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

Investigators

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Introduction

The purpose of this project is to develop new understanding of the atomic-scale structure and dynamics of oxide ion conducting ceramic materials that are at the heart of solid oxide fuel cells ("SOFC's"), with the aim of more effectively optimizing their performance, lowering operating temperatures, size, and costs. Given the high efficiencies of fuel cells and their likely central role in future hydrogen-based fuel systems, SOFC's may eventually play an important part in the GCEP mission of reducing total CO_2 emissions to the atmosphere.

An especially powerful experimental tool, which has received only limited application to such materials, is high-resolution, solid-state Nuclear Magnetic Resonance spectroscopy (NMR). We are using NMR to characterize the structure of oxide ion conductors, in particular the nature of the order or disorder among dopant cations, which is difficult or impossible to obtain by other methods. We are studying the effects of composition, temperature, and processing conditions on this structure, including exciting new thin film materials being developed in a related program by the group of Professor Fritz Prinz. We are also using the unique capability of NMR to detect the dynamics of ion motion with *in situ*, high temperature experiments. We will relate both types of results to state-of-the-art electrical conductivity measurements, also in collaboration with the Prinz group. The combination of these approaches should lead to more fundamental understanding of the mechanism of ionic conduction in SOFC materials and hence provide new tools for engineering their properties.

This report summarizes the background and motivation for this project as presented in our previous report, and describes the considerable progress made since research began in February of 2004, as well as future plans.

Background

Fuel cells, which directly convert the energy released by fuel oxidation to electricity, have been studied for decades as power sources that are cleaner and more efficient than conventional combustion-based systems. In most designs, the primary reaction involved is the oxidation of hydrogen by oxygen. In systems under development for use in the existing fossil fuel-based energy systems, the H_2 reactant is generally produced by "reforming" of gaseous hydrocarbons. In the short term, therefore, growing use of high-efficiency fuel cell-containing systems will contribute to net reductions in the rate of CO_2 emissions to the atmosphere primarily by lowering the amount of hydrocarbons that must be oxidized per unit of energy produced. In the longer term, however, movement

towards a hydrogen-based fuel economy will be greatly facilitated by advanced fuel cell technology, which is ideally suited to the direct utilization of H_2.

Most commonly used types of fuel cells are designed around gas-impermeable solid barriers that separate the H_2-rich fuel gas from the O_2-rich oxidant, but which allow rapid transfer of either H^+ or O^{2-} by ionic conduction. The latter process is most common, using oxide anionic conducting electrolytes (most typically yttrium-stabilized zirconia or "YSZ"). The potential efficiencies of SOFC's, especially when combined with cogeneration systems to fully utilize the byproduct heat, their modularity and unit size flexibility, and their environmental advantages (low SO_2, NO_x, and particulate emissions), have lead to major government and industry research and development efforts and the beginnings of installation of multi-megawatt commercial systems in distributed generation applications.

Typical SOFC's must be operated at the relatively high temperatures (600 to 1000 °C) where electrolyte conductivity is sufficient to reduce resistive energy losses to acceptable values. Although high temperatures have the advantage of rapid redox reaction kinetics, and the ability to reform hydrocarbon fuels internally, they may limit the use of SOFC's in applications that are critical to restructuring global energy systems, in particular to powering automobiles. (Note however that existing SOFC technologies are already being tested for powering long-range buses and trucks.) Other types of fuel cells that operate at lower temperatures have thus been developed, for example those involving proton-conducting electrolyte membranes ("PEM" cells). Further advances in SOFC's for some such applications will depend on increasing oxide membrane conductivity, by designing new materials and/or by developing new methods of fabricating much thinner electrolyte layers and integrating them into robust, miniaturizable fuel cell systems with fast warm-up times. The latter is one of the goals of another GCEP project, led by Professor Prinz.

