New Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells

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Objectives

- The specific objectives are to develop cathode materials that meet the electrode performance targets
  - 1.0 W/cm^2 at 0.7 V in combination with YSZ at 700 ºC and with GDC at 600 ºC.

- The research strategy is to:
  - investigate both established classes of materials and new candidates as cathodes;
  - determine fundamental performance parameters such as bulk diffusion, surface reactivity and interfacial transfer;
  - couple these parameters to performance in single cell tests;
  - use model thin film structures to isolate specific features of oxygen reactivity and transport at surfaces and interfaces

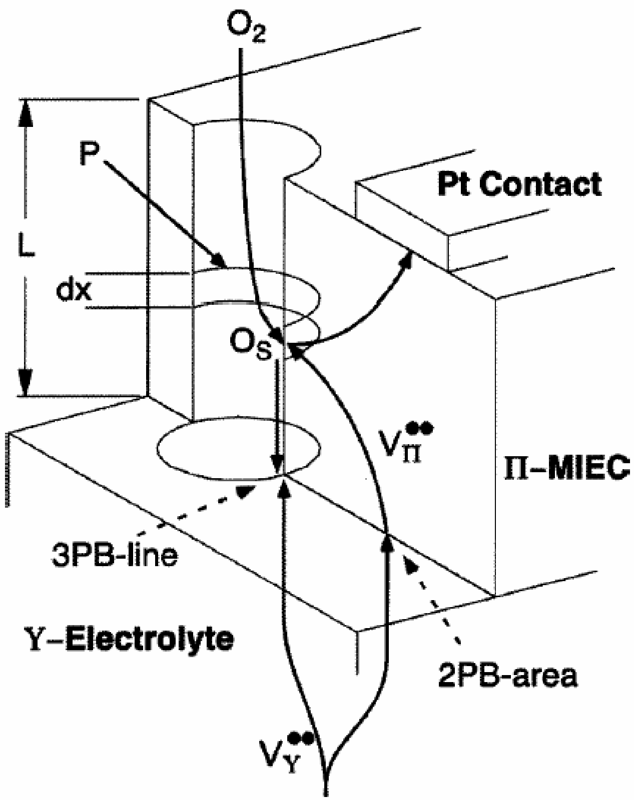
Overview

New Materials → Bulk Properties → Electrode Performance → Electrode/ Electrolyte Structure

Model Systems → Surfaces/ Interfaces → Electrode Polarization → Modeling

Optimized electrode /electrolyte combinations

SOFC Cathode Performance



$$1/2O_2(g)+S(II)\underset{k_{rdes}}{\overset{k_{fads}}{\rightleftarrows}}O_s(II)$$

$$V_O^{\bullet\bullet}(II)+O_s(II)\underset{k_{rex}}{\overset{k_{fex}}{\rightleftarrows}}S(II)+2h^{\bullet}(II)+O_O^{\times}(II)$$

$$V_O^{\bullet\bullet}(Y,II)+O_{tbp}(II,Y)\underset{k_{rTBP}}{\overset{k_{fTBP}}{\rightleftarrows}}S(II)+2h^{\bullet}(II)+O_O^{\times}(Y)$$

$$V_O^{\bullet\bullet}(Y,II)\underset{k_{rDBP}}{\overset{k_{fDBP}}{\rightleftarrows}}V_O^{\bullet\bullet}(II,Y)$$

$$D_O(II), D_s(II)$$

Both surface and bulk diffusion considered

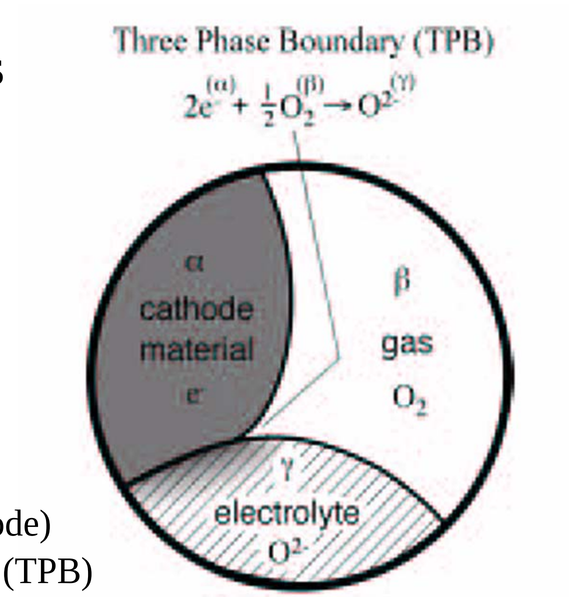
from Coffey *et al. JECS* 150, A1139 (2003)

Oxygen Activation Mechanisms

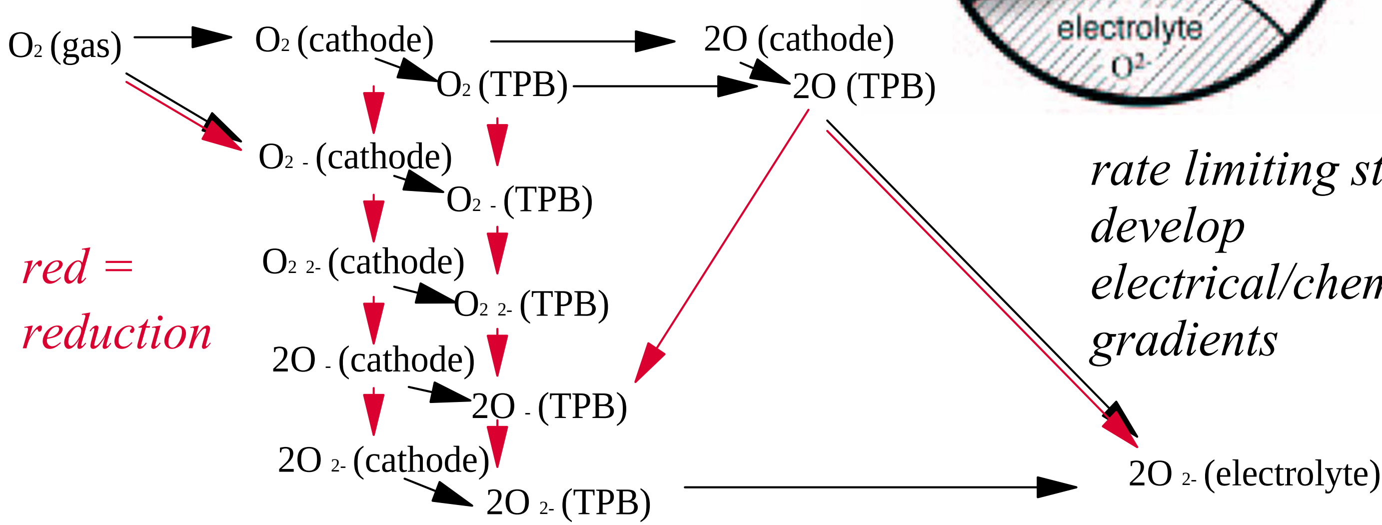
"Simple" overall cathode reaction involves

-3 phases (+ current collector)

O_2 (gas) + $4e^-$ (cathode, collector) = 2 O^{2-}(electrolyte)



-and multiple (largely unknown) elementary reaction steps



red = reduction

rate limiting steps develop electrical/chemical gradients

SOFC Cathodes

A model that does not consider surface diffusion gives the cathode resistance in terms of the diffusion coefficient (D_O^*) and the surface exchange rate (k_O^0) (cm/s units)

$$R_{cathode} = \frac{RT}{2F^2}\left[\frac{\tau}{(1-\varphi)Sc_O^2 D_O^* k_O^0}\right]^{1/2}$$

where τ, φ and S are the electrode tortuosity, porosity and surface area

D_O and k_O can be measured by:

Isotope exchange and depth profiling (IEDP)

Electrical conductivity relaxation (ECR)

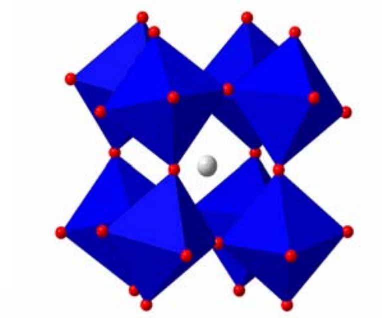
(Adler *et al*. J. Electrochem. Soc. (1996) *143* 3554)

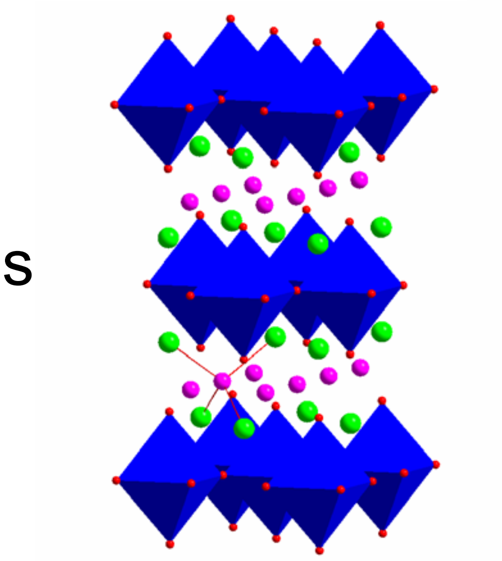
Experimental Methods

– Stoichiometry measurements
– Conductivity and Conductivity relaxation
– Isotope exchange and depth profiling (IEDP)
– Photoelectron spectroscopy / Kelvin probe
– AC impedance on symmetric cells
– Half cell measurements
– Thin film synthesis of model structures

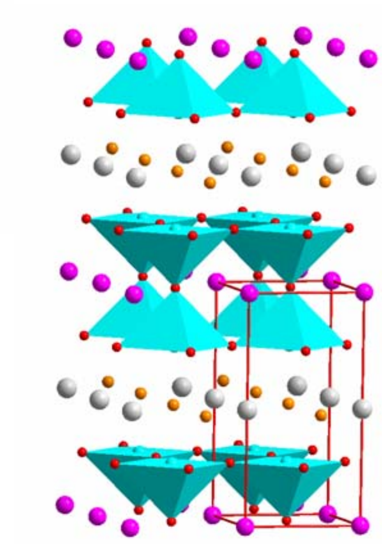
Materials Classes

- perovskite ferrites
  - *oxygen vacancies*
    - $La_{1-x}Sr_xFeO_{3-x}$, x= 0.2, 0.3
    - $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-x}$





- perovskite related structures
  - *oxygen interstitials*
    - La_2NiO_{4+x}
    - Pr_2NiO_{4+x}

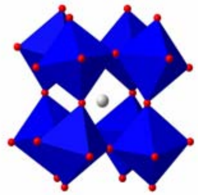


- perovskite oxides with ordered A cations
  - *2 dimensional vacancies*
    - $PrBaCo_2O_{5+x}$
    - $LaBaCuFeO_{5+x}$,

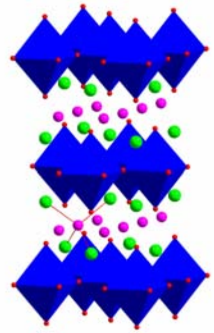
Jacobson Mims Rieke

Previous Results

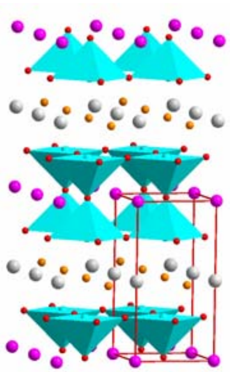
- perovskite ferrites
  - *Stoichiometry, conductivity, measured for* $La_{1-x}Sr_xFeO_{3-x}$ *and* $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-x}$
  - *Both share strange, sluggish stoichiometry changes with other ferrites at intermediate* p_{O2}



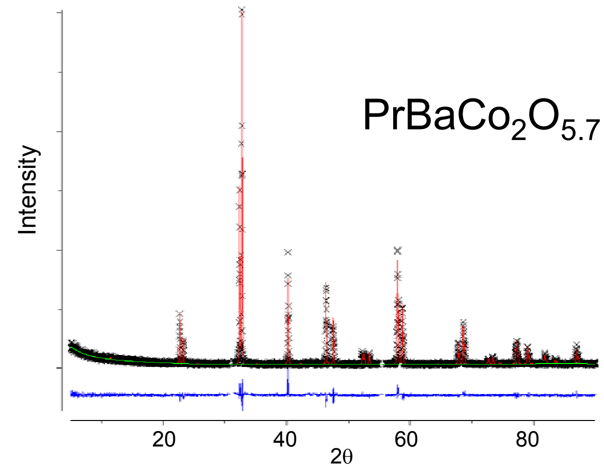
- perovskite related structures
  - *Stoichiometry, conductivity, IEDP, ECR measured for* La_2NiO_{4+x}, Pr_2NiO_{4+x}
  - *Symmetric cells (YSZ and CGO electrolyte) ASR = 1 ohm at 600C*

