New Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells

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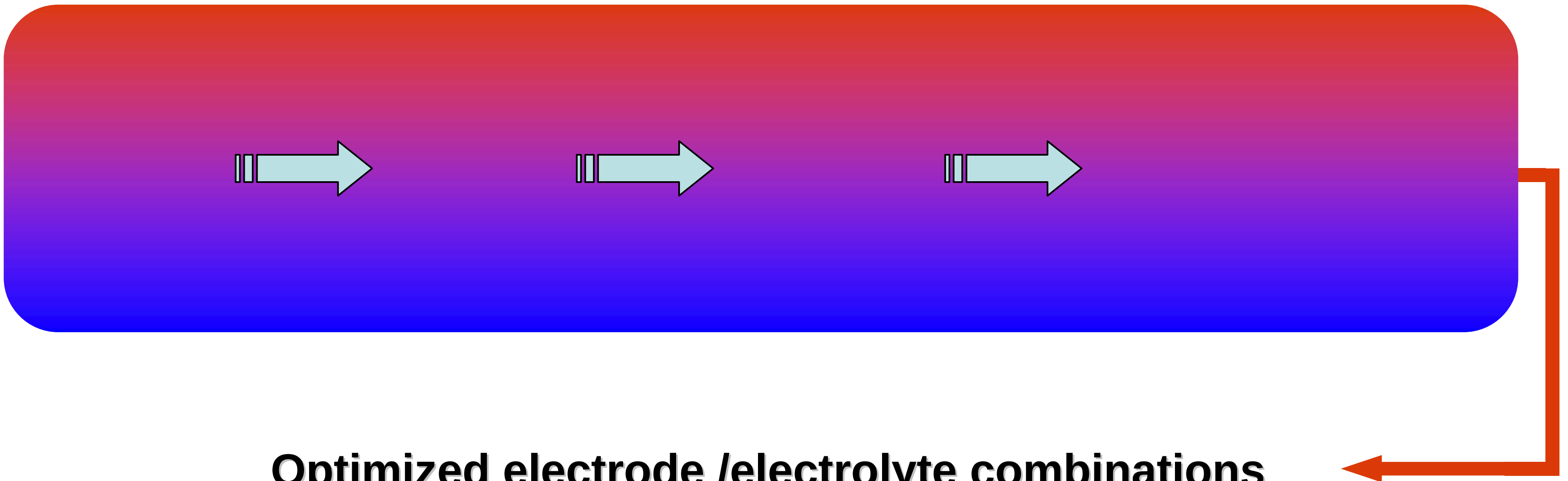
Objectives

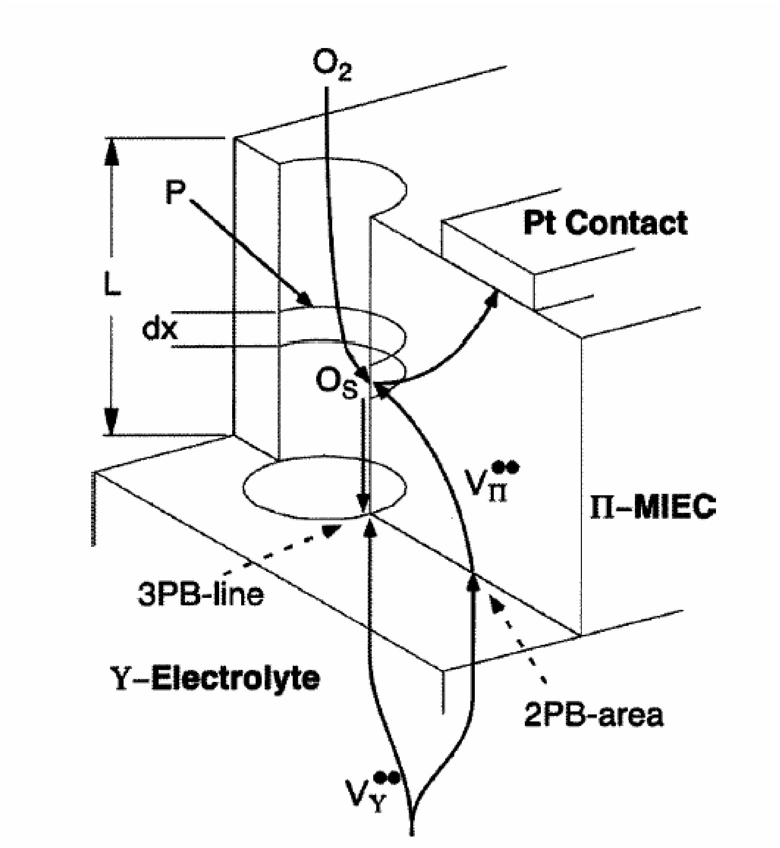
- The specific objectives are to develop cathode materials that meet the electrode performance targets
  - 1.0 W/cm^2 at 0.7 V in combination with YSZ at 700 ºC and with GDC at 600 ºC.

- 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



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)

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)

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

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

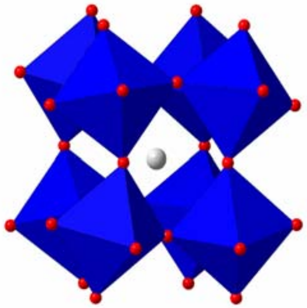
D_O and k_O can be measured by:

Isotope exchange and depth profiling (IEDP)

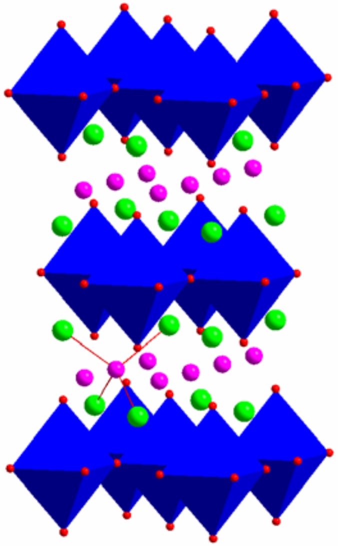
Electrical conductivity relaxation (ECR)

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

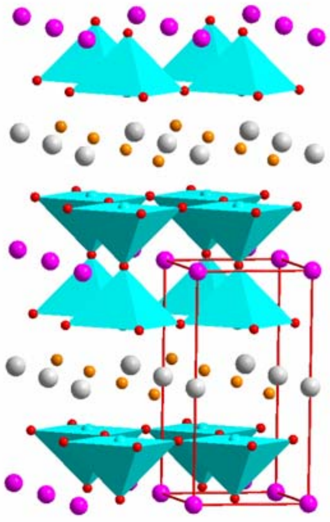
Materials Classes



- 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*
    - $PrBaCo_2O_{5+x}$
    - $LaBaCuFeO_{5+x}$,

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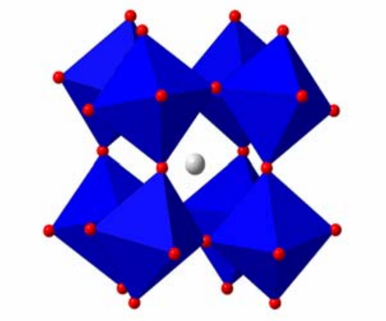
Experimental Methods

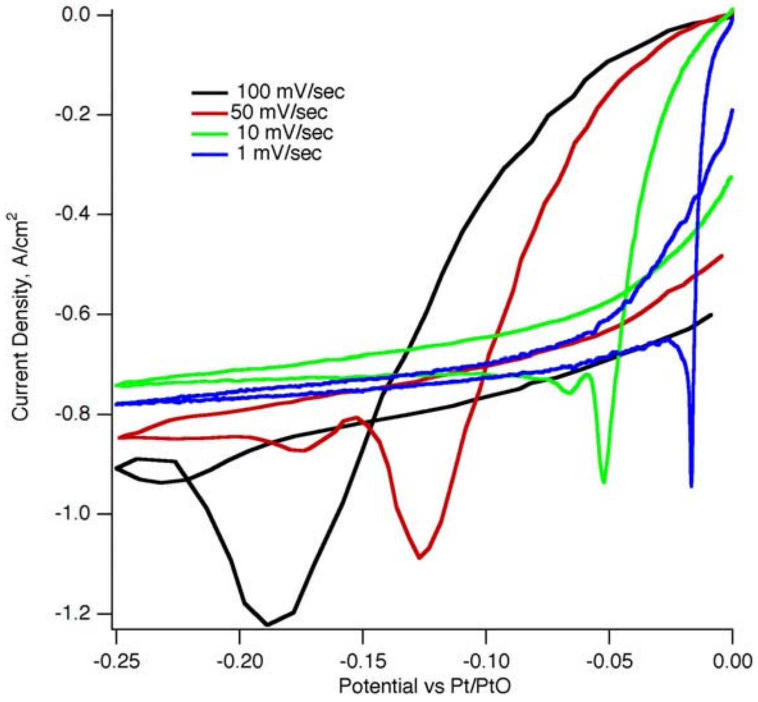
- Stoichiometry measurements
- Conductivity and Conductivity relaxation
- Photoelectron spectroscopy / Kelvin probe
- AC impedance on symmetric cells
- Isotope exchange and depth profiling (IEDP)
- Half cell measurements
- Thin film synthesis of model structures

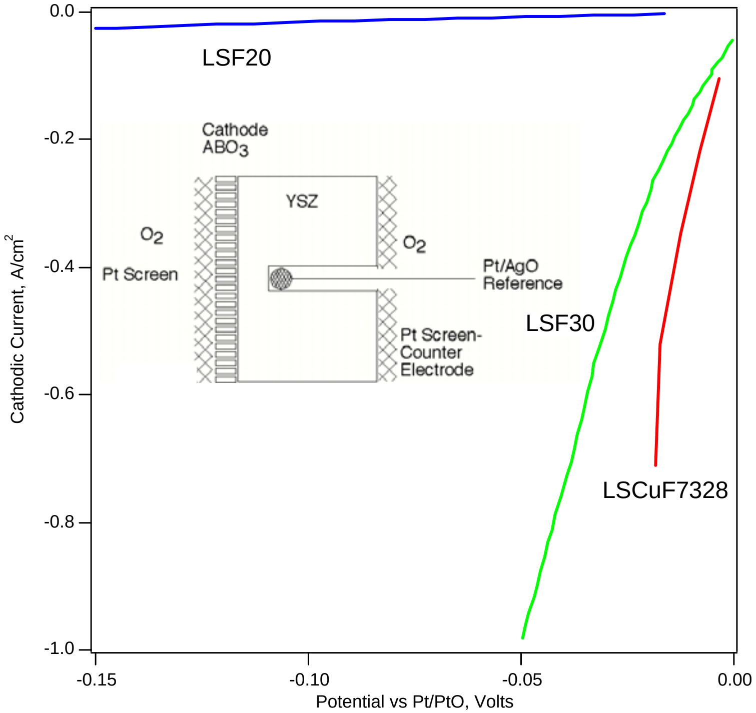
Materials Classes

- perovskite ferrites
  - *oxygen vacancies*
    - $La_{1-x}Sr_xFeO_{3-x}$, x= 0.2, 0.3
      - Extensive measurements of D_O, k_{ex}, and δ
    - $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-x}$
      - Stoichiometry
      - Interfacial chemistry