The general principles of oxide ion conduction in ceramics have long been understood: O^{2-} ions diffuse through the crystal lattice at a rate that depends primarily on the concentration, distribution, and mobility of anion vacancies in the structure. Vacancies are most commonly introduced by creating solid solutions with cations having formal valances that are reduced from that of the host phase. A lack of information about atomic-scale structure and dynamics of these materials has hindered full development of predictive models of their properties. In particular, most oxide conductors have complex but poorly-characterized degrees of cation and/or vacancy disorder that may vary with composition, temperature, and even the partial pressure of O_2. The extent and type of ordering can have major effects on conductivity. However, commonly-applied analytical techniques have been of limited utility in directly characterizing and quantifying such disorder. X-ray and neutron diffraction, for example, only reveal the structure averaged over long range, and can only hint at the energetically more significant short-range order/disorder.

Methods of observing atomic-scale mechanisms of dynamics (the hopping from site to site that controls diffusivity and conductivity) are even more limited, and for the most part rely on modeling of bulk property data collected over ranges of temperature,

composition, and external conditions. Information about preferred structural pathways for ion migration, about frequencies of ion exchange among locally different types of sites, and about mobility of populations of ions in energetically distinct sites can in general thus be only inferred. Over the last twenty years, solid state nuclear magnetic resonance (NMR) has developed into a powerful new method for elucidating the short-range structure of disordered oxide materials [1]. Even more uniquely, NMR can often directly sample ion dynamics at the microsecond to second time scales required to characterize diffusion in disordered crystalline systems [2, 3, 4].

NMR provides information primarily about local structure around isotopes of specific elements in crystalline, amorphous, or liquid materials. Spectra are thus primarily controlled by the number and spatial distribution of first and second atomic neighbors. In many cases it is this short- to intermediate-range structure that has the greatest energetic importance in controlling disorder and ion mobility. Among spectroscopic methods, NMR is unusual in that the strength of the observed signal in a properly designed experiment is directly proportional to the concentration of atoms in a given structural environment, providing an often unique approach to quantitatively measuring site occupancies and hence the ordering state.

The common (and structurally predominant) element in all of these materials is of course oxygen. However, the only NMR-active stable isotope of oxygen, ^{17}O, has a natural abundance of only 0.035%. Isotopic enrichment by up to >1,000 times is usually needed to observe high-quality spectra. Such enrichment is not inexpensive, but is feasible. Because of the great potential of this approach for obtaining structural and dynamical information on a wide range of oxide ceramics, we have chosen to emphasize it in our planned research. A very few studies of this kind on oxide ion conductors have been made using low-resolution, high temperature ^{17}O NMR of yttria-doped ceria [5], zirconia [6] and barium indate [7]. Recent breakthroughs in high-resolution ^{17}O NMR at elevated temperatures on materials such as bismuth vanadates, by the group of Clare Grey at SUNY Stonybrook, have demonstrated that this approach can be very revealing of the rates and pathways for oxide ion diffusion [8].

Several important dopant cations in SOFC's have abundant isotopes that can also yield NMR spectra that potentially provide important additional constraints on both structure and dynamics, in particular ^{45}Sc and ^{89}Y. Only a very few studies of these nuclides in any oxide material have been reported, and these were all done at ambient temperature [9-13].

Experimental approaches that we are taking are described below, so that they may be illustrated by our recent results. All NMR spectra shown use the "magic angle spinning" (MAS) technique, in which samples are spun at very high rates (here, 5 to 20 kHz) to eliminate some types of line broadening that result from orientation-dependent interactions. Data were collected at external fields of 9.4, 14.1, and 18.8 Tesla in labs at Stanford. The first two are maintained by the P.I., the third is part of the Stanford Magnetic Resonance Laboratory, run by Professor J. Puglisi of the Medical School. We have acquired a specially-built, high temperature MAS NMR probe capable of operating

to over 700 ˚C (Doty Scientific, Inc.). Only a handful of such instruments are in use, worldwide. Our group pioneered in the application of an early version of this technology to ionicly conductive oxides [14].

