

Solid-State NMR Studies of Oxide Ion Conducting Ceramics for Enhanced Fuel Cell Performance

Stanford Global Climate and Energy Project

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Global Climate & Energy Project
STANFORD UNIVERSITY

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web site version

fuel cells: some context

early work (many decades)

- direct conversion of energy of fuel oxidation to electricity:
higher efficiency than combustion
- high energy density
- low S, NO_x, particulate emissions

CO₂ emissions/sequestration

- higher efficiency may reduce CO₂ emissions per kw,
even with hydrocarbon fuels (e.g. natural gas)
- with hydrocarbon fuels, CO₂ separation from exhaust gas
(CO₂ + H₂O only) is easier than for combustion systems
- efficient candidate for future, H₂-based energy systems
- generally still too expensive for widespread applications,
but prototype systems are well-developed

fuel cells: prototype applications

Toyota fuel cell hybrid vehicle

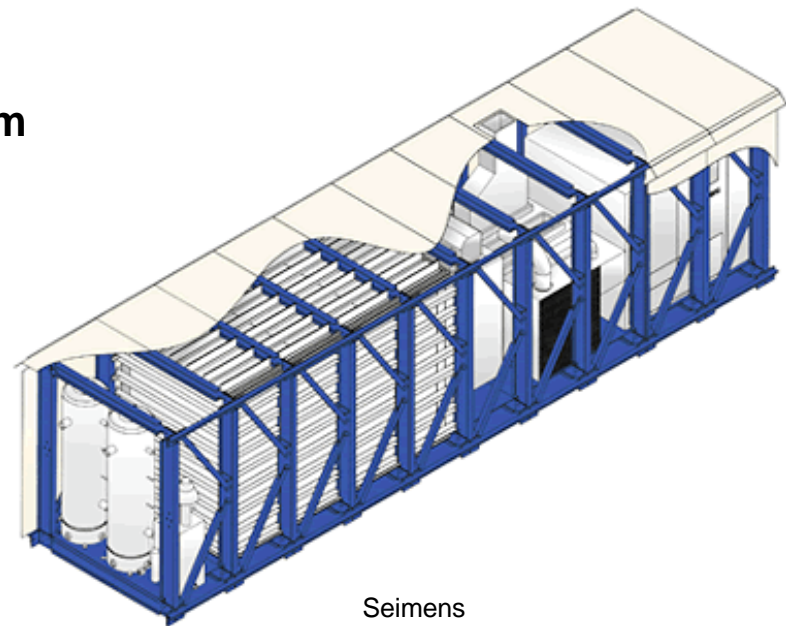
- “Polymer Electrolyte Membrane” (PEM) fuel cell
- high pressure hydrogen gas fuel
- storage battery to recover braking energy
- 90 kw power



Toyota

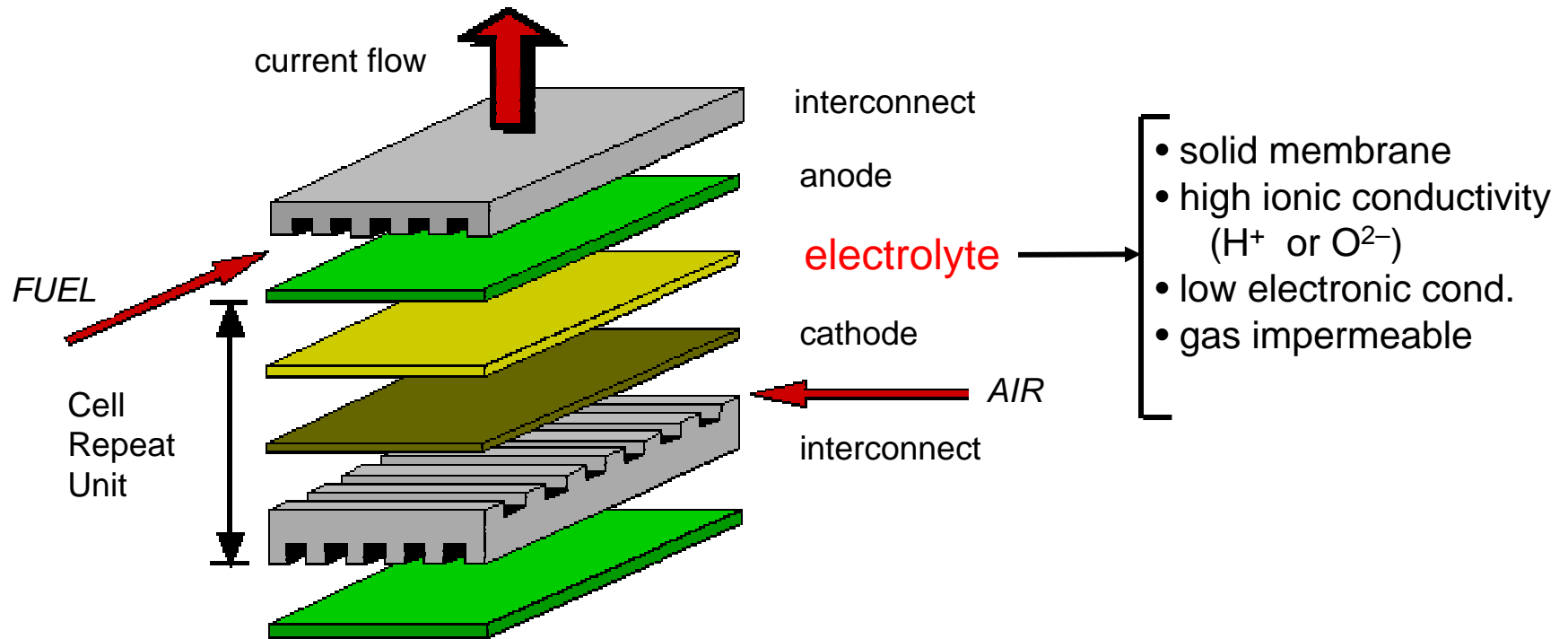
Siemens Westinghouse cogen power system

- “Solid Oxide Fuel Cell” (SOFC)
- methane fuel, integral “reforming” system to make $H_2 + CO$
- 50% electrical efficiency
- 80 % overall efficiency
- 250 kw



