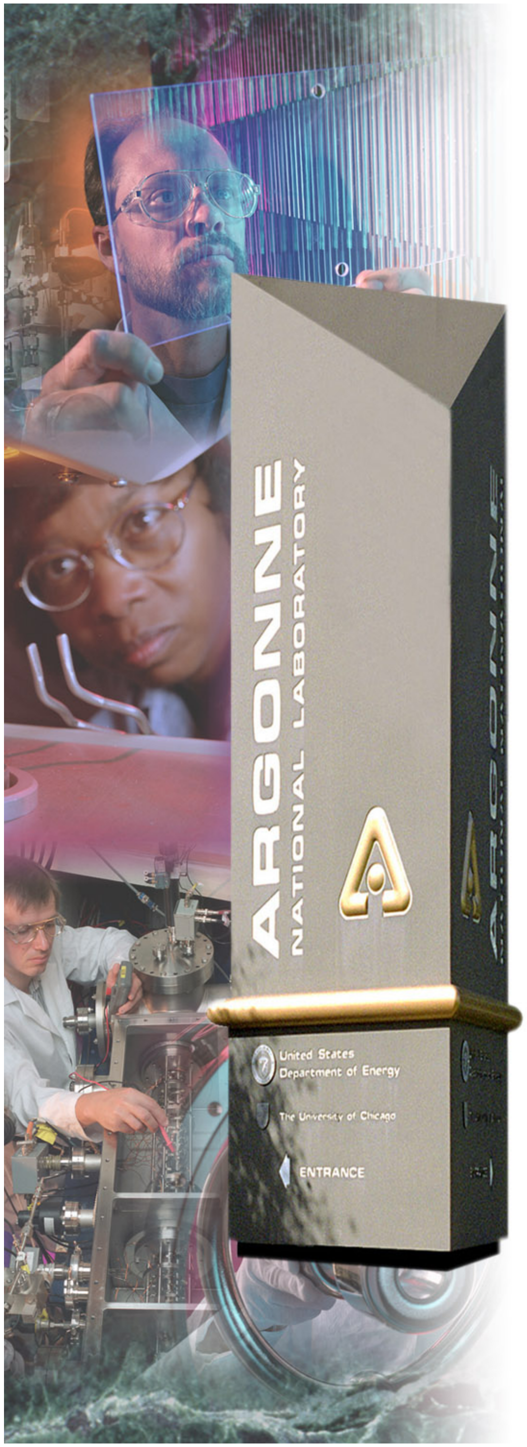

Ceramic Membranes for Gas Separation and Fuel Cell Applications: Opportunities for Neutron Scattering Research

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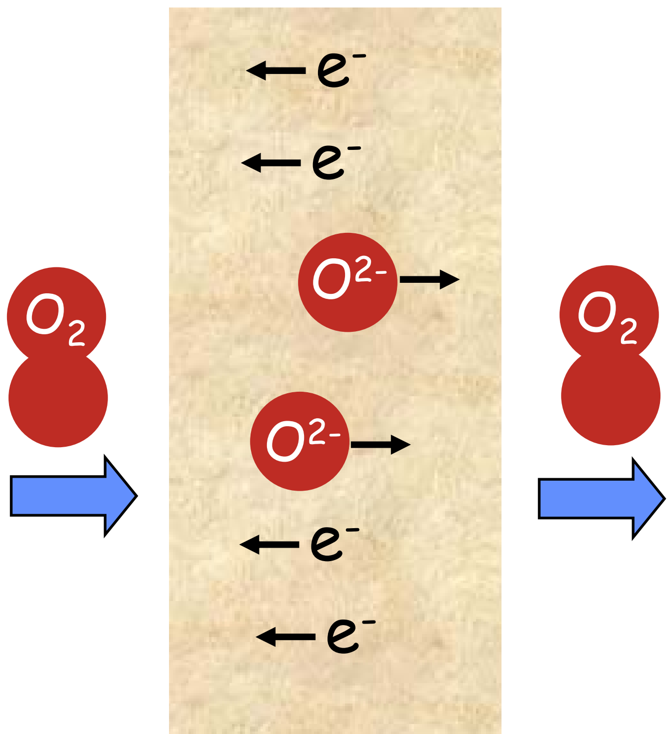
B. Dabrowski & O. Chmaissem, Dept. of Physics, Northern Illinois Univ.

What is a ceramic membrane?

A dense ceramic membrane that supports ionic transport by (vacancy or interstitial) diffusion. A mixed conducting membrane also supports electronic transport

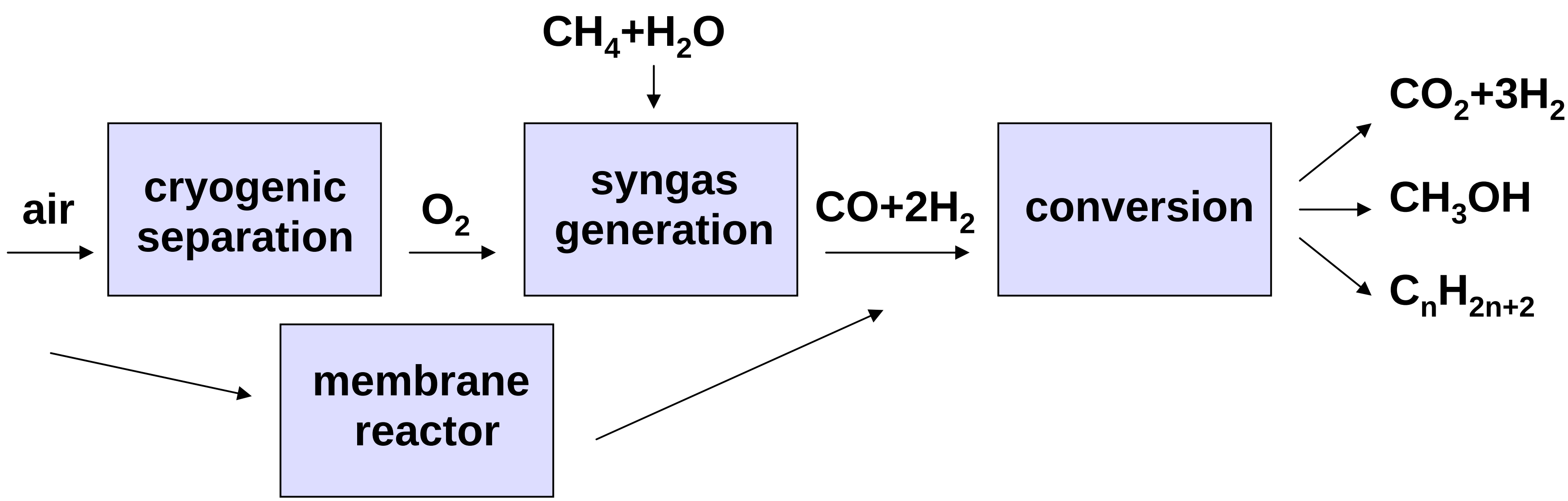


Oxygen-transport ceramic membranes are perhaps the most common in energy production and utilization technologies.

