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 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 reports, and describes the considerable progress made in the last 12 months of the project.

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 recent GCEP project, lead 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 ("aliovalent") 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 indirectly characterize the energetically often 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 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 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 several approaches to obtaining suitable SOFC electrolyte materials for NMR experiments. So far, we have synthesized most of our samples in our own laboratory, using modified "Pechini" methods as well as high temperature sintering of oxide powders. The first 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 + citric acid), 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 have been chosen specifically to explore the information content of NMR spectra of zirconia-based SOFC materials, as well as other potentially useful oxide conductors with related structures. 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 relatively 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. 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 continued our application of ^{45}Sc NMR to oxide ion conductors by synthesizing "doubly-doped" zirconias containing Sc^{3+} as well as other aliovalent ions, including Ca^{2+}, Mg^{2+}, and Y^{3+}, which are especially interesting because they retain the optimal cubic structure to considerably higher dopant (and thus vacancy) levels. We have also synthesized Sc-doped versions of fluorite-structured $Y_2Zr_2O_7$ (known to have considerable oxide ionic conductivity) and the related pyrochlore-structured $Y_2Ti_2O_7$, and several Sc-doped variations of the perovskite phase $CaZrO_3$, of interest as a possible protonic conductor when vacancies are associated with H^+ ions.

Going farther afield with application of ^{17}O NMR, we have synthesized and characterized isotopically-enriched samples of Y-doped CeO_2, of widespread interest as a

possible SOFC material, as well as Y-doped Bi_2O_3. Ceria, even in pure form, retains the cubic structure over the entire temperature range up to its very high melting point, although there is a tendency for some Ce^{4+} reduction to Ce^{3+} at high T and low oxygen pressure, which can introduce electronic as well as ionic conductivity. Ceria can be doped with high concentrations of trivalent rare earth and other cations, generating unusually high oxide ion vacancy contents [15, 16]. Yttria-doped Bi_2O_3, like zirconia, is stabilized in a high temperature, apparently disordered fluorite structure, that can have oxide ionic conductivity higher than zirconia. Although applications to SOFC's have been limited so far by a tendency for Bi^{3+} reduction at low oxygen pressure and by volatility, this group of materials has received widespread study [17, 18].

We have taken 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). 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.

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 synthesized a number 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 $ScVO_4$ and $ScPO_4$.

Sc-45 NMR, Sc-stabilized ZrO₂

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, few solid-state NMR studies of this nuclide have been published. To learn about technologically interesting scandium-doped zirconias (which have the best conductivities in this class of materials), we thus developed optimized experimental methods for this nuclide, and derived the first empirical correlations between local structure and NMR observables for ^{45}Sc. It is clear that this approach

holds real promise: there is a well-defined correlation between the number of oxygens coordinating the Sc cation and the isotropic chemical shift, as described in our previous GCEP report and in our paper in review in Chemistry of Materials.

Sc-45 NMR peaks for SSZ samples lie between the values for six- and eight-coordination. Again as described previously, analysis of NMR data from samples with a variety of dopant levels and heat treatments, collected at fields of 9.4, 14.1, and 18.8 T, indicates a mean coordination number of Sc that is surprisingly low, suggesting some ordering of vacancies with Sc cations. To explore this effect, we have collected ^{45}Sc MAS