Results

Materials synthesis and isotopic enrichment

We have taken three approaches to obtaining suitable SOFC electrolyte materials for NMR experiments. So far, we have synthesized most of our samples in our own laboratory, primarily using "Pechini" methods. This approach is known to produce materials that have relatively homogeneous distributions of dopant and major-element cations, because it does not rely on long-range solid-state diffusion in the final oxide product. Here, aqueous solutions of the precursor cations (most often as nitrates) are gelled by addition of a soluble polymer precursor (e.g. ethylene glycol plus citric acid), followed by heat treatment. Here, aqueous solutions of the precursor cations (most often as nitrates) are gelled by addition of a soluble polymer precursor (e.g. ethylene glycol), followed by heat treatment. Initial precipitation of intimately mixed, "nano-scaled" oxide particles, dispersed in the gel matrix, is followed by devolatilization of nitrates, organics, and of water. A higher temperature "calcining" step then allows the formation of crystalline oxide particles and equilibration to a variety of possible phases, depending on the type and level of dopant.

The compositions synthesized so far have been chosen specifically to explore the information content of NMR spectra of zirconia-based SOFC materials. For example, scandium-doped ("stabilized") zirconia (SSZ) is known to have the highest ionic conductivity of this family of materials, and ^{45}Sc is a potentially feasible (although nearly unexplored) NMR nuclide. We thus began by making several SSZ samples with a wide range of Sc_2O_3 contents (2 to 8 mol%) and a corresponding range of crystal symmetries (monoclinic to cubic). Ca- and Mg-doped zirconia (CSZ and MSZ), while known to have lower conductivities, are well-studied as structural ceramics. In addition, we expected that the presence of Sc^{3+} vs. Y^{3+} vs. Ca^{2+} vs. Mg^{2+} cation neighbors will have significant effects on the ^{17}O NMR response, especially on the chemical shift δ_{iso}. We have thus synthesized two other series of zirconia samples with 10 to 20 mol% CaO, and with 10 to 15% MgO. We characterized all samples by powder x-ray diffraction to determine phase purity and the long-range average crystal structure and symmetry.

We have begun a second approach to sample synthesis in collaboration with the group of Professor Prinz, with the goal of better understanding the thin-film SOFC materials that are a focus of one of their major projects. Here, films of yttria-stabilized zirconia (YSZ) are grown by deposition of mixed metal layers followed by oxidation. For the sample masses needed for NMR, layers are grown that are unusually thick (about 1 micron). Conveniently, induced stresses in such layers result in their easy detachment from the substrates, yielding as much as a few 10's of mg per wafer. Although this amount is small by conventional solid-state NMR standards, it is sufficient for obtaining high-quality spectra with the small-sample probes and high field instruments that we have available at Stanford. We have also begun to study commercial YSZ samples, which are available in a range of compositions and particle sizes.

For ^{17}O NMR, we have developed methods for ^{17}O enrichment from a gas source of the isotope. In a specially-constructed apparatus, we dispense a known amount of enriched oxygen gas (currently 40% ^{17}O, although higher levels are available) into a silica glass vessel containing the powdered oxide sample in an open Au tube. We then seal the tube with a valve, and heat the sample-containing zone in a tube furnace, typically at 800 °C for 12 to 24 h. We have found that because the high oxide ion conductivity of these materials equates to high oxygen diffusivity, isotope exchange under these conditions is rapid enough to yield enrichment sufficient for high-quality NMR spectra, generally without changing the crystal structure inherited from previous, higher temperature annealing. In addition, the temperature is apparently low enough to lead to negligible ^{17}O loss through exchange with the SiO_2 glass reaction vessel.

We have also begun syntheses of ordered, crystalline model compounds needed to help relate observed NMR spectra to local structural parameters such as cation coordination number. For example, to characterize Sc in the type of eight-coordinated environment expected when substituted into ZrO_2, we synthesized the known-structured $ScVO_4$ by sintering of oxide starting materials.