Outline of the Talk

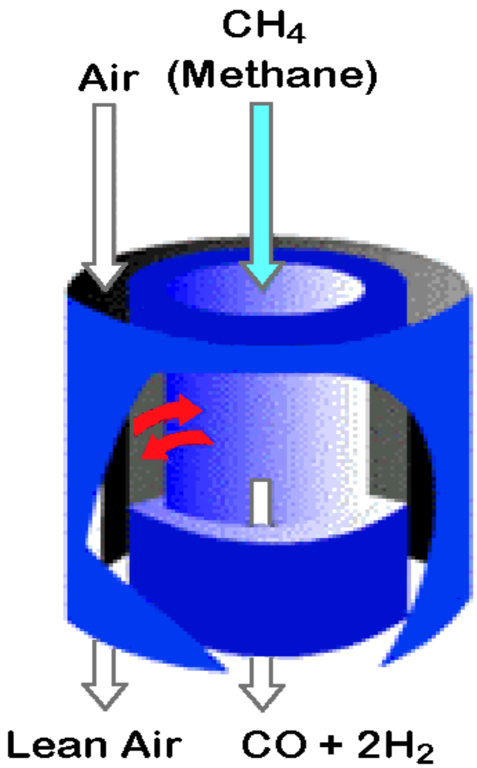
- The roles of ceramic membranes in present and emerging energy technologies
- Materials requirements that define crosscutting research opportunities
- Recent examples of neutron diffraction studies of ceramic membranes
- Research opportunities

Natural Gas Conversion to Hydrogen, Methanol, Hydrocarbons



- 25-40 TCF natural gas in Alaska, 1700 TCF in Russia
- Partial oxidation and steam reforming
- ~60% capital expense is in syngas generation
- 2500MT/day MeOH, 1600MT/day O_2

A Ceramic Membrane Reactor for Conversion of Natural Gas to Syngas



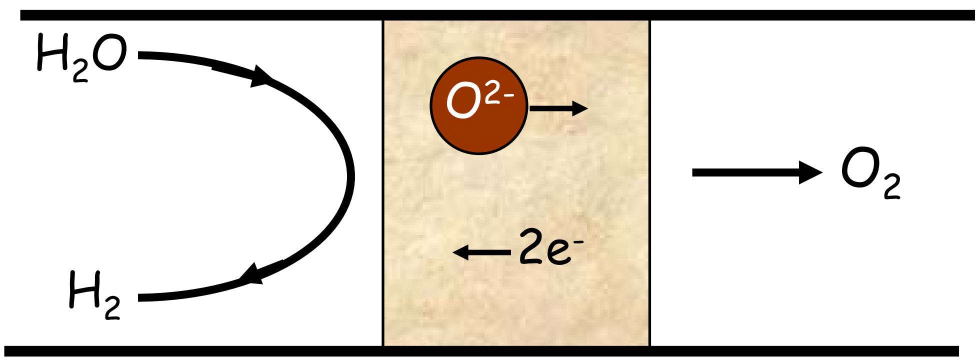
<u>Ceramic membrane requirements:</u>

- Oxygen ionic transport
- Electronic transport
- Chemical and thermal stability

Water Separation Using a Ceramic Membrane

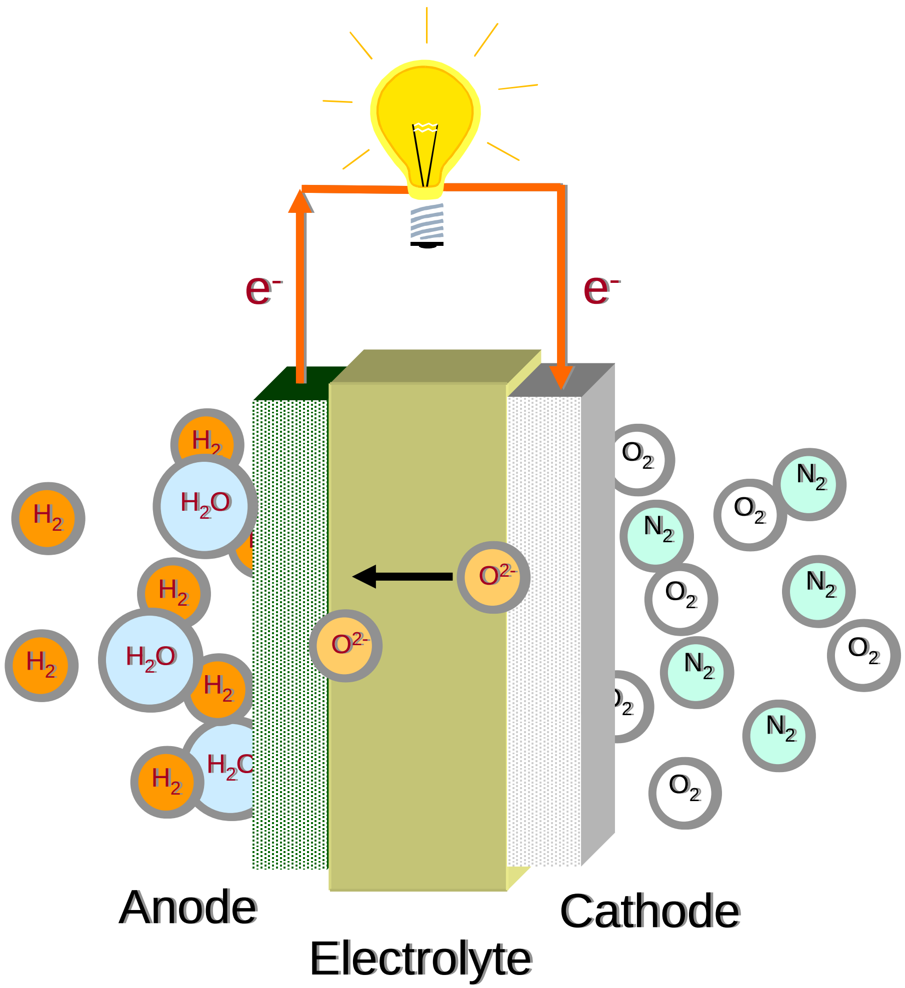
$$H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2$$

The amounts of hydrogen and oxygen in equilibrium with water are very small, even at high temperatures, but significant amounts of hydrogen or oxygen can be generated at modest temperatures if the reaction is shifted towards water dissociation by removing either hydrogen or oxygen using a mixed-conducting membrane.



Balchandran et al. have achieved H production of ~10cm^3(STP)/min-cm^2 at 900°C.

Solid Oxide Fuel Cells



Ceramic membrane requirements:

Electrolyte

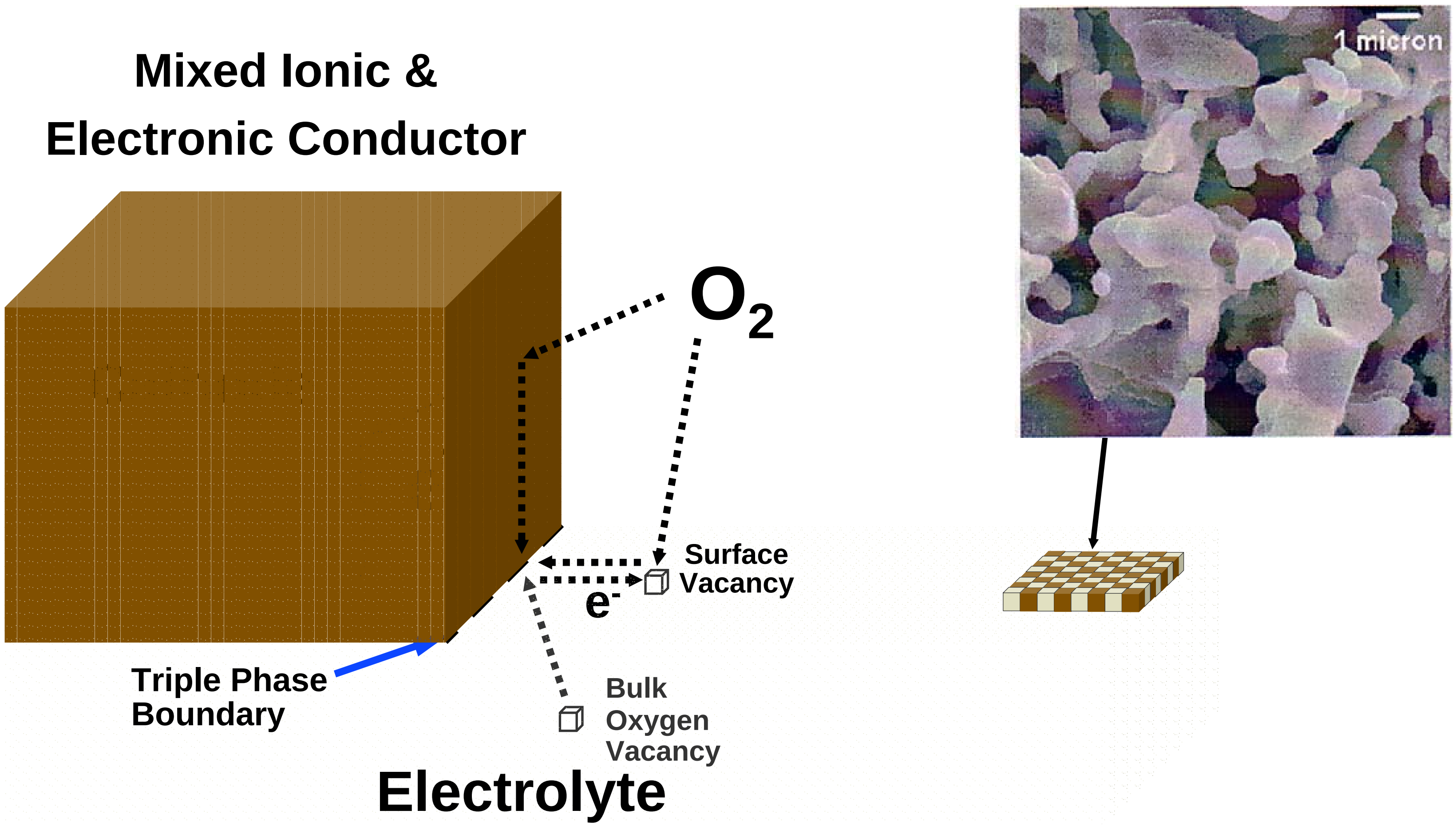
- Ionic transport
- Electrically insulating

Electrodes

- Ionic transport
- Electronic transport

Both bulk and surface properties are important.

The SOFC Cathode



Crosscutting Research Opportunities

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

<u>Example -- a specific challenge:</u>

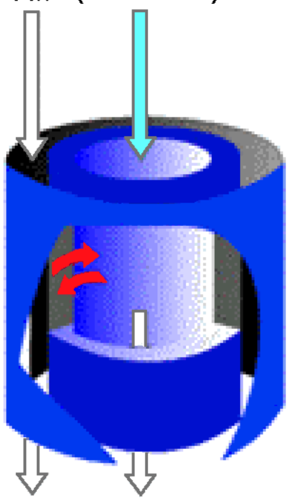
Achieve good oxygen ionic and electronic transport in a ceramic membrane material at 500-600° C.

What can be done with neutron scattering?

- Structure
- Defect location, concentration, and ordering
- Phase transitions vs. chemical composition, temperature, & oxygen partial pressure
- Detailed information about the synthesis chemistry from *in situ* diffraction studies
- Phase separation & decomposition
- Phase behavior in *in situ* dynamic ion-conducting environments
- Vibration and diffusion properties of the mobile species

In situ studies under conditions that simulate the ceramic membrane operating environment are especially important because they provide information that cannot be obtained in any other way.

Example: The SFC-2 Ceramic Membrane



Ceramic Membrane Technology

In previous ANL/Amoco work:

- A material called SFC-2 achieved 98% methane to syngas conversion efficiency in tests up to 1000 hr.
- However, the phase composition and crystal structure of this material was not known.

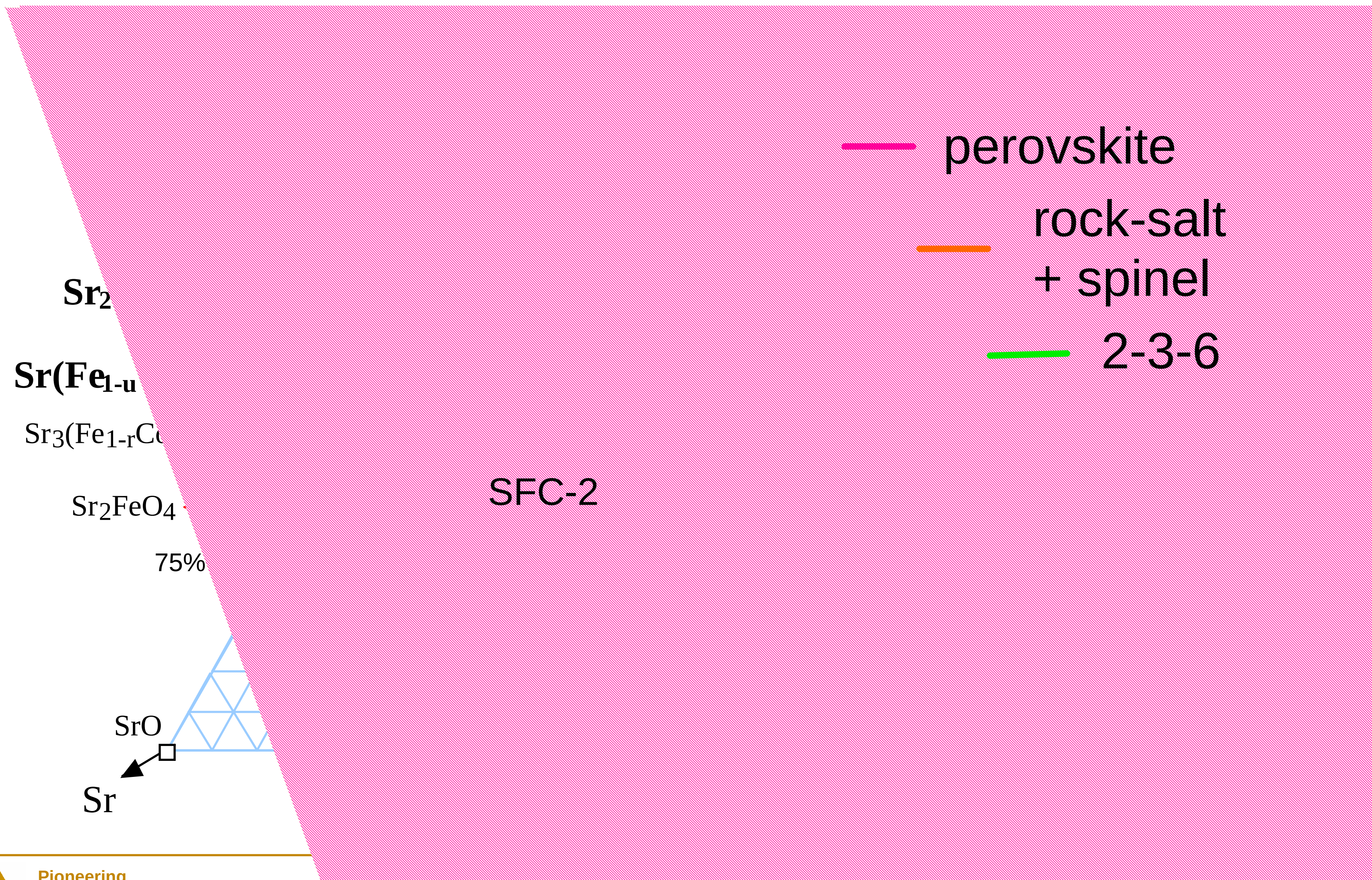
From neutron powder diffraction, we learned:

SFC-2 ($Sr_2Fe_2CoO_{6+\delta}$) is a mixed-phase compound:

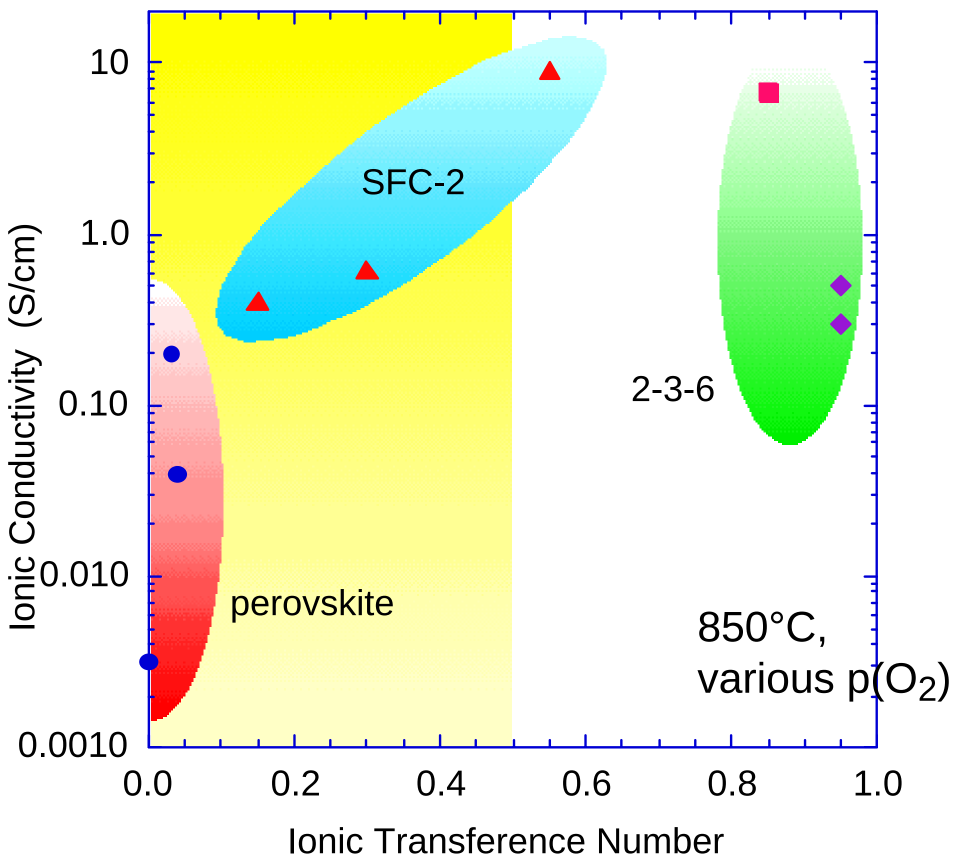
20-30%	$Sr(Fe_{1-x}Co_x)O_{3-\delta}$ perovskite	
50-70%	$Sr_2(Fe_{1-x}Co_x)_3O_{6+\delta}$	2-3-6 phase
5-15%	$(Co_{1-x}Fe_x)O$	rock salt
	$(Co_{1-x}Fe_x)_3O_4$	spinel

Relative weight fractions are determined by synthesis and operating conditions.

Sr-Fe-Co Composition Diagram



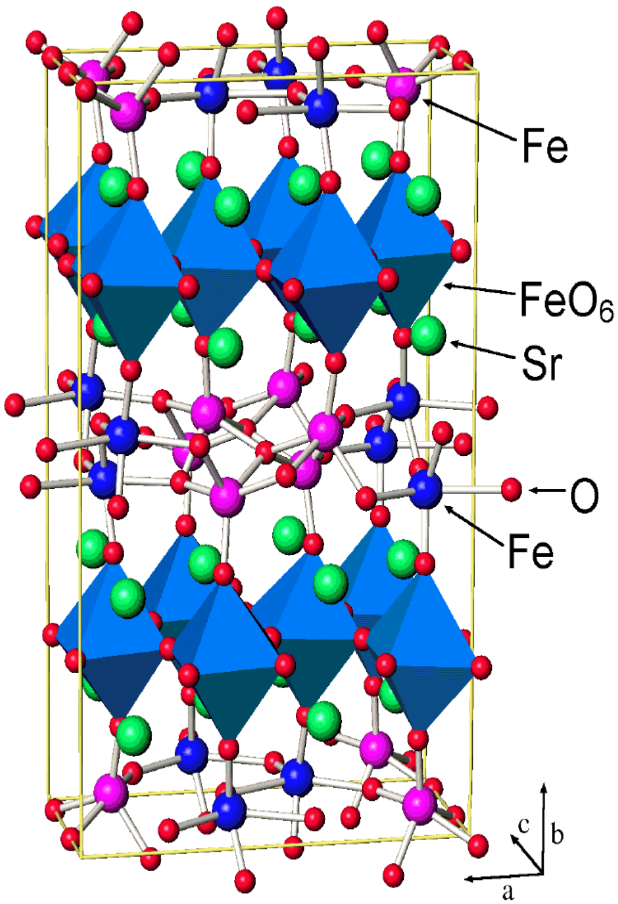
Ionic conductivity vs. ionic transference number for the active components of SFC-2



An ideal mixed-conducting membrane exhibits:

- High ionic conductivity
- $t_i = \sigma_{ionic}/\sigma_{total} \leq 0.5$

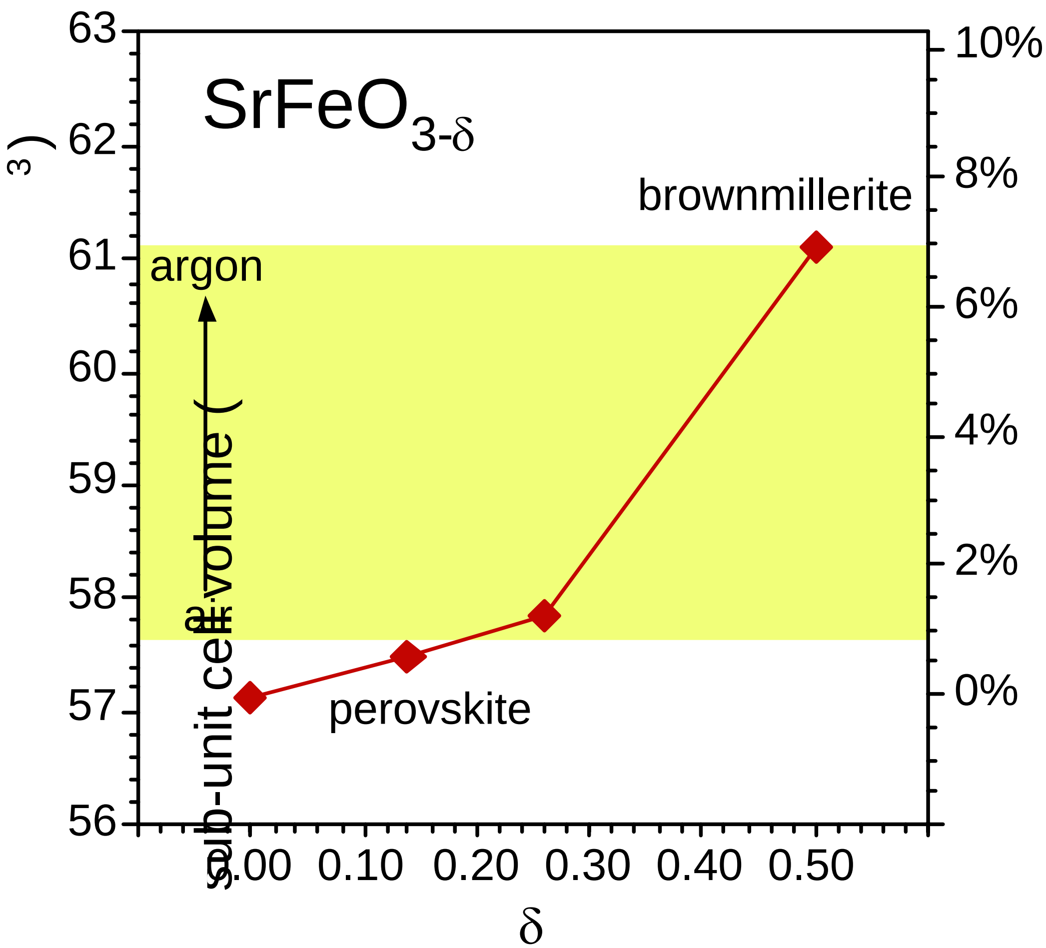
The 2-3-6 phase: A new layered ionic conductor