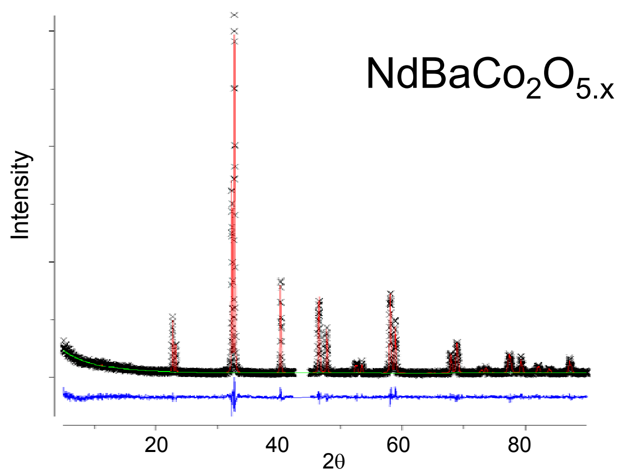


- perovskite oxides with ordered A cations
  - $PrBaCo_2O_{5+x}$ *films ECR, IEDP*

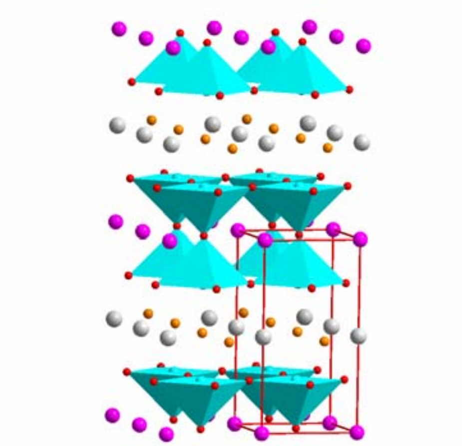


Bulk Powders of Double Perovskites





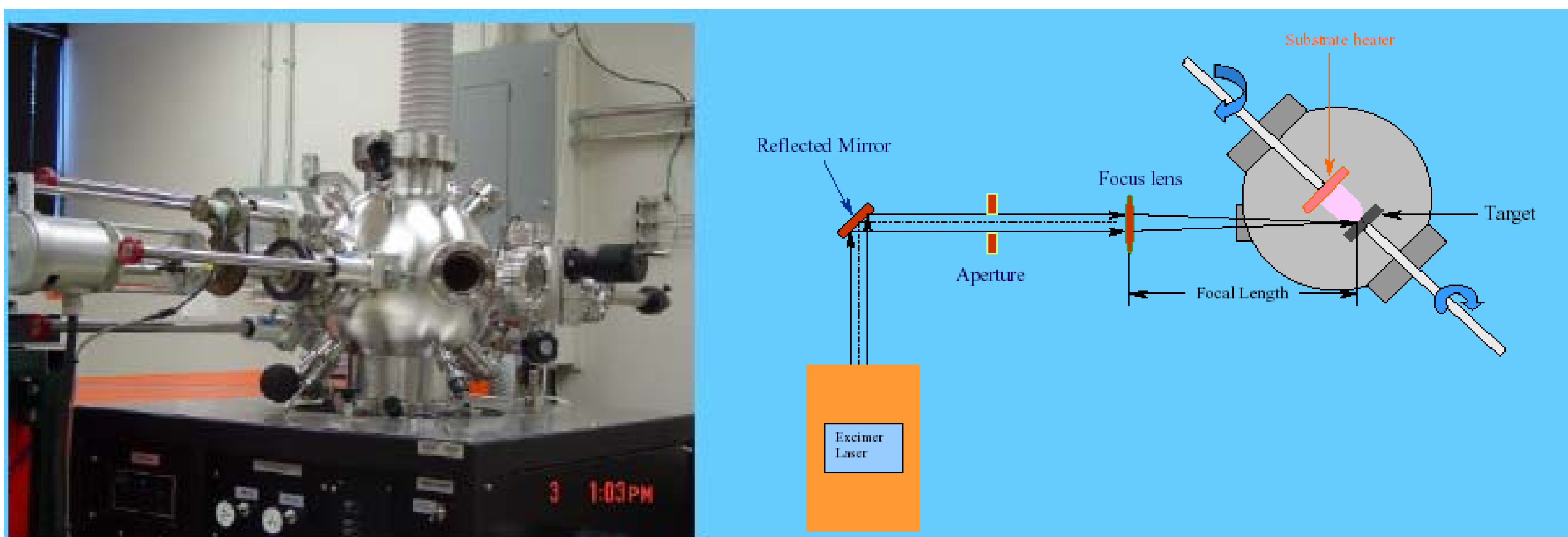
Rietveld refinement of PrBaCo$_2$O$_{5.7}$
a = 3.9084(1) Å b = 3.9053(1) Å c = 7.6343(2) Å.



Powders synthesized for ceramic (bulk) samples, cell electrodes and targets for thin films

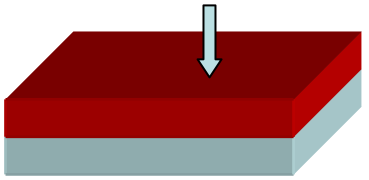
PLD Film Deposition

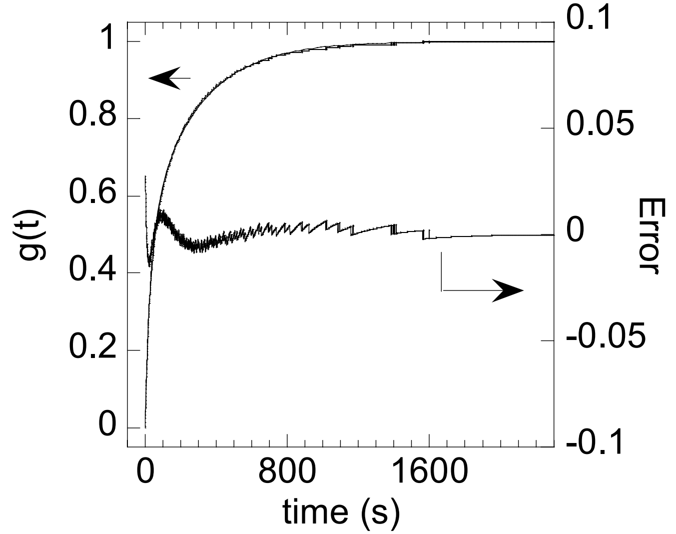
- (100) $LaAlO_3$ $SrTiO_3$ and YSZ single crystal substrates
- PBCO at 300 mTorr oxygen partial pressure with a substrate temperature of 880 °C.
- LNO at 300 mTorr and 840 °C
- KrF excimer laser with pulse frequency of 7 Hz.
- Films 2000 to 5000 Å



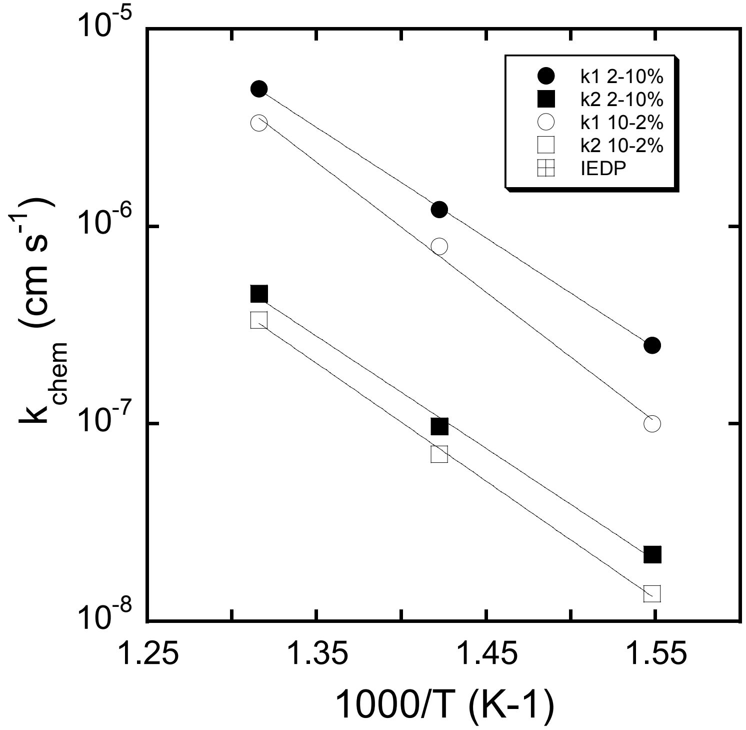
Oxygen Activation on PBCO Films

ECR involves oxygen pressure jump
Conductivity change results from stoichiometry change (O uptake).
Two time constants used to fit data



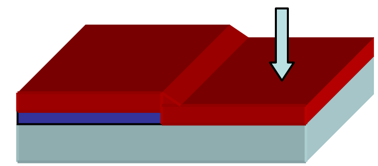


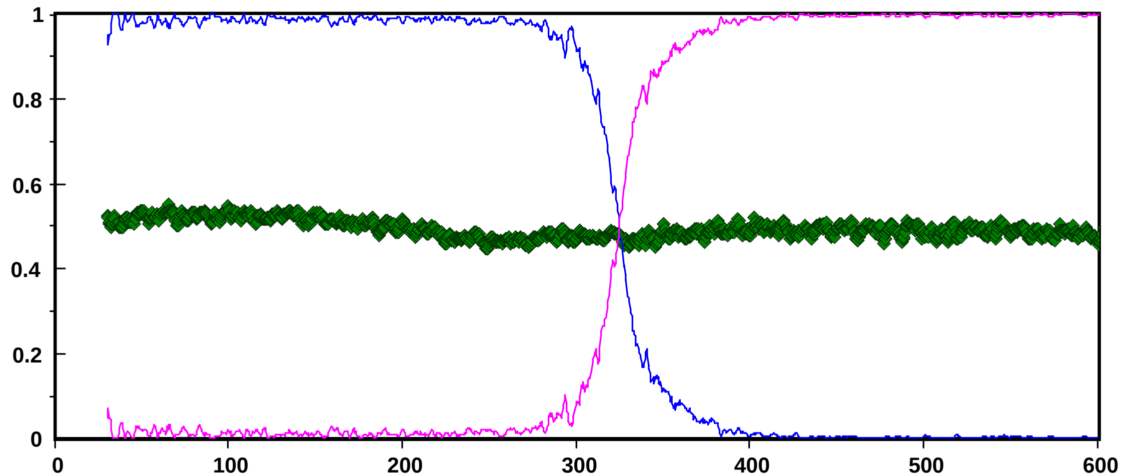
$PrBaCo_2O_{5.7}$ on STO



Thin film PBCO on YSZ (100)

