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Fuel cell related materials using in situ neutron diffraction

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Intense Pulsed Neutron Source
Argonne National Laboratory

U.S. Department of Energy

UChicago
Argonne LLC

Office of Science
U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory
managed by UChicago Argonne, LLC

Overview

Ceramic membranes

- Fuel cell electrodes and electrolytes
- Water dissociation
- Gas separation

Materials properties and role of neutron diffraction

- Bulk phase composition
- Mixed ionic/electronic conductivity - cation and oxygen vacancies
- pO_2 gradients - gas mixtures to control pO_2 on both sides of membranes
- Kinetics - time-resolved studies

Examples with current instrumentation

- SFC2 - $Sr_2(Fe,Co)_3O_{6.5+\delta}$
- LSFC - $(La,Sr)_1(Fe,Co)_2O_{6-\delta}$
- CY20 - $Ce_{0.8}Y_{0.2}O_{1.9-\delta}$

Future prospects

- Higher neutron flux - more detail from each point, shorter runs
- Higher spatial resolution
- New analysis capabilities

Mixed-conducting ceramic membranes

Technologically important membranes with unique properties

- High oxygen/hydrogen conductivity along with electronic conductivity
- Long-term structural stability under steep pO_2 gradients
- Typically perovskite-based oxides with oxygen vacancies
- Typical dimensions: 1-3 mm thick (future applications require 1-100 µm)

Cross-cutting research opportunities

- Understand bulk and surface ionic transport in insulating and electronically-conducting materials
- Learn to tailor the properties of materials
- Achieve chemical and thermal stability and surface catalytic properties while maintaining the required transport

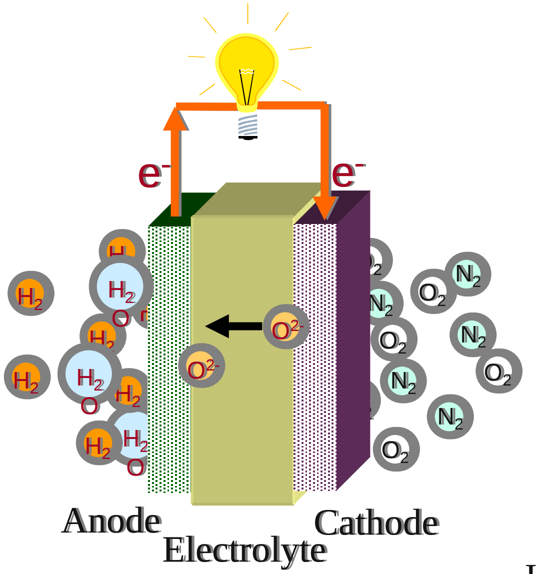
Applications

- Solid-oxide fuel cells: e.g., $Ce_{0.8}Y_{0.2}O_{1.9-\delta}$, $(La,Sr)(Fe,Co)O_{3-\delta}$
- Gas separation: e.g., $Sr(Fe,Co)O_{3-\delta}$, $(La,Sr)_3(Fe,Co)_2O_{3-\delta}$
- Hydrogen production: e.g., $Ba(Ce_{0.7}Zr_{0.2}Yb_{0.1})O_{3-\delta}$

Solid oxide fuel cells and water dissociation

Solid oxide fuel cells

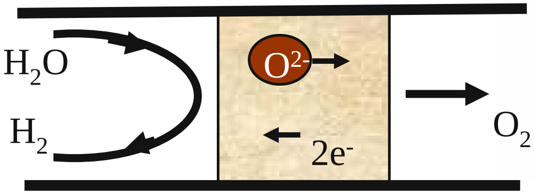
- Multi-component assemblies that generate electricity from chemical dissociation
- Wide variety of applications and materials

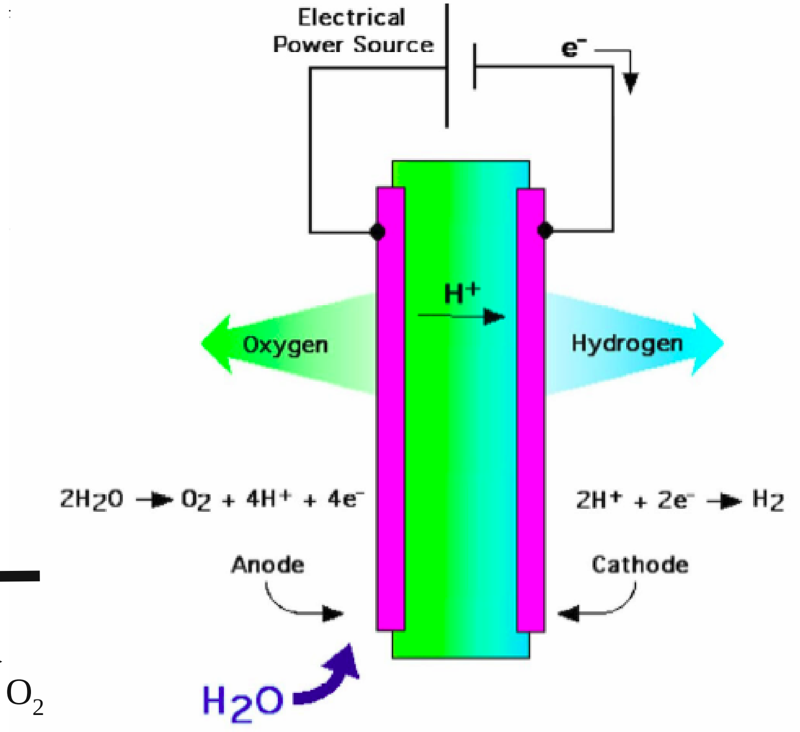


Water dissociation

- Shifts water decomposition reaction toward dissociation - $H_2O = H_2 + {}^1/_2O_2$
- e.g., $Ba(Ce_{0.7}Zr_{0.2}Yb_{0.1})O_{3-\delta}$ proton conductor

$$H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2$$





SOFC components

Complex electrochemistry

- Electrodes “painted” on electrolyte

Cathode

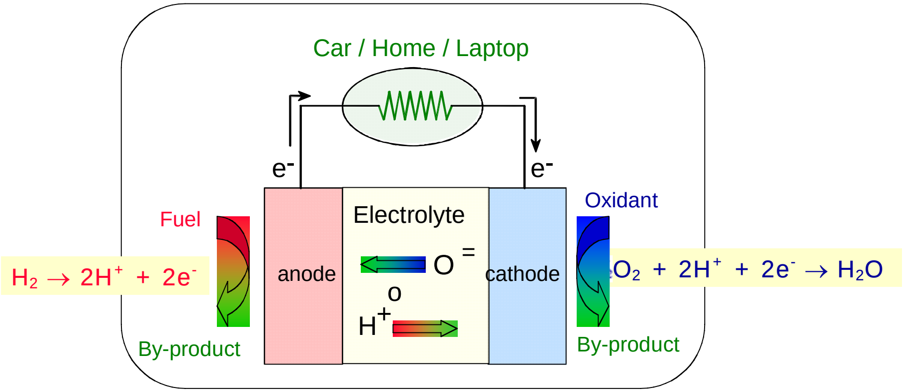
- Reduction, dissociation of O_2
- Operates at comparatively high pO_2
- e.g., $(La,Sr)(Fe,Co)O_{3-\delta}$

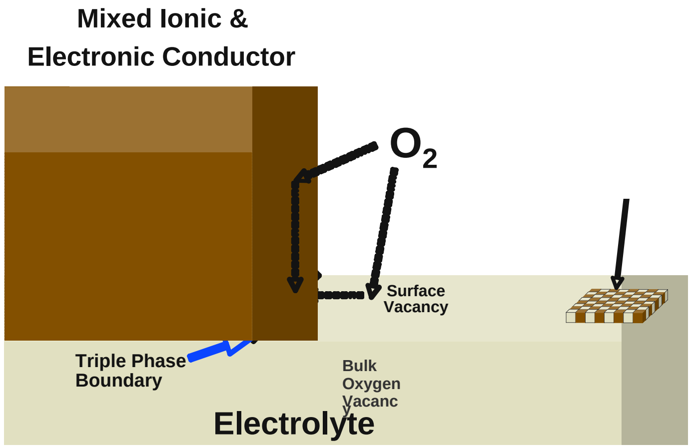
Anode

- Oxidation, dissociation of e.g. H_2O or H_2
- Operates at low pO_2
- e.g., Ni or Ni/stabilized zirconia

Electrolyte

- Ionic only or O^{2-}/H^+ mixed conduction
- Nanoscale connectivity critical
- Triple phase boundary - ion, electron, gas conduction: need to avoid “blockages”
- e.g., Sm-, Gd-, Y-doped ceria

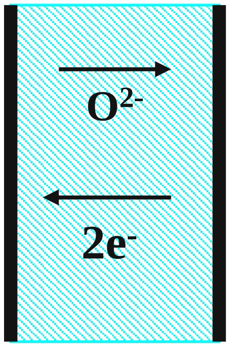




Gas separation

Typical application is conversion of CH_4 to syngas ($CO + H_2$)

- Membrane activated simply by passing gases across opposing surfaces
- pO_2 gradient generated: $pO_2 = 10^{-0.5}$ (air), 10^{-18} (CH_4)
- Oxygen ions permeate through membrane to react with CH_4
- Single-phase, e.g., $Sr(Fe,Co)O_{3-\delta}$ and multi-phase, e.g., $Sr_2(Fe,Co)_3O_{6.5-\delta}$



Oxidizing Atmosphere

Air (O_2/N_2)

Half reaction
$\frac{1}{2} O_2 + 2e^- = O^{2-}$

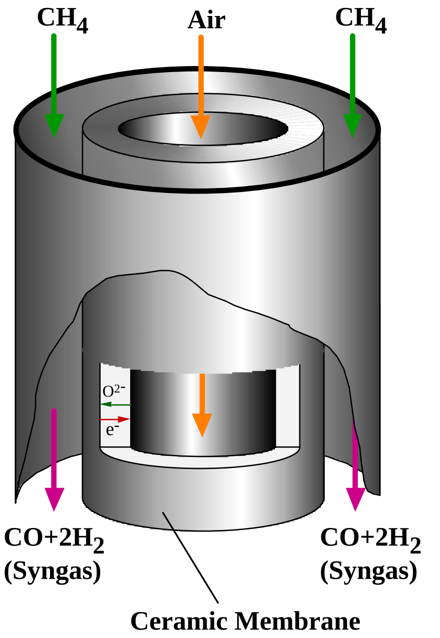
Reducing Atmosphere

Methane (CH_4)