$Sr_2(Fe_{1-x}Co_x)_3O_{6+\delta}$

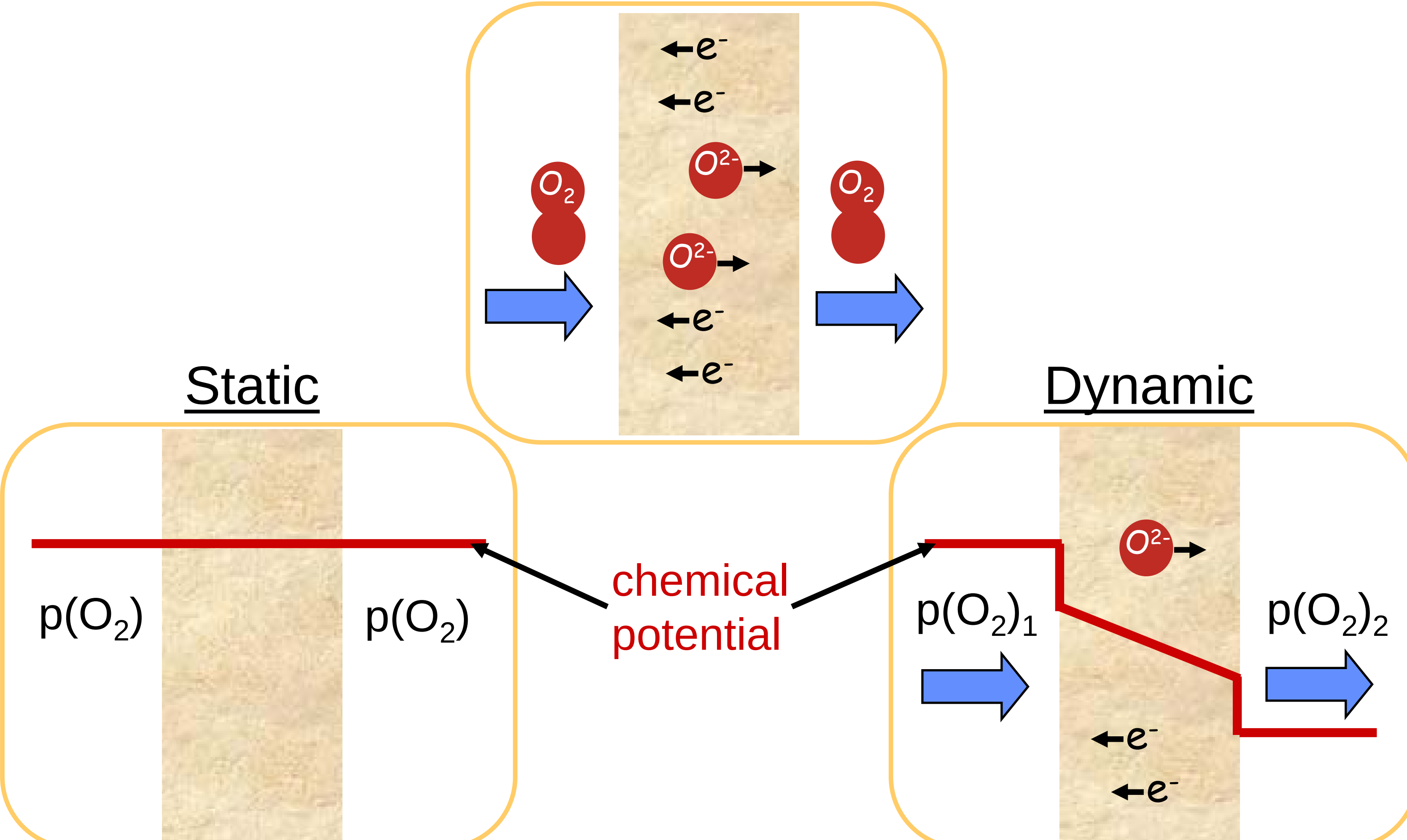
The 2-3-6 phase is a layered compound that supports oxygen ionic conductivity and is mechanically and chemically stable in the reactor environment. It has poor electronic conductivity.

Volume of perovskite phases vs. oxygen content (large changes lead to mechanical instability)

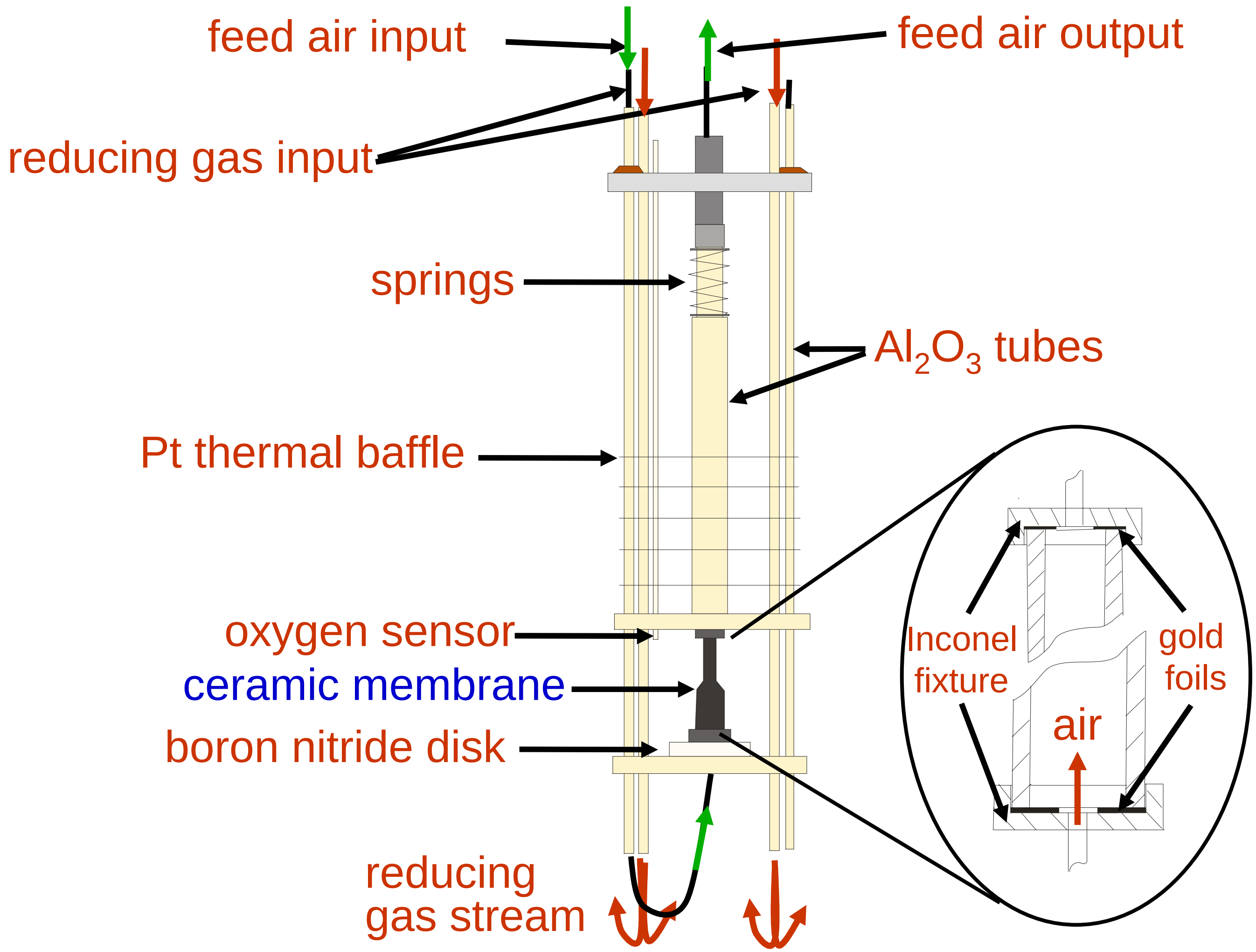


The perovskite phase has good electronic conductivity, but is mechanically unstable in the reactor environment because of large changes in oxygen content as a function of external $p(O_2)$, which affect the cell volume.

