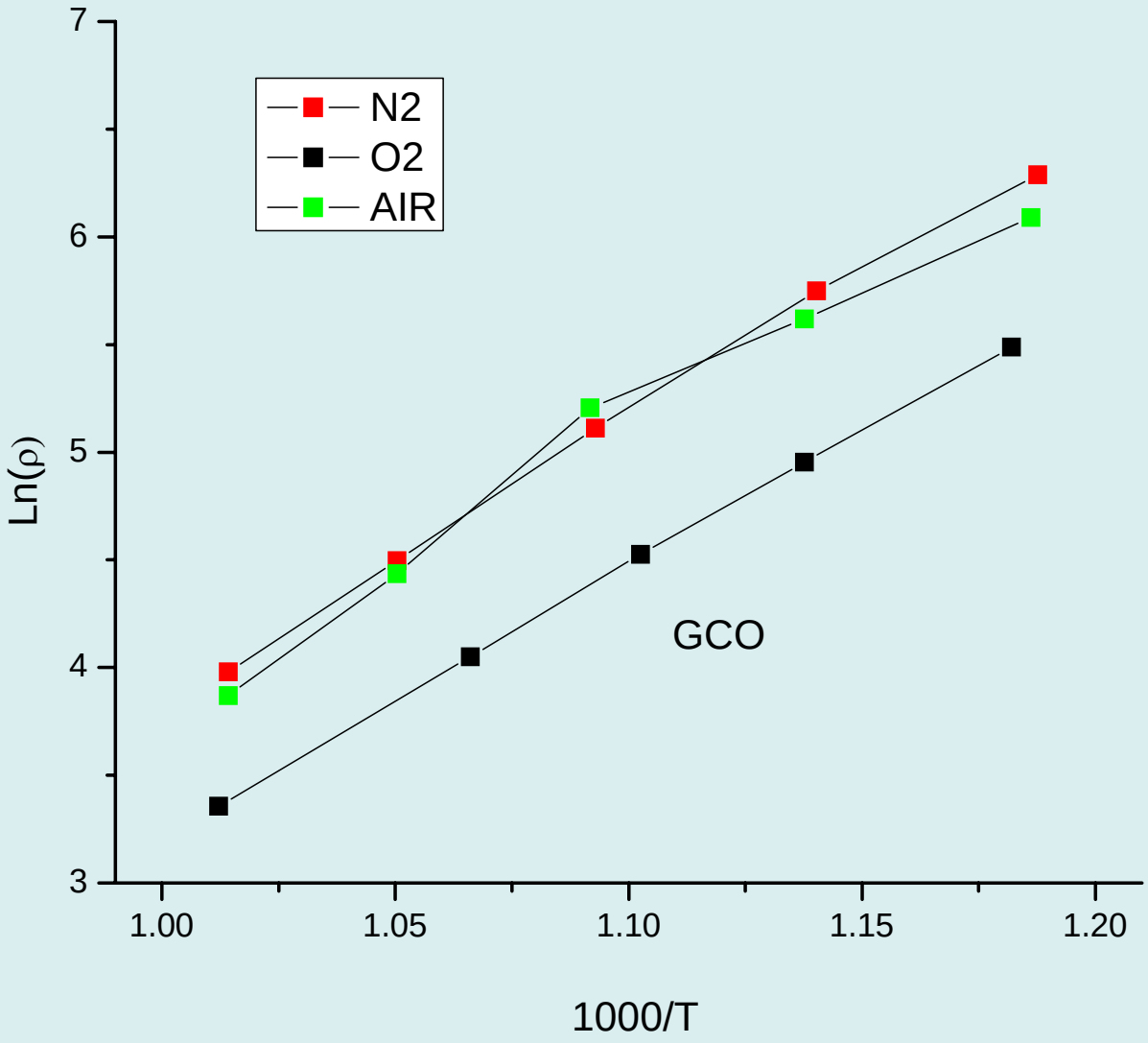
Conductivity study of multilayered films