Seimens

fuel cell “stack”: simplified, expanded view



Craig Fisher

zirconia (ZrO₂) - based solid electrolytes

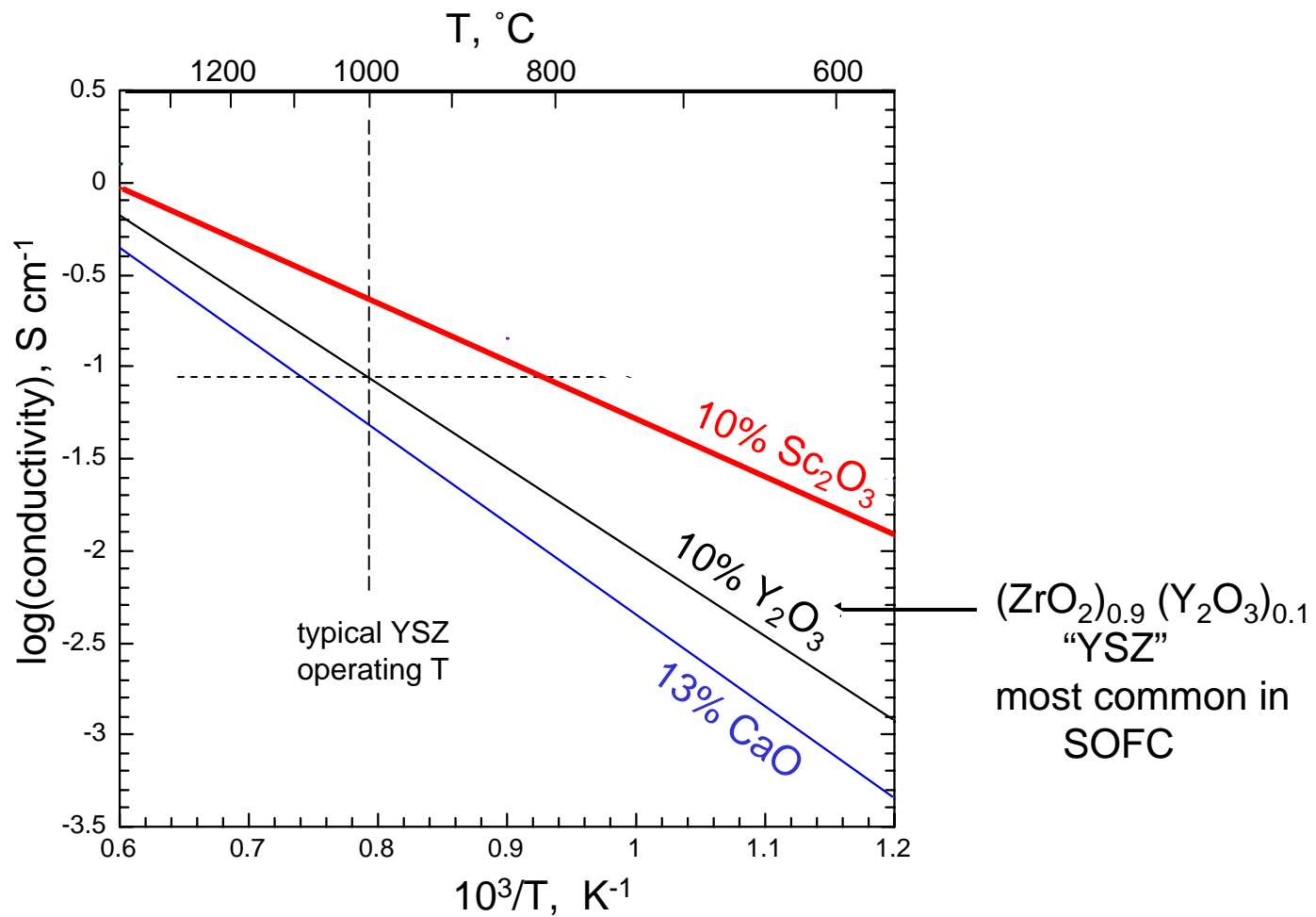
- well developed technology (O₂ sensors, fuel cells, etc.)
- excellent ionic conductor at 800 to 1000° C
- stable in O₂ and H₂ at high T

- can this be improved?
- better conductivity? lower operating T?
- thinner? cheaper?

- better understanding of mechanism of conduction, and relation to composition and structure, are needed to optimize properties