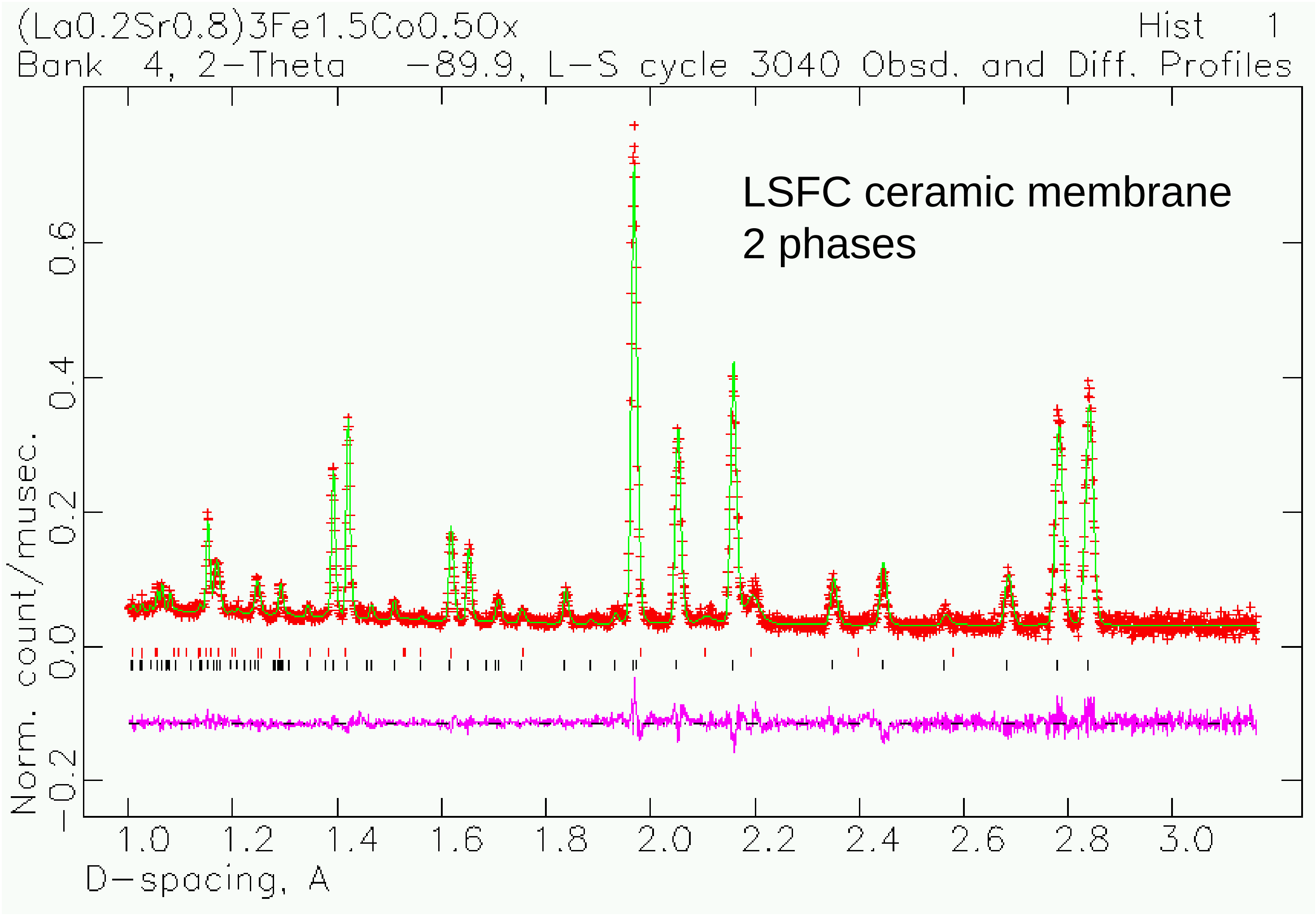
In Situ Neutron Powder Diffraction Under Dynamic Conditions: What Can We Learn?



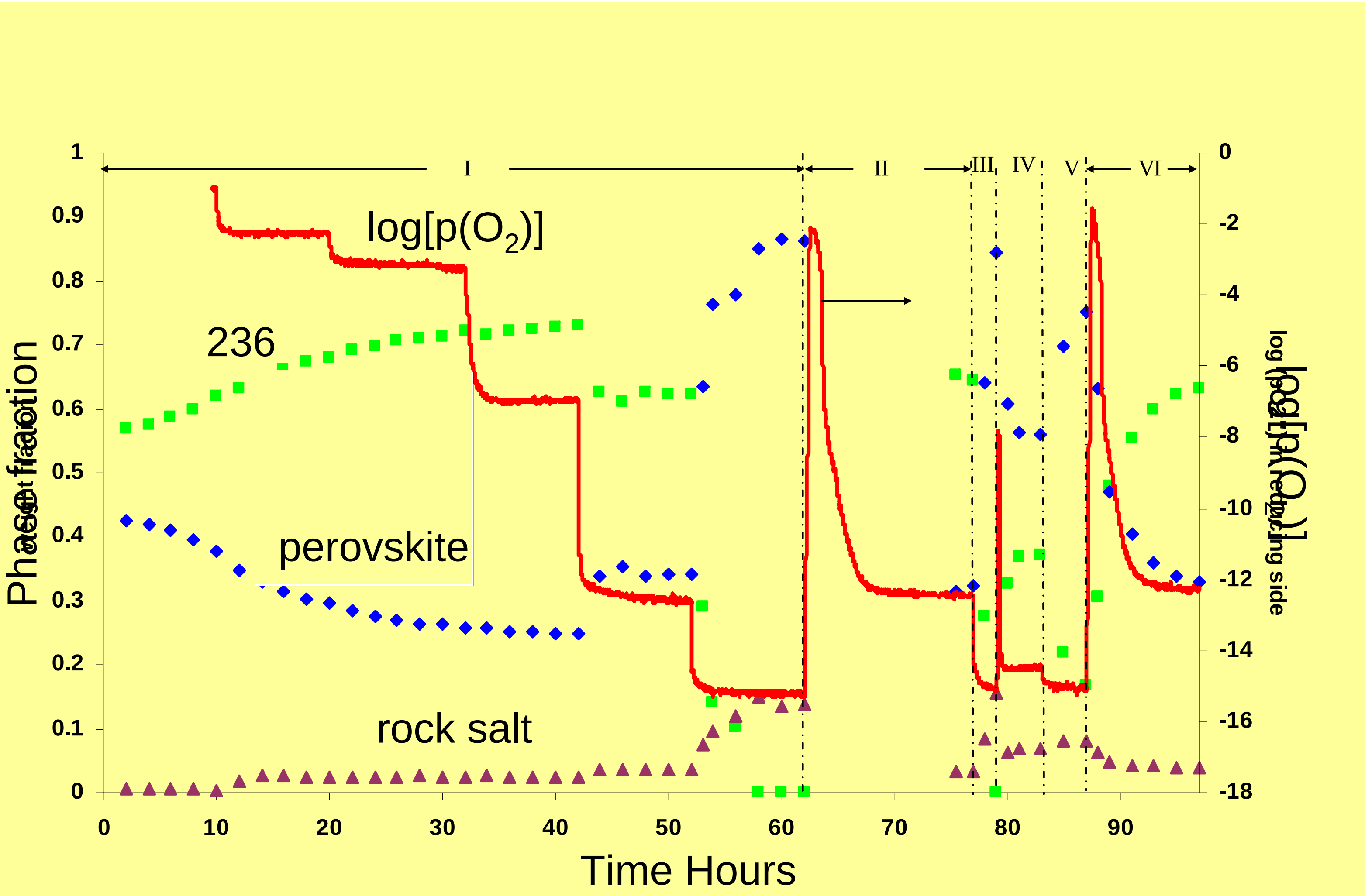
Furnace at the IPNS for Dynamic In Situ Studies of Ceramic Membranes (J. W. Richardson, E. Maxey, & Y. Li)