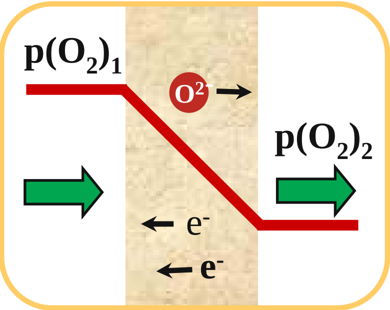
Half reaction
$CH_4 + O^{2-} = CO + 2H_2 + 2e^-$

Overall reaction

$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ (syngas)



Membrane properties and role of neutron diffraction



Phase composition

- Most membranes have complex chemical composition
- Some membranes are multi-phase; may vary with pO_2
- ***Neutrons:*** bulk measurement tracks composition, phase separation, decomposition *in situ*

Oxygen vacancy concentration and distribution

- Control conducting properties
- Mechanical stress - lattice parameter changes with cation reduction, gradient across membrane could jeopardize mechanical stability
- ***Neutrons:*** oxygen is strong scatterer - defect location, concentration and ordering
- ***Neutrons:*** *in situ* lattice parameters and peak shapes resolve issues related to stress

Hydrogen / deuterium

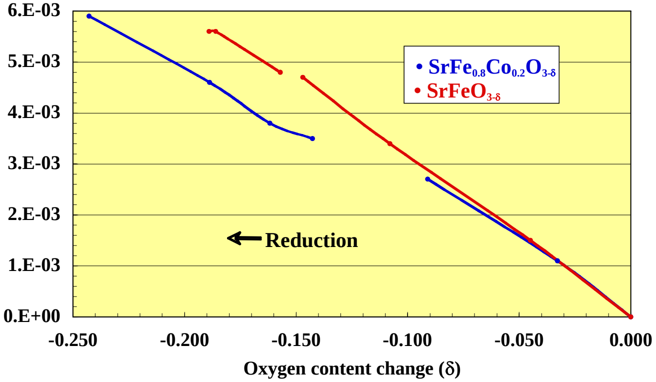
- ***Neutrons:*** $b_H = -3.7$, $b_D = 6.7$, $b_O = 5.8$, $b_{Fe} = 9.5$, $b_{Sr} = 7.0$ fm

Surface oxygen exchange and bulk chemical diffusion

- ***Neutrons:*** Time-resolved variation in lattice parameter

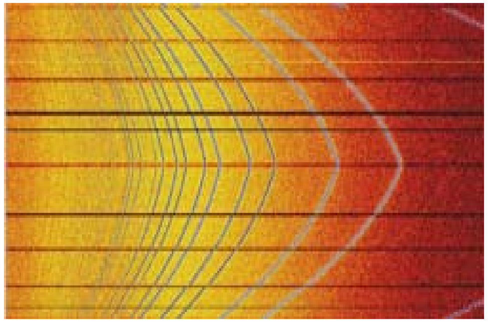
Oxygen / hydrogen flux

- Measure gas conversion

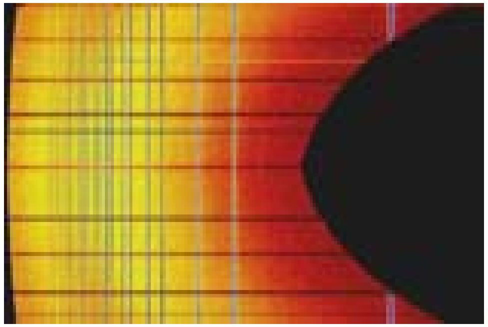


Powder diffractometer (GPPD at IPNS)

Raw (vs. time-of-flight)



Time-focused (vs. d)



Built in 1981 - x70 intensity increase @ d = 2Å, $2\theta = 145°$

(POWGEN3 ~50x current GPPD)

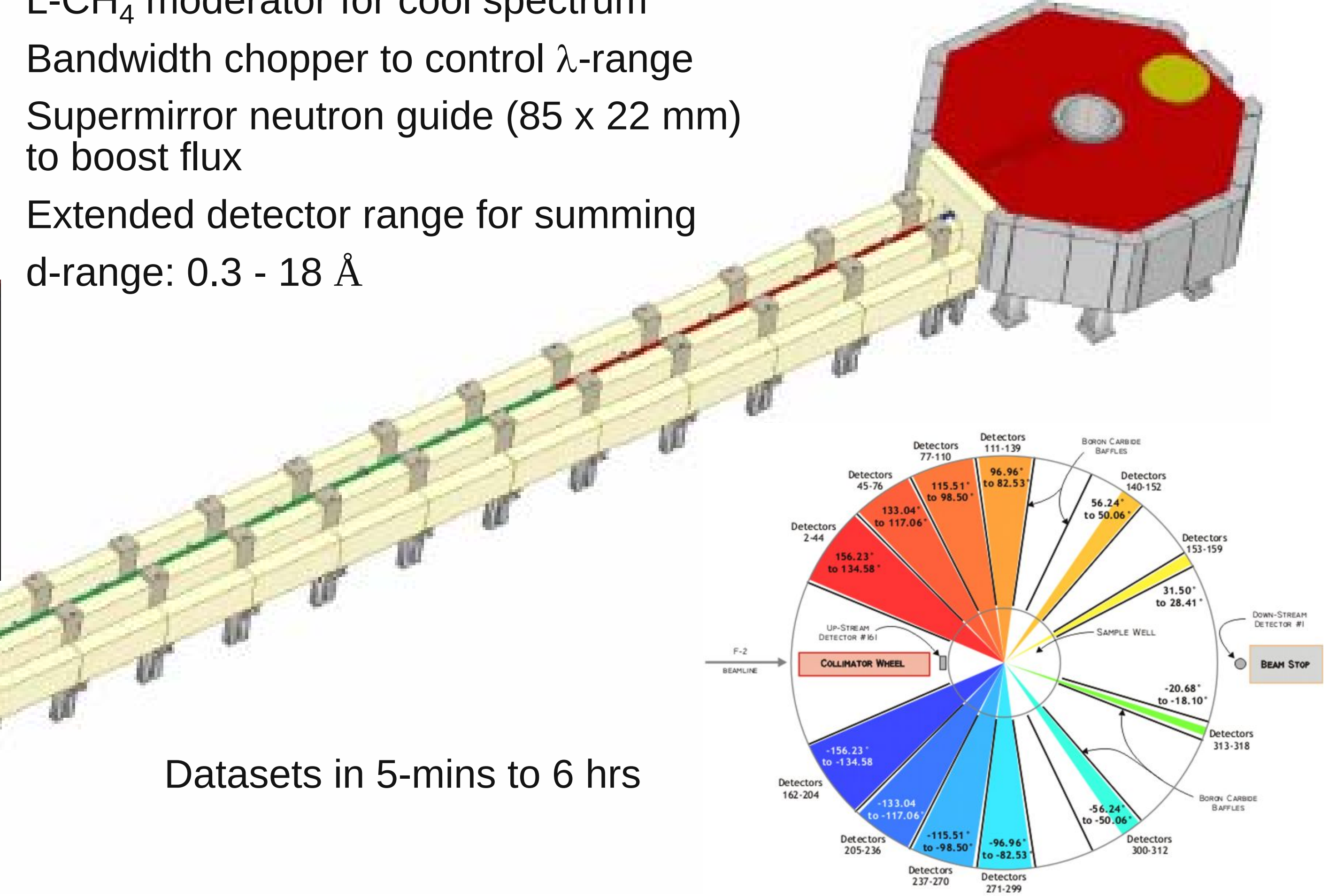
$L\text{-}CH_4$ moderator for cool spectrum

Bandwidth chopper to control λ-range

Supermirror neutron guide (85 x 22 mm) to boost flux

Extended detector range for summing

d-range: 0.3 - 18 Å



Datasets in 5-mins to 6 hrs

Controlling atmosphere at high temperature

Controlled atmosphere furnace

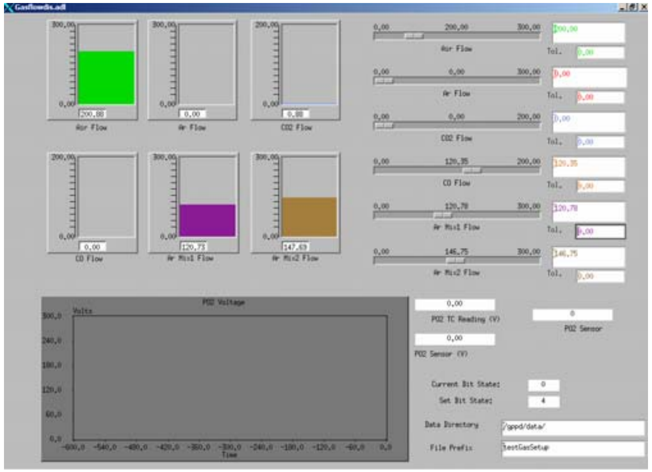
- Gases include: Air, Ar, CO_2, CO, CH_4, H_2/Ar,He

Automated flow control

- pO_2 control on both sides of membrane

On-line mass spectrometer

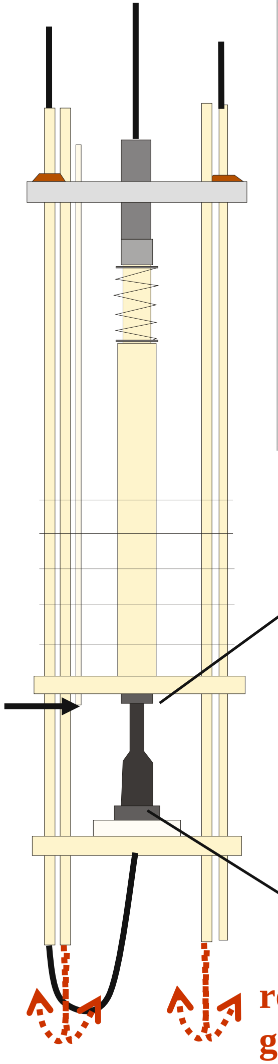
- Allows composition analysis of gas effluents from either side