Sc-45 NMR

100% of natural Sc is ^{45}Sc, an isotope with nuclear spin= 7/2 and a conveniently high NMR resonant (Larmor) frequency, similar to those of other commonly studied nuclides such as ^{13}C and ^{27}Al. However, very few solid-state NMR studies of this nuclide have been published. To learn about technologically interesting scandium-doped zirconias, we are thus having not only to develop optimized experimental methods for this nuclide, but to derive the first empirical correlations between local structure and NMR observables. Nonetheless, it already appears that this approach holds real promise.

In inorganic materials, one of the most commonly observed structural correlations is between isotropic chemical shift (δ_{iso}) and cation coordination number. For many nuclides, including ^6Li, ^{11}B, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{39}K, and ^{41}Ca, we and others have found that the largest single effect on δ_{iso} is a shift towards lower frequency (to the right with standard plotting conventions) with increased coordination. (The opposite effect is often seen for anions, including ^{19}F, ^{35}Cl, and in some cases, ^{17}O.) Our data that confirm that ^{45}Sc spectra are similarly affected, and show as well the very large range of δ_{iso} for this nuclide, providing a great deal of sensitivity to local structure.

Sc-45 NMR peaks for SSZ samples lie between the values for six- and eight-coordination. The observed line shapes are broadened by both distributions of δ_{iso} resulting from structural disorder (ranges of coordination number, bond distances, and second neighbor populations) and by second-order quadrupolar effects. These can be in part separated by collecting data at not only the "high" magnetic field of 14.1 T, but also at the "medium" field of 9.4 T and the "very high" field of 18.8 T, which is available at only a few labs in the world. Preliminary analysis of the variation of line shape with field suggests a mean coordination number (CN) for the Sc in 8% SSZ is about 7. This is surprisingly low: a random distribution of vacancies in this composition would yield a

mean CN of 7.8, while the localization of all vacancies next to Sc cations would yield 7.5. The observed result suggests that there may be significant Sc pairing next to vacancies, which may have important bearing on future studies of the effects of heat treatment on conductivity.

Oxygen-17 NMR, ambient temperature

Pure ZrO_2 has a cubic crystal structure at high temperature, but transforms to lower, monoclinic symmetry on cooling to room T. This structure has two distinct oxygen sites, with three and four coordination by Zr, respectively. For compositions with relatively small dopant levels, similar transitions occur. Thus, the [17]O MAS spectrum of 2% Sc_2O_3-doped zirconia has two main peaks, consistent with an ordered, monoclinic structure, as previously reported from ^{17}O NMR on pure ZrO_2 [15]. We observe two smaller peaks that may be due to oxygens with one Sc and three Zr neighbors. At higher dopant levels, the high T, high-symmetry structure can be "stabilized" at lower temperatures, because of at least long-range disorder among the Zr and dopant cations. Such disordered phases result in broad NMR peaks, which result from more-or-less continuous ranges of local structural variables, as illustrated by the spectrum for 8% Sc_2O_3 doped zirconia. At intermediate compositions, mixtures of phases, and perhaps some intermediate ordering, may occur, as for the 5% Sc_2O_3 sample.

The [17]O-enriched SSZ provides an opportunity to test a "double resonance" NMR method, is which [17]O is observed simultaneously with pulsed excitation of the [45]Sc spin system. Because [45]Sc -[17]O nuclear dipolar interactions are expected to be relatively strong for O atoms located next to Sc atoms, a systematic perturbation of the spectrum is expected. Preliminary results of such "TRAPDOR" NMR experiments are intriguing, but will require further work to interpret in detail.

Calcium-doped zirconia (CSZ) is also monoclinic at low dopant levels, but again is stabilized in the cubic phase at higher concentrations. Thus, a 10 mole % CaO sample is comprised of a mixture of the monoclinic phase, again with two narrow ^{17}O NMR peaks, and a disordered cubic phase with a much broader peak. Remarkably, however, the single phase cubic CSZ samples (15 and 20% CaO) have partially resolved sub-peaks for at least three distinct types of O environments, suggesting the possibility of substantial short-range order that could result from the larger size and charge difference between Ca^{2+} (1.12 A) and Zr^{4+} (0.84 A) relative to Sc^{3+} (0.87 A). This ordering is not apparent in the long-range (x-ray) average structure. (Y^{3+} has an intermediate radius of 1.02 A.)