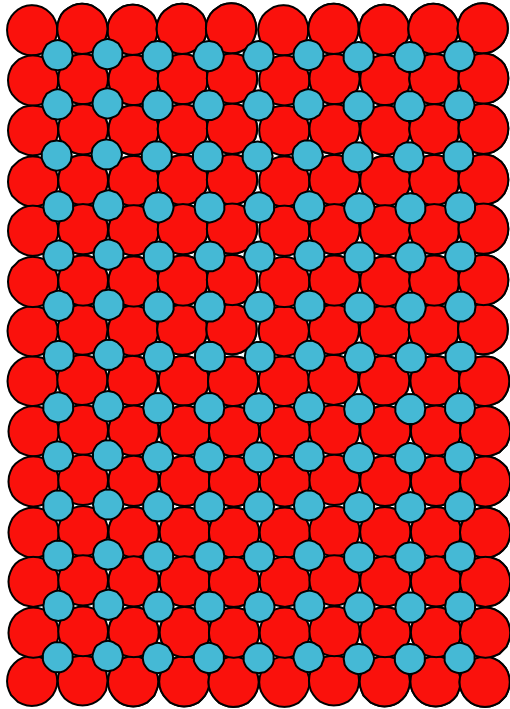
- inherently *disordered* solids:
few available experimental tools to quantify local structure and dynamics... [solid-state NMR](#)

conductivities of ZrO₂-based ion electrolyte ceramics

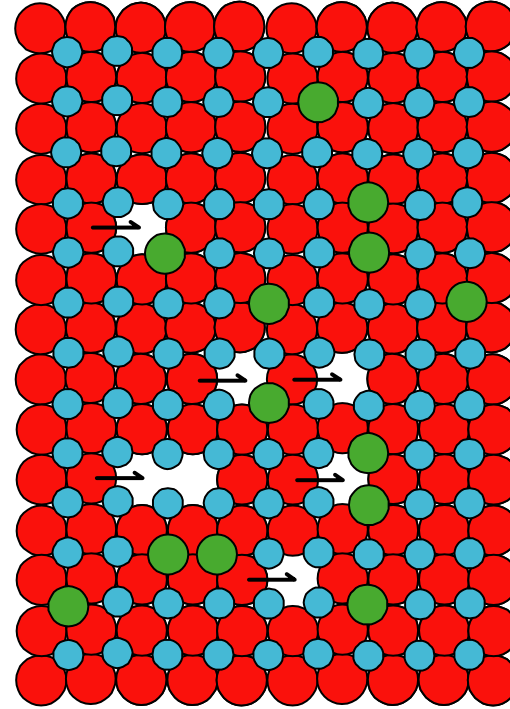


Yamamoto, 2003

2-D sketch of oxide-ion conductor



pure ZrO₂ (zirconia)



yttrium-stabilized zirconia (“YSZ”)

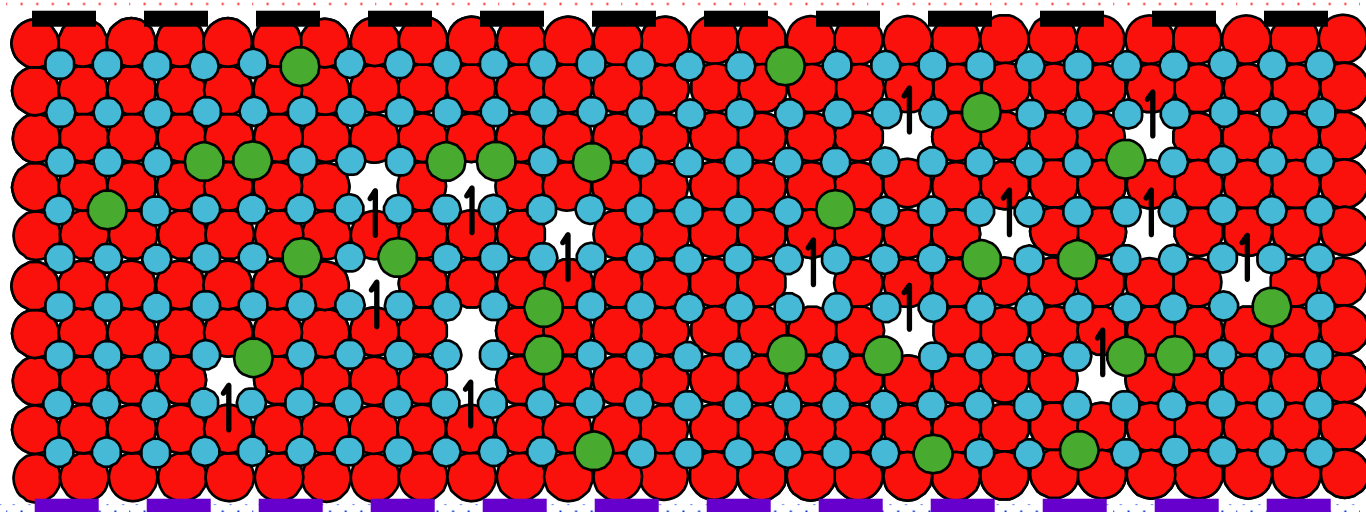
“stabilized” in high T crystal symmetry
by solid solution: ZrO₂ – YO_{3/2}

Zr⁴⁺ + 1/2 O²⁻ = Y³⁺ + O vacancy
disordered, but *how and how much?*

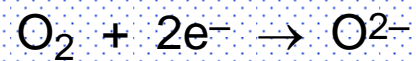
H₂ gas



permeable electron conductor
(stable in H₂)



electron flow
(power!)