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





Linear Scan Voltammetry

Charge under peak corresponds to
~ 1 electron reduction of B site metal

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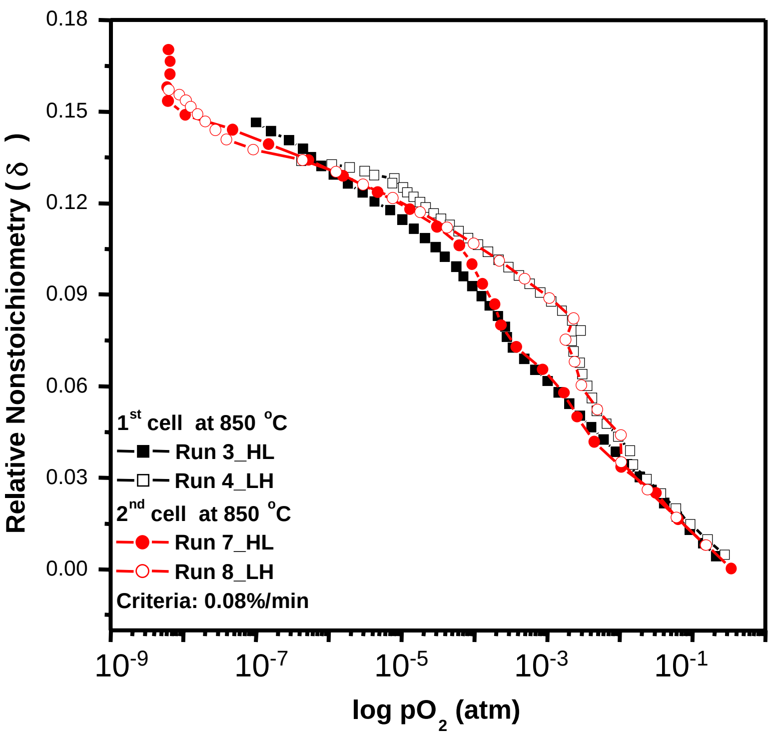
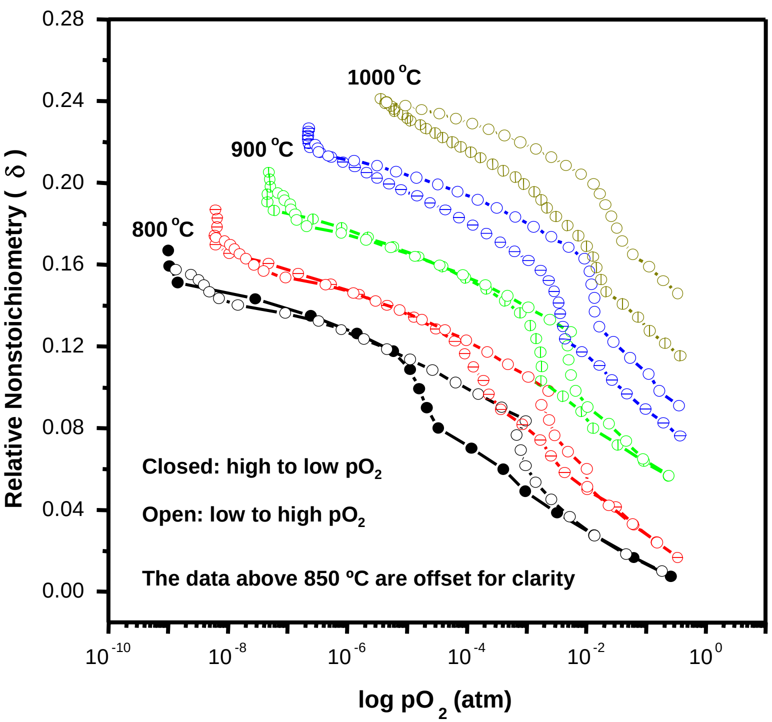
$La_{0.7}Sr_{0.3}Fe_{0.8}Cu_{0.2}O_{3-x}$ Stoichiometry

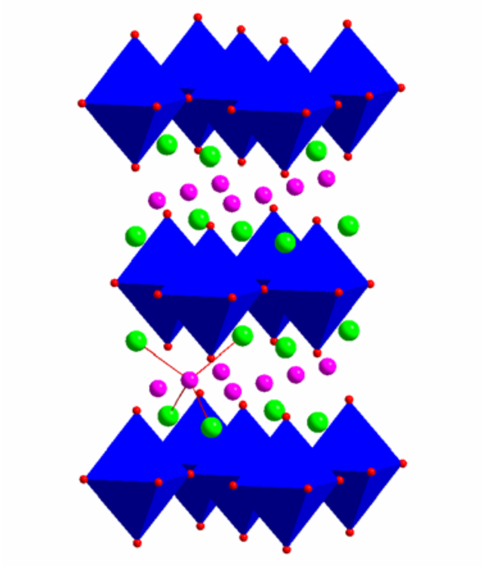




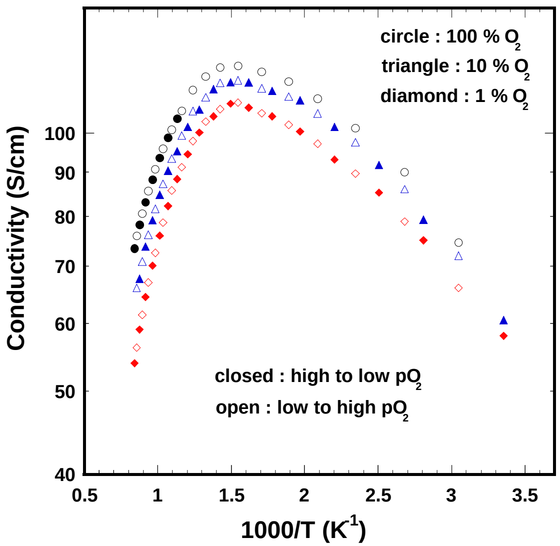
Measurements made in an electrochemical cell with Pt|YSZ|Pt as sensor and pump

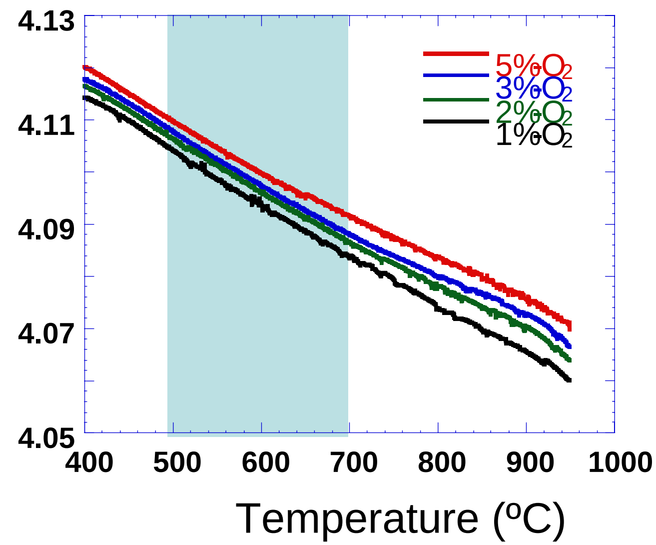
Materials Classes

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

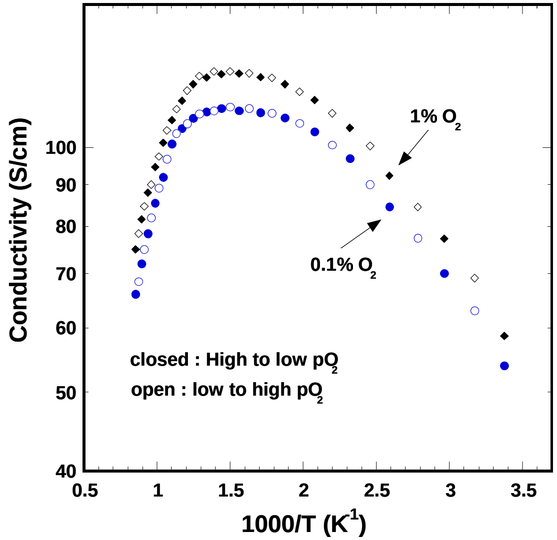


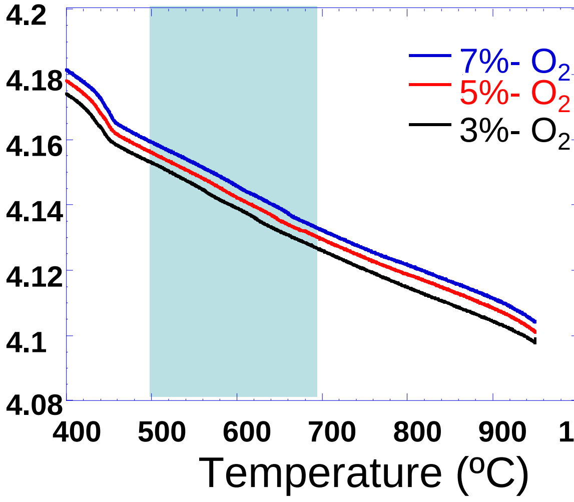
Conductivity and Stoichiometry





LNO





PNO

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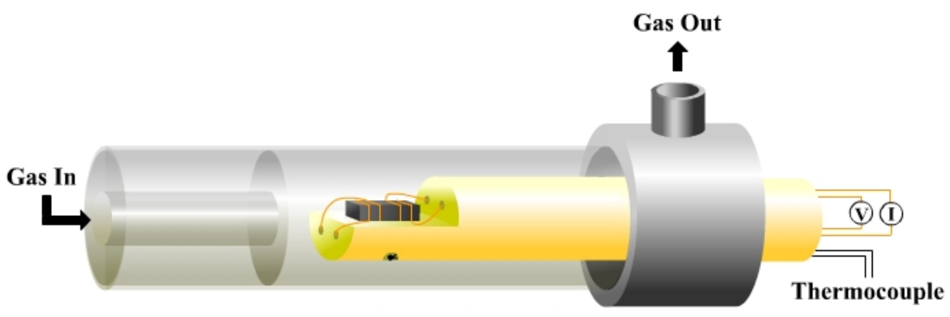
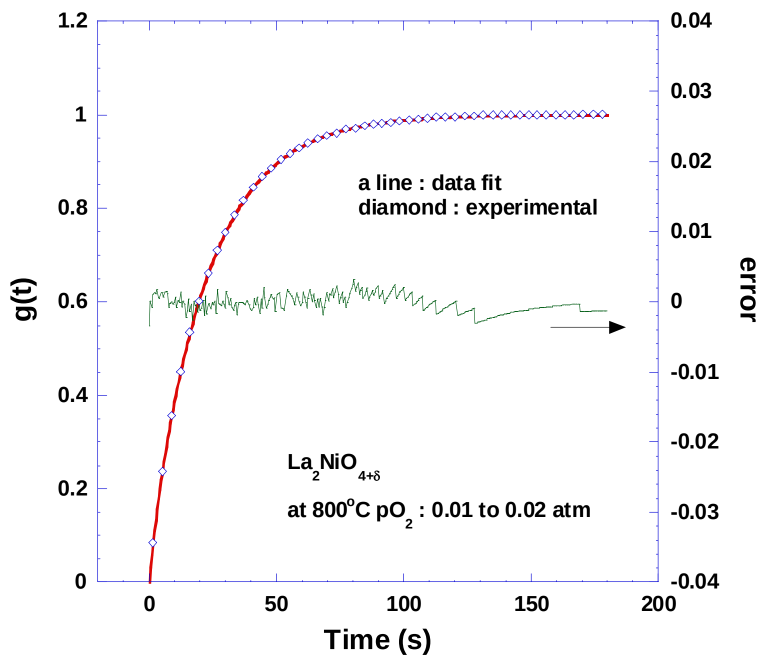
Electrical Conductivity Relaxation