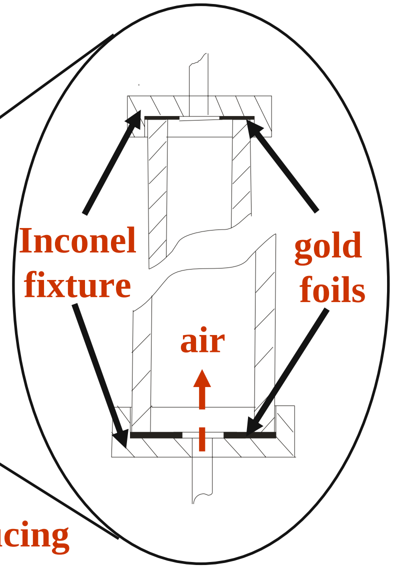


Air Flow: 200,88
Ar Flow: 0,00
CO2 Flow: 0,00
CO Flow: 0,00
Ar Mix1 Flow: 120,73
Ar Mix2 Flow: 147,63

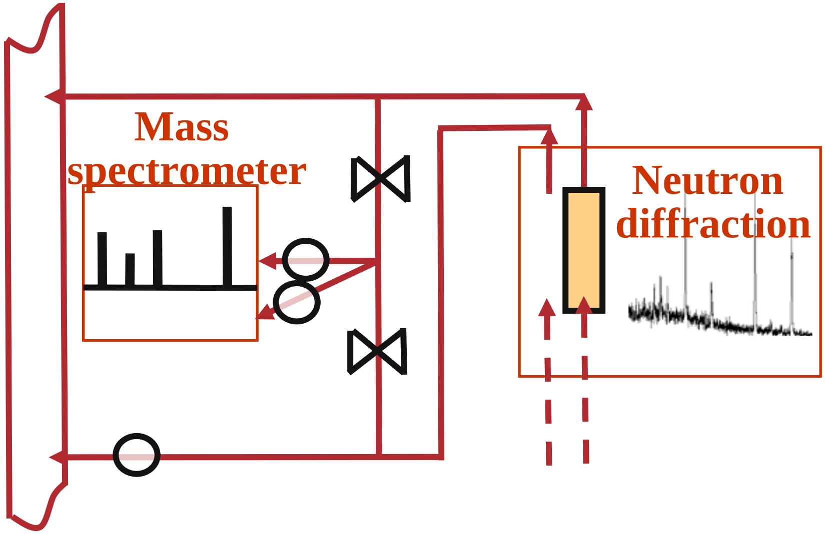
Air Flow 0,00 200,00 300,00: 200,00 Tol. 0,00
Ar Flow 0,00 0,00 300,00: 0,00 Tol. 0,00
CO2 Flow 0,00 0,00 200,00: 0,00 Tol. 0,00
CO Flow 0,00 120,35 200,00: 120,35 Tol. 0,00
Ar Mix1 Flow 0,00 120,78 300,00: 120,78 Tol. 0,00
Ar Mix2 Flow 0,00 146,75 300,00: 146,75 Tol. 0,00

PO2 TC Reading (V): 0,00
PO2 Sensor (V): 0,00
PO2 Sensor: 0
Current Bit State: 0
Set Bit State: 4
Data Directory: /gppd/data/
File Prefix: testGasSetup





reducing gas stream

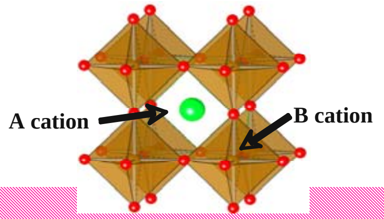


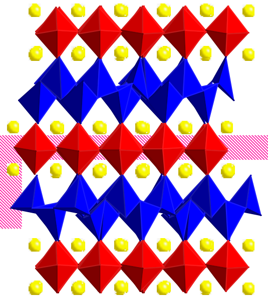
Work of Yaping Li (IPNS-ANL)

Phase composition: e.g., $Sr_2Fe_2CoO_{6+x}$ (SFC2)

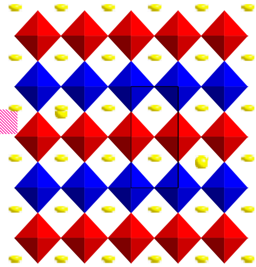
Candidate for syngas production

- Multi-phase mixed conductor with phase composition dependent on pO_2
- Chemical composition changes within each phase
- 15 - 60 minute runs; slow kinetics





$Sr_2(Fe,Co)_3O_{6+x}$

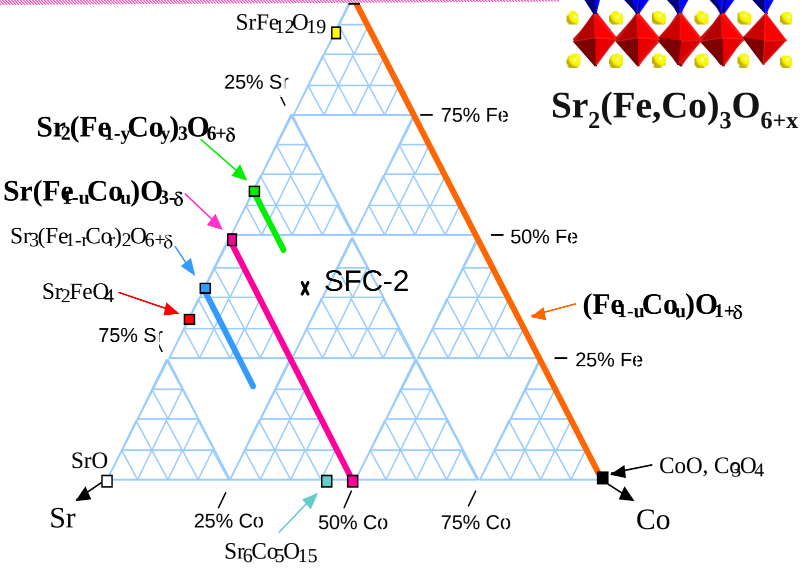


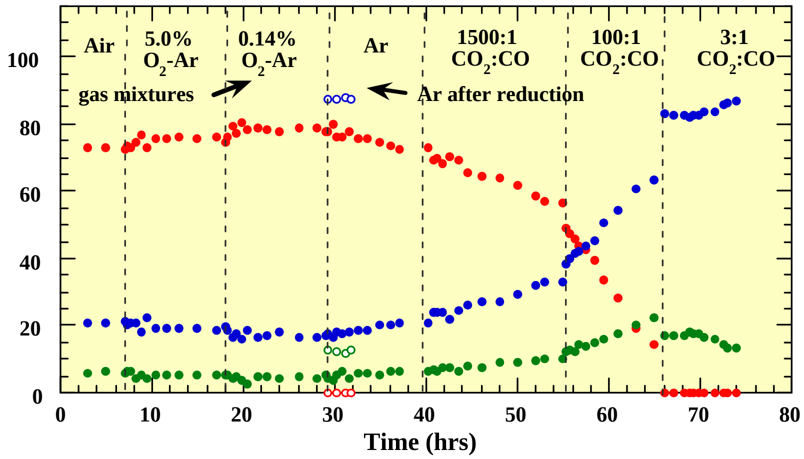
$Sr(Fe,Co)O_{3-y}$

time

QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

d-spacing→





Lattice strain across SFC2 membrane

Perovskite lattice expansion

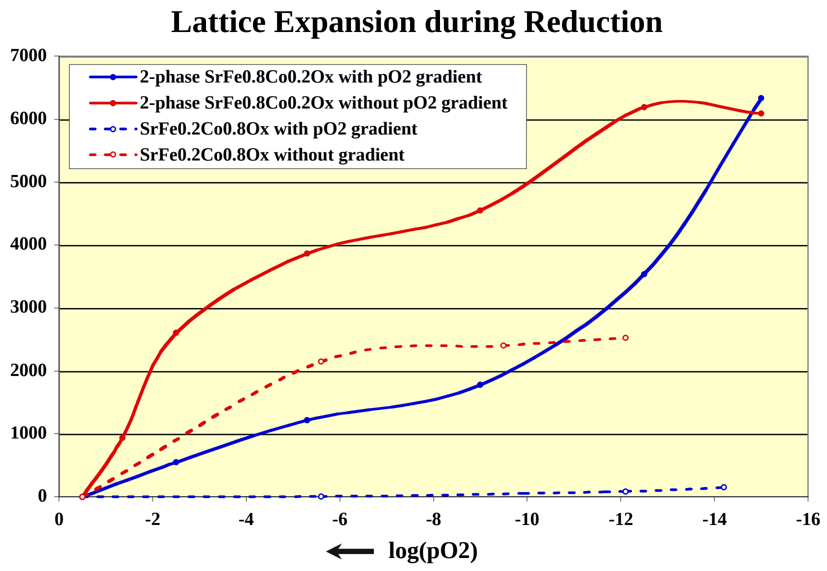
- From Fe^{4+} to Fe^{3+} and Co^{3+} to Co^{2+} reduction