10 and 20% MgO-doped zirconia, both of which appear to be cubic by powder XRD, have dramatically different [17]O spectra. At the higher concentration level, the peak is very broad, indicating considerable disorder, while at the lower level, the much narrower peak (and indications of partially-resolved sub-peaks) again suggests the possibility of short-range ordering.

The spectrum for an [17]O-enriched, commercial yttria-doped (8% Y_2O_3) zirconia resembles that of the corresponding Sc phase, and is broad and unresolved. Intriguingly, the spectrum for a thin-film sample of similar composition is much broader, perhaps

because it is more defective or disordered. This, in turn, could result from its lower synthesis temperature, which could lead to non-equilibrium distributions of cations and/or vacancies. We are pursuing studies of the effects of higher-T annealing on this kind of sample.

High temperature NMR results

The acquisition of a specially built, high temperature MAS NMR probe has allowed us to record the first truly high-resolution spectra of doped zirconias at temperatures where oxygen site hopping becomes significant, although low-resolution spectra at high T have been briefly described [6]. This instrument, built by Doty Scientific, Inc., can spin samples up to 6 kHz (360,000 rpm) at temperatures to 750 ˚C, while recording high-quality NMR data. (Conventional MAS NMR probes generally cannot exceed 250 ˚C because of materials limitations, severe challenges of maintaining precise tolerances, and problems such as the large effects of temperature on the viscosity of the gas used to drive the spinner.) After several months of installation and testing, we have now been able to collect high T ^{17}O data on several of the samples described above. These were done at a field of 9.4 T, but the probe is designed to work equally well in our 14.1 T system as needed.

The first data collected were on the monoclinic, 2% Sc_2O_3-doped zirconia, chosen because of the clear separation of the peaks for 3- and 4-coordinated oxygen. As temperature increases above about 500 ˚C, both NMR peaks begin to broaden. The most likely explanation of this phenomenon, as is seen more completely in other samples (see below), is a process known to NMR spectroscopists as "chemical exchange." This requires a physical exchange of atoms of the observed nuclide between the local bonding environments that give rise to different peak positions. In this case, this exchange can be caused only by hopping of oxide anions between 3- and 4- coordinated sites: cations in these materials are known to diffuse much more slowly. For such exchange to be detectable in normal one-dimensional spectra, it must reach an average rate similar to the frequency separation of the peaks, which in this case is about 4 kHz. If chemical exchange were the only process occurring, at even higher temperatures the peaks would merge together and eventually form a narrow new peak whose position is the weighted average of the low T peaks. This occurs when the exchange frequency reaches 10's to 100's of time greater than the peak separation frequency. Instead in this sample, a separate, broad peak begins to grow into the spectrum, which resembles the low T spectra of the higher-Sc, cubic phase. This indicates that at least part of the sample is indeed transforming to a disordered, high-symmetry phase, as expected from known phase relations in this system.

The disordered cubic phase with 8% Sc_2O_3 indeed shows this complete averaging of all of its (unresolved) component peaks, with noticeable narrowing at temperatures below 300 ˚C and complete "coalescence" at about 400 ˚C. This contrasts with the behavior of the cubic, high-T phase seen in the 2% Sc_2O_3 sample, which remains broad even at 700 ˚C. This large difference in oxygen site exchange rate is consistent with the known, much lower conductivity at the lower dopant level.

The Ca-doped materials are unique among those examined so far in having partially-resolved subpeaks. This makes the high temperature chemical exchange process even more clear. In this case, it is obvious that all oxygen sites in the structure are participating in the exchange, and thus that the material is indeed a single, homogeneous phase and not a mixture. This may help to constrain the nature of the ordering that we suspect in this material.