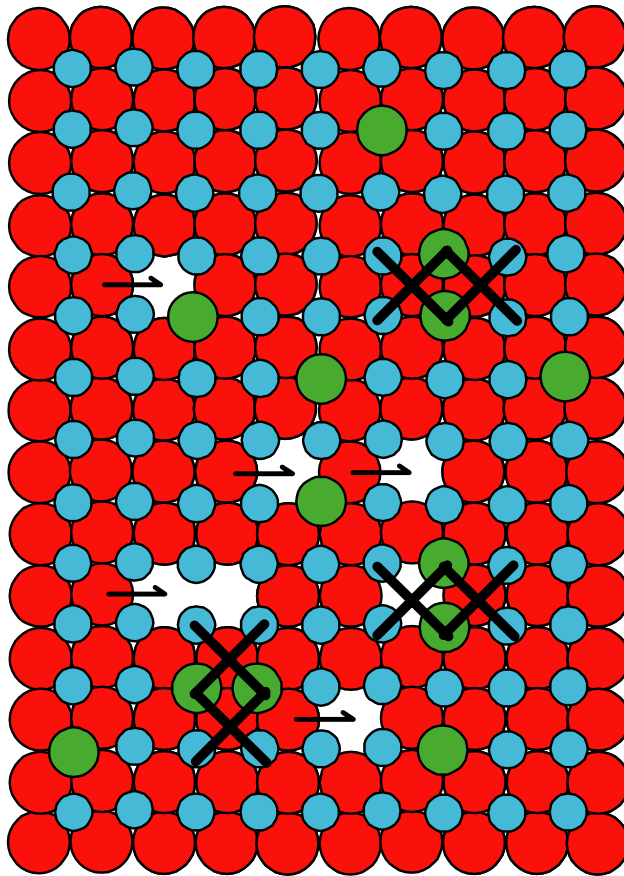


permeable electron conductor
(stable in O₂)

O₂ gas

not to scale!!

interplay between short-range structure and dynamics (therefore *conductivity!*)



local structure,
e.g. defect order/disorder
will strongly affect **ion mobility**
(and thus fuel cell performance)

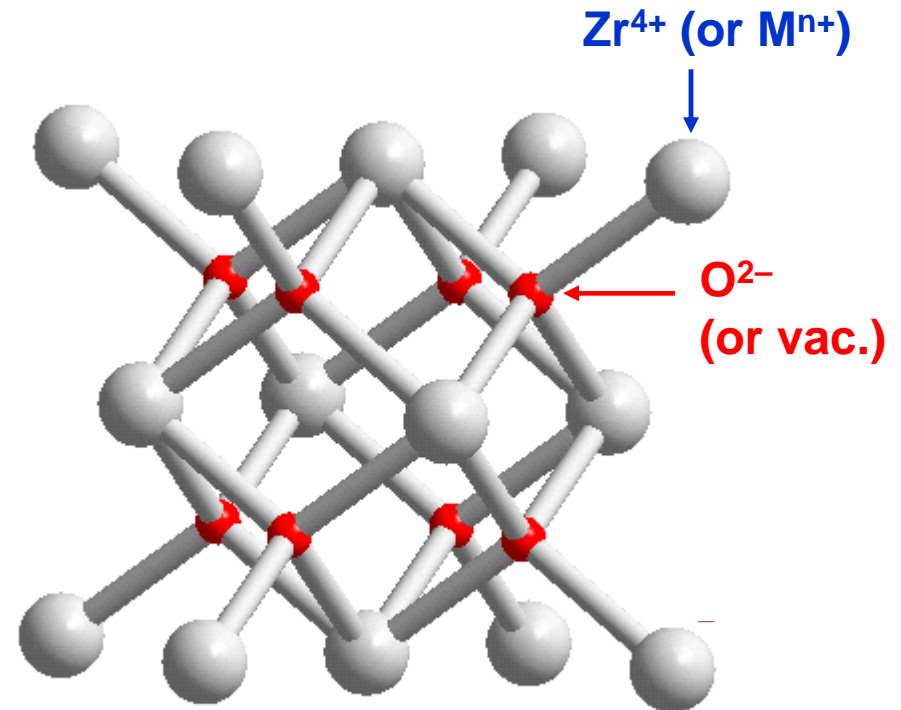
need to probe **short-range dynamics**
at **high temperature**
with **structure-sensitive** tool

▶ **high-resolution, solid-state NMR**

cubic zirconia (ZrO_2): the real material

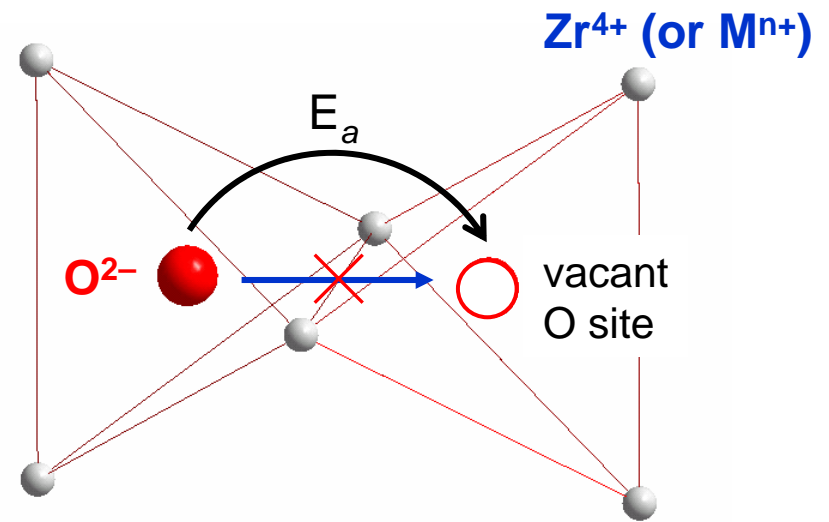
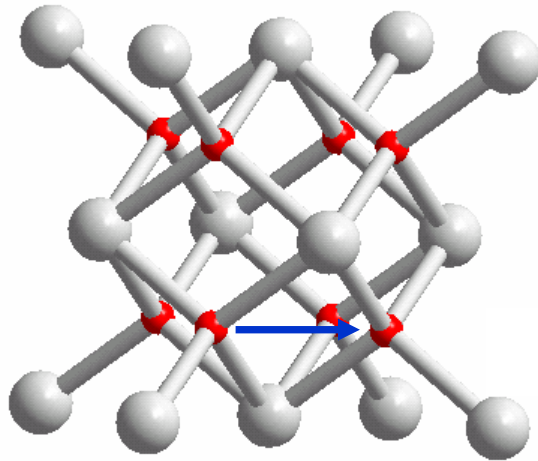


(not just fuel cells
and O_2 sensors!)