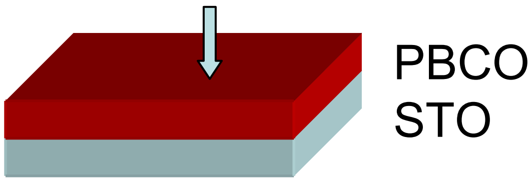
^{18}O at 700 °C,
pO_2 = 0.2 atm

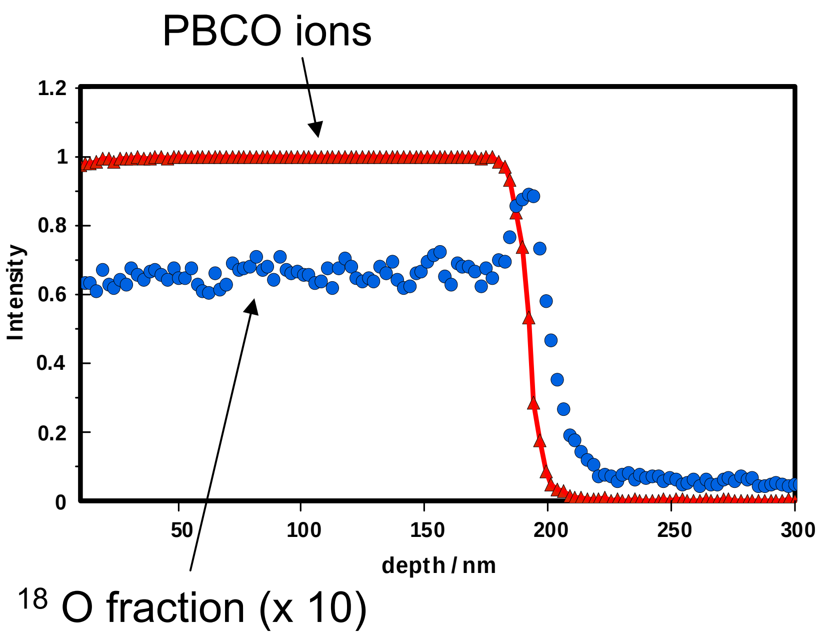


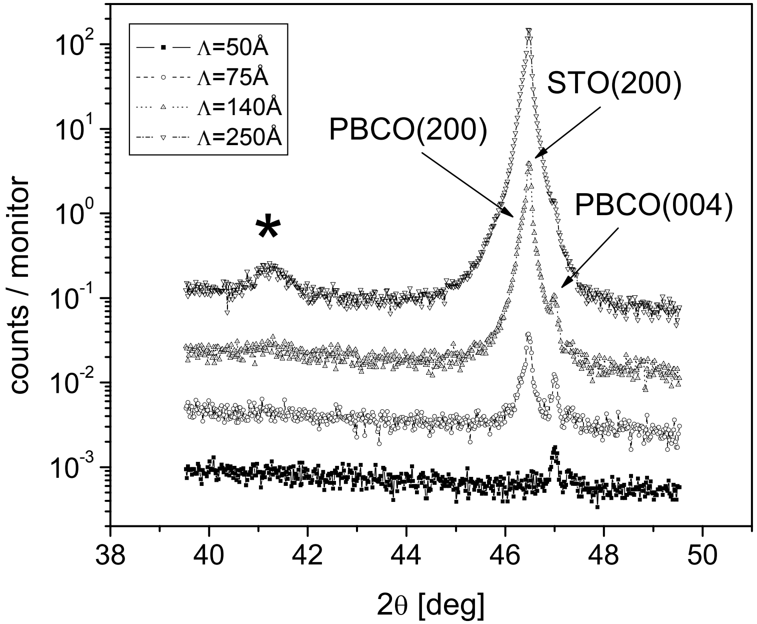


- Insignificant interfacial transfer barriers
- Exchange limited by surface $k_{O,PBCO}$ and $D_{O,\ YSZ}$

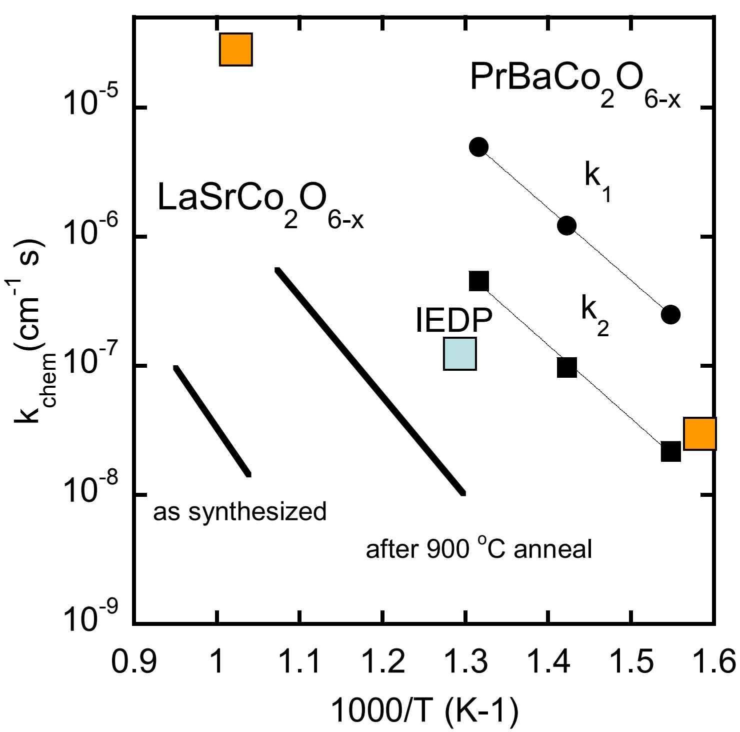
Epitaxial PBCO Thin Films







Surface k_O Values on PBCO Films



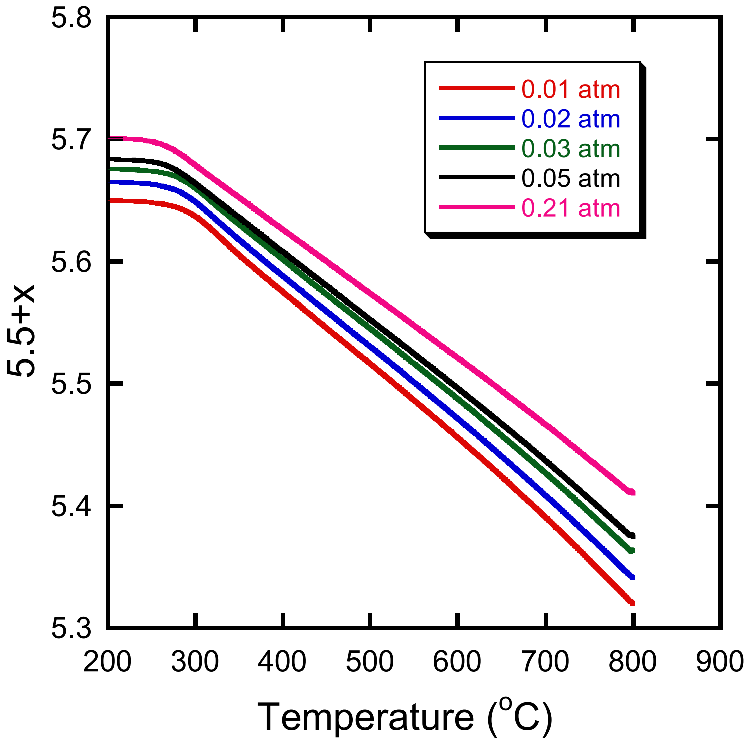
- Higher surface rates than LSCO
- Sensitivity to surface preparation/ history

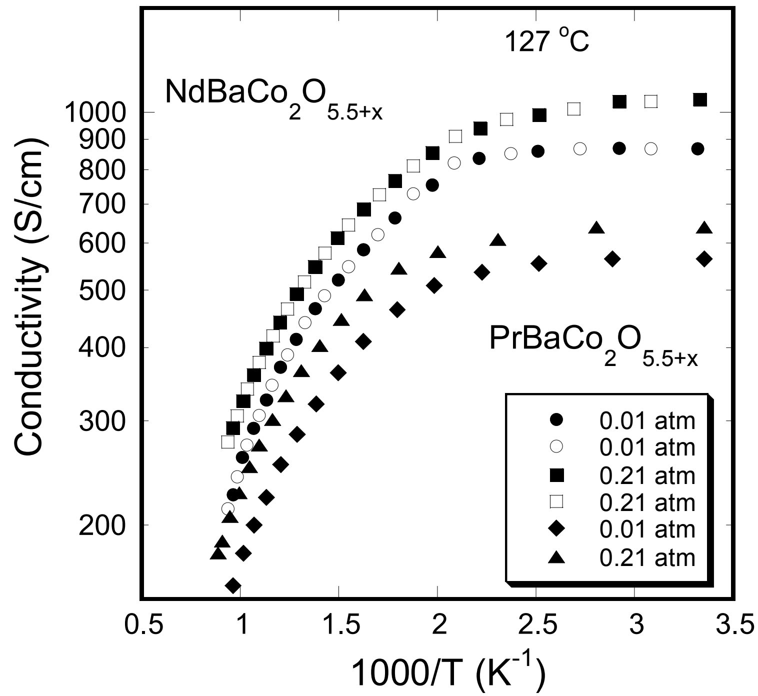
PBCO/YSZ

PBCO/STO (epitaxial)

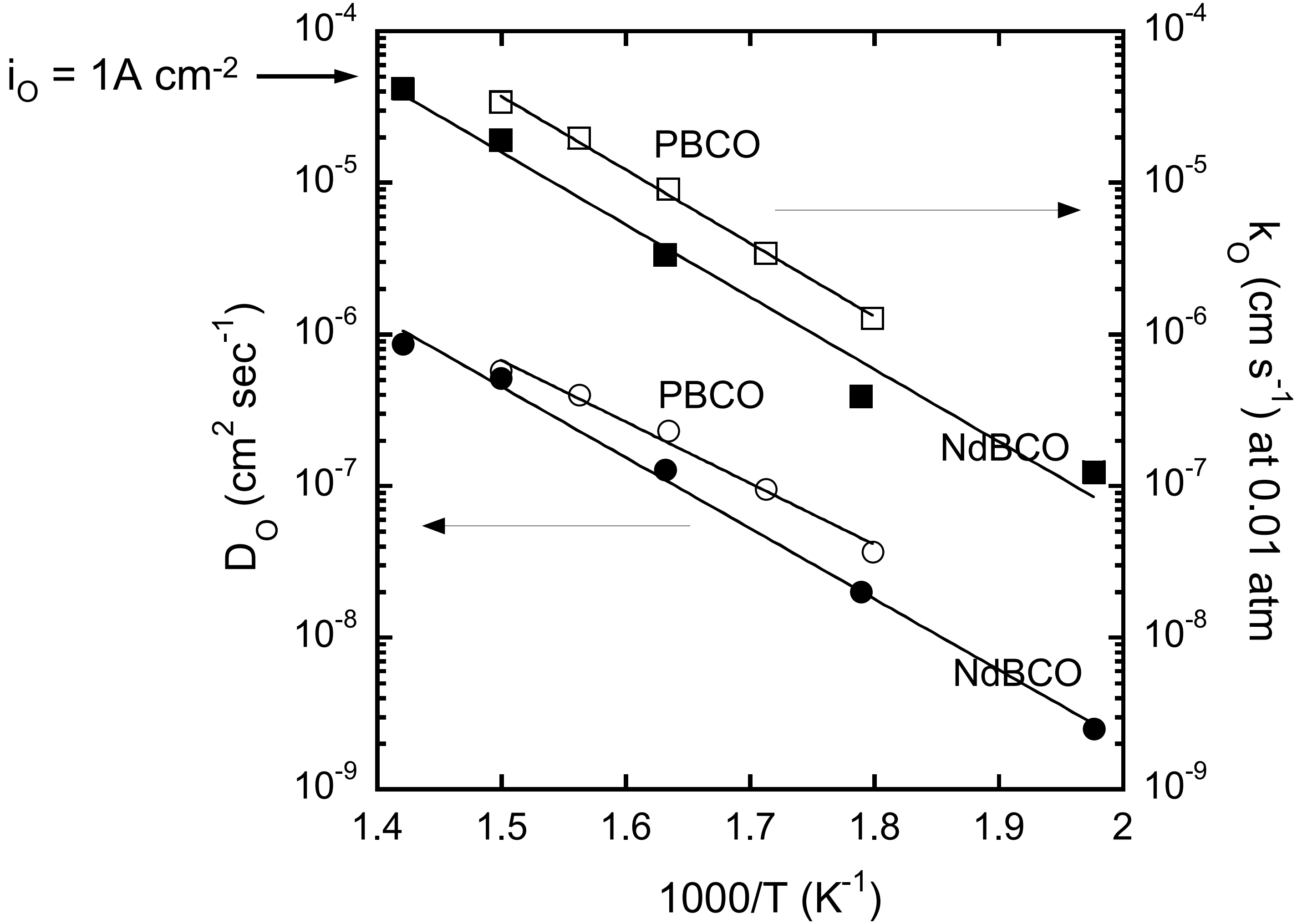
Accepted Appl. Phys. Lett. (2005)