- 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 $$k_{ex} = k_{chem} / \Gamma_O$$

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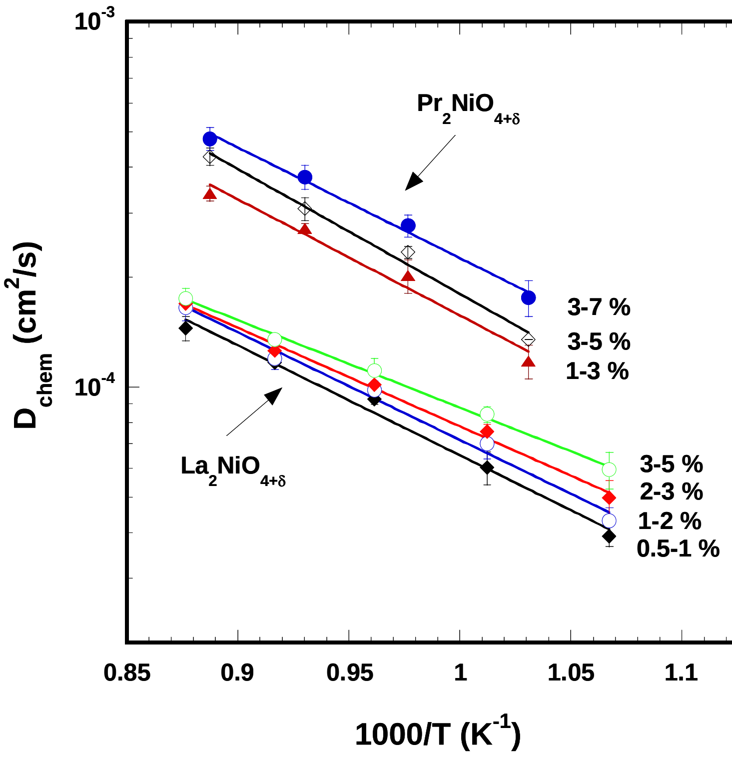
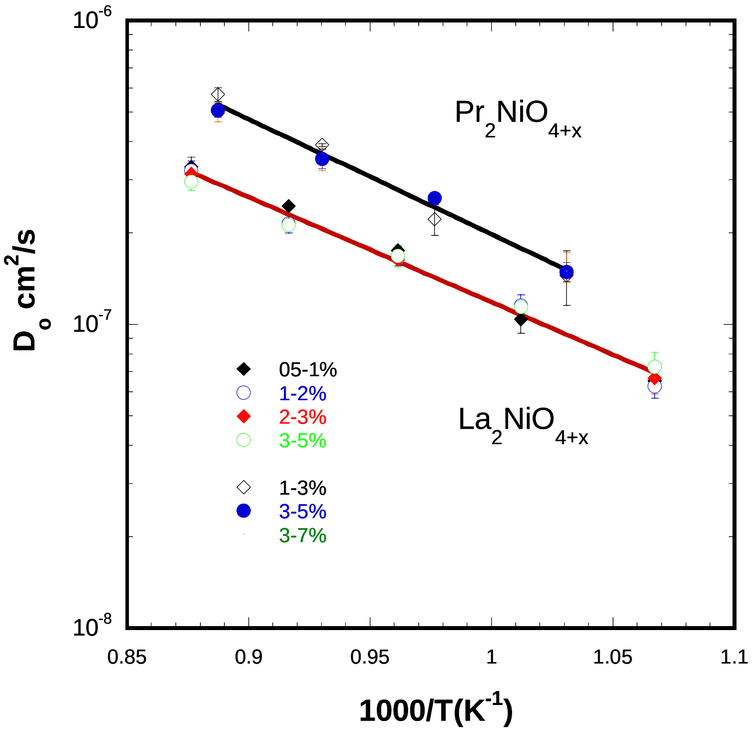
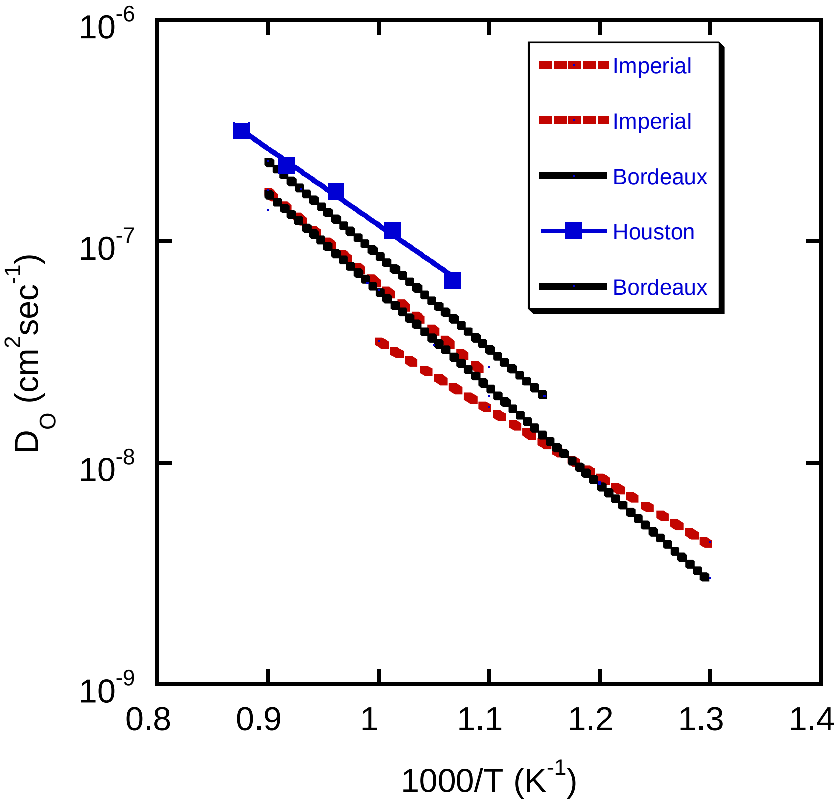
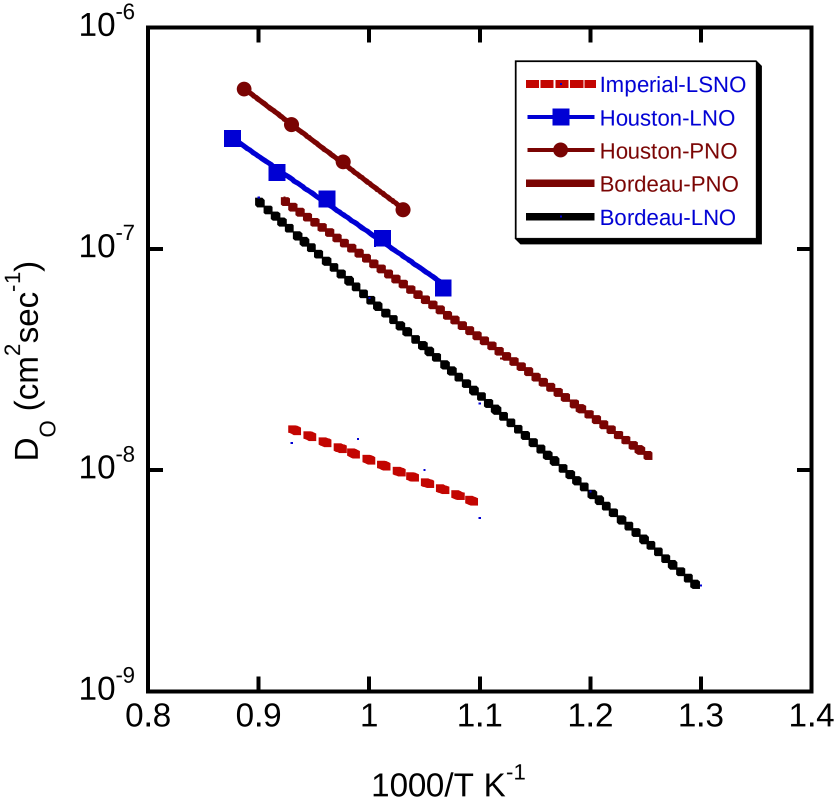
Oxygen Diffusion Coefficients for La_2NiO_4 and Pr_2NiO_4