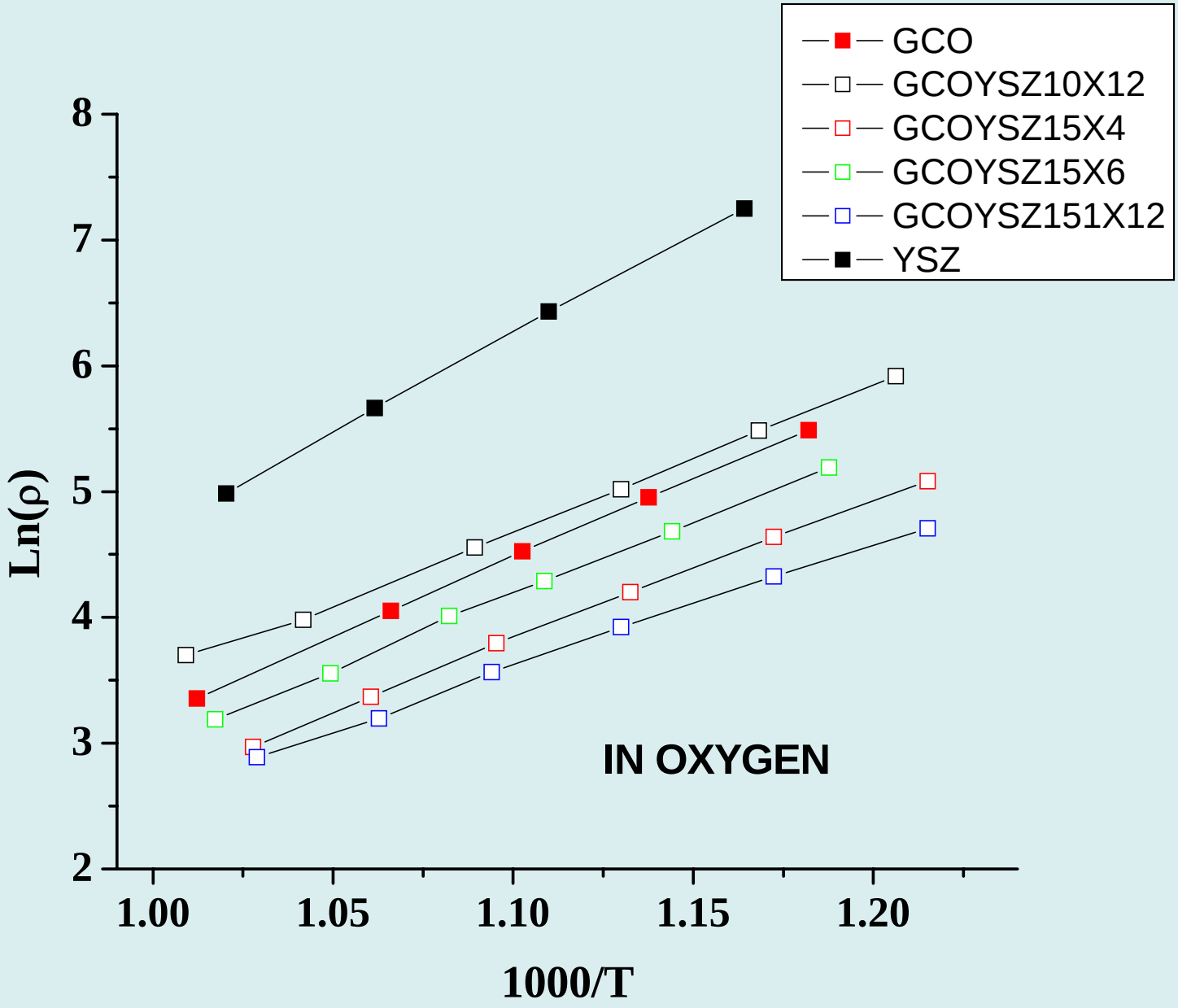
Conductivity study of multilayered films



Conductivity study of multilayered films



Summary of conductivity study

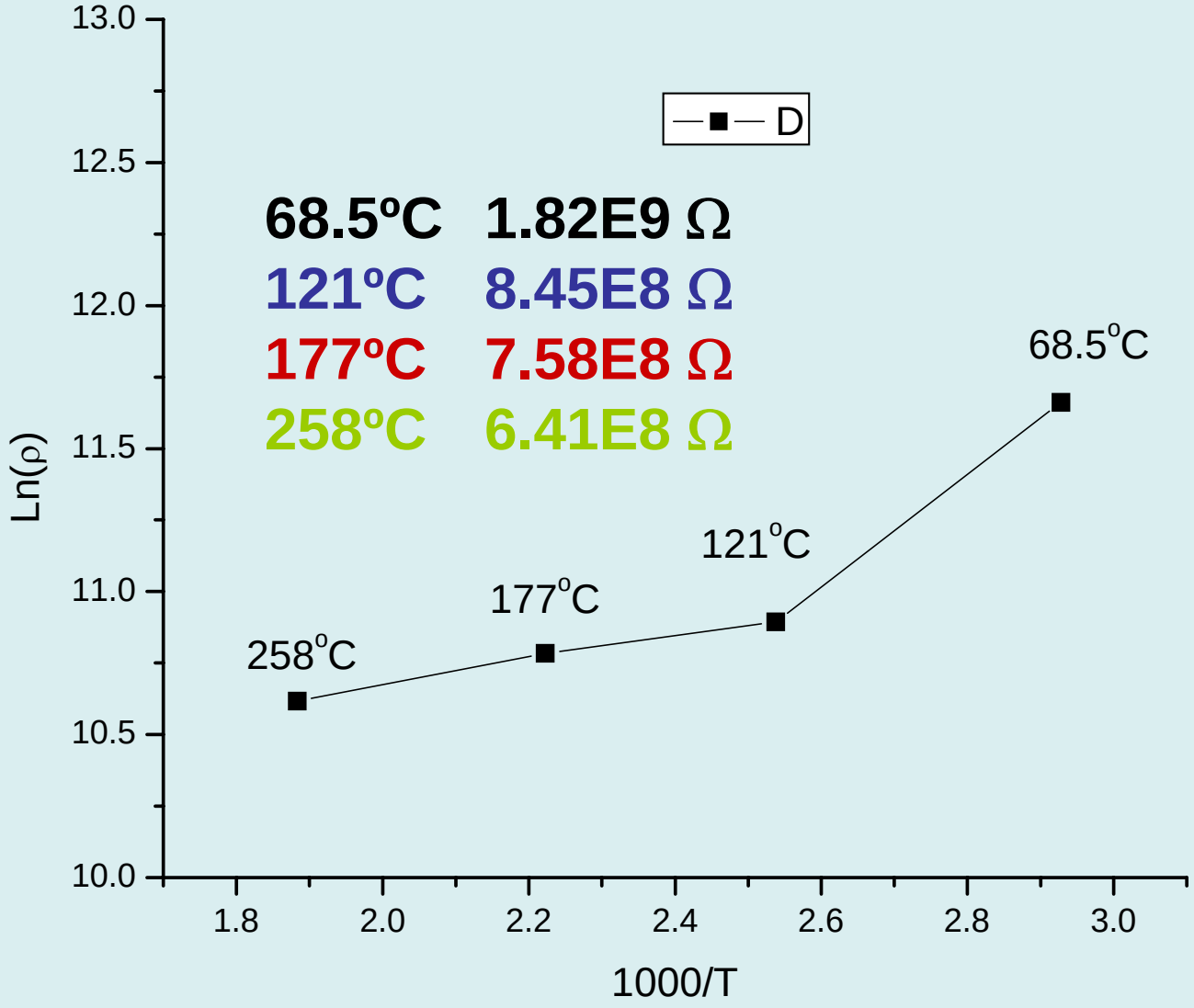


Summary of multilayered structures

sample	GCO:YSZ	stack#	test envirovemt	activation energy (eV)	conductivity at 600 C(Scm)
1018	10:1	12	O2	0.986191524	0.005374982
			Air	1.027593086	0.005949191
			N2	1.063014058	0.004960246
1022	15:1	4	O2	0.97254059	0.013183358
			Air	1.091869326	0.009446604
			N2	1.011961567	0.008526298
1023	15:1	6	O2	1.013997384	0.009039061
			Air	1.092743545	0.005761255
			N2	1.169550545	0.004475219
1024 a	15:1	12	O2	0.853716709	0.017528976
			Air	0.94359557	0.015045144
			N2	0.90199897	0.013931539

4%H_2 with 3% H_2O in N_2

annealed 1 hour at 607ºC



Summary: Electrolytes

- Multilayered GCO/YSZ thin film structures have been successfully fabricated and characterized.

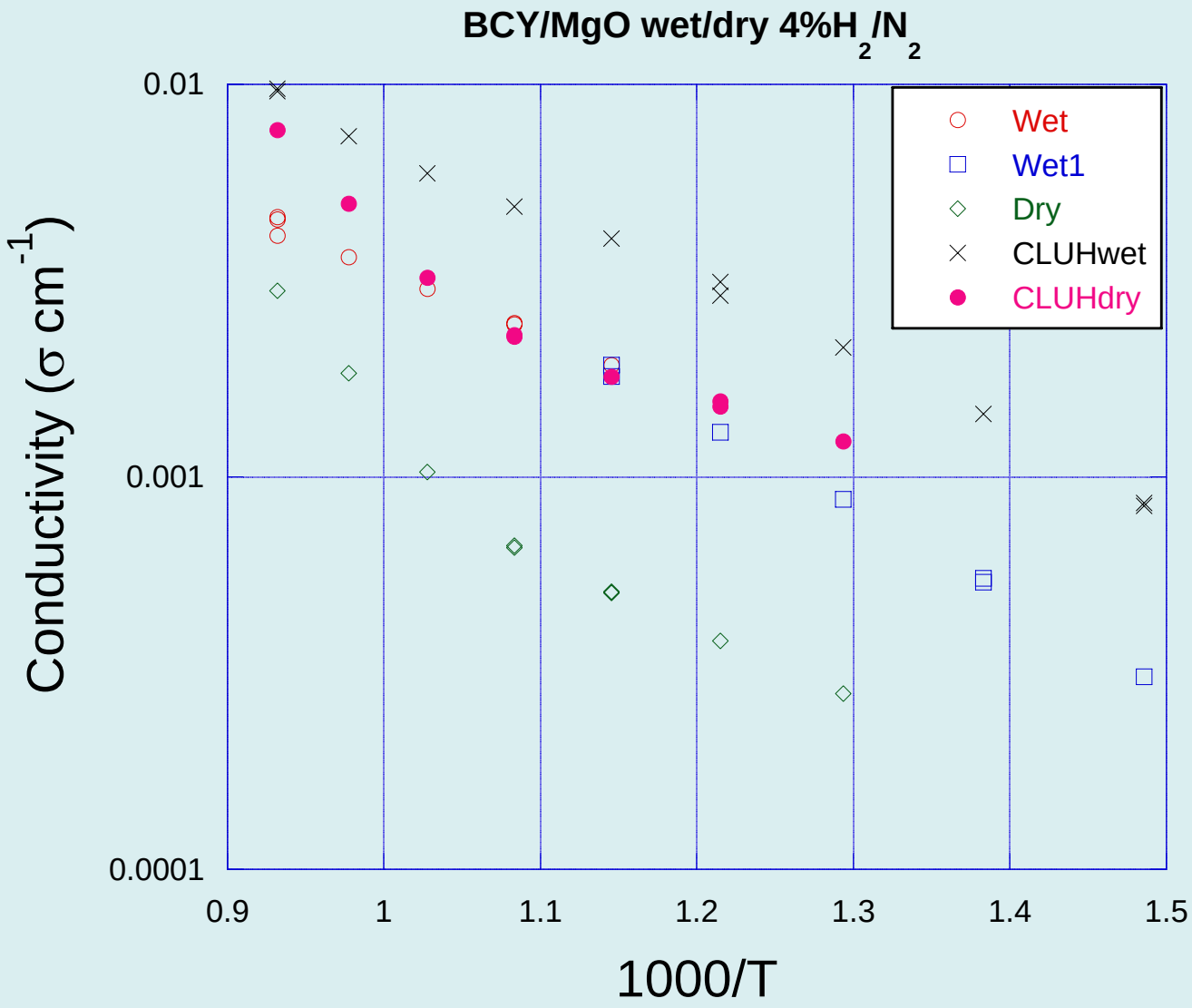
- Textured GCO/YSZ thin film structures have excellent intermediate temperature (600-700 ^{o}C) ionic transport properties with low electronic conductivity.

- The temperature dependence of the electrical conductivity gives an activation energy of 0.85 eV for the optimized GCO/YSZ structures.

Anode Materials

- Ni and Zr composites
- Pd and Ru particles
- $Ba(Y,Ce)O_3$

YBCO Results



Recent Publications

- C. L. Chen, J. Liu, G. Collins, “2008.024.UTSA: ***Multilayered YSZ/GCO structure for intermediate temperature fuel cell applications***, patent disclosure.
- Z. Yuan, J. Liu, **C. L. Chen**, C. H. Wang, X. G. Luo, X. H. Chen, G. T. Kim, D. X. Huang, S. S. Wang, A. J. Jacobson, and W. Donner, “Epitaxial Behavior and Transport Properties of PrBaCo2O5 Thin Films on (001) SrTiO3”, ***Appl. Phys. Lett***., **90** (2007) 212111.
- J. Liu, G. Collins, C. L. Chen, J. C. Jiang, E. I. Meletis, “Ionic Transport Properties in Multilayered GCO/YSZ structures”, submitted to ***Solid State Ionics***.
- J. Liu, G. Collins, C. L. Chen, J. C. Jiang, E. I. Meletis, and A, J, Jacobson: “Strain Effects in Transport Properties of PrBaCo2O5 Thin Films”, submitted to ***Appl. Phys. Lett***.
- C. L. Chen (invited talk), “Remarkable new class of ionic conductive oxide thin films for intermediate temperature fuel cells”, the **2008 International Materials Research Conference**, Chongqing, P. R. China, June 9-12, 2008.
- C. L. Chen (invited talk), “Remarkable new class of ionic conductive oxide thin films for intermediate temperature fuel cells”, the Summer School Workshop on Advanced Materials, Shenyang, P. R. China, July 7-9, 2008.
- C. L. Chen (invited talk), “Remarkable new class of ionic conductive oxide thin films for intermediate temperature fuel cells”, the **08 Materials Sciences and Technology**, Pittsburgh, Pennsylvania, Oct. 5-9, 2008.

Future Works

- Continue on the fabrication and characterizations of mixed conductive PBCO thin films with various multilayered ionic conductive GCO/YSZ half-cell structure combinations
- Understand the interface behavior and ionic transport dynamics of oxygen in the PBCO-GCO/YSZ multilayered structures.
- Model the YSZ layer in the multilayered structures for blocking the electronic conduction
- Enhance the quality of the electrolyte materials and to lower the operation temperature from 800 oC to 600 oC.
- Optimize the half–cell structures from PBCO/YSZ and PBCO/GCO to determine the best interface structures for the cathode/electrolyte interface.
- Fabricate and characterize the advanced proton conductive YxBaCe1-xO3 (YBCO) for anode use; systematically study the physical properties and ionic transport behavior of each material (YBCO, PBCO, and multilayered GCO/YSZ structures).
- Fabricate various crystal structures and different crystal grain sizes, and will comprehensively analyze the physical properties and interface phenomena of each material and the effects from interface, size, and strain.
- Final goal to demonstrate the thin film multilayered structures for intermediate temperature SSFC.

Thank you very much!