Composition and Total Conductivity of Bulk $PrBaCo_2O_{5+\delta}$

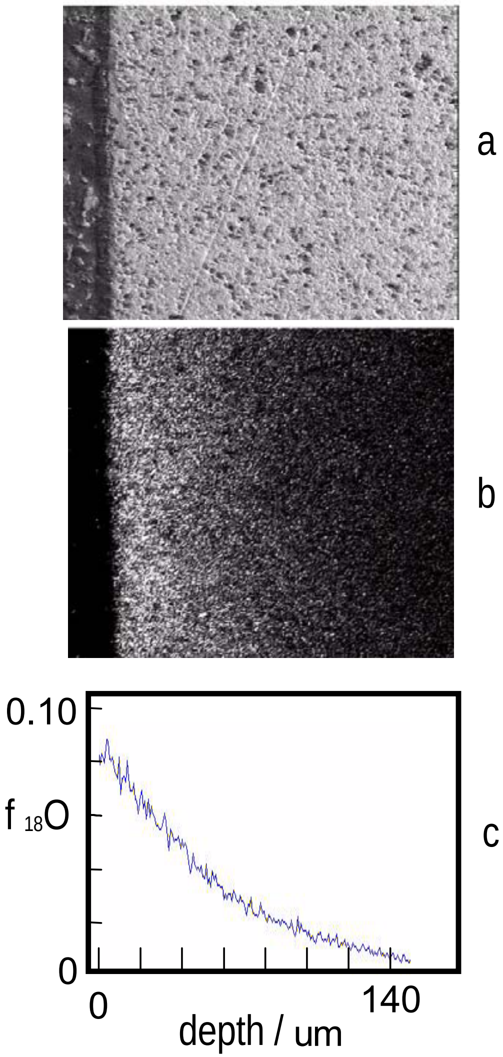




Kinetics on Bulk Materials

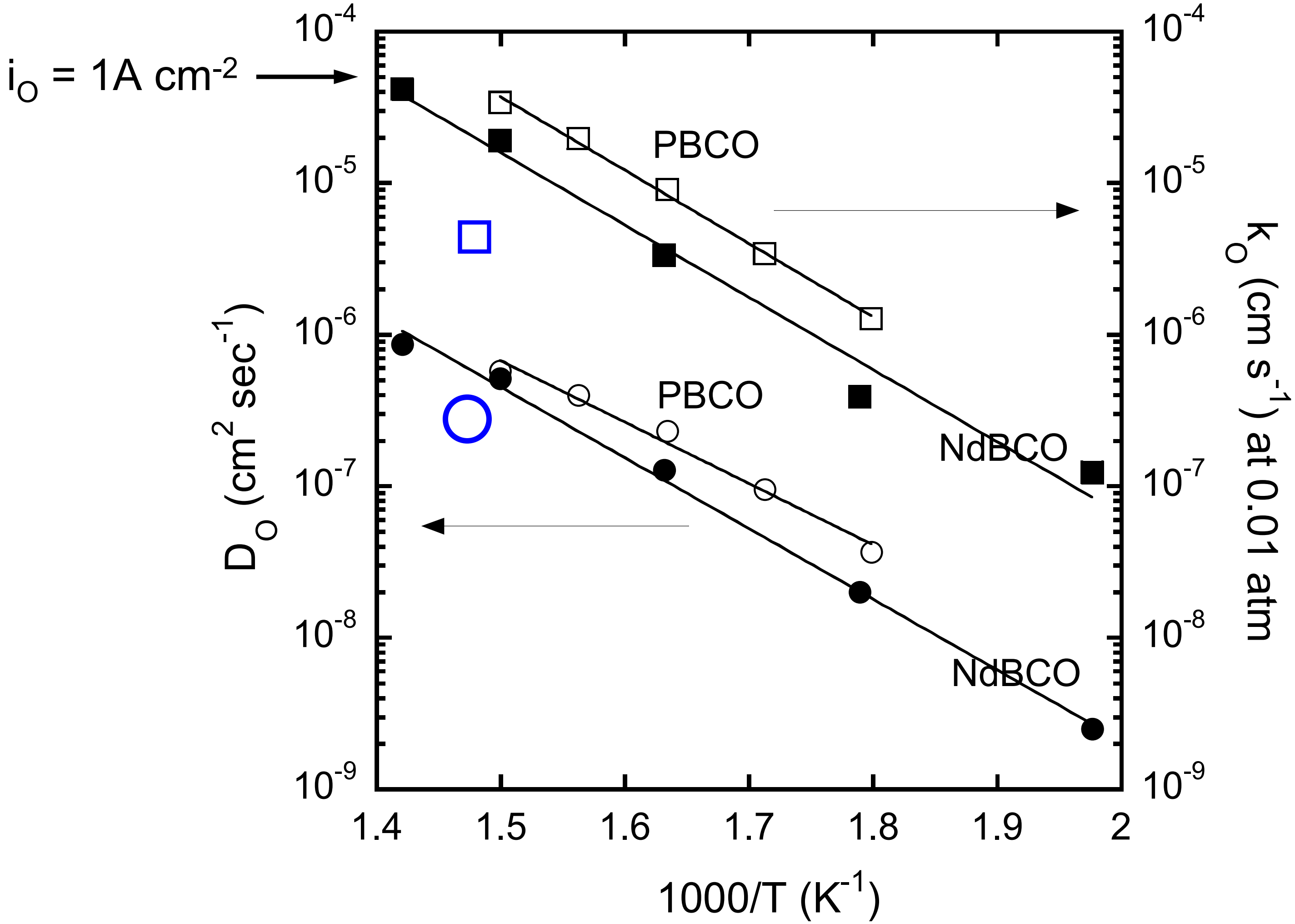


PBCO D_o and k_o Results (IEDP)



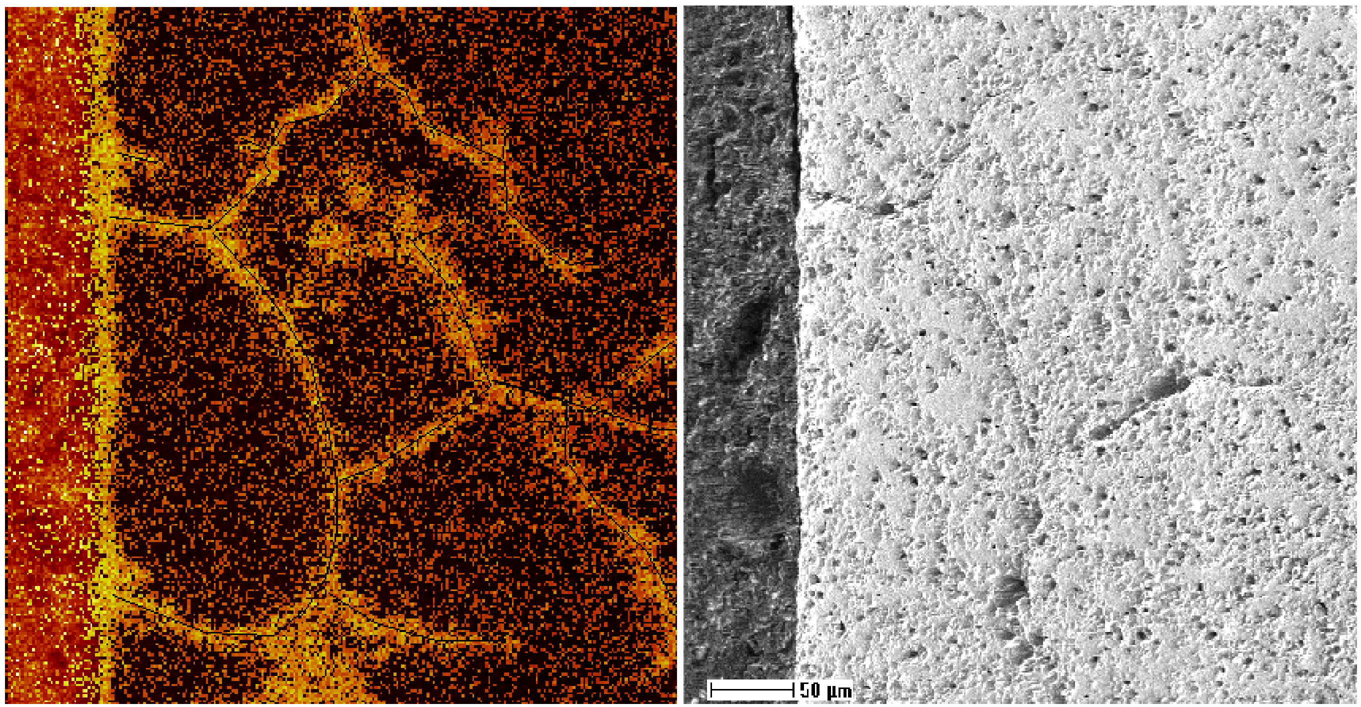
- 400°C – 5 minutes – polished cross section - ToFSIMS
- Secondary electron image
- ^{18}O image
- ^{18}O profile and fit

Kinetics on Bulk Materials



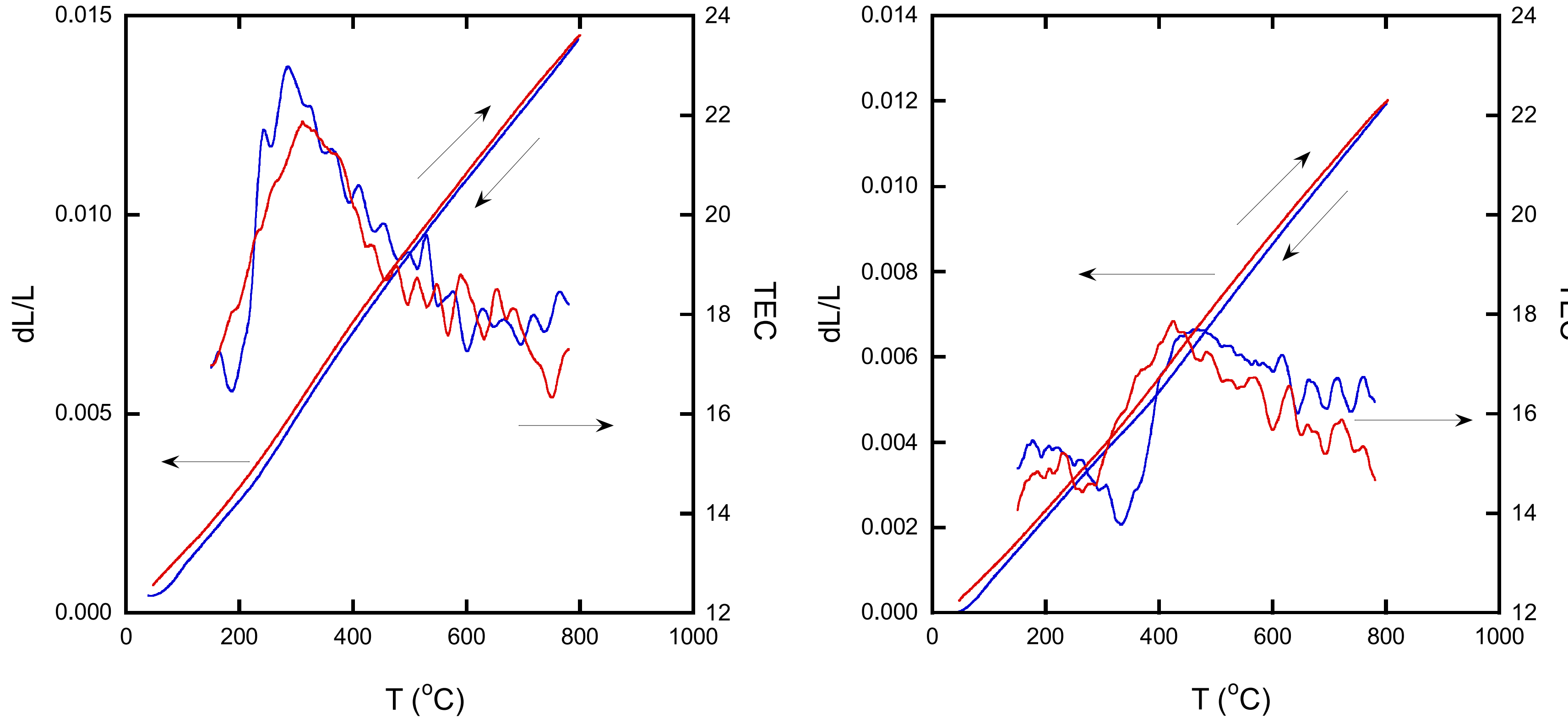
NBCO D_o and k_o Results (IEDP)

^{18}O / ^{16}O — Secondary Electron



- D_O less than 0.05 x PBCO

TECS for $PrBaCo_2O_{5+\delta}$ and $NdBaCo_2O_{5+\delta}$



$PrBaCo_2O_{5+\delta}$ $NdBaCo_2O_{5+\delta}$

Summary

- PBCO kinetic parameters are superior to previous cobaltites
- Cell tests underway - initial batch of powder did not make good electrodes

Plans

- Cell tests (Pt anode) with PBCO cathodes

- Patterned films for IEDP
- Ink jet printed compositional ferrite series (underway)
- Surface studies

Model materials to study individual steps

Single phase material

Surface and bulk

Two phase (films on single xtals)

Surface, interface and bulk(s)

Patterned materials
(masked films, printed patterns)