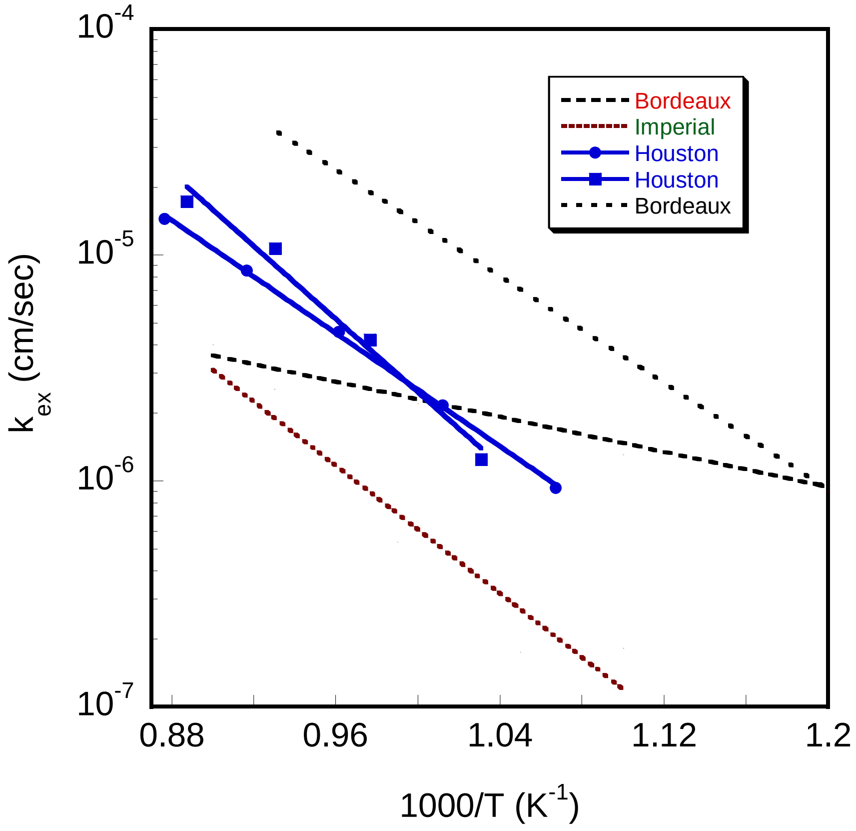


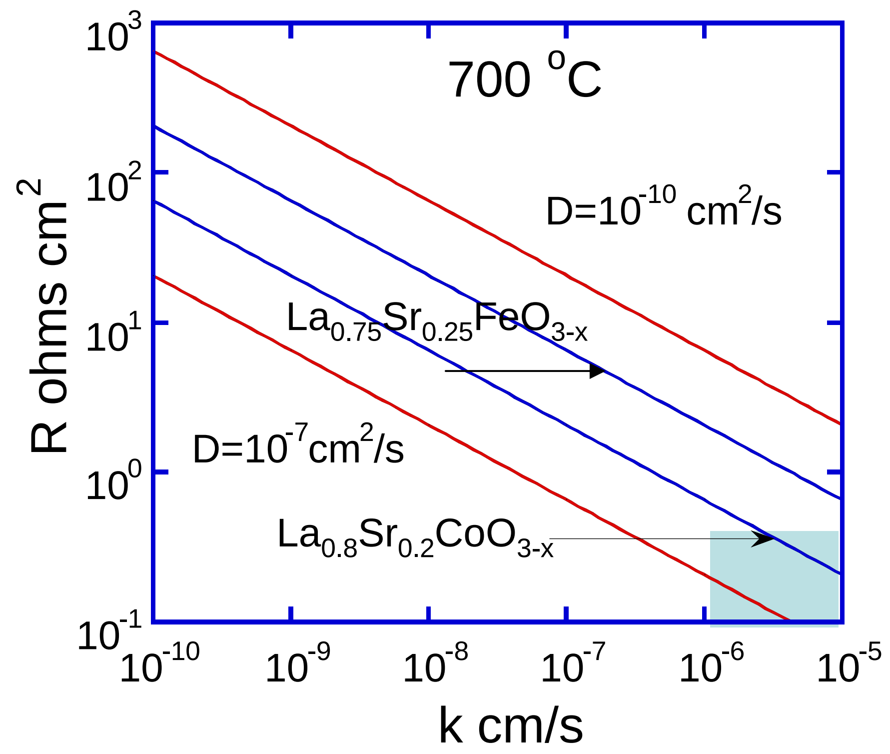
Oxygen Diffusion Coefficients for LNO and PNO





Surface Exchange Rates

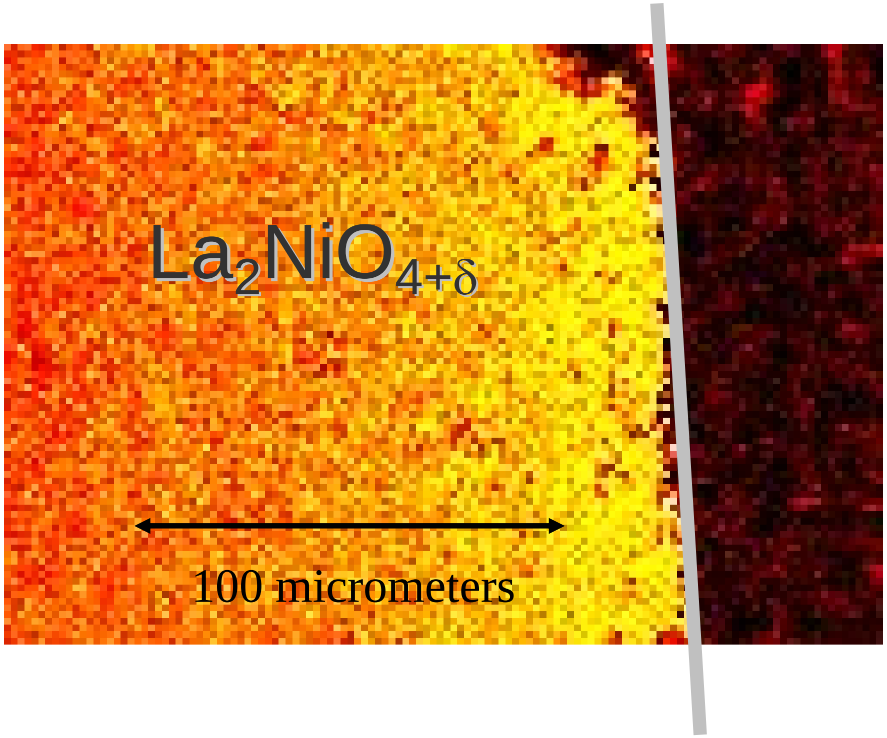




TOF- SIMS Profile in Cross-section

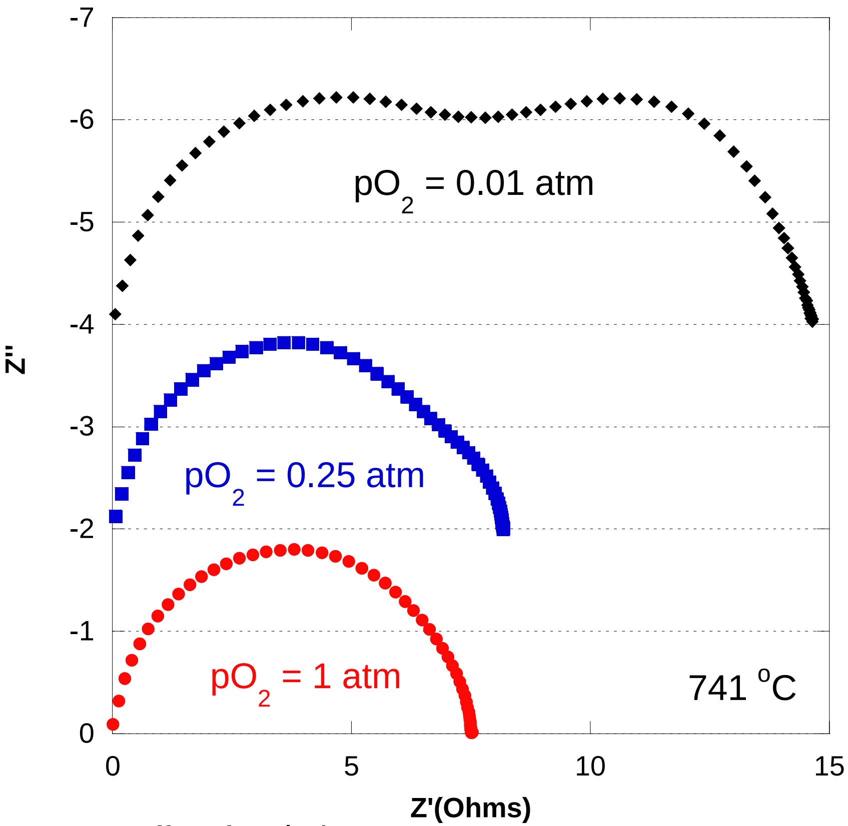
Cross section after O-18 infusion of $La_2NiO_{4+\delta}$

700 ºC, 5 min, pO_2 = 0.2 atm

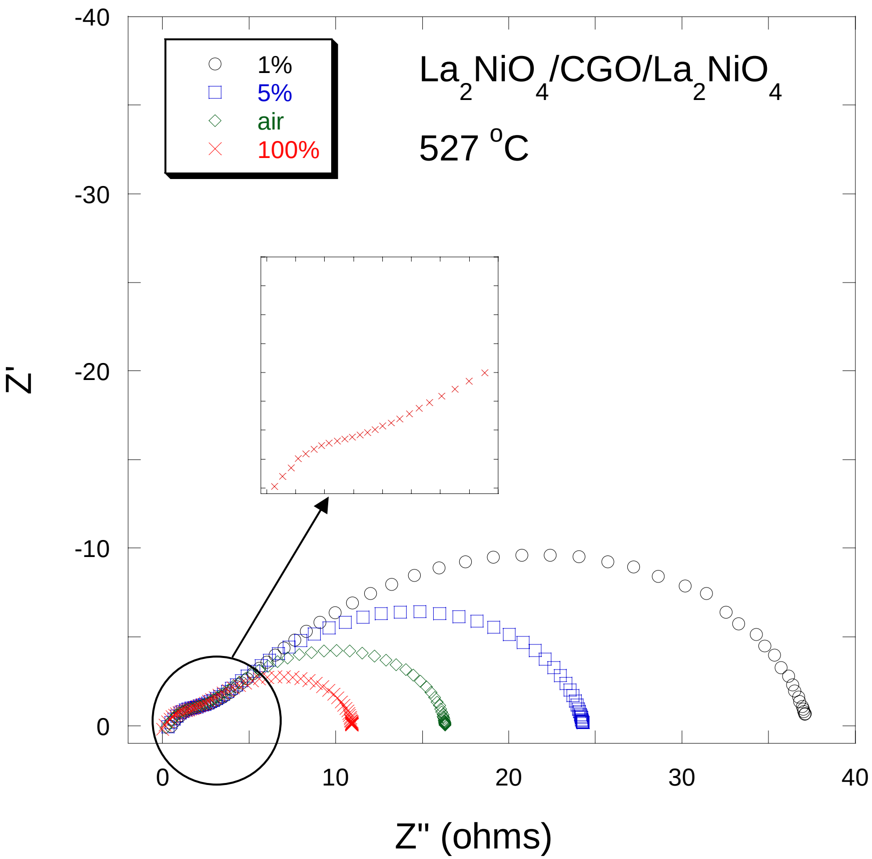


A fit of the ^{18}O profile to k_O and D_O gives values in agreement with the ECR data