Example of TOF Neutron Powder Diffraction Data from the *In Situ* Furnace

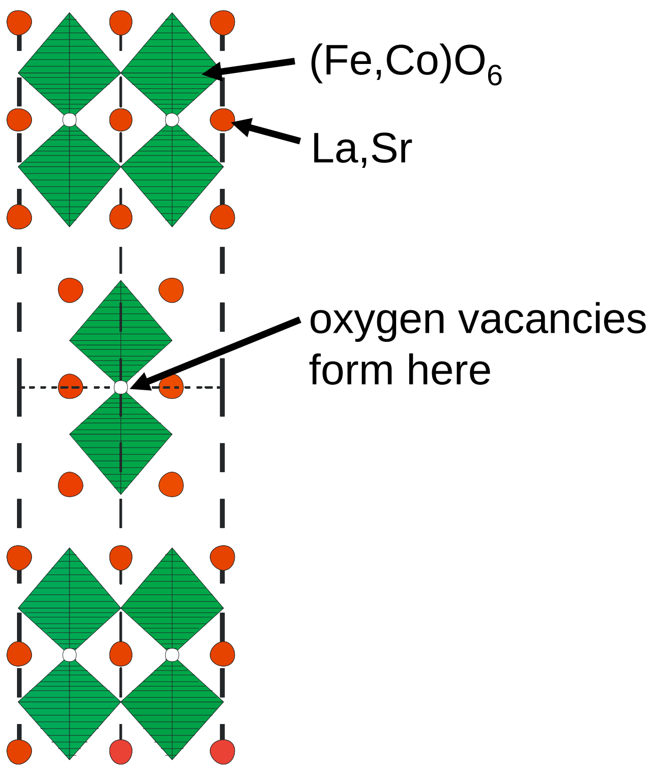


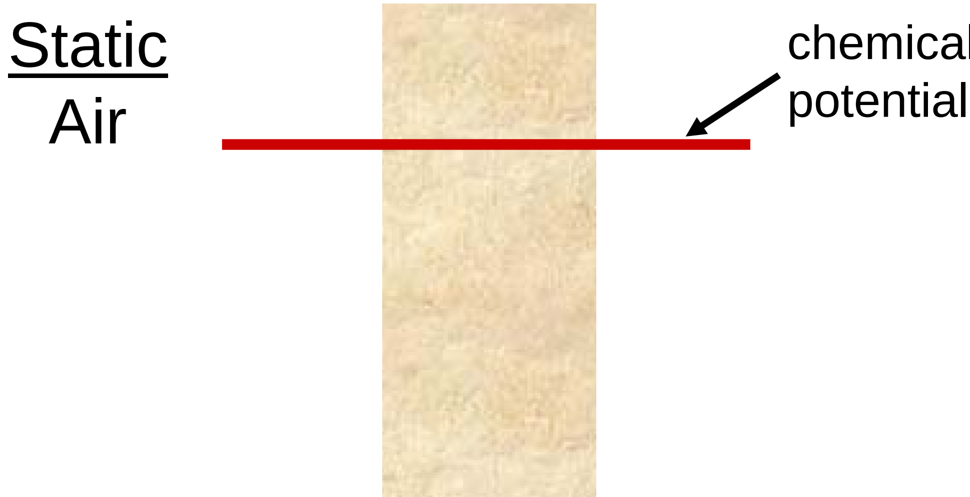
In Situ Phase Behavior of SFC-2 Three-Phase Ceramic Membrane vs. Time While Changing $p(O_2)$

