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

Stanford Global Climate and Energy Project

Jonathan Stebbins, prof., Geological and Environmental Sciences
Fritz Prinz, prof., Mechanical Engineering;
Materials Science and Engineering
Namjun Kim, postdoc, G&ES
Cheng-Han Hsieh, grad student, MSE
Hong Huang, research associate, ME

GCEP symposium, June 15, 2005
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\textsubscript{x}, particulate emissions

CO\textsubscript{2} emissions/sequestration
- higher efficiency may reduce CO\textsubscript{2} emissions per kw,
  even with hydrocarbon fuels (e.g. natural gas)
- with hydrocarbon fuels, CO\textsubscript{2} separation from exhaust gas
  (CO\textsubscript{2} + H\textsubscript{2}O only) is easier than for combustion systems
- efficient candidate for future, H\textsubscript{2}-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

Siemens Westinghouse cogen power system
• “Solid Oxide Fuel Cell” (SOFC)
  • methane fuel, integral “reforming” system
even to make $H_2 + CO$
  • 50% electrical efficiency
  • 80 % overall efficiency
  • 250 kw
fuel cell “stack”: simplified, expanded view

- solid membrane
- high ionic conductivity (H⁺ or O²⁻)
- low electronic cond.
- gas impermeable

Craig Fisher
zirconia (ZrO$_2$) - based solid electrolytes

- well developed technology (O$_2$ sensors, fuel cells, etc.)
- excellent ionic conductor at 800 to 1000° C
- stable in O$_2$ and H$_2$ 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 ZrO$_2$-based ion electrolyte ceramics

\[ \log(\text{conductivity}), \text{S cm}^{-1} \]

T, °C

\[ 1200 \quad 1000 \quad 800 \quad 600 \]

10$^3$/T, K$^{-1}$

-3.5 -3 -2.5 -2 -1.5 -1 -0.5 0 0.5

0.6 0.7 0.8 0.9 1 1.1 1.2

Yamamoto, 2003

conductivities of ZrO$_2$-based ion electrolyte ceramics

most common in SOFC

(ZrO$_2$)$_{0.9}$ (Y$_2$O$_3$)$_{0.1}$

"YSZ"

10% Sc$_2$O$_3$

10% Y$_2$O$_3$

13% CaO

typical YSZ operating T
Zr<sup>4+</sup> O<sub>2</sub><sup>−</sup> 

Pure ZrO<sub>2</sub> (zirconia)     yttrium-'stabilized' zirconia  ('YSZ')

Zr<sup>4+</sup> + 1/2 O<sub>2</sub><sup>−</sup> = Y<sup>3+</sup> + O vacancy

2-D hypothetical models of an oxide-ion conductor

2-D sketch of oxide-ion conductor

pure ZrO<sub>2</sub> (zirconia)       yttrium-stabilized zirconia ("YSZ")

"stabilized" in high T crystal symmetry by solid solution:  ZrO<sub>2</sub> – YO<sub>3/2</sub>

Zr<sup>4+</sup> + 1/2 O<sub>2</sub><sup>−</sup> = Y<sup>3+</sup> + O vacancy

disordered, but how and how much?
\[ O_2^- + H_2 \rightarrow H_2O + 2e^- \]

\[ O_2 + 2e^- \rightarrow O_2^- \]

permeable electron conductor (stable in H₂)

permeable electron conductor (stable in O₂)

H₂ gas

O₂ gas

not to scale!!

electron flow (power!)
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 ($\text{ZrO}_2$): the real material

(not just fuel cells and $\text{O}_2$ sensors!)

$\text{Zr}^{4+}$ (or $\text{M}^{n+}$)

$\text{O}^{2-}$ (or vac.)

$\text{ZrO}_2$

(ideal fluorite structure)
cubic zirconia ($\text{ZrO}_2$): 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 $E_a$:

$$E_a = \text{migration energy} + \text{association energy between dopant and vacancy}$$
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. $^{17}\text{O}$, $^{45}\text{Sc}$, $^{89}\text{Y}$, $^{91}\text{Zr}$

• 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
18.8 Tesla NMR magnet
(800 MHz $^1$H 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

**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

Doty Scientific, Inc.
oxygen is the predominant element in oxide materials (!) (volumetrically, numerically, dynamically)

challenges of $^{17}\text{O}$ NMR of oxide ion conductors

0.04% natural abundance:
  • usually requires isotopic enrichment ($\ldots$)
  • 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 $Y_2Sn_xTi_{2-x}O_7$

“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 \div \frac{NMR frequency difference}{100}

1
2
0.5
10
0.1
4
0.25

NMR frequency

faster exchange
higher temperature

Δω
high-T, high resolution $^{17}$O NMR of Bi$_4$V$_2$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.)

- $\ln(\text{rate}) = A - \frac{E_a}{k_B T}$
- slope gives $E_a \sim 0.69$ eV
- measured $E_a$ for conduction $\sim 0.8$ 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 ZrO$_2$-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!