Symmetric cells
LNO|YSZ|LNO and LNO|CGO|LNO



Data offset for clarity



Interface effects on both YSZ and CGO

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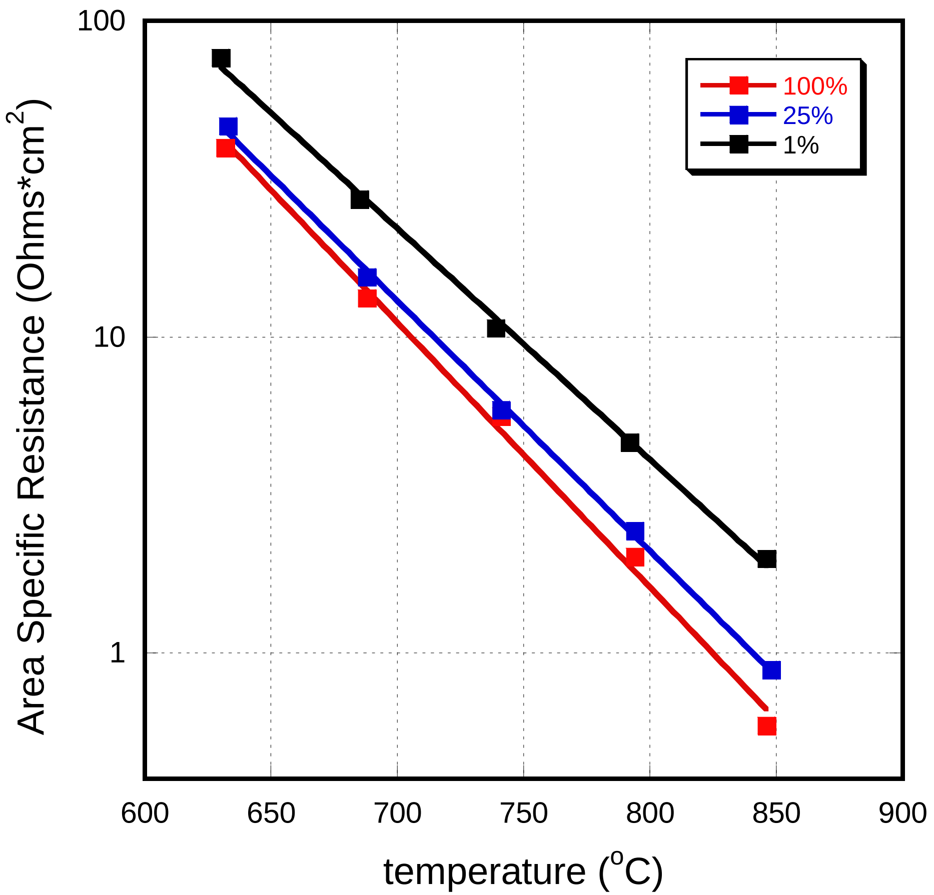
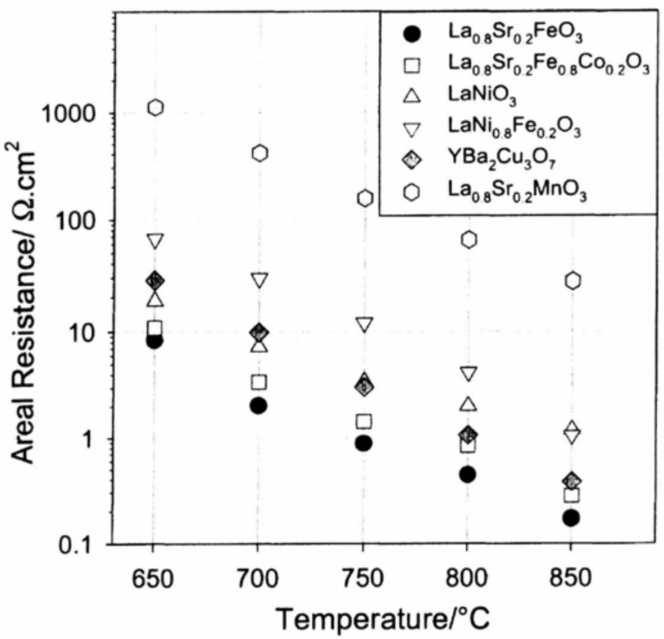
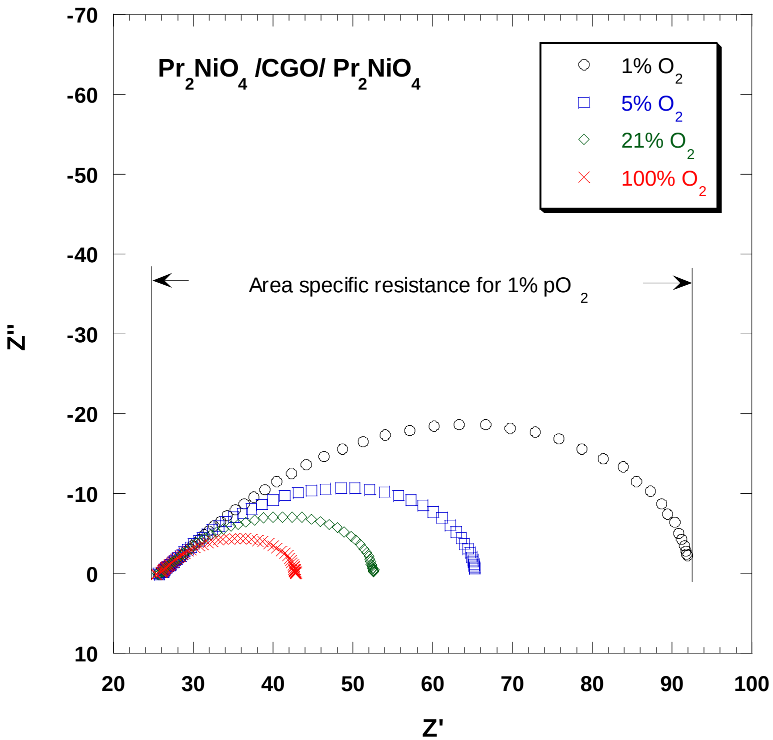
Area Resistances on YSZ

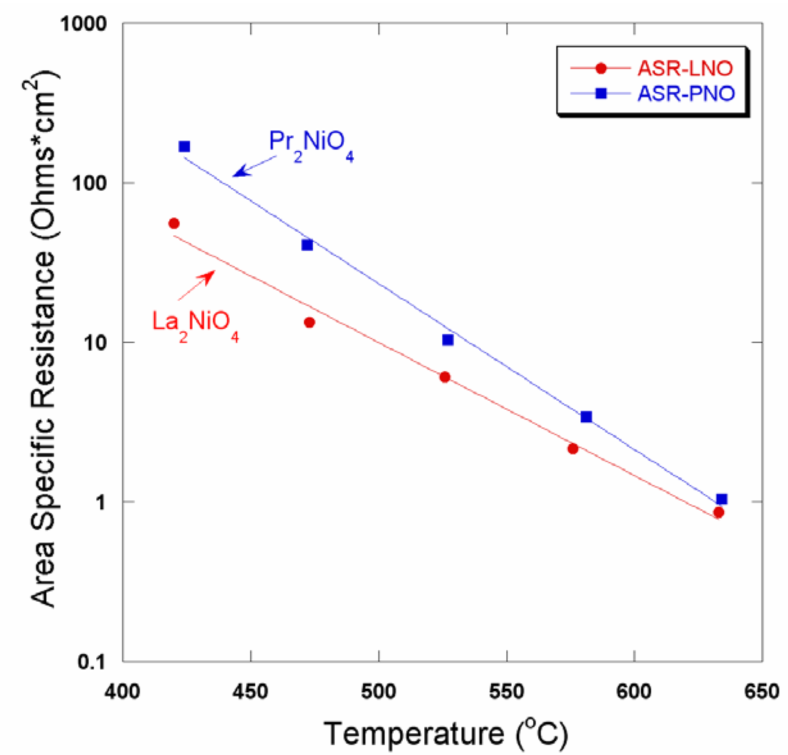




Ralph et al., in *Solid Oxide Fuel Cells VII*, PV 2001-16, p. 466, 2001.

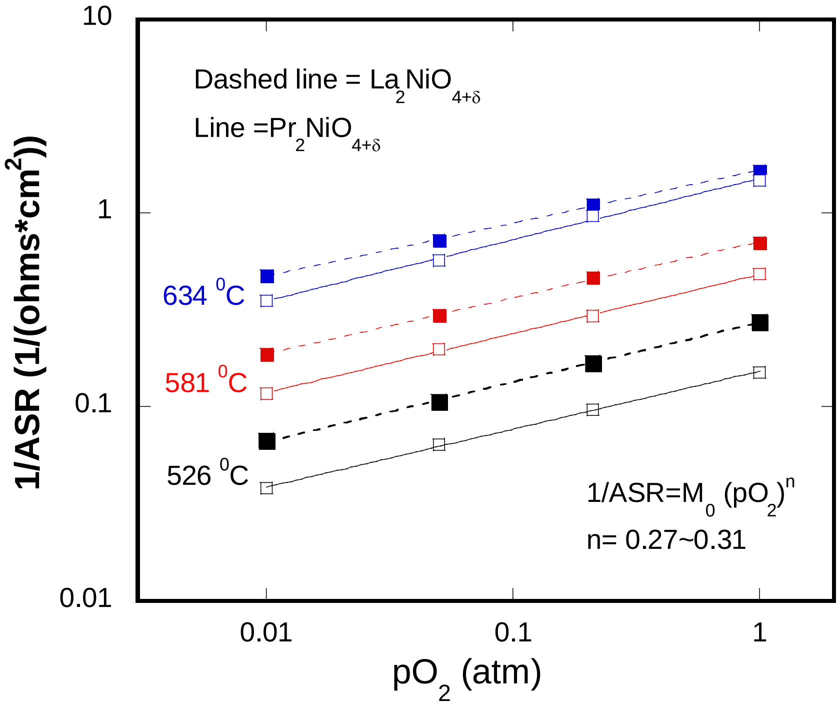
Symmetric cells
LNO|CGO|LNO and PNO|CGO|PNO

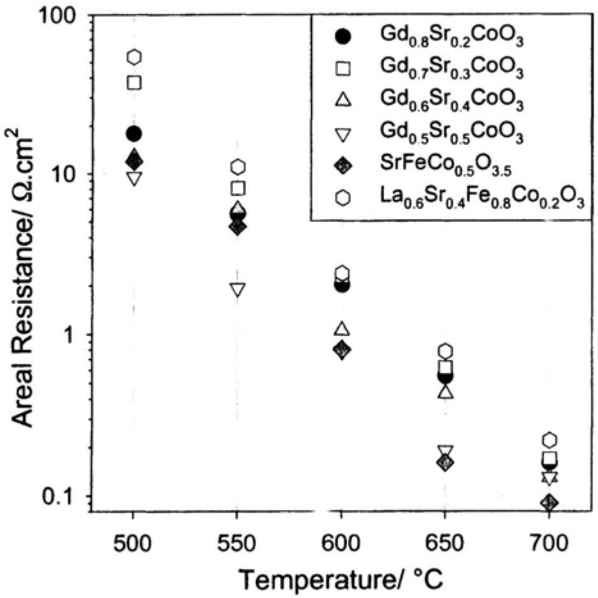




Representative impedance spectra of the Pr_2NiO_4 electrochemical cell: Pr_2NiO_4 /CGO/ Pr_2NiO_4 (T= 527 °C).