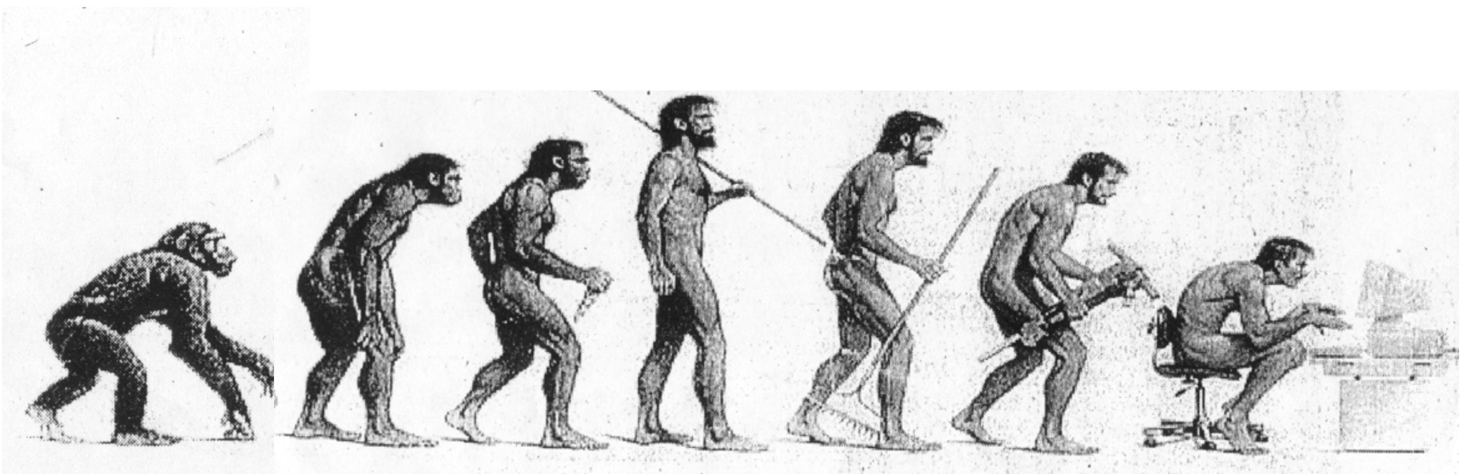
Surfaces, interface, bulk(s) and TPB
Combinatorial investigations

Synthesis: Pulsed Laser Deposition and Ink Jet Printing

Surface Studies

WHAT WE DON'T KNOW

- Mechanistic sequence of oxygen activation
- Role of adlineated sites
- Surface structure (including vacancies) of perovskite oxides
- Surface oxygen vacancy concentration as function of p_{O2}

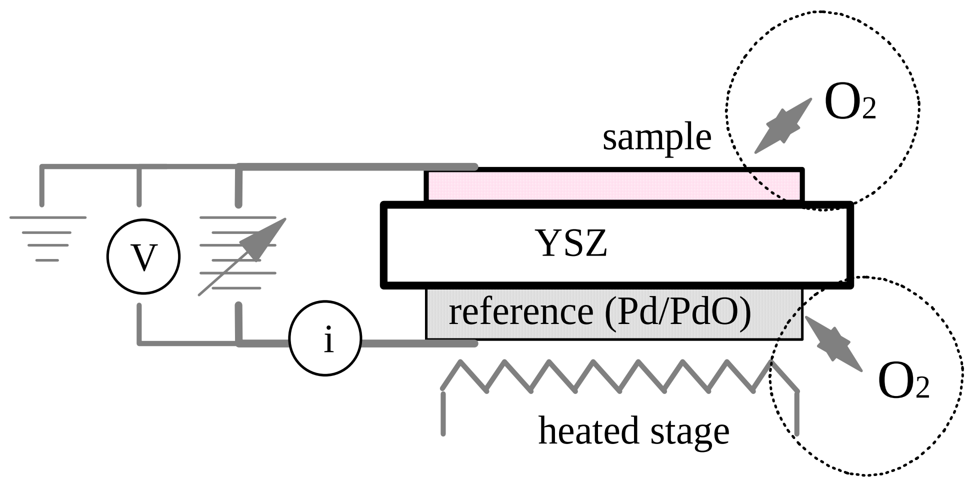


Surface Studies

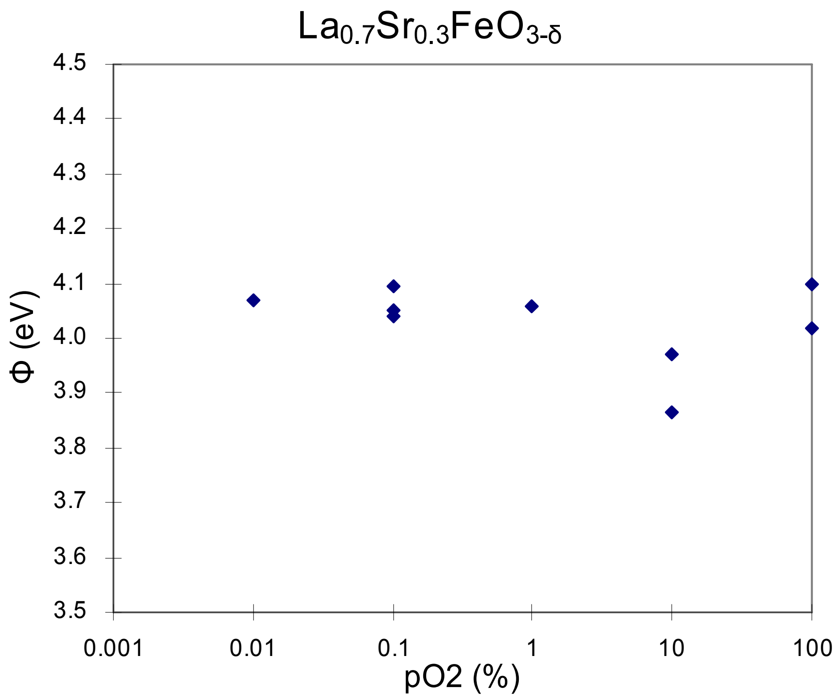
- Photoelectron spectroscopy and work function measurements + other techniques (STM)

- Probe molecules

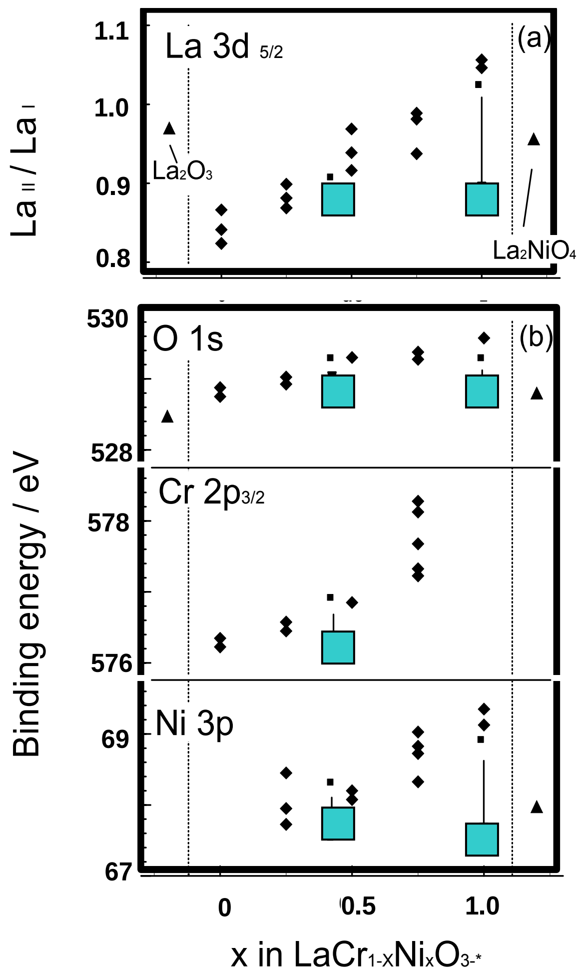
- Surface studies of electrochemically polarized materials