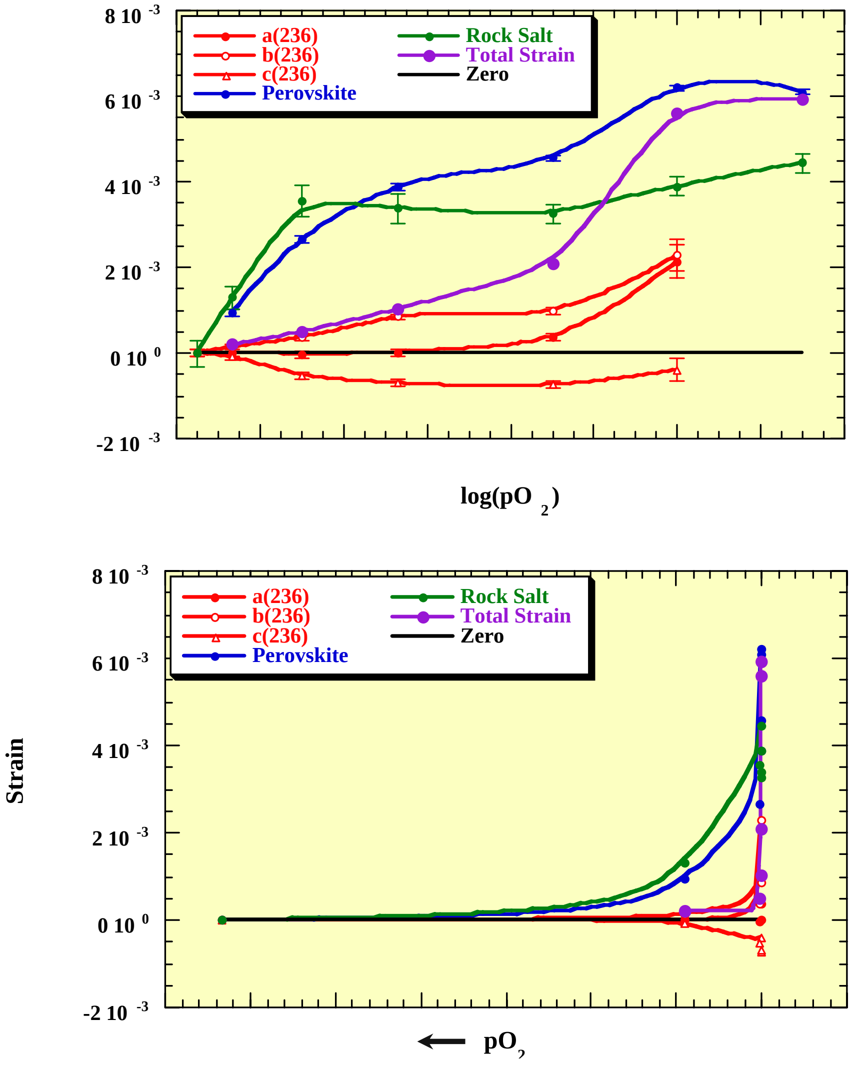
Possible mechanical strain in gradient

- Large changes for perovskite, layered phase
- Total, weighted by volume fractions, intermediate

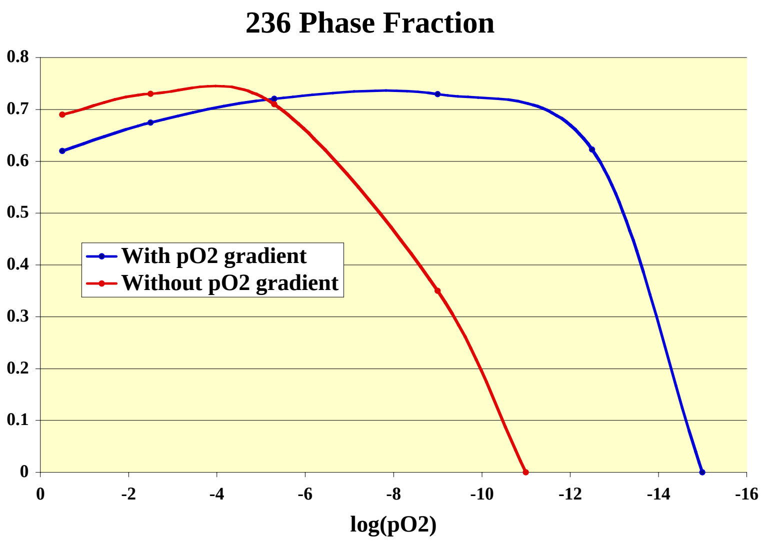
Lattice parameters in gradient

- Minimal lattice expansion in gradient





SFC2: Effect of pO_2 gradient

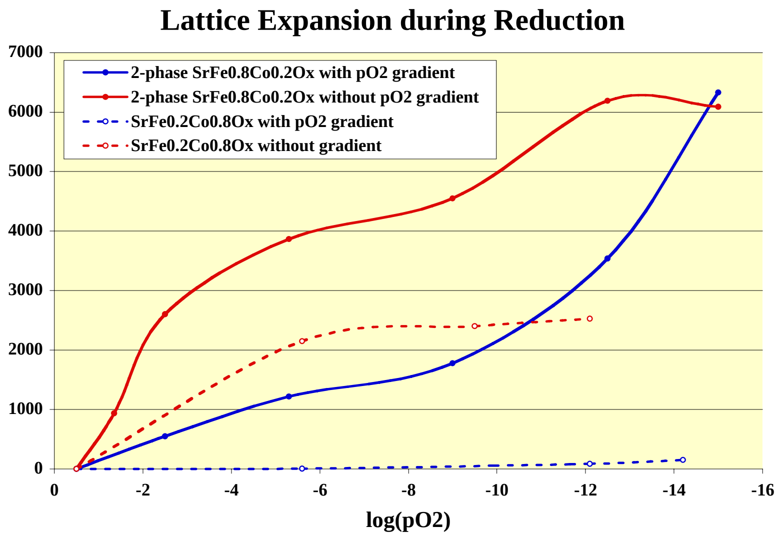


Phase stability:

- Layered phase stable in oxidizing conditions
- Presumably important to mixed conducting properties
- Stability extended to lower pO_2 in gradient

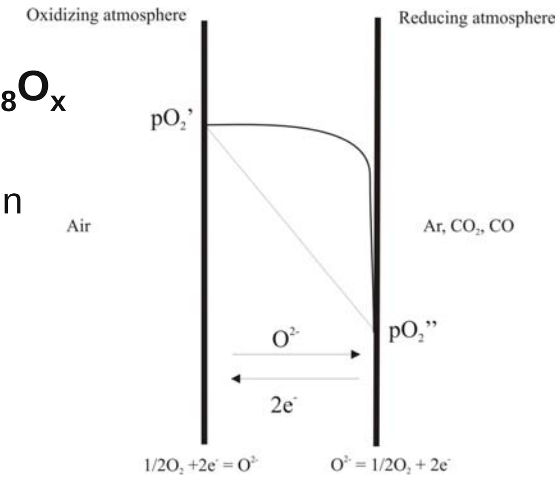
Perovskite phase lattice parameter:

- Expansion from Fe^{4+} to Fe^{3+} and Co^{3+} to Co^{2+} reduction
- Larger changes in Fe-rich perovskite (with and without gradient)



Single phase $SrFe_{0.2}Co_{0.8}O_x$

- Good oxygen conductor
- Minimal lattice expansion in gradient
- Lean air on inside (RGA)



[a] B. J. Mitchell et al., *MRS Bulletin*, 35, 491-501 (2000).

[b] Y. Li et al., *J. Am. Ceram. Soc.*, 88 (5), 1244-1252 (2005).

Oxygen vacancies: $La_{0.6}Sr_{2.4}Fe_{1.5}Co_{0.5}O_{7-\delta}$ (LSFC)

Ruddlesden-Popper (RP) series

- $A_{n+1}B_nX_{3n+1} = AX + nABX_3$

n=2 member in Sr-La-Fe-Co-O system

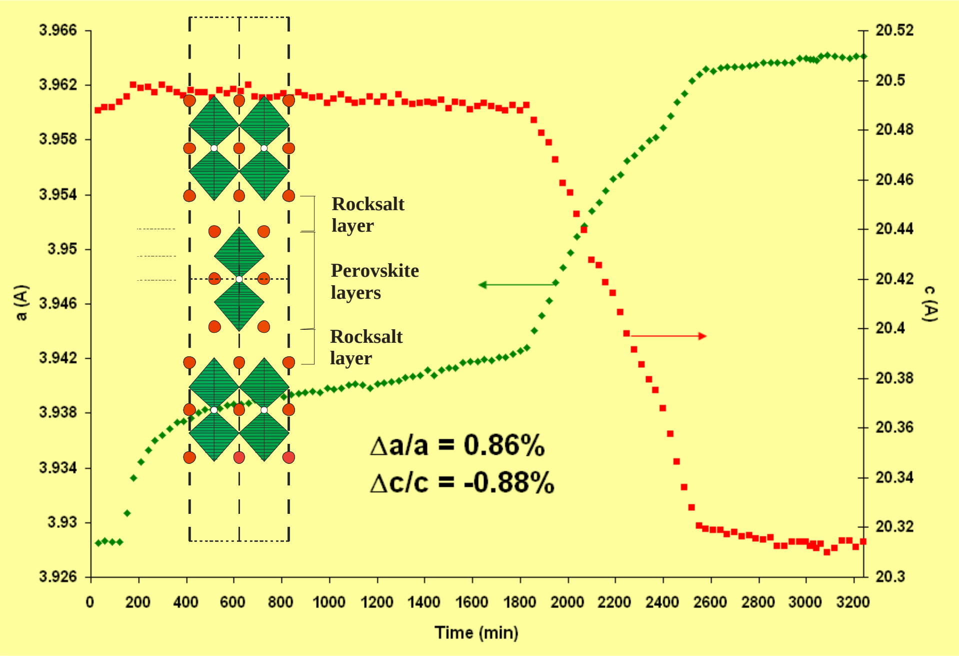
- $(La_{0.2}Sr_{0.8})_3(Fe_{0.75}Co_{0.25})_2O_x$
- *I4/mmm*, *a* = 3.87, *c* = 20.18 Å