Comparisons on CGO





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

Model materials to study individual steps

Single phase material

Surface and bulk

Two phase (films on single xtals)

Surface, interface and bulk(s)

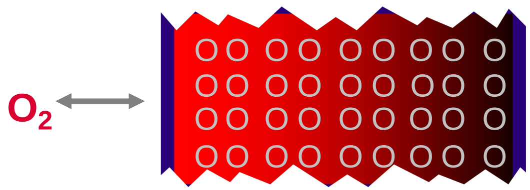
Patterned materials
(masked films, printed patterns)

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

Synthesis: Pulsed Laser Deposition and Ink Jet Printing

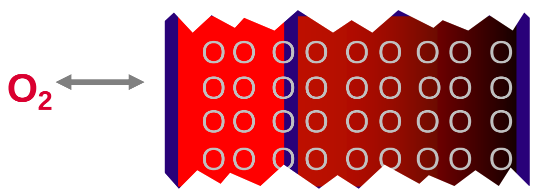
Isotope exchange - SIMS analysis

^{18}O represented by red color



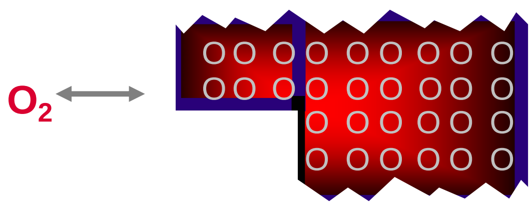
Single phase material

Surface and bulk



Two phase (films)

Surface, interface and bulk(2)



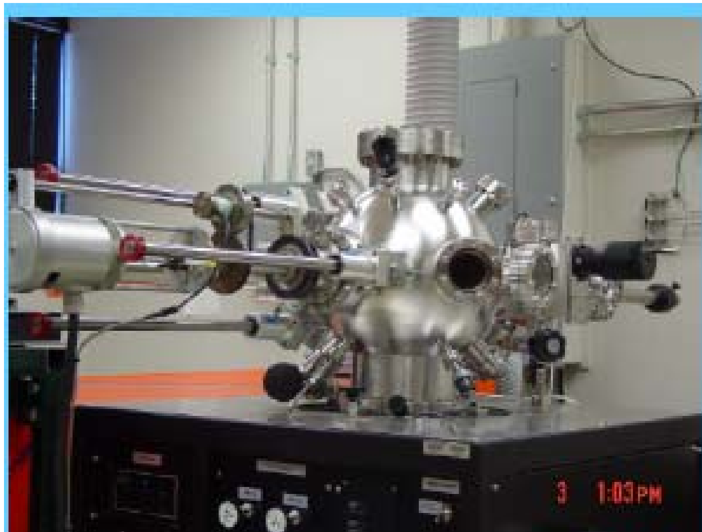
Patterned materials (printed films, patterns)

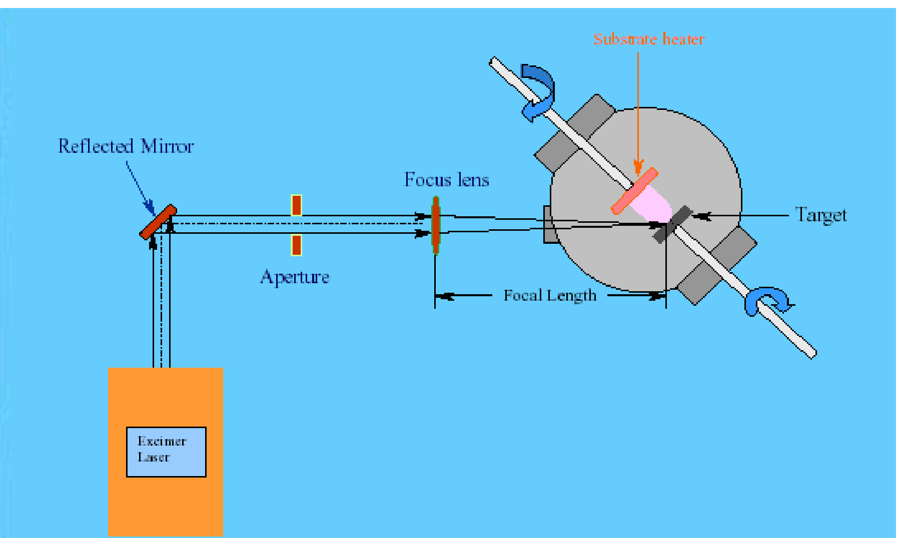
Surfaces (2), interface, bulk(2) and TPB

+ *Functioning cathodes*?

PLD Film Deposition

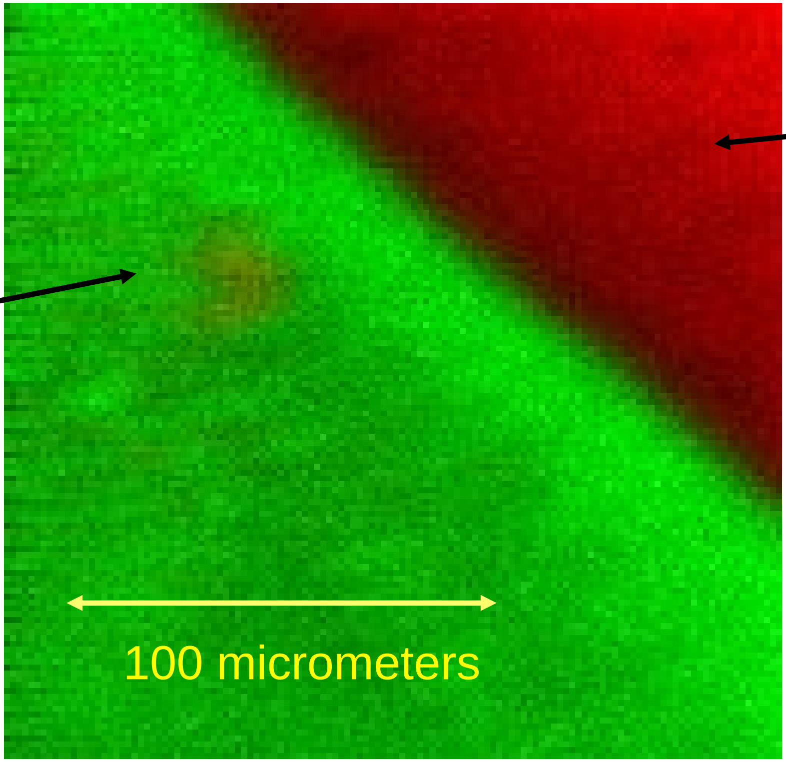
- (100) $LaAlO_3$ $SrTiO_3$ and YSZ single crystal substrates
- PBCO at 300 mTorr oxygen partial pressure with a substrate temperature of 880 °C.
- LNO at 300 mTorr and 840 °C
- KrF excimer laser with pulse frequency of 7 Hz.
- Films 2000 to 5000 Å





Ink - Jet printing on YSZ(100)