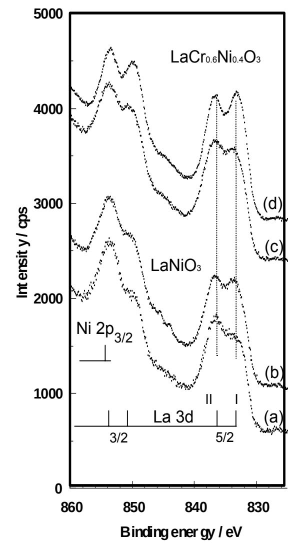


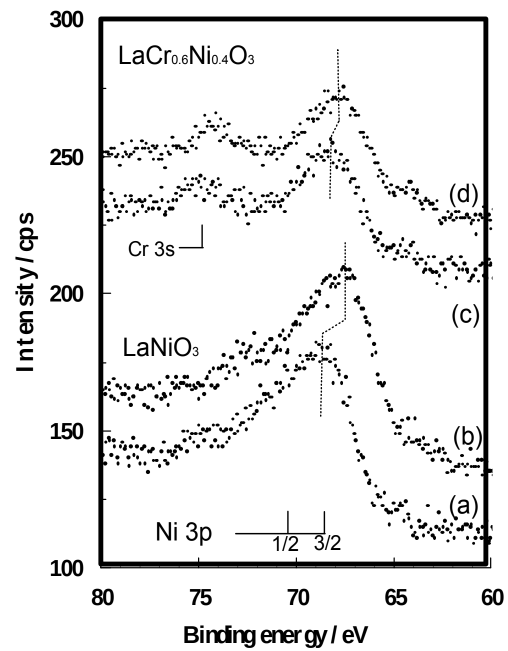
Work function measurements



$LaCr_{1-x}Ni_xO_{3-y}$ XPS Under Polarization

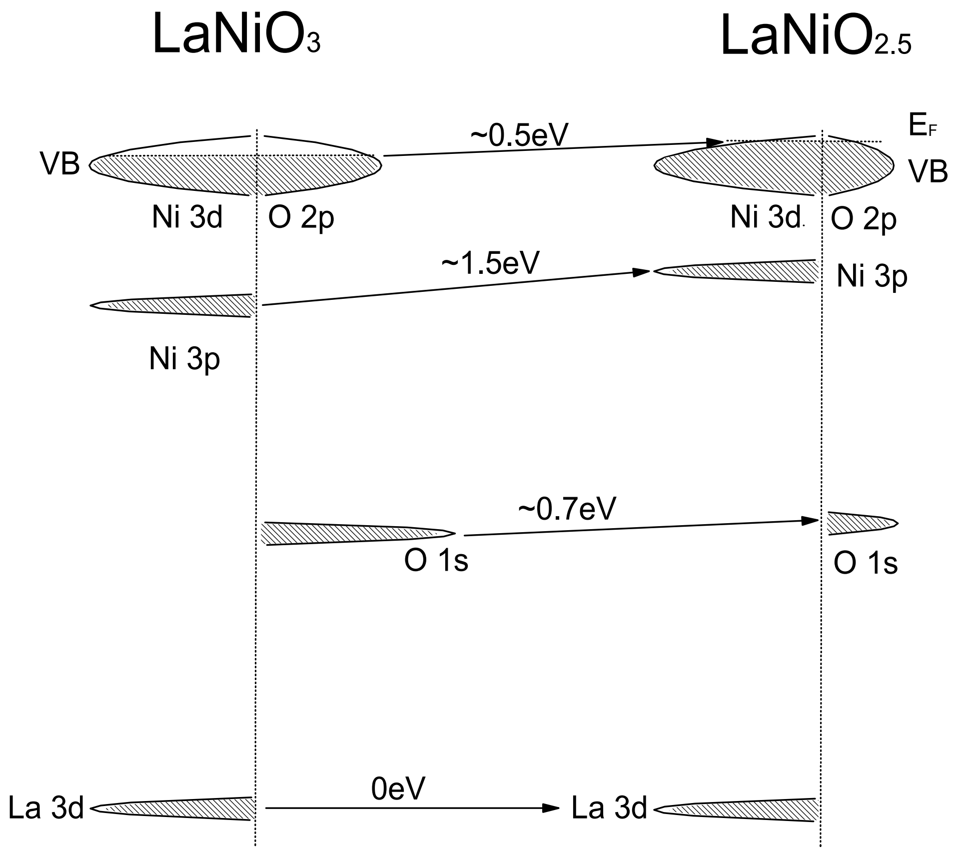




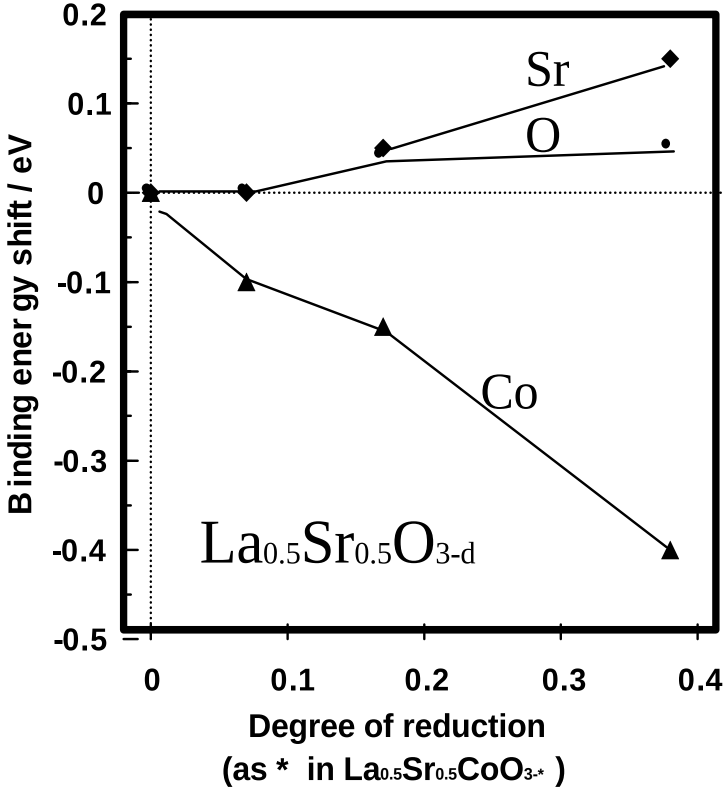


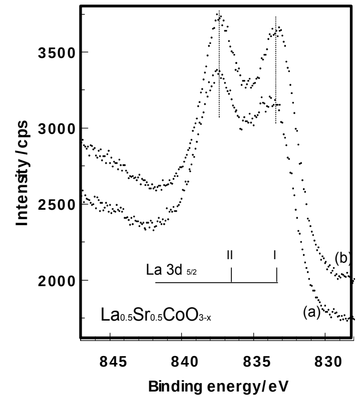
Reduced to Ni^{2+} stoichiometry

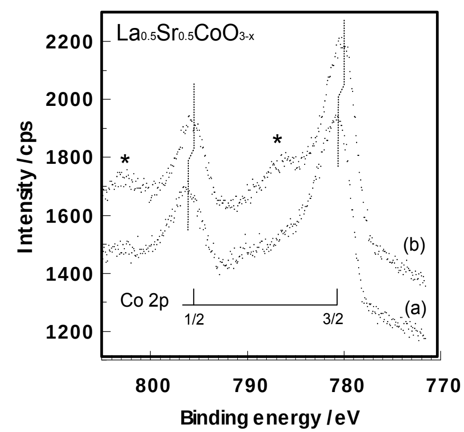
Oxygen Activation Mechanisms



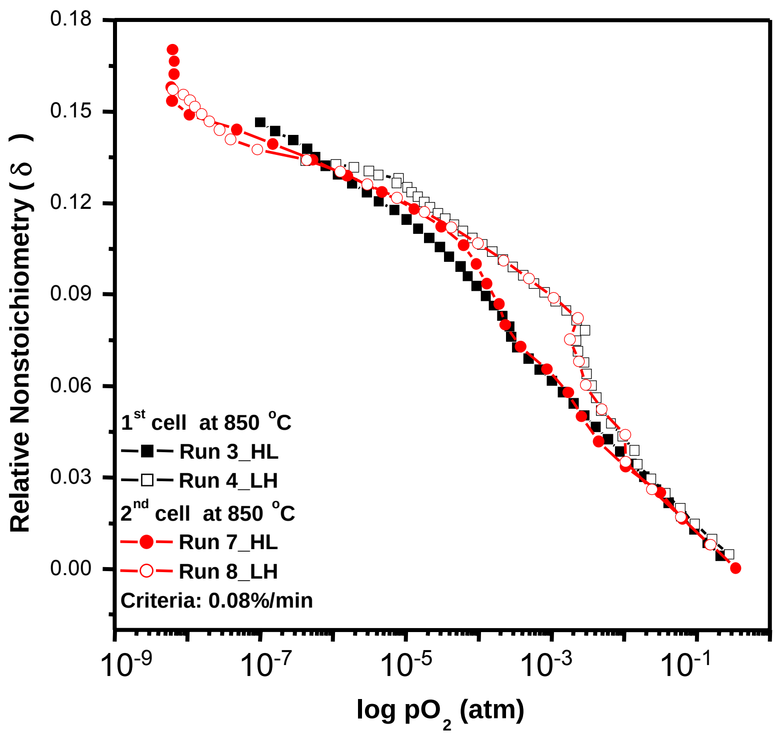
Oxygen Activation Mechanisms

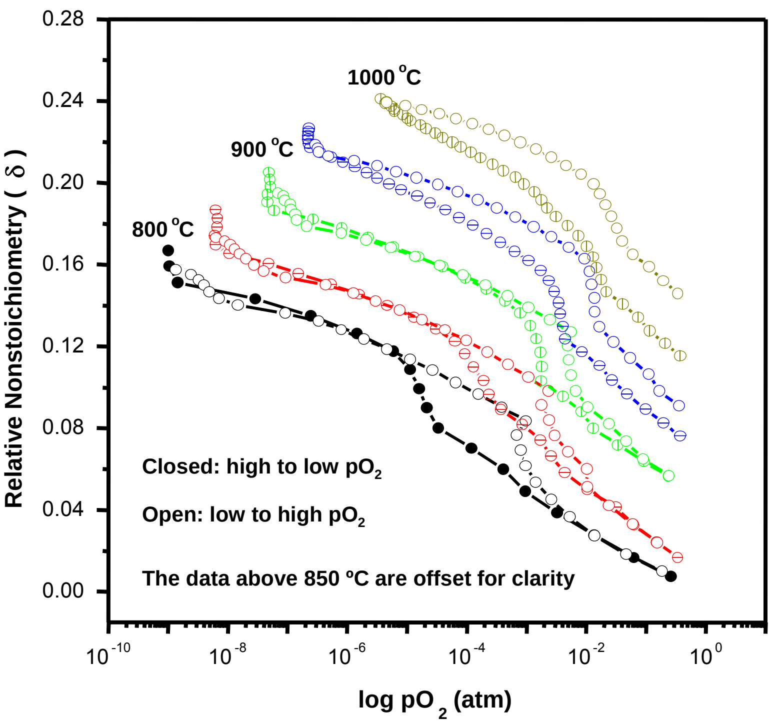






$La_{0.7}Sr_{0.3}Fe_{0.8}Cu_{0.2}O_{3-x}$ Stoichiometry



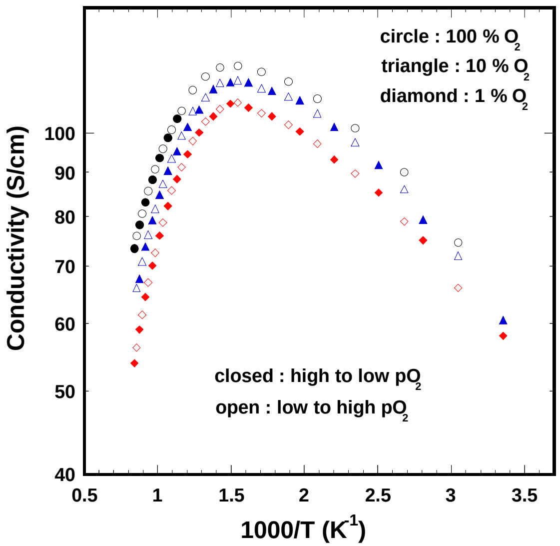


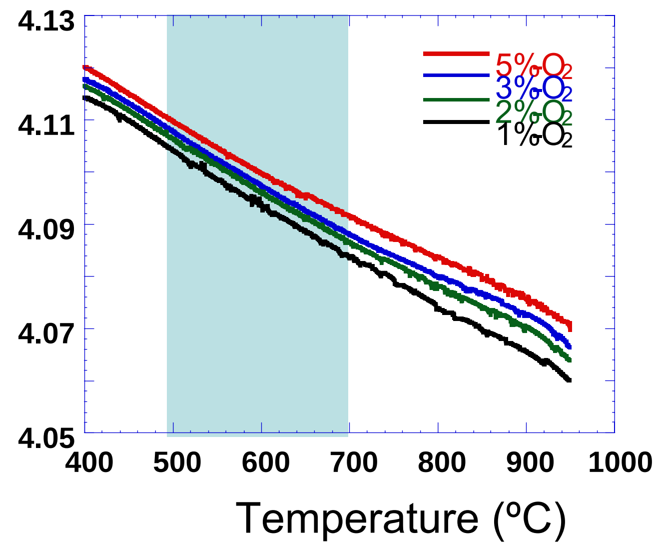
Measurements made in an electrochemical cell with Pt|YSZ|Pt as sensor and pump

Thank You

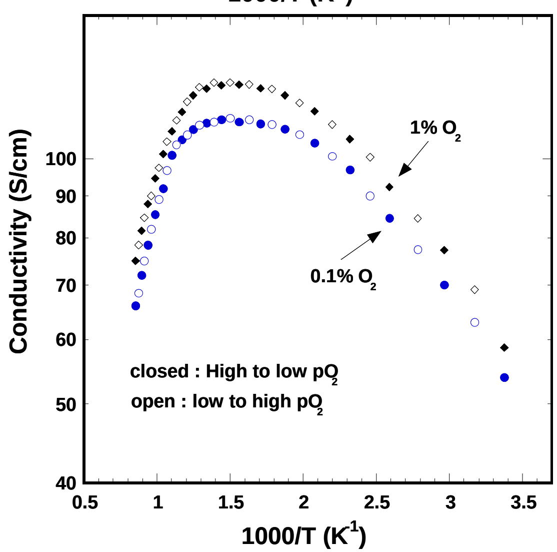
Extra Slides →

Conductivity and Stoichiometry

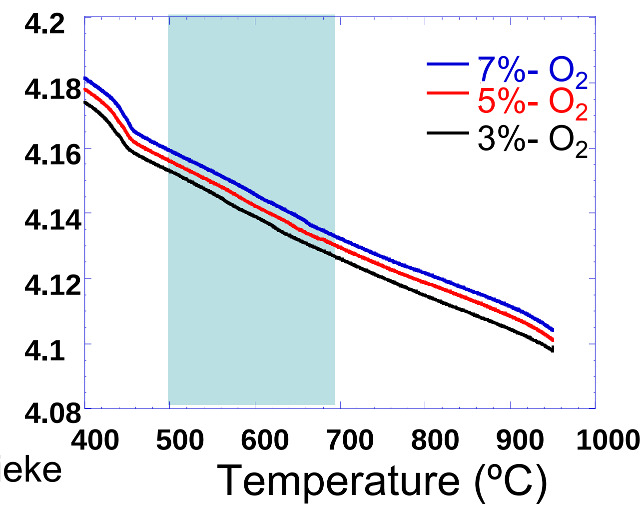




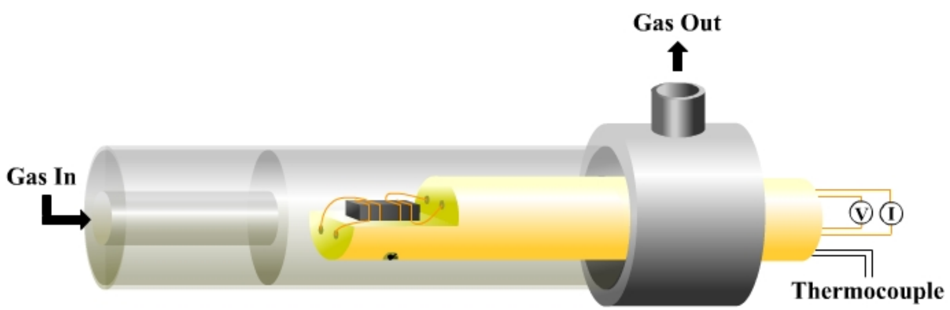
LNO



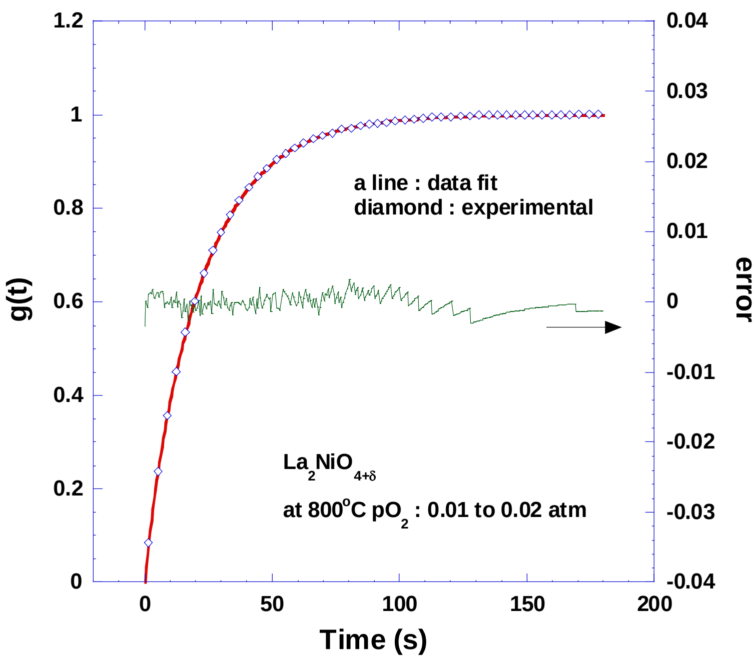
PNO



Electrical Conductivity Relaxation



- The normalized conductivity data *g(t)* are fit to a model that includes D_{chem} and k_{chem} as variables
- The surface exchange coefficient (k_{ex}) and the self diffusion coefficient (D_O) were obtained using the relationships below :