ZrO_2
(ideal fluorite structure)

cubic zirconia (ZrO_2): mechanism of oxide ion conductivity



- direct path is too high in energy – must squeeze past two cations
↪ low energy path through tetrahedral face

charge, size, and distribution of dopant cation effects conductivity and activation energy E_a :

E_a = migration energy + association energy between dopant and vacancy

what is NMR (Nuclear Magnetic Resonance)?

- nuclear spin transitions in (high!) magnetic fields
- small changes in energy levels caused by:
 - local distribution of electrons (“chemical shift”)
 - local electric field gradients (for “quadrupolar” nuclides)
- isotope specific, e.g. ^{17}O , ^{45}Sc , ^{89}Y , ^{91}Zr
- sensitive to local structure:
 - coordination numbers
 - first and second atom neighbors
 - bonds distances, types (e.g. covalency)
 - symmetry
- peak areas are usually quantitative of site populations
- sensitive to dynamics (e.g. ion site hopping at s to 10 ns time scales)
- spectra usually with frequency relative to a standard, in ppm



Stanford Magnetic Resonance Lab

18.8 Tesla NMR magnet
(800 MHz ^1H frequency system):
Stanford Magnetic Resonance Lab

14.1 T and 9.4 T systems
(600 and 400 MHz):
Stebbins group labs

- all are fully equipped, multichannel spectrometers with full solids capability
- variety of state-of-the-art, high power, high spinning speed NMR probes

state-of-the art “conventional” magic-angle spinning (MAS) NMR probe

50 mm

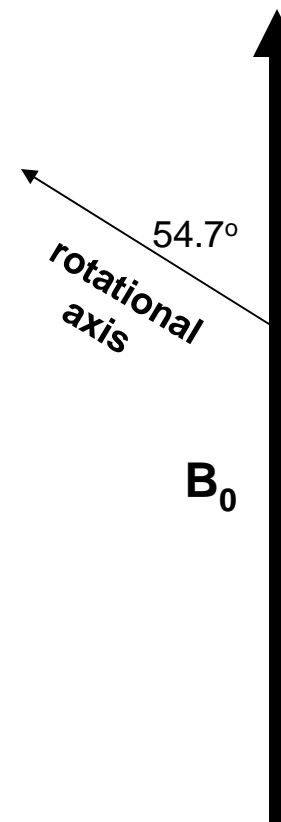
stator housing

- contains NMR coil (radio antenna!),
sample rotor (3 to 7 mm diam.),
high-precision air bearings

- spinning rates to 24 kHz
(1,440,000 rpm...> 500 mph)

tuning electronics

- pulse powers to
1 kW
- typical frequencies
50 -200 MHz



Doty Scientific, Inc.

700° C high temperature MAS NMR probe
(special fabrication by Doty Scientific, Inc.)

stator housing (silicon nitride ceramic) →

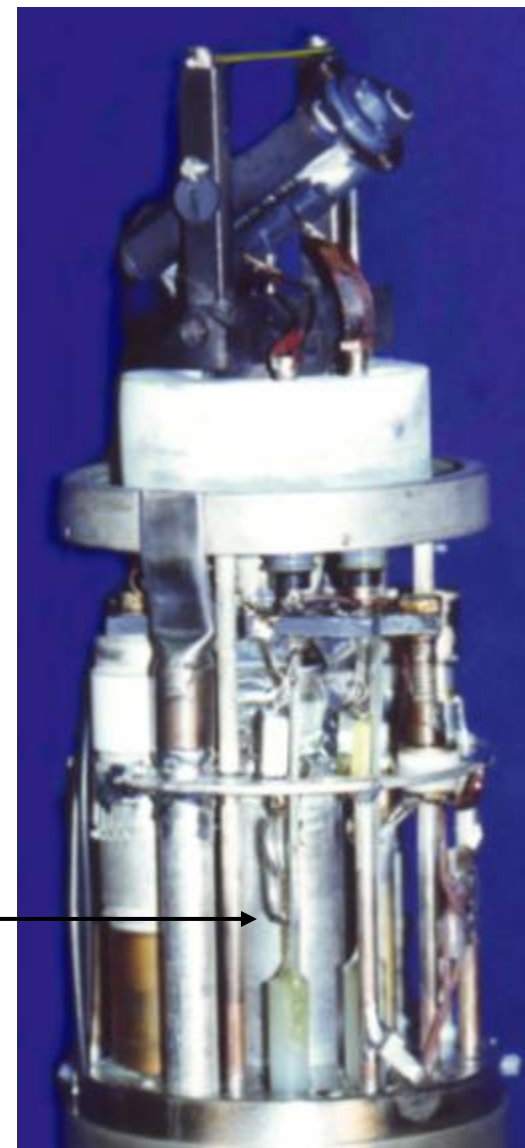
- spinning rates to 6 kHz

thermal insulation →

tuning electronics —

**gas heater
and supply line** →

← 70 mm →



Doty Scientific, Inc.

**oxygen is the predominant element in oxide materials (!)
(volumetrically, numerically, dynamically)**

challenges of ^{17}O NMR of oxide ion conductors

0.04% natural abundance:

- usually requires isotopic enrichment (\$\$\$!)
- but! these materials readily exchange oxygen, making this easier

“quadrupolar” nuclide (spin=5/2)...can lead to broadening of peaks

- best results at “very high” magnetic fields (e.g. 14.1 and 18.8 T)

effects of structure on spectra still largely empirical

- theoretical calculations are rapidly improving

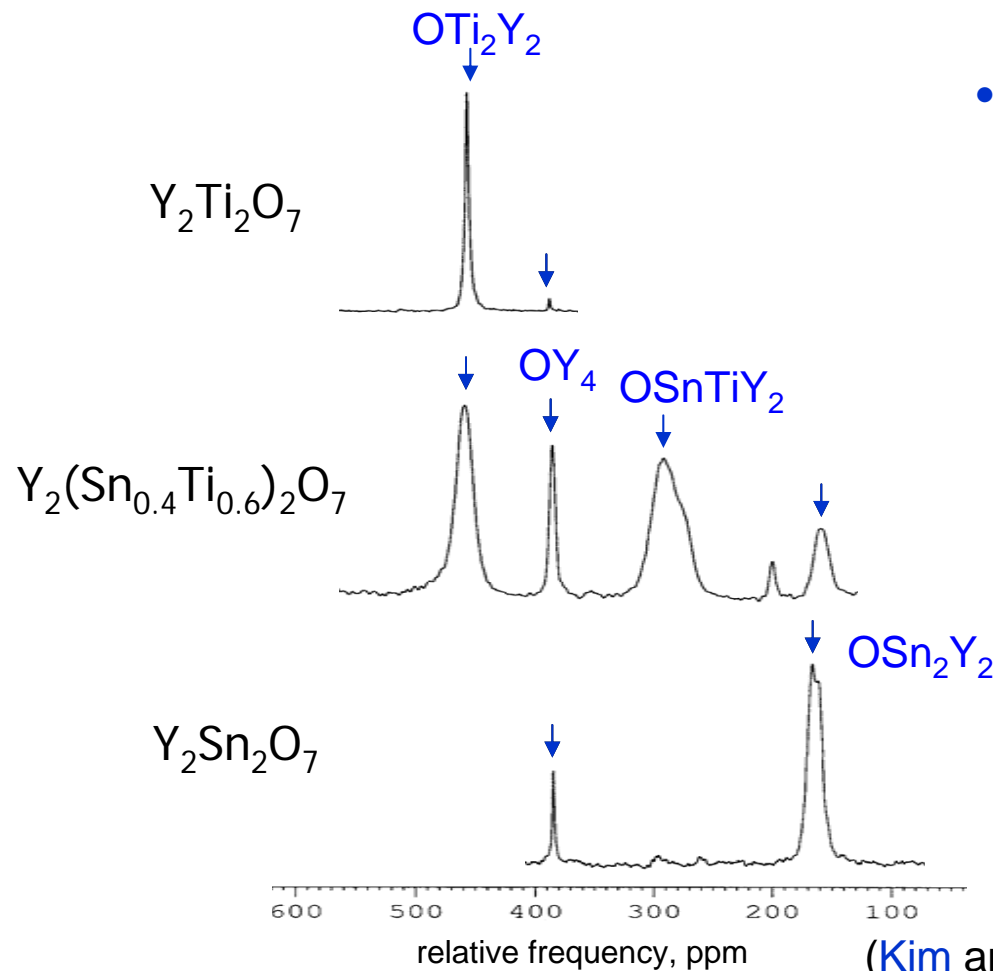
previous work shows low resolution in spectra of YSZ

- start with more promising model systems, e.g. Sc- and Ca-doped
- move to YSZ, etc.

^{17}O MAS NMR of $\text{Y}_2\text{Sn}_x\text{Ti}_{2-x}\text{O}_7$

“pyrochlore” structure

(like ZrO_2 , but with fixed O vacancy content)



- for cations with relatively large differences in size, charge, and/or electronic structure, chemical shift of ^{17}O is systematically affected by number and type of neighbor

(Kim and Grey, 2003, SUNY Stony Brook)

NMR and dynamics at high temperature

one-dimensional exchange spectroscopy:

- applicable when peaks for distinct sites are resolvable
- with increasing T, exchange rate among sites speeds up
- merging or “coalescence” of peaks may be seen
- simulation gives exchange rate
- typical range of frequencies: 100 to 100,000 Hz
- new approach for these materials

two-dimensional exchange spectroscopy

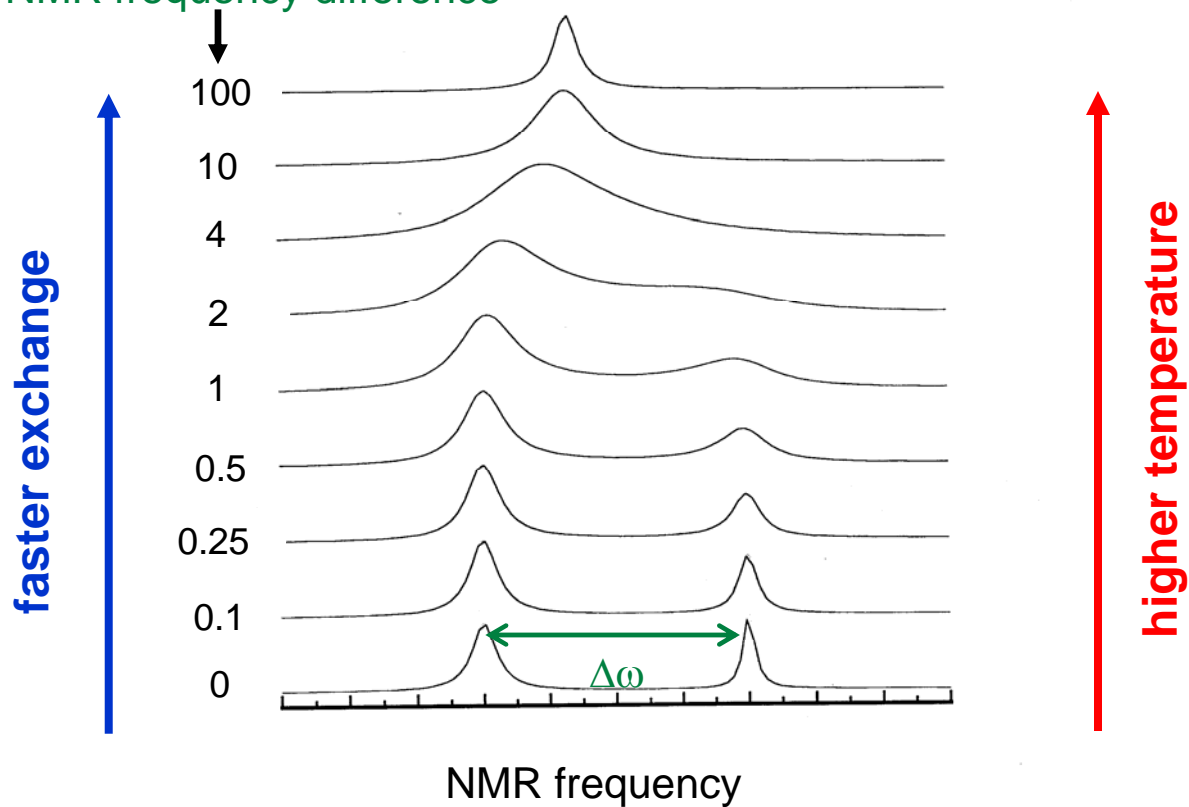
- even slower exchange rates
- more complex to implement
- planned for future work

spin-lattice relaxation measurements

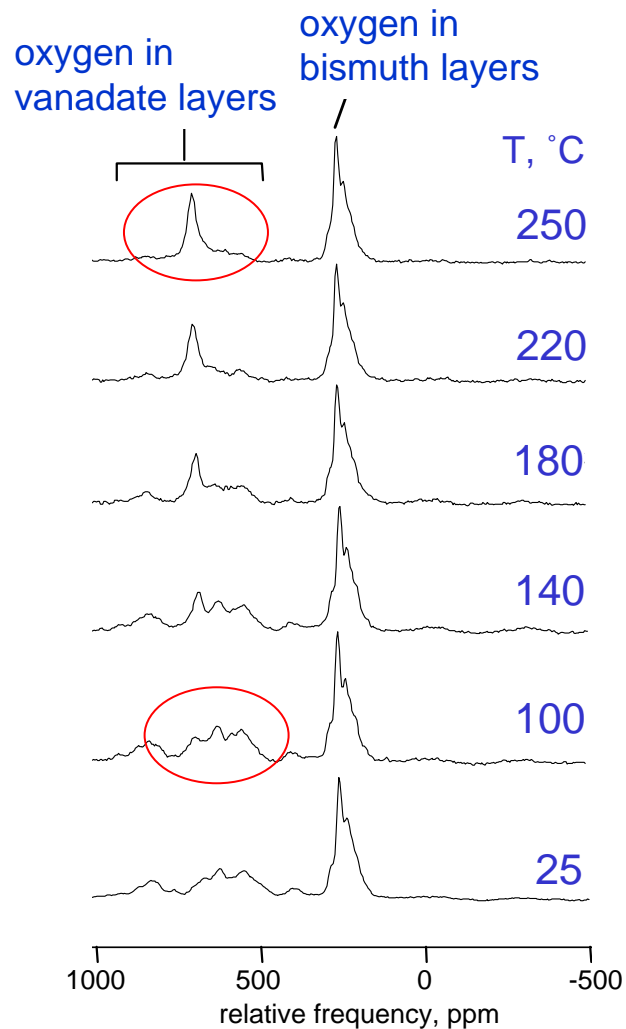
- long history for ionic conductors
- applicable to almost any system and nuclide
- often complex, model-dependent interpretation
- may prove useful here

“coalescence” of NMR peaks: two-site exchange (hypothetical spectra)

exchange frequency ÷
NMR frequency difference



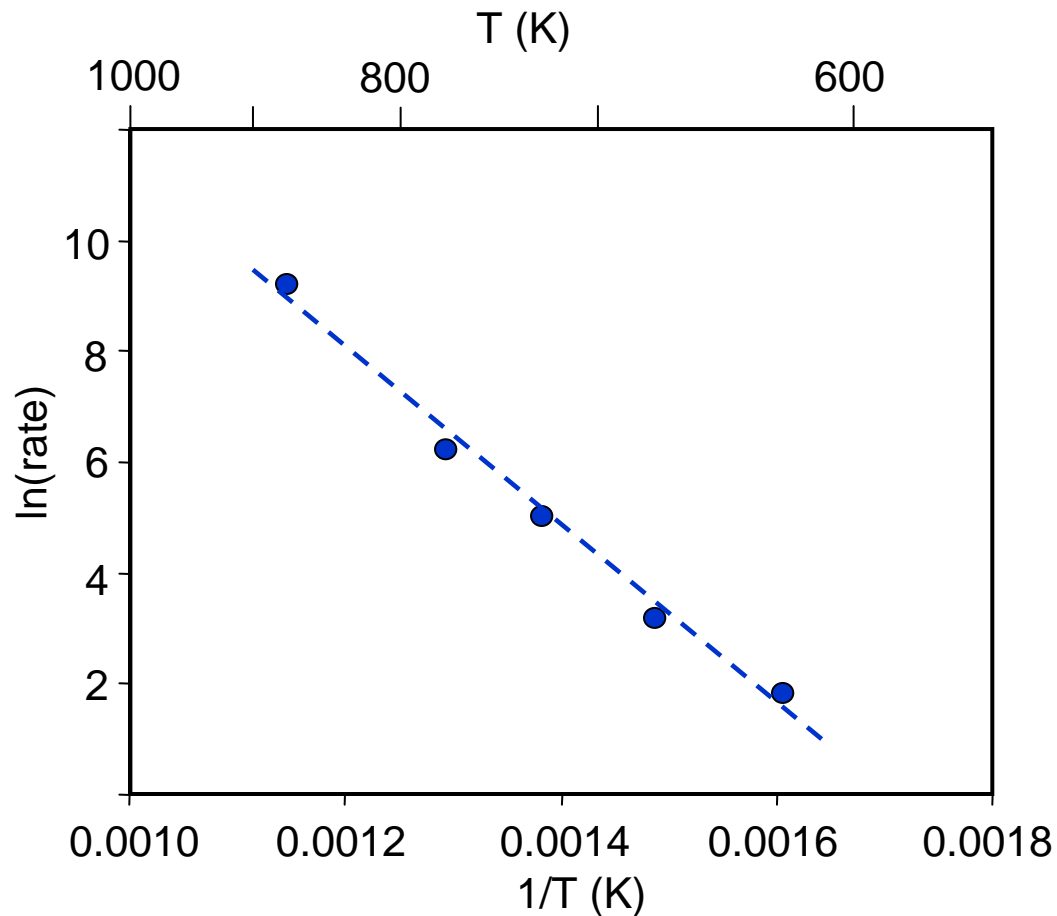
high-T, high resolution ^{17}O NMR of $\text{Bi}_4\text{V}_2\text{O}_{11}$ oxide ion conductor



- layered structure with oxygen vacancies in “vanadate” layer: high ionic conductivity
- separate peaks for different oxide ions in “vanadate” layer merge together at higher T: oxide ion hopping among these sites only
- gives hopping rate *and* pathway through structure

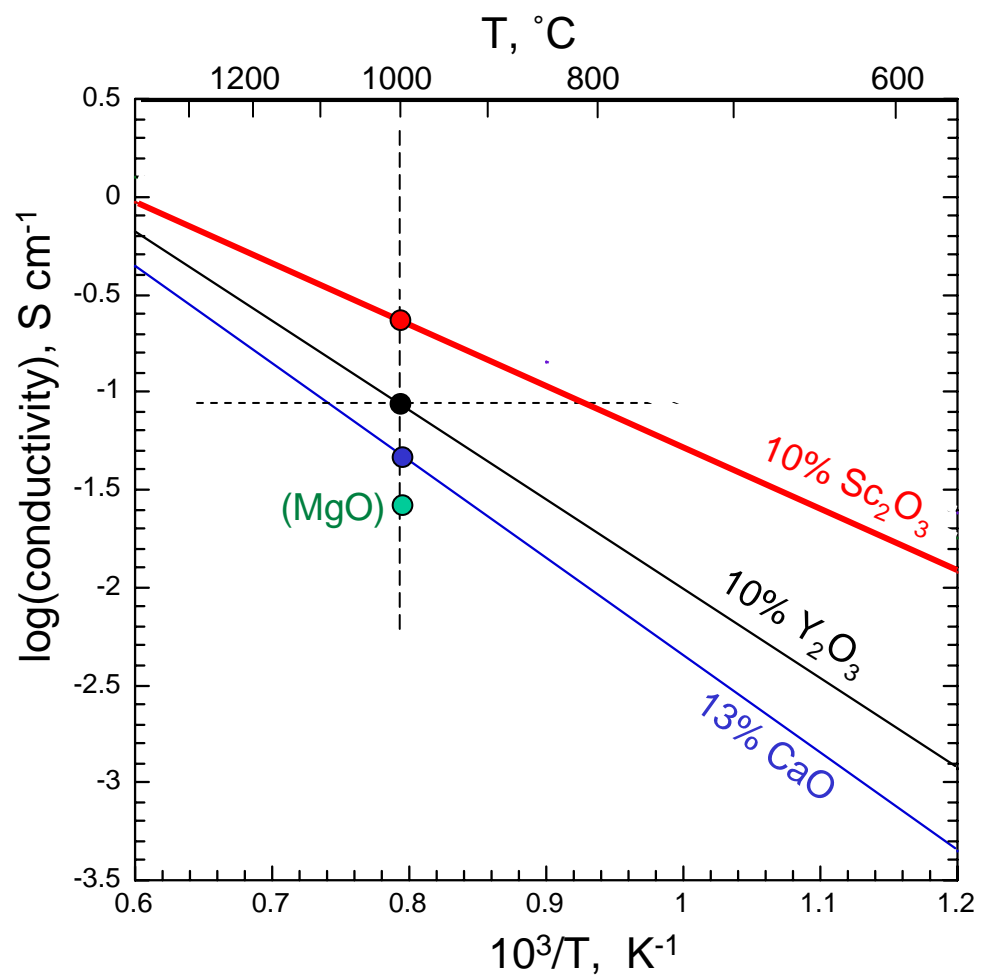
Kim and Grey (2002)

activation energy from NMR exchange data (3 peak sim.)



- $\ln(\text{rate}) = A - E_a/k_B T$
- slope gives $E_a \sim 0.69$ eV
- measured E_a for conduction ~ 0.8 to 1.0 eV
- conduction largely controlled by oxide ion site hopping
- no surprise, but this is indeed a useful new tool for dynamics at atomic scale

conductivities of ZrO₂-based ion electrolyte ceramics



Yamamoto, 2003

closing thoughts

- even “simple” material such as “doped” ZrO_2 has complexities that need to be explored with method that reveals details of cation and vacancy order/disorder and transport dynamics
- solid state NMR at ambient and high T is proving a very interesting new approach to this problem
- we are beginning to see affects of composition and synthesis history on local structure
- in-situ, high T NMR studies show oxide ion site exchange that makes sense in terms of energetics of conduction
- much left to be explored!