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

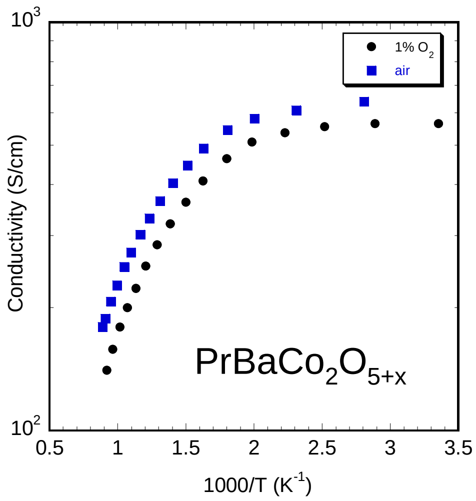


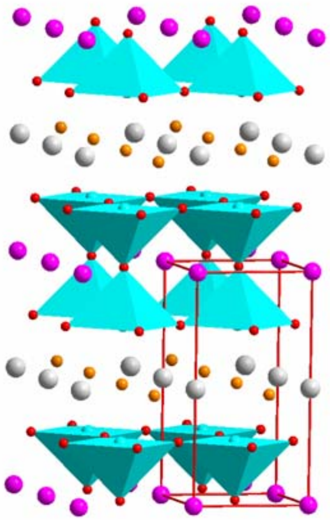
Materials Classes

perovskite oxides with ordered A cations

– 2 dimensional vacancies

- $PrBaCo_2O_{5+x}$ (PBCO)
- $LaBaCuFeO_{5+x}$, $LaBaCu_xFe_{1+x}O_{5+x}$

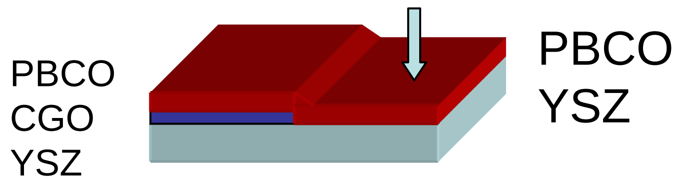


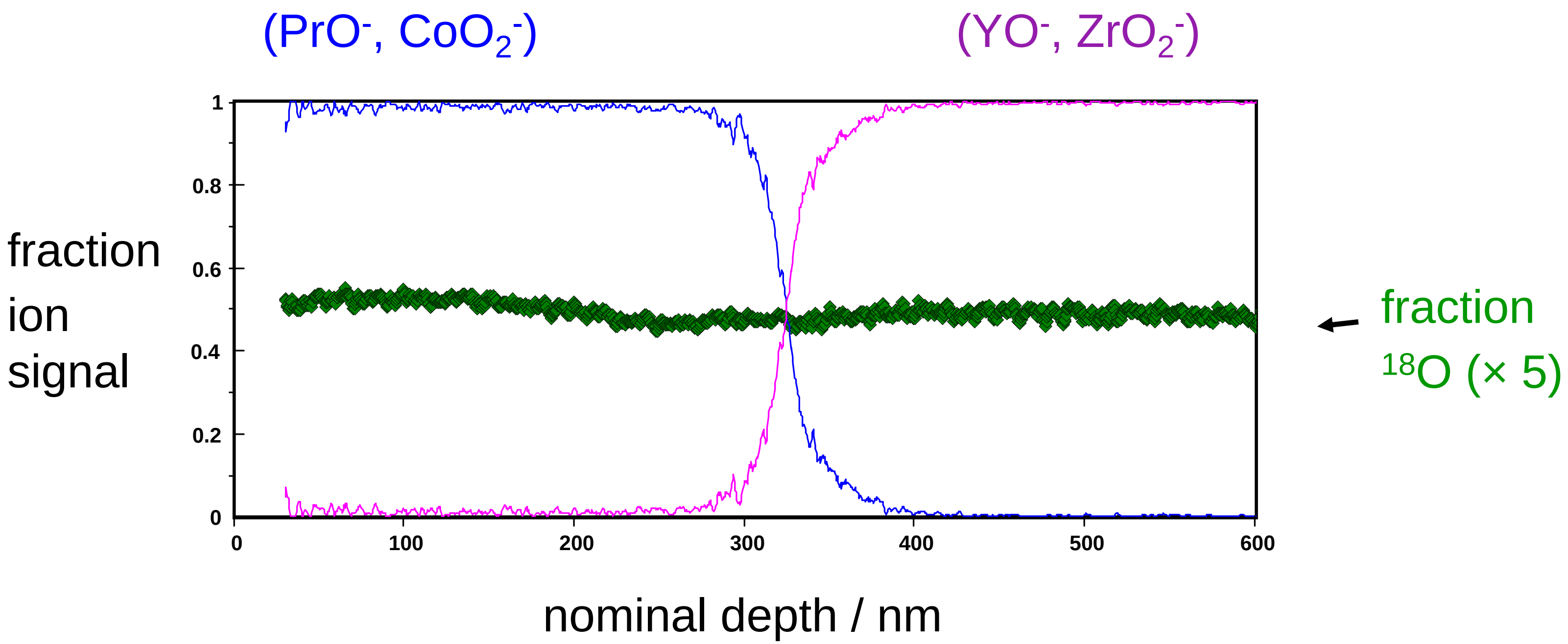


Thin film PBCO on YSZ (100)

^{18}O at 700 °C,

pO_2 = 0.2 atm





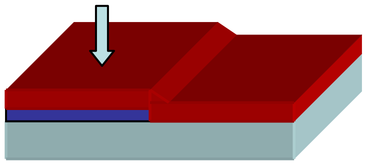
- Insignificant interfacial transfer barriers
- Exchange limited by surface $k_{O,PBCO}$ and $D_{O, YSZ}$

Thin films PBCO + CGO on YSZ (100)

^{18}O at 700 °C,

pO_2 = 0.2 atm

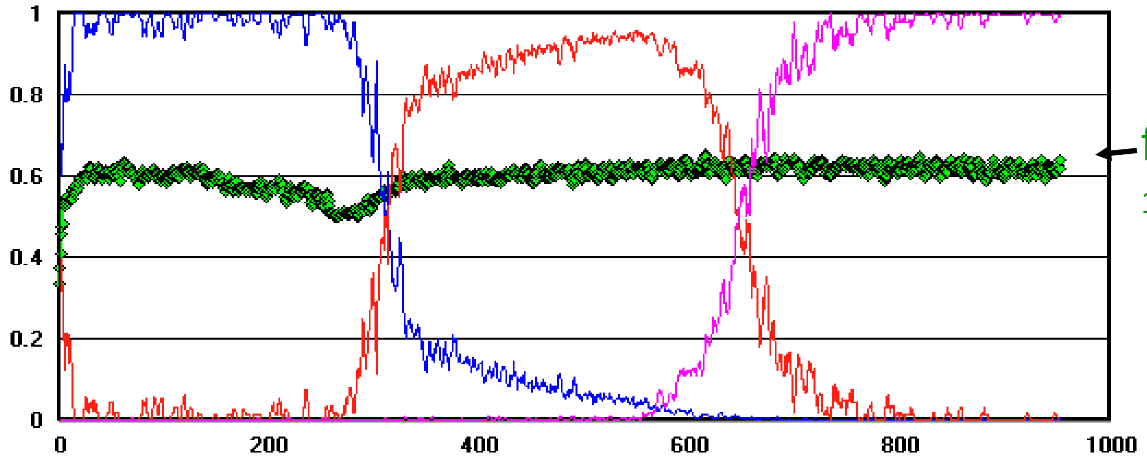
PBCO
CGO
YSZ



PBCO
YSZ

(PrO^-, CoO_2^-) (CeO^-, GdO^-) (YO^-, ZrO_2^-)

fraction ion signal

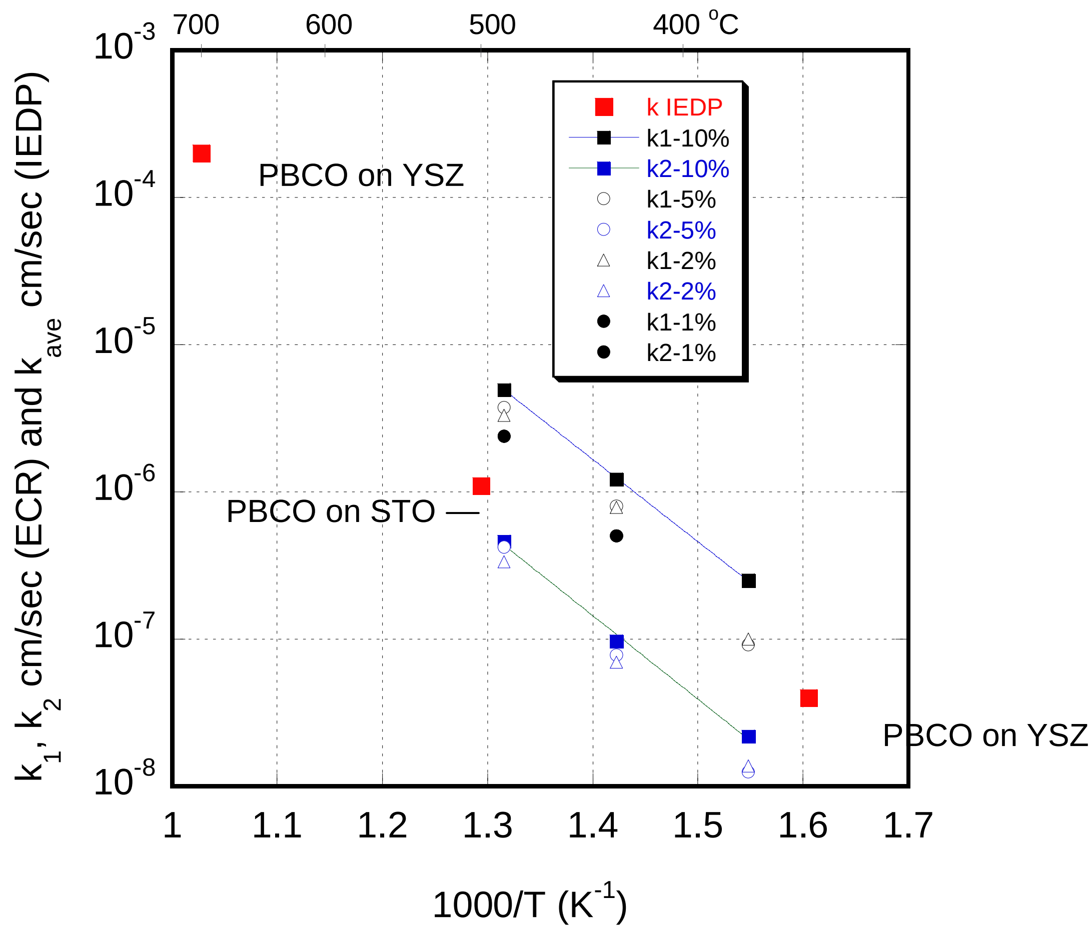


fraction ^{18}O (× 5)

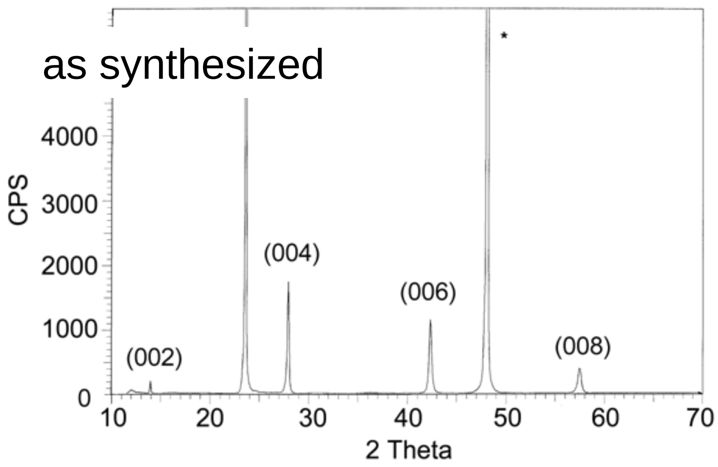
nominal depth / nm

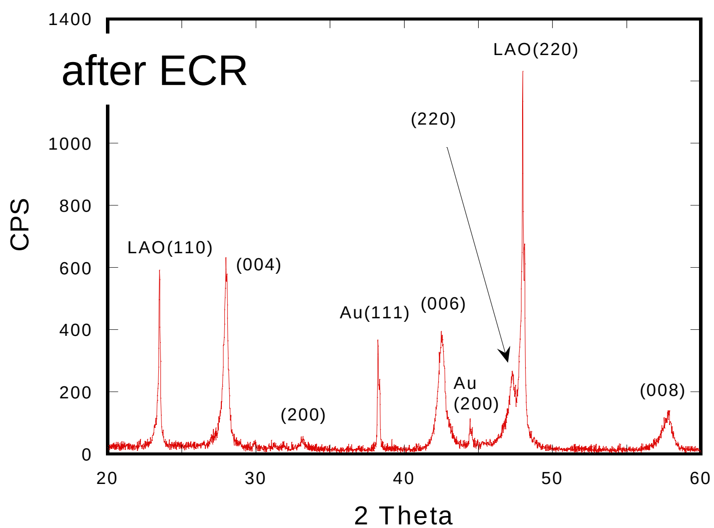
- Insignificant interfacial transfer barriers
- Exchange limited by surface $k_{O,PBCO}$ and $D_{O, YSZ}$