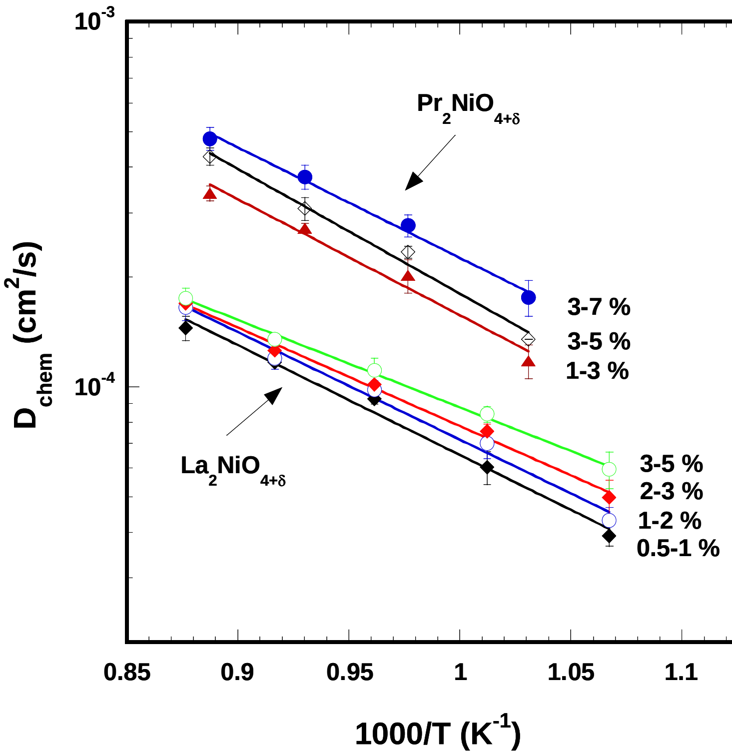


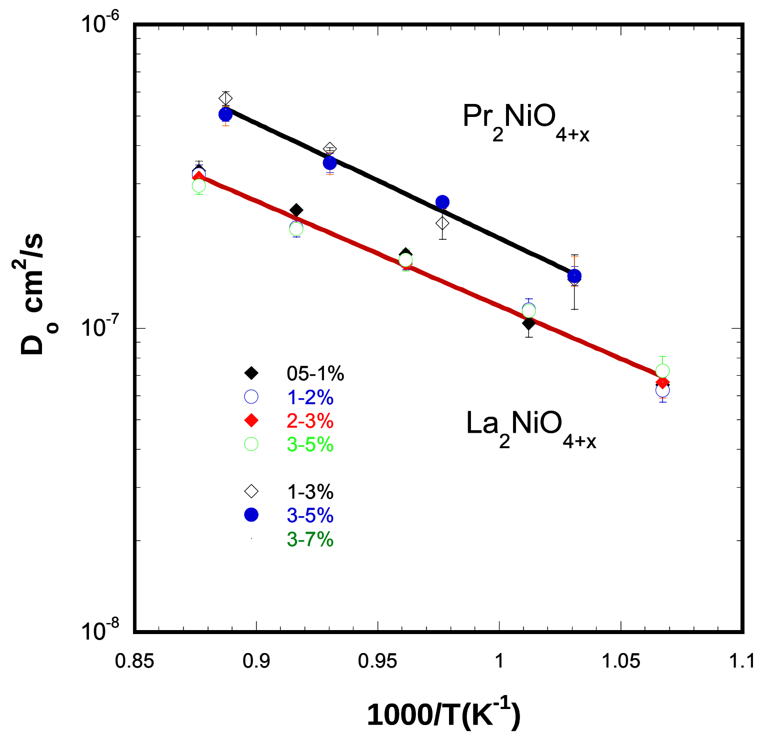
Thermodynamic factor $$\Gamma_O = \frac{1}{2} \cdot \frac{\partial ln\, pO_2}{\partial ln\, C_{O^{2-}}}$$

Self diffusion coefficient $$D_{O^{2-}} \approx D_{chem} / \Gamma_O$$

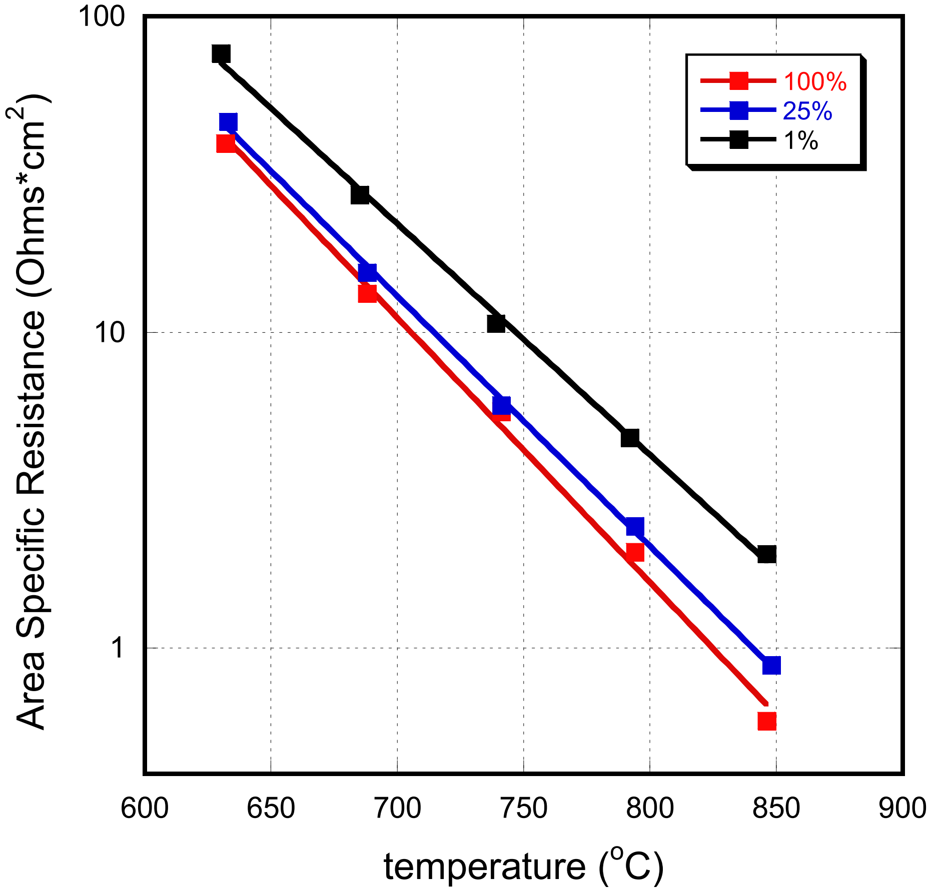
Surface exchange coefficient $$k_{ex} = k_{chem} / \Gamma_O$$

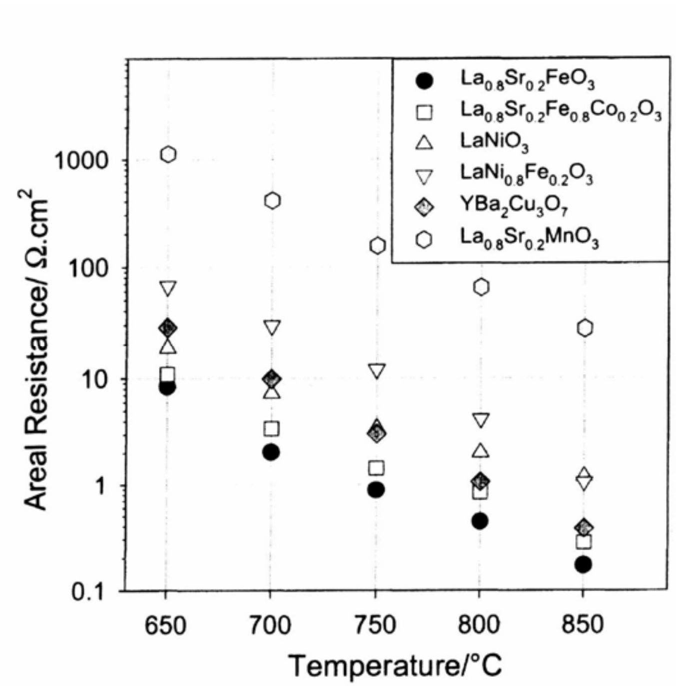
Oxygen Diffusion Coefficients for La_2NiO_4 and Pr_2NiO_4





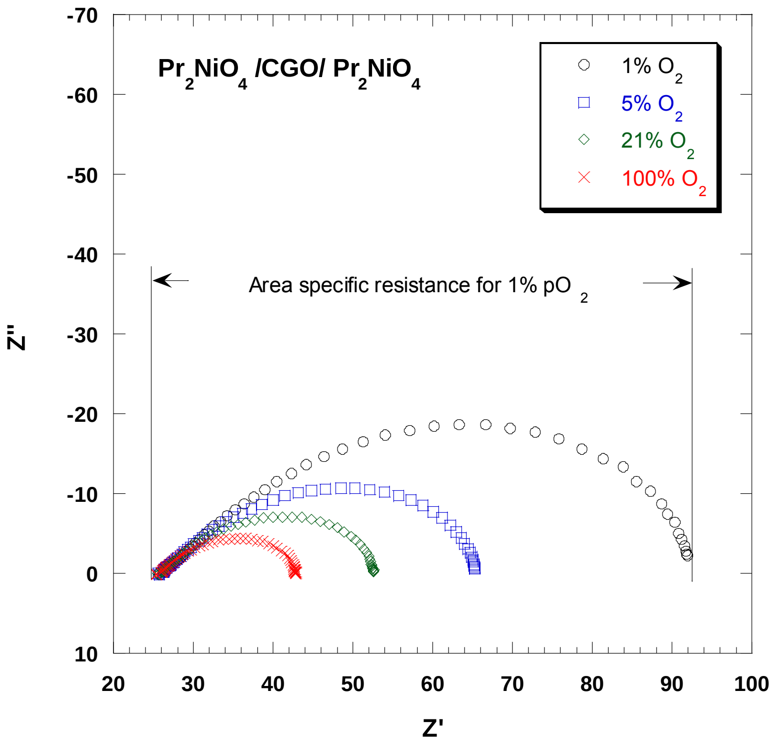
Area Resistances on YSZ

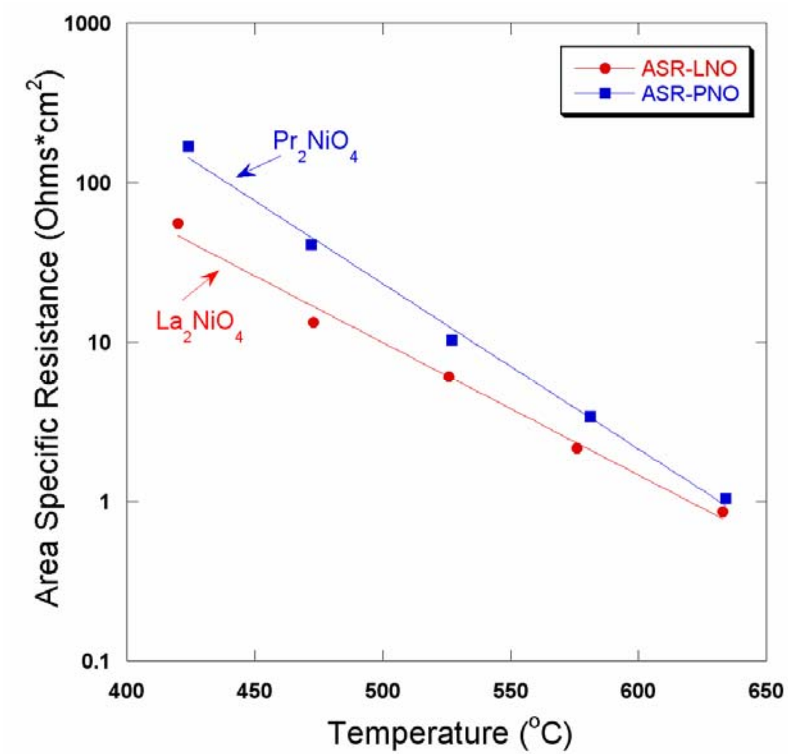




Ralph et al., in *Solid Oxide Fuel Cells VII*, PV 2001-16, p. 466, 2001.