High temperature spectra for the Mg- and Y-doped zirconias also shown clear signs of complete chemical exchange and line narrowing, well within the temperature range that can be reached with this probe. It is also quite clear that spectrum of the faster-conducting YSZ narrows at a much lower temperature than that for MSZ. In fact, comparison of spectra collected at 400 ˚C for all the differently doped samples indicates at least a qualitative agreement with the known order of conductivities, with SSZ>YSZ>CSZ>MSZ [16]. This preliminary finding strongly suggests that as expected, the ^{17}O spectra are indeed responding to the same kind of dynamics that are responsible for the anionic conduction.

We have begun to extract quantitative site exchange data from our high temperature NMR spectra with a software package that can simulate spectra for multiple sites, each pair of which exchanges at a different rate. Even with an initial approximation that all rates the same, we have been able to at least roughly reproduce the observed high T line shapes for CSZ. Plotting the logarithm of these means rates vs. inverse temperature yields activation energies that are similar to those for ionic conduction, again indicating that the NMR is "seeing" oxygen site hopping that is closely related to desired engineering properties.

Progress

It is too early in this project to predict in detail its specific consequences for reduction in global CO_2 emissions. However, its most important overall goal is to provide the mechanistic understanding of fundamental processes in fuel cells that is needed to optimize their performance sufficiently to allow them to take their role as key elements in future hydrogen-based energy systems. If such systems do indeed become a major part of a global, reduced-CO_2 energy economy as is being explored by GCEP and many other research efforts, then the impact of our planned studies may be quite significant.

Future Plans

We will continue to synthesize doped zirconia samples of varying composition and thermal history, as well as ordered model compounds, to better understand the relationships between local structure and NMR observables. To make assignments of spectral components more robust, we will explore possibilities for calculating chemical shifts for hypothesized structures, using advanced *ab initio* quantum mechanical methods, possibly in collaboration with a colleague whom we have contacted at U.C. Berkeley. We plan to explore the utility of other nuclides in these materials, in particular ^{89}Y. Although a few studies of this isotope in solid oxides have been reported, it is somewhat challenging because of its low Larmor frequency. However, we have special equipment required for such studies on our 14.1 T spectrometer.

Our high T NMR studies have only just begun. We intend to carry out more studies of oxygen site exchange rates with ^{17}O NMR peak shape analysis, and we will also attempt to collect high temperature spectra on other nuclides, in particular ^{45}Sc. We will expand our line shape simulations, developing more flexible software if needed. We are particularly excited by the possibility of collaborating with Professor Prinz's group, which is doing theoretical optimizations of the structures of doped zirconias, calculating site exchange energies, and modeling conduction with Monte Carlo simulations. We hope to be able to couple such results with NMR line shape calculations to be able to test such complex dynamical models against our data directly.

Also with the Prinz group, we will continue our studies of thin-film oxide ion conductors, in order to better understand how they differ in structure from more conventional bulk materials. We plan as well to make dense ceramics of some of the materials that we have synthesized for NMR studies, to allow detailed electrical measurements to be made in the Prinz lab.

We are beginning to develop methods to explore a second NMR approach to dynamics, the measurement of spin-lattice relaxation times (always denoted in the NMR literature as "T_1"). Spin-lattice relaxation, which is the transfer of energy out of the nuclear spin system into random thermal energy of the atoms surrounding the nuclide observed, depends on local-scale fluctuations in magnetic field and/or electric field gradients, and so can be very sensitive to ion hopping dynamics. Interpretations of T_1 data can be complex and theoretically challenging, but provide an independent sampling of dynamics that may be a useful complement to line shape studies.

Publications

1. N. Kim, C.-H. Hsieh, and J.F. Stebbins, Scandium-stabilized zirconia: high-resolution NMR assessment of cation ordering. In preparation.
2. N. Kim, C.-H. Hsieh, and J.F. Stebbins, Oxygen site exchange and ionic conductivity in zirconias: a high-resolution, high-temperature NMR study. In preparation.

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