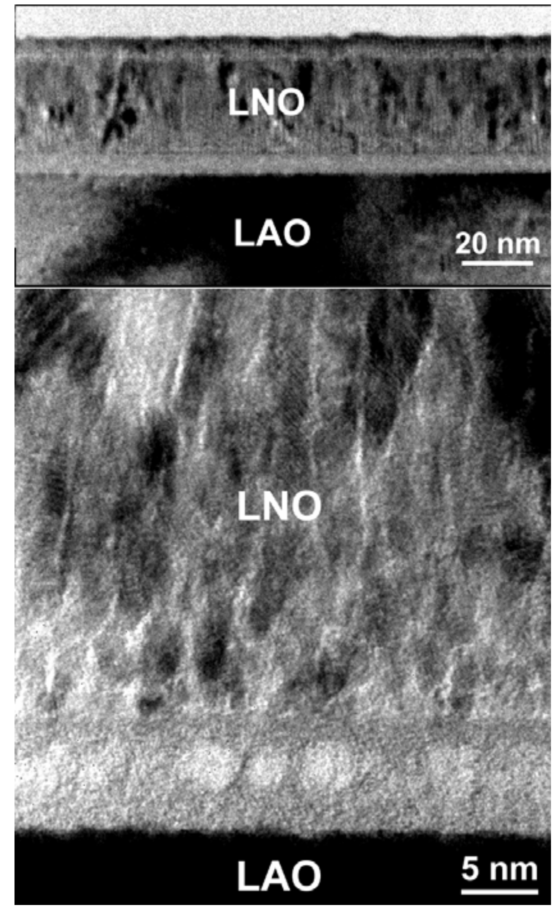
Surface Exchange on PBCO Thin Films



Structural Characterization of La_2NiO_4 Thin Films on LAO

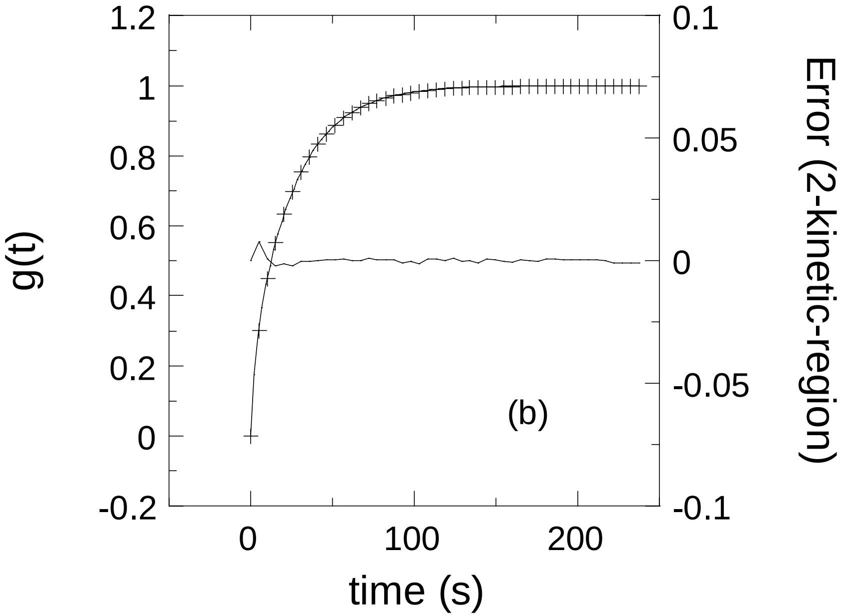


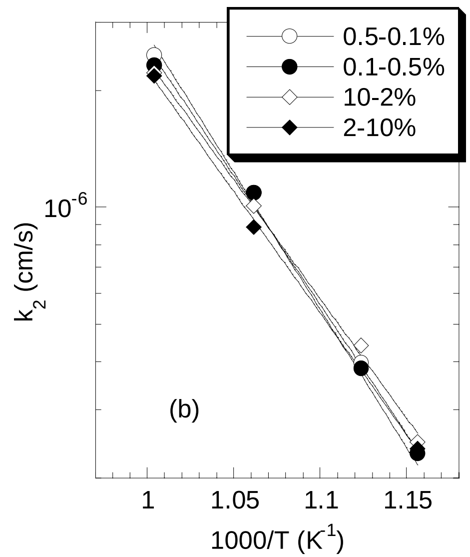


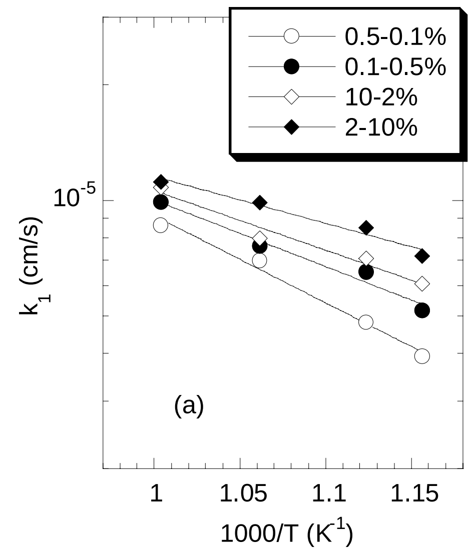


HRTEM cross section before ECR

Surface Exchange Kinetics on La_2 NiO_4 Films





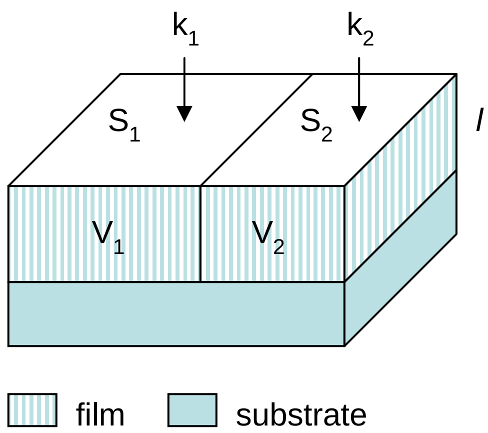


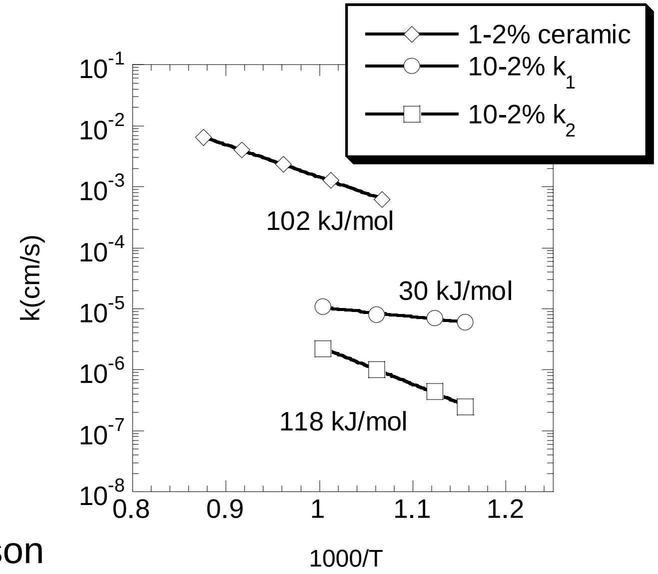
A single exponential model does not fit the data – requires two time constants

$$g(t) = \frac{\bar{c}(t) - \bar{c}(0)}{\bar{c}(\infty) - \bar{c}(0)} = 1 - A_1 \exp(-\frac{t}{\tau_1}) - A_2 \exp(-\frac{t}{\tau_2})$$

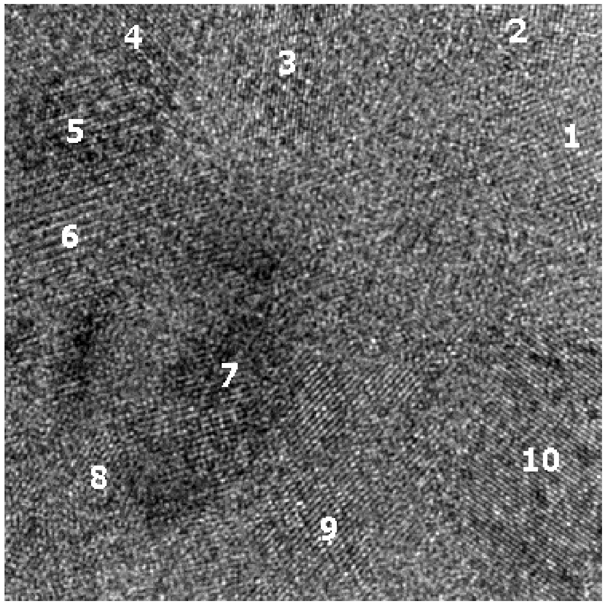
La_2NiO_4 Surface Exchange Model

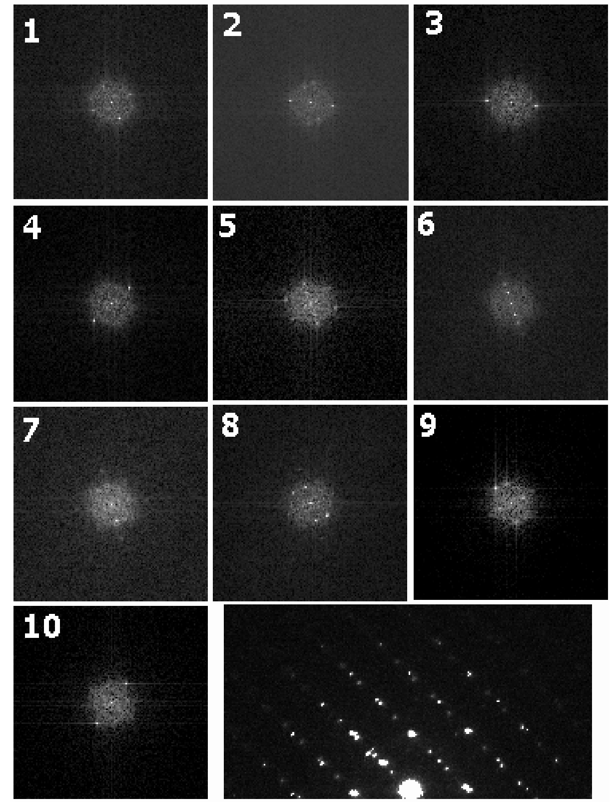
switch / T(ºC)	2%-10%			10%-2%			0.1-0.5%			0.5-0.1%		
	A_1	A_2	A_1+A_2	A_1	A_2	A_1+A_2	A_1	A_2	A_1+A_2	A_1	A_2	A_1+A_2
592	0.17	0.83	1.00	0.17	0.83	1.00	0.17	0.85	1.02	0.20	0.81	1.01
617	0.42	0.58	1.00	0.19	0.81	1.00	0.32	0.70	1.02	0.21	0.79	1.00
669	0.22	0.78	1.00	0.22	0.78	1.00	0.22	0.78	1.00	0.28	0.72	1.00
723	0.23	0.77	1.00	0.21	0.79	1.00	0.42	0.62	1.04	0.46	0.61	1.07





HRTEM on La_2NiO_4 after ECR





- Films show columnar growth
- c axis oriented on synthesis
- Reconstructs during ECR experiment but still mainly c axis oriented
- Two kinetic pathways due to the anisotropy

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

Future Plans

- Further analysis of the stoichiometry behavior of $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-x}$
- Thin film deposition of $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-x}$ (target prepared) for interface studies
- Clarify the potential advantage of Pr vs La systems with respect to interface reactivity
- Symmetric cell tests of Pr_2NiO_4 on YSZ
- Evaluation of PBCO and related compositions in bulk form
- Electrochemical performance studies of LNO, PNO and PBCO

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