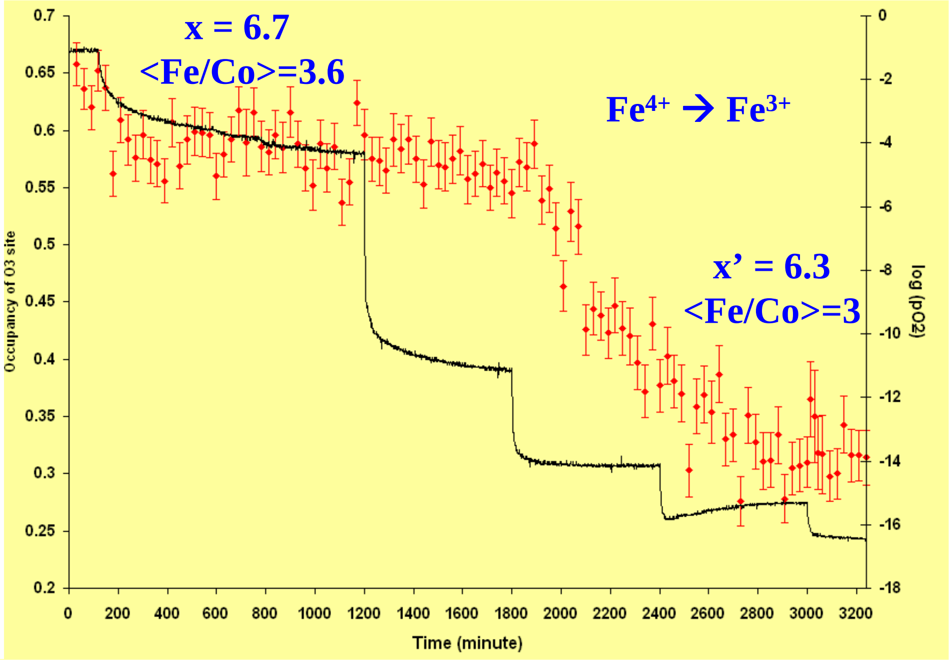
Lattice expansion

- Fe^{4+}, Co^{3+} in air, Fe^{3+}, Co^{3+} in reduced
- Lattice parameter changes anisotropic; magnitudes high, $\pm 9 \times 10^{-3}$

Oxygen vacancies

- Primarily on one oxygen site
- Variation: δ = 0.3-0.7

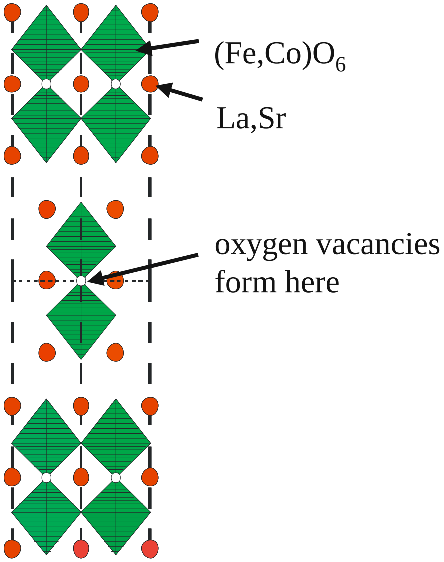


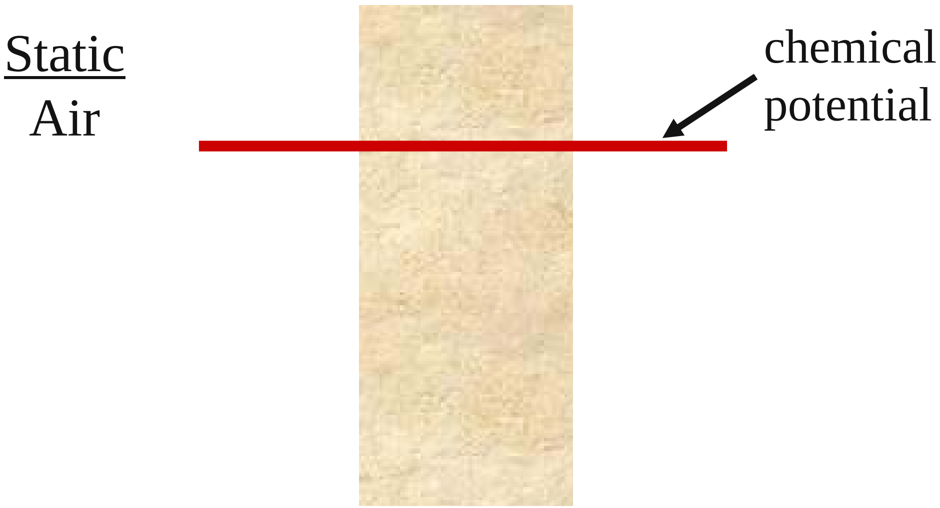


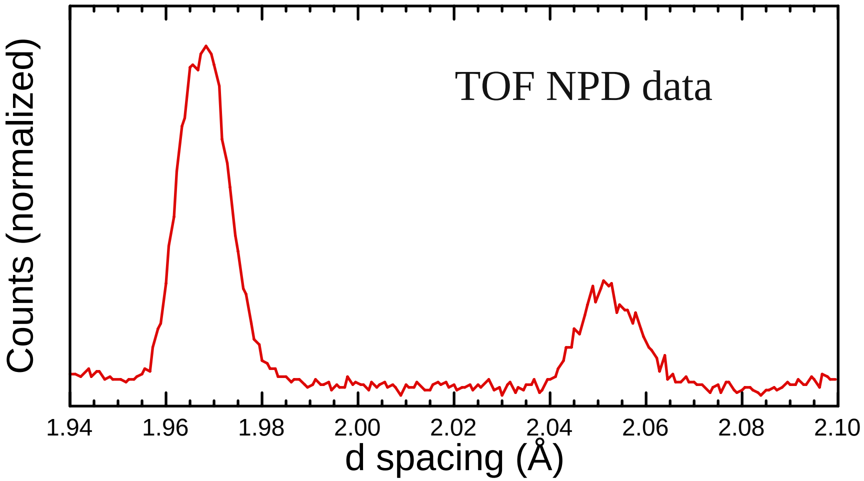
Y. Li et al., *Solid State Ionics*, in press (2007).

LSFC:
In air

LSFC
$La_{0.6}Sr_{2.4}Fe_{1.5}Co_{0.5}O_{7-\delta}$





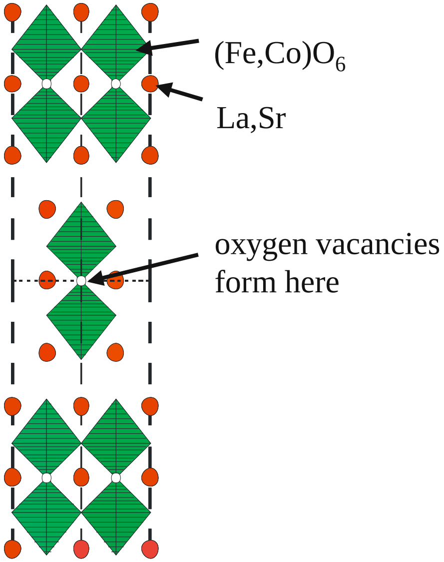


Neutron diffraction measures:

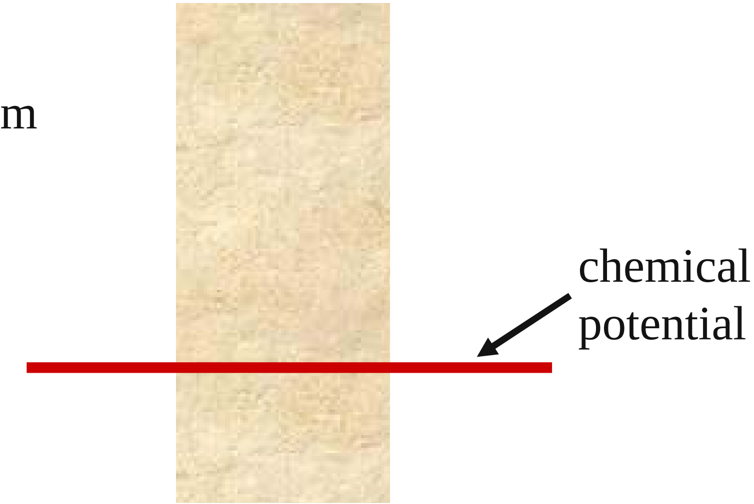
- Structure including lattice parameters and oxygen vacancy concentration
- Measured as function of time (30 min. increments) and pO_2 ($10^{-0.5}$ to 10^{-20})

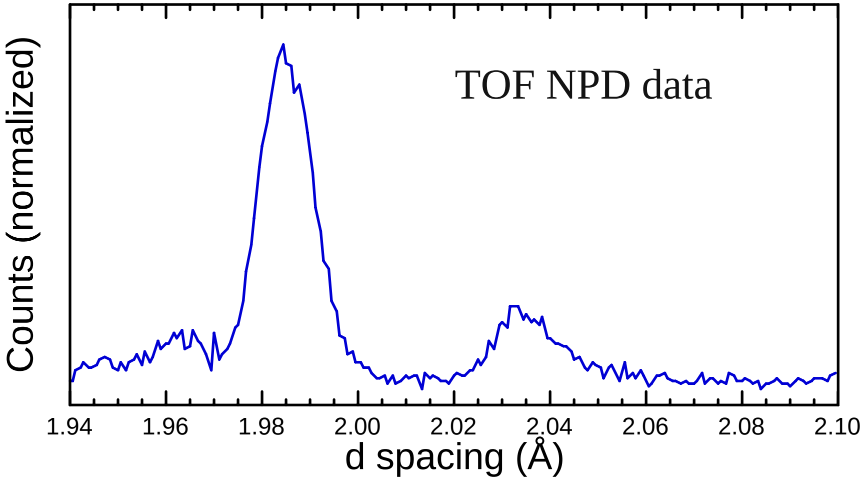
LSFC:
Response to low pO_2

LSFC
$La_{0.6}Sr_{2.4}Fe_{1.5}Co_{0.5}O_{7-\delta}$



Static
$p(O_2)=10^{-16}$ atm





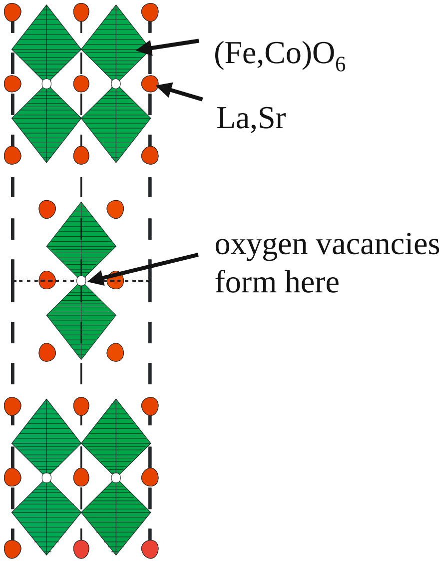
Change in pO_2 produces:

- Shift in peak positions
- Increase in oxygen vacancy concentration

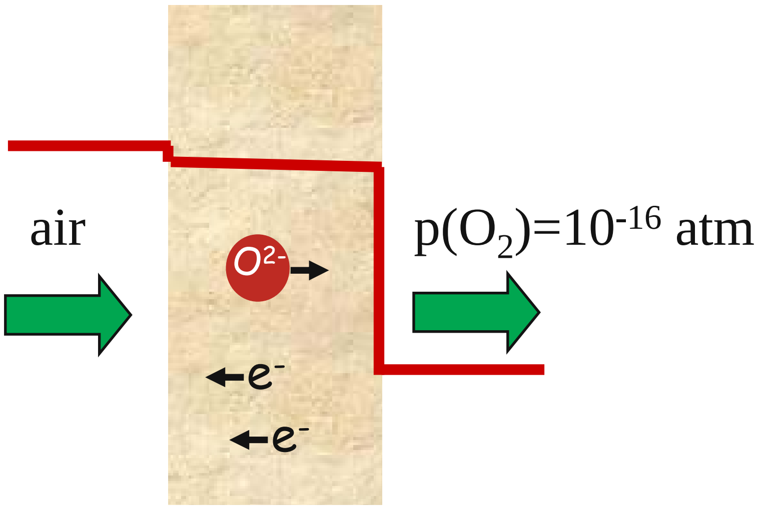
LSFC:
Response in pO_2 gradient

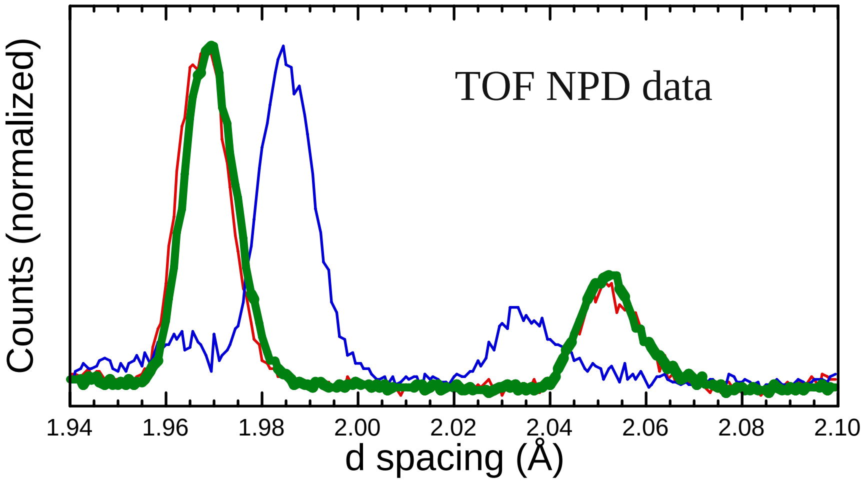
LSFC

$La_{0.6}Sr_{2.4}Fe_{1.5}Co_{0.5}O_{7-\delta}$



Dynamic





Peak positions and oxygen vacancy content consistent with values in static air

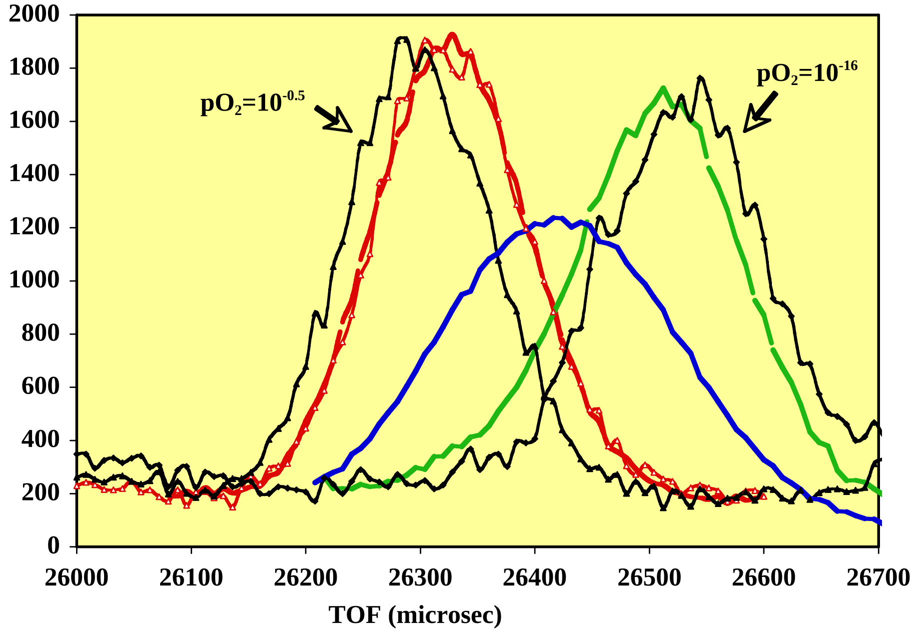
- Suggests that majority of membrane has comparatively high effective pO_2
- Performance limited by reaction at reducing side of membrane

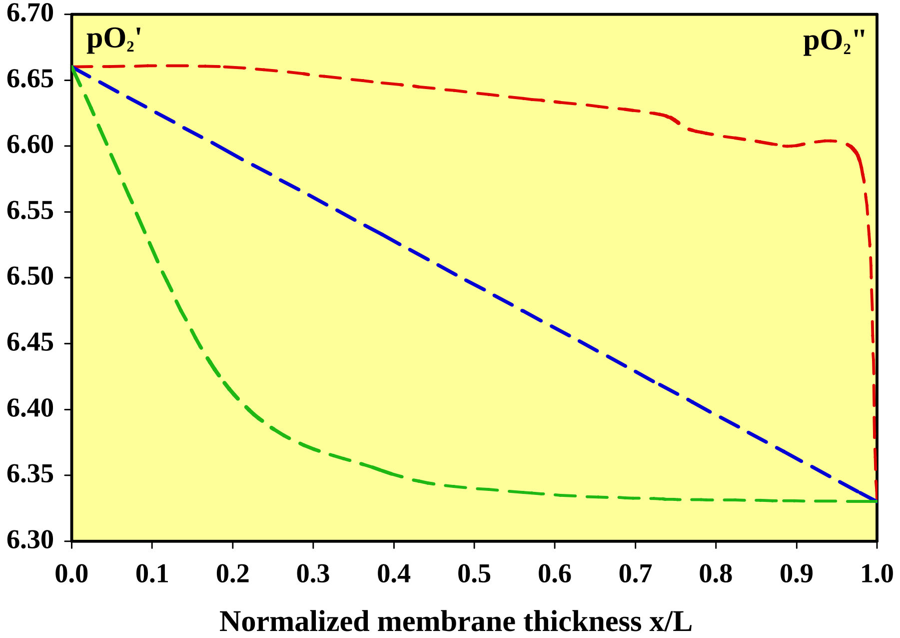
LSFC:
Calculated pO_2 profile across membrane

Peak from static measurement used as template to reproduce peak profiles in dynamic mode

- From static measurements, each pO_2 value corresponds to unique peak position
- Projected peak profiles for two possible pO_2 gradients not at all representative of actual profile
- Calculated profile suggests very strong gradient at reducing surface

Proprietary coatings typically used on surface



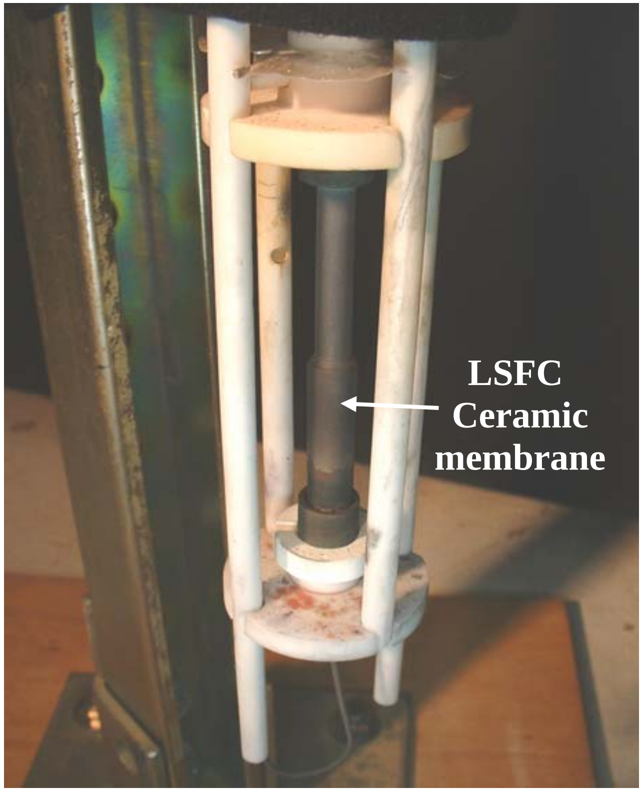


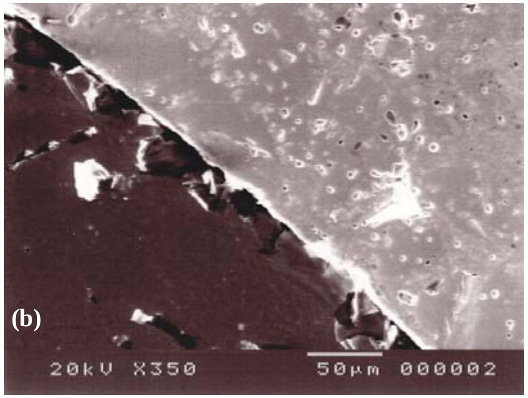
LSFC:
Microstructure of LSFC after neutron experiment

Membrane intact after experiment - ~10 hrs in gradient

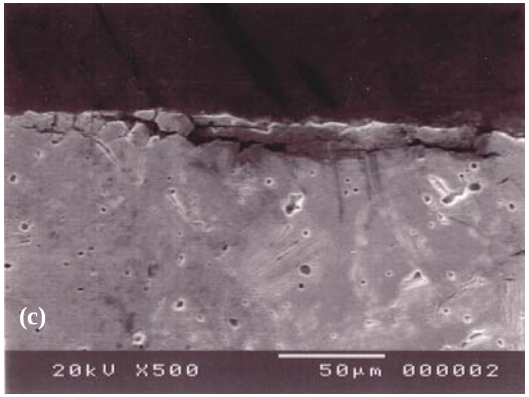
Micrographs of air and methane surfaces

- Methane (reducing) surface degraded



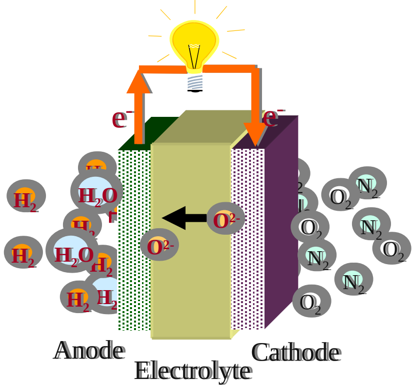


Air side



Methane side

Kinetics: Solid-oxide fuel cell electrolyte: $Ce_{0.8}Y_{0.2}O_{1.9-\delta}$ (CY20)



Well-studied material

- Intrinsic vacancies from Y-doping; Ce^{4+}, Y^{3+}
- Extrinsic vacancies generated under reduction; some Ce^{4+} to Ce^{3+}
- Ionic conductor in oxidizing environment
- Electronic conductor in reducing
- Some degree of mixed conduction in between

Behavior under reduction

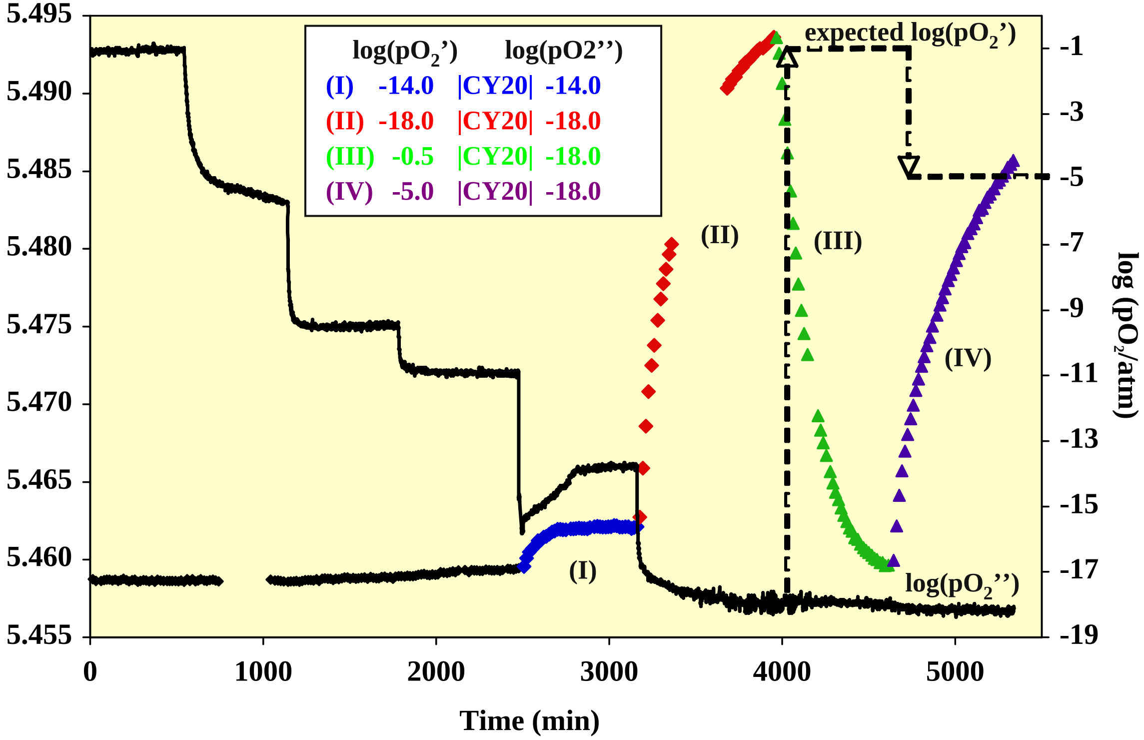
- No lattice parameter change down to $\log(pO_2) = -11$
- Expansion at log(pO2) = -14, -18

Gradient

- -0.5 |CY20| -18: shift to air value
- -5.3 |CY20| -18: near -18 value

Switch-like behavior

- Minor change on oxidizing side
- In and out of mixed-conducting regime?



Kinetics of CY20 reduction

Time-resolved lattice parameter evolution

- Based on linear relationship between lattice parameter and oxygen vacancy concentration
- Parameter plotted is fraction of progress from start to finish

Kinetics parameters

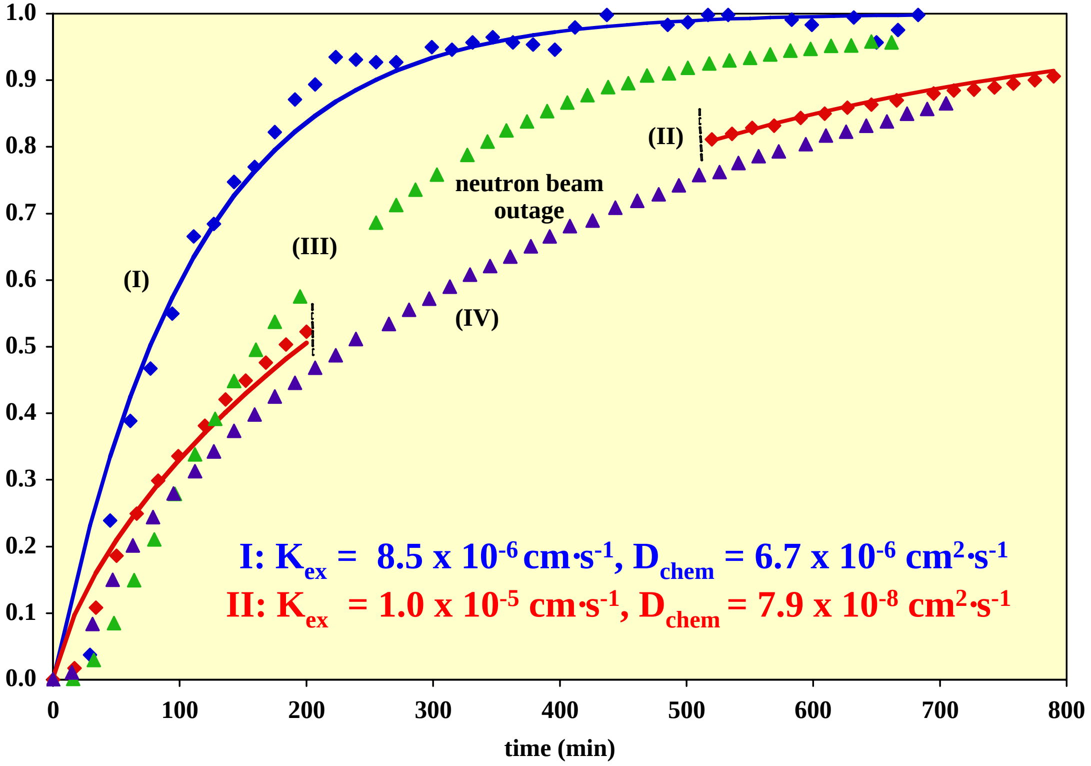
- K_{ex}: surface oxygen exchange constant
- D_{chem}: bulk diffusion coefficient

Static measurements

- Traditional relaxation
- (I): $\log(pO_2) = -11$ to -14
- (II): $\log(pO_2) = -14$ to -18

Gradient measurements

- Not traditional relaxation
- Model not known, although behavior similar
- (III): $\log(pO_2) = -0.5\ |CY20|\ -18.0$
- (IV): $\log(pO_2) = -5.3\ |CY20|\ -18.0$

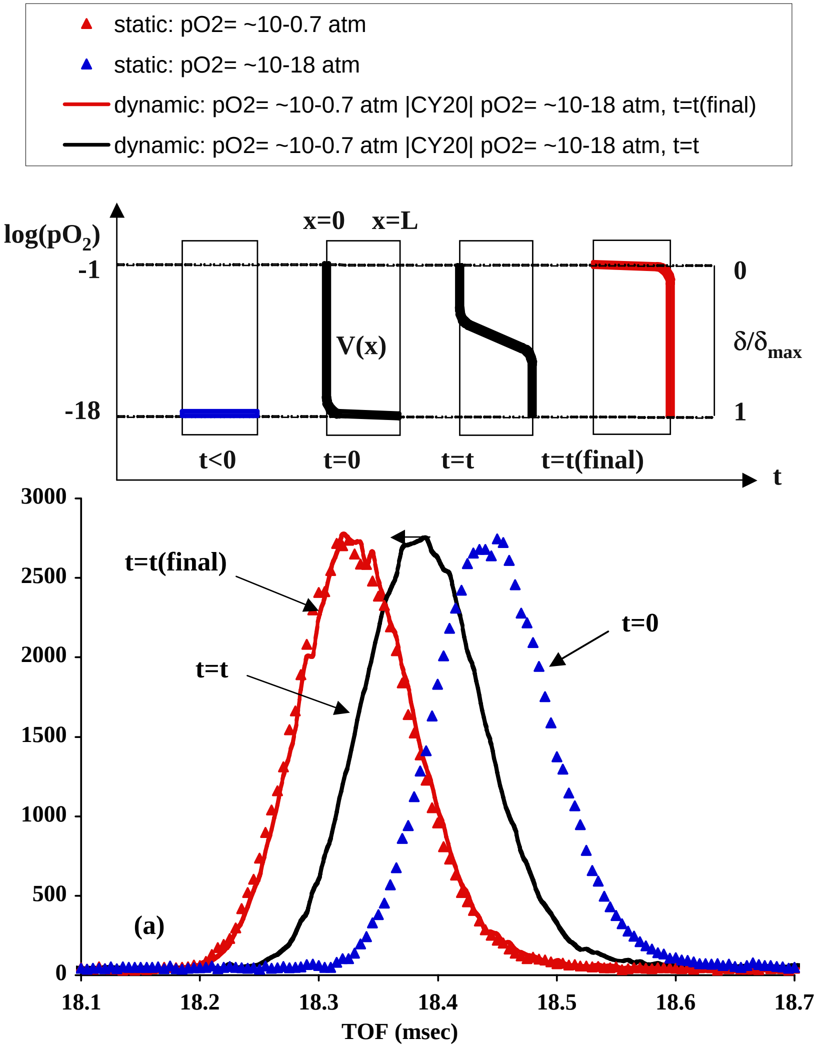


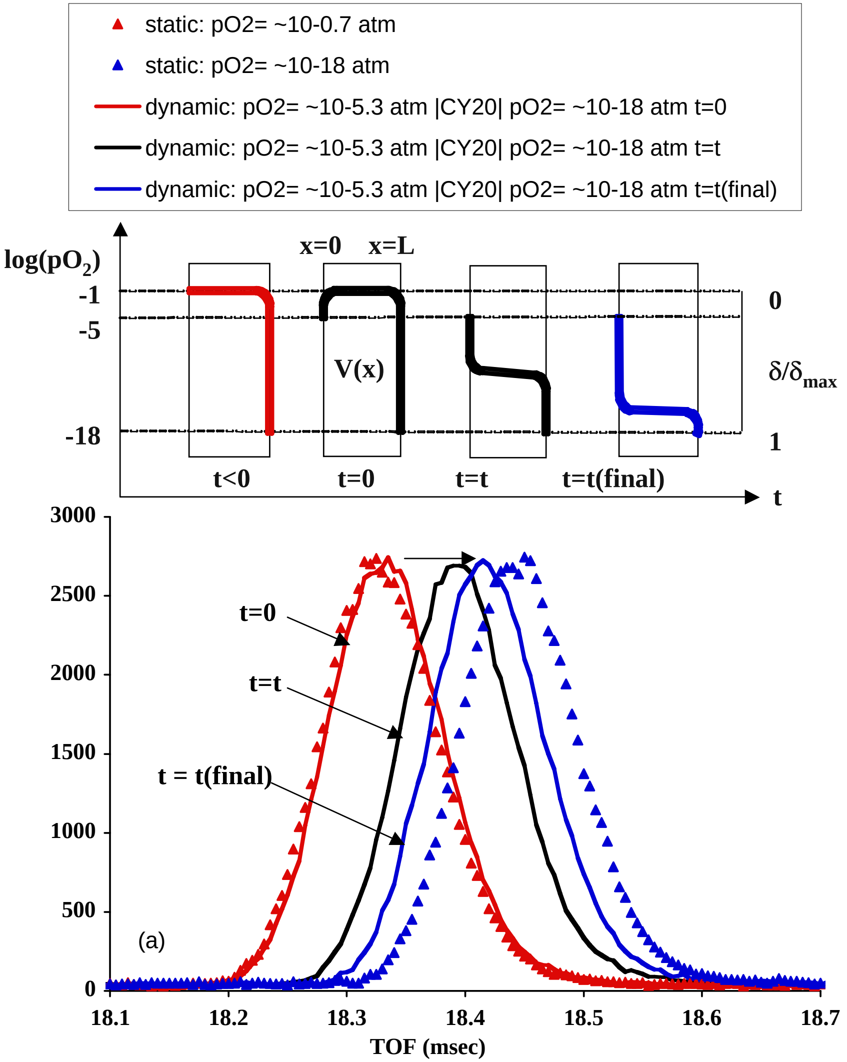
Trends

- K_{ex} doesn't change; D_{chem} increases with increasing pO_2

Li, Maxey, Richardson, *J. Am. Ceram. Soc.* (2007) in print.

pO_2 gradient progression in CY20





Future prospects in neutron powder diffraction

Higher flux

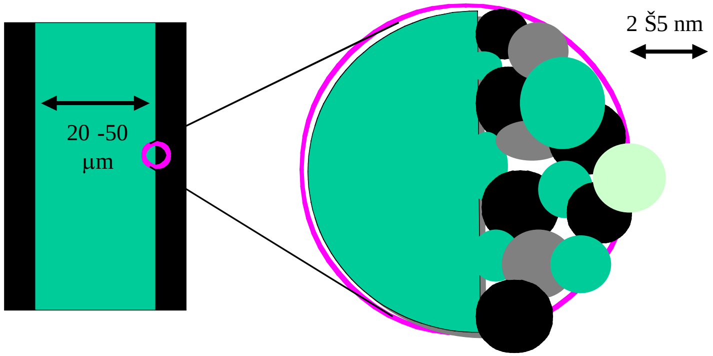
- More detail from each point, shorter runs
- Local structure changes
- Nanocrystalline components
- Chemical kinetics

Higher spatial resolution

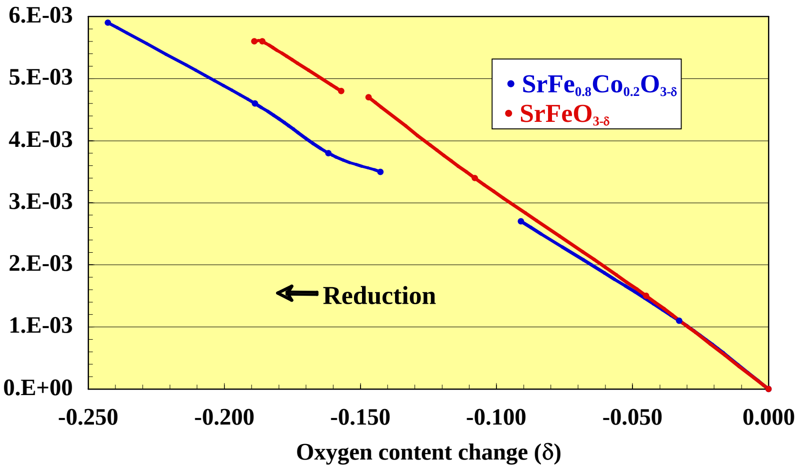
- Multi-component systems
- Mapping across gradients
- Directly probe interfaces

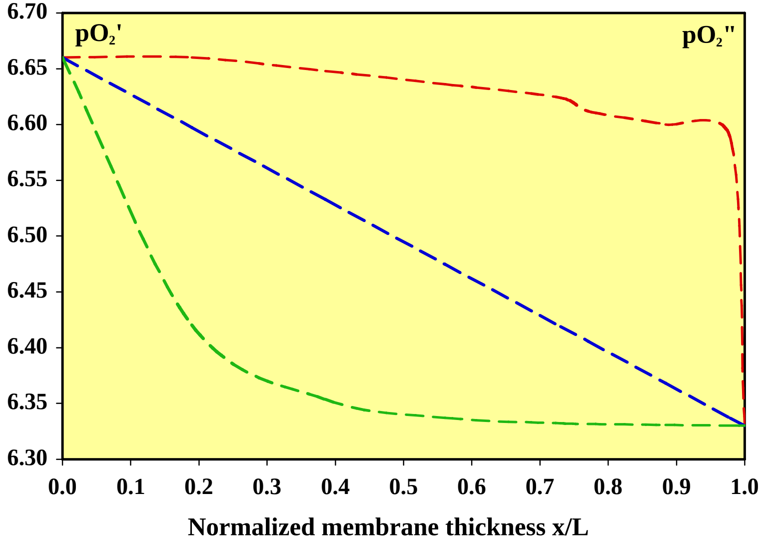
Electrode/Membrane Design

Very challenging. Electrodes need to support several percolation networks: electronic, ionic, fuel/oxidizer/product access.



From BES Workshop on Basic Research for Hydrogen Production, Storage, and Use





New analysis capabilities - e.g. MMM

Modified Maximum entropy with Monte carlo (MMM)

- Developed by Ryoji Kiyanagi (IPNS-ANL)

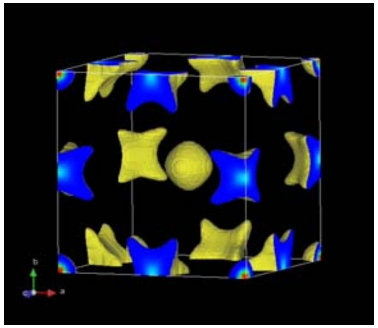
Methodology

- Utilizes integrated intensities of reflections
- Density is described as continuous distribution, not discrete atomic positions
- Nuclear density is adjusted to minimize constraint equation
- Find most disordered representation consistent with data

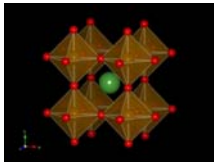
$$C = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|F_{MEM}^{i} - F_{obs}^{i}\right|^{2}}{\sigma_{i}^{2}}$$

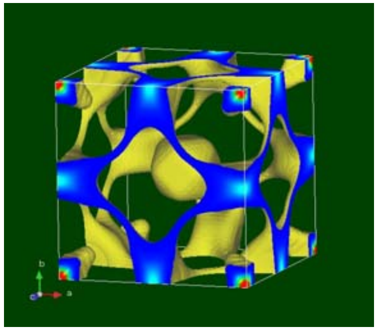
Application to ceramic membranes

- Oxygen and/or cation vacancies and oxygen migration
- Local coordination often deviates significantly from octahedral
- Up to 5-10% of oxygens de-localized



$La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-\delta}$ at RT





$La_{0.8}Sr_{0.2}Ga_{0.65}Fe_{0.35}O_{3-\delta}$ at 1200°C

Summary

Current neutron powder diffraction instrumentation can probe:

- Phase composition
- Lattice expansion / strain
- Oxygen / hydrogen vacancy concentration
- Diffusion kinetics

Future instrumentation may probe:

- 1-100 µm thick membranes
- Structural relaxation kinetics - local structure changes
- Distributions within thin membranes - spatially resolved

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