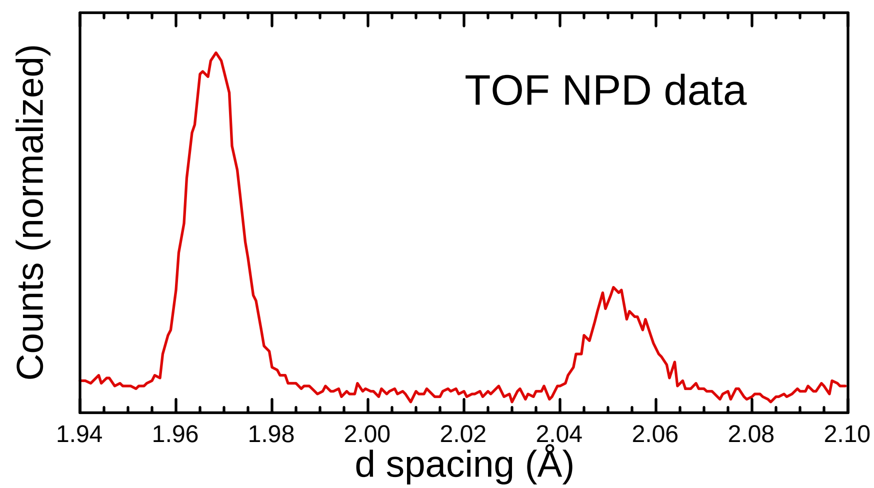


In situ NPD Data for LSFC Ceramic Membrane under Static and Dynamic Conditions

LSFC
$La_{0.2}Sr_{0.8}Fe_{1.5}Co_{0.5}O_{6-\delta}$







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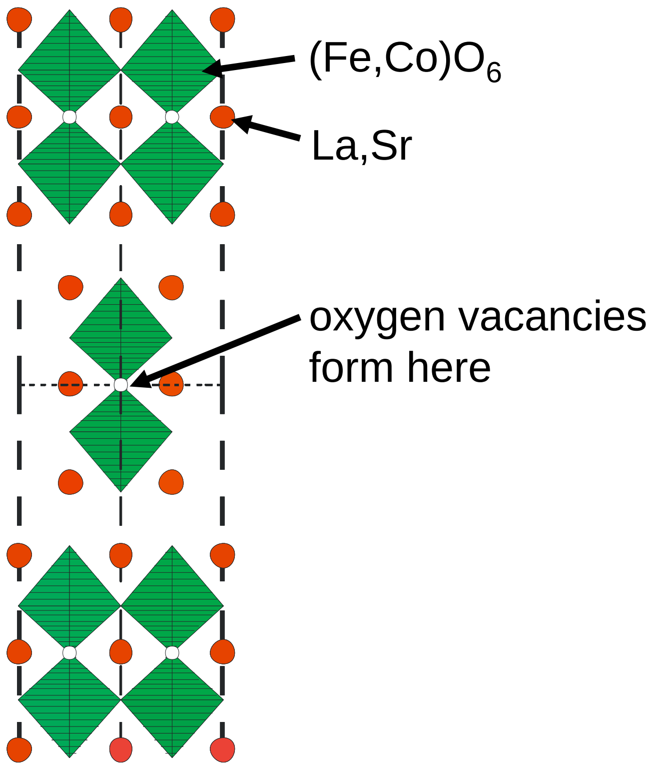
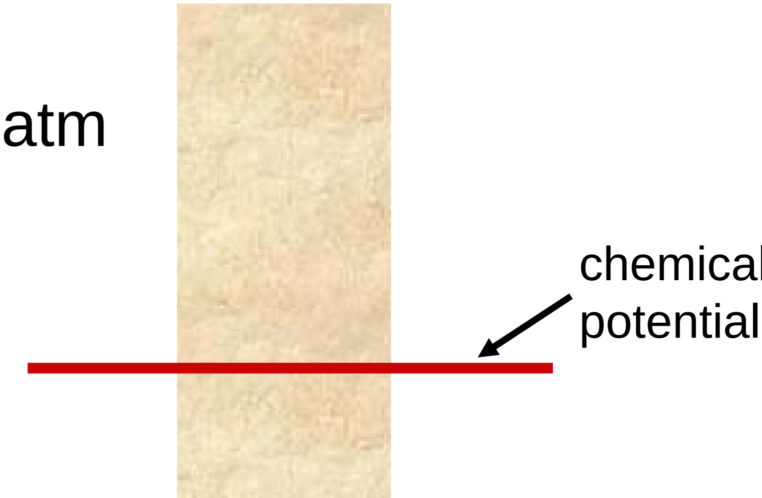
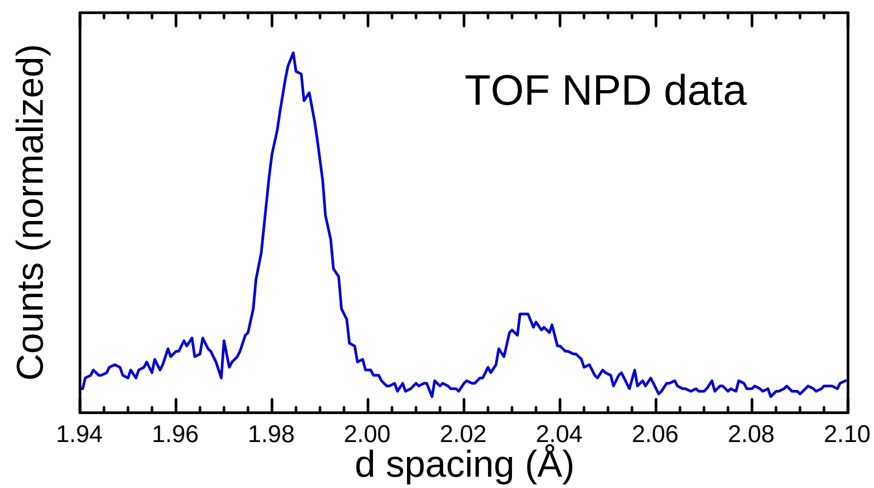


<u>Static</u>

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





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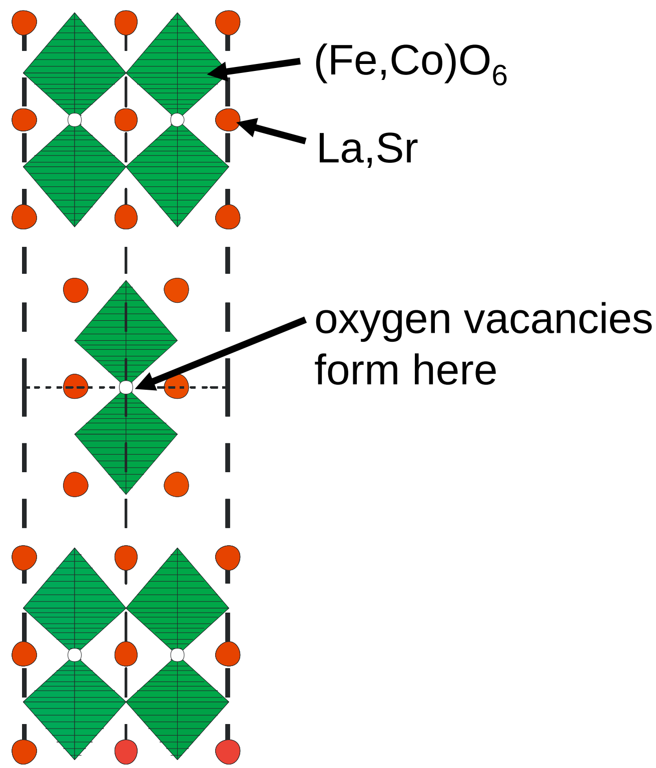
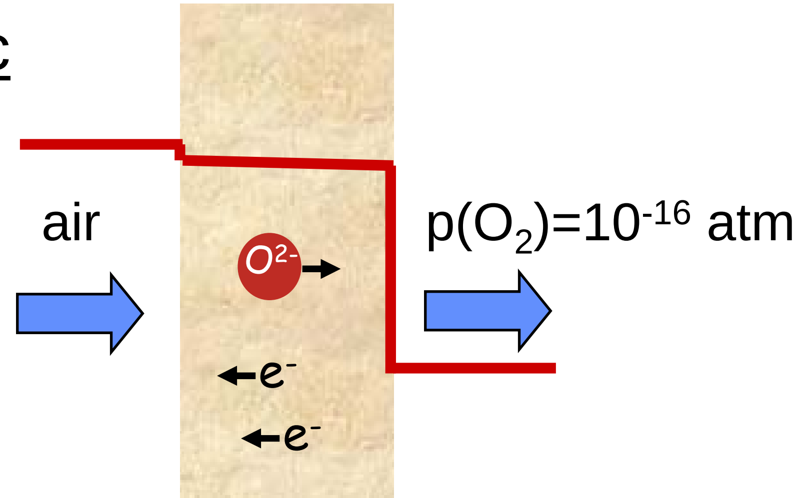
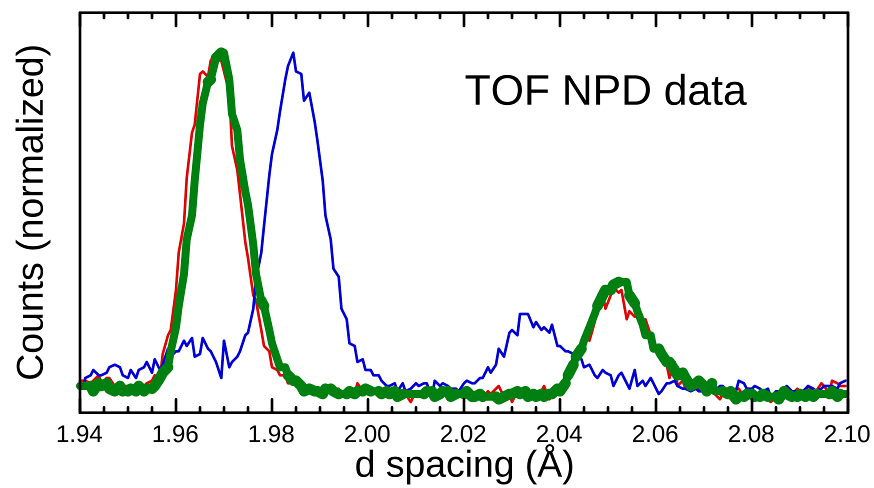


Dynamic





Summary

- Ceramic membranes are widely used in existing and emerging energy technologies.
- Because of the large costs involved, even incremental improvements in performance are important.
- Breakthroughs in ceramic membrane materials (e.g., higher transport at lower temperature) could have dramatic impact.
- Neutron scattering (especially in situ studies) provides unique information about both bulk and surface properties.
- These techniques need to be extended to other types of ceramic membranes -- e.g., hydrogen or CO_2 transport membranes.