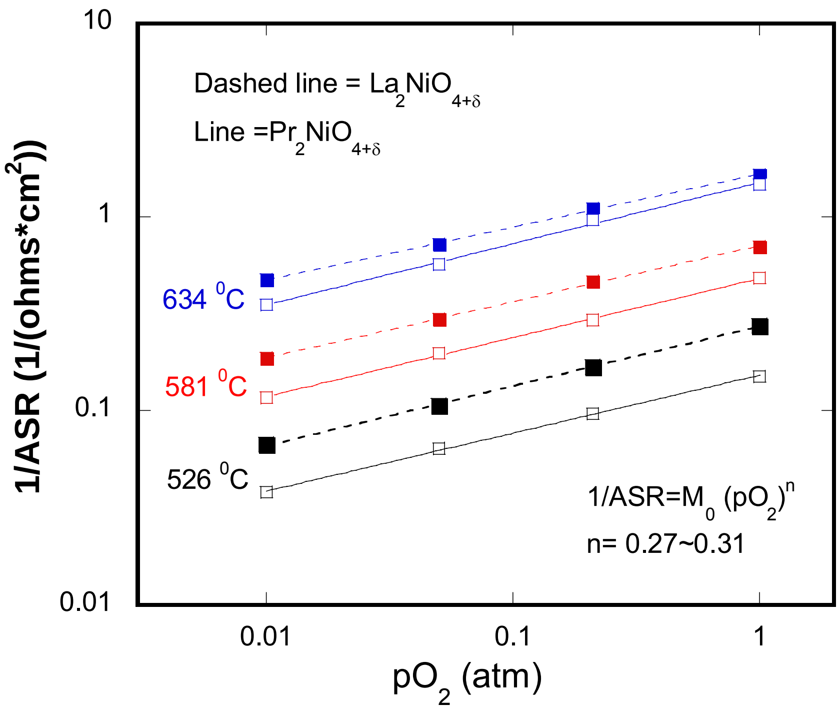
Symmetric cells
LNO|CGO|LNO and PNO|CGO|PNO

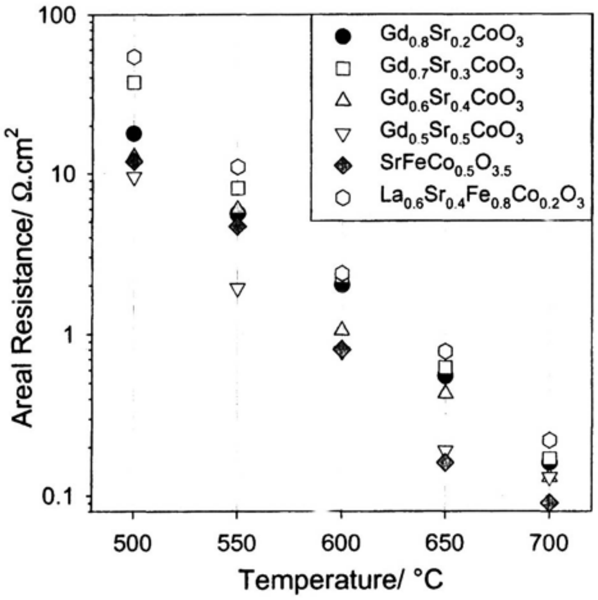




Representative impedance spectra of the Pr_2NiO_4 electrochemical cell: Pr_2NiO_4 /CGO/ Pr_2NiO_4 (T= 527 °C).

Comparisons on CGO

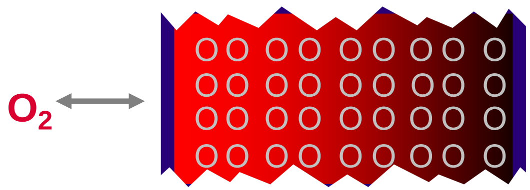




Ralph et al., in *Solid Oxide Fuel Cells VII*, PV 2001-16, p. 466, 2001.

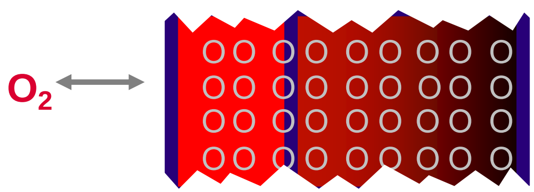
Isotope exchange - SIMS analysis

^{18}O represented by red color



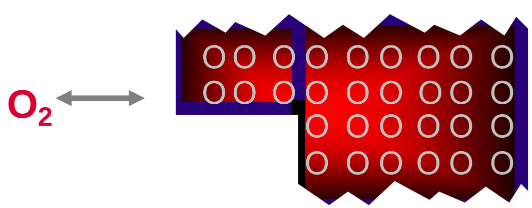
Single phase material

Surface and bulk



Two phase (films)

Surface, interface and bulk(2)



Patterned materials (printed films, patterns)

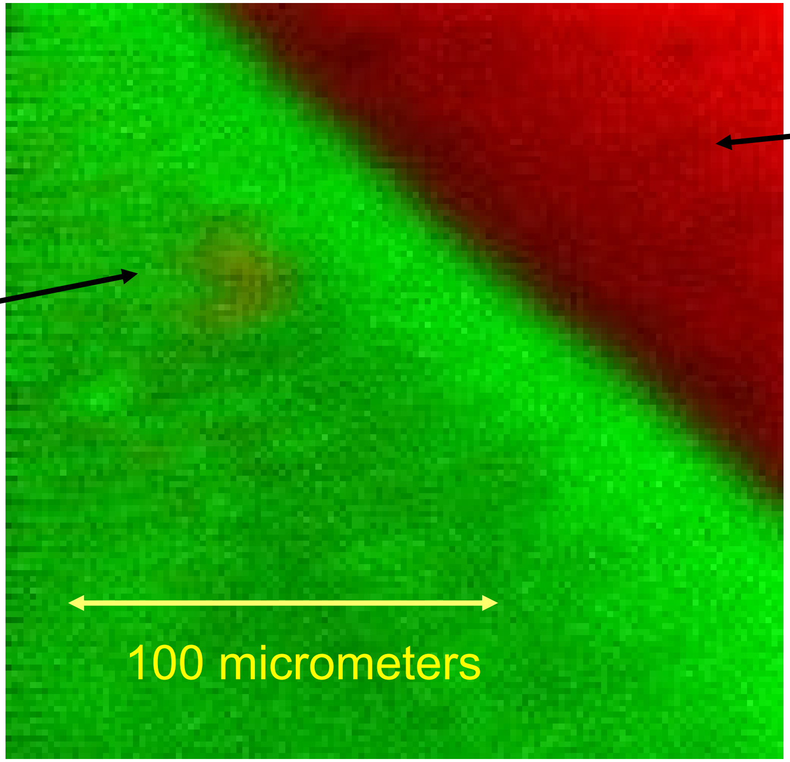
Surfaces (2), interface, bulk(2) and TPB

\+ *Functioning cathodes*?

Ink - Jet printing on YSZ(100)

TOF-SIMS image - portion of a circle (dia. 4mm, linewidth 500 micron)

CGO ions
(Ce^+,CeO^+,
Gd^+,GdO^+,etc.)

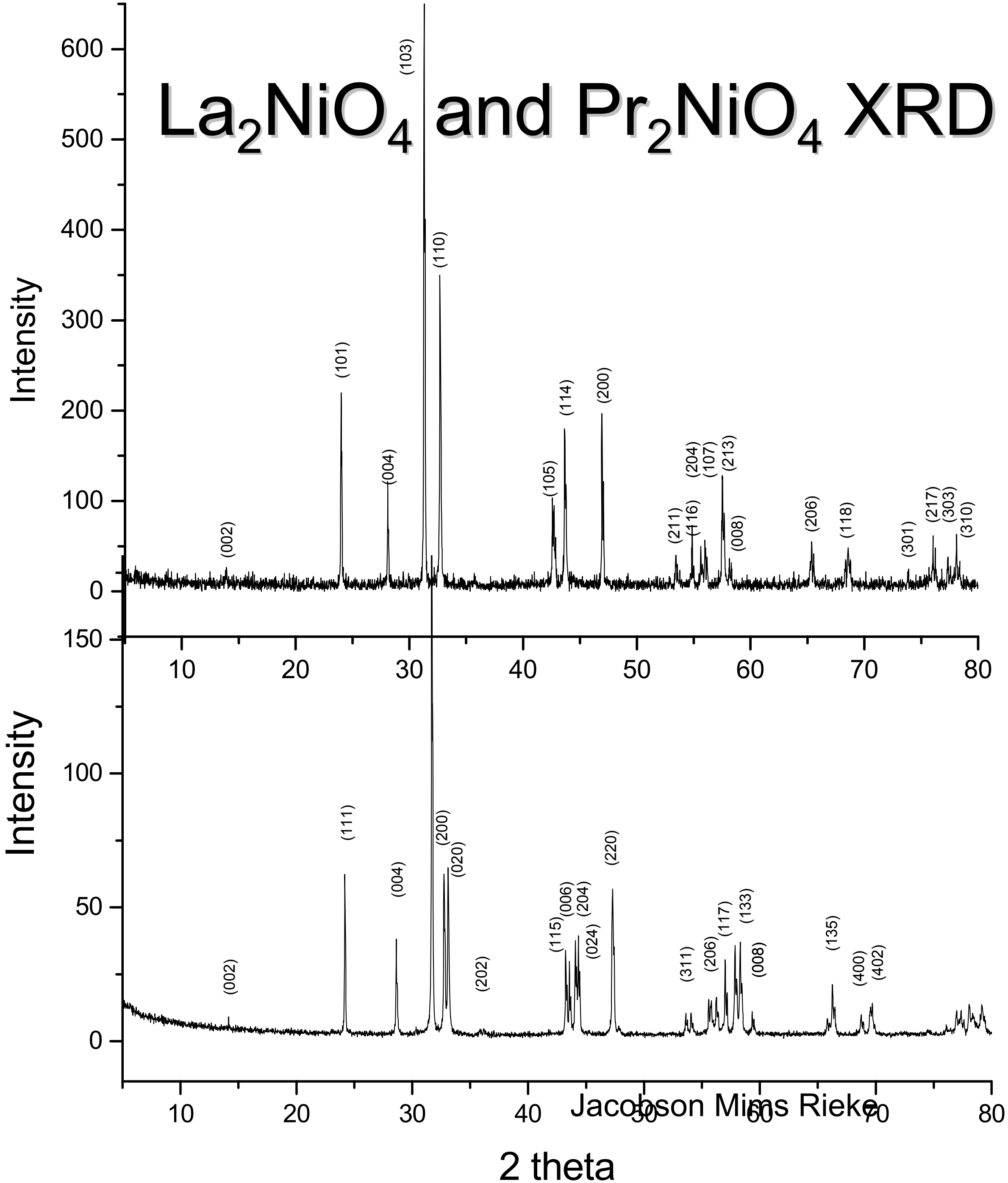


YSZ ions
(Y^+,YO^+, Zr^+,
ZrO^+, etc.)

Some Conclusions

- $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-x}$ shows complex phase behavior
  - Further structural data needed
- Pr_2NiO_4 is a promising material
  - appears to be less reactive with YSZ than La_2NiO_4
- $PrBaCo_2O_{5+x}$ thin films have:
  - very fast surface kinetics;
  - good interfaces on YSZ and CGO;
  - bulk materials require further study.
- Anisotropic materials show two surface kinetic pathways in addition to anisotropic bulk diffusion

La_2NiO_4 and Pr_2NiO_4 XRD Data



$La_2NiO_{4+\delta}$
I4/mmm
a=3.8635 Å
c=12.6667 Å

$Pr_2NiO_{4+\delta}$
Fmmm
a = 5.4523 Å
b = 5.3962 Å
c = 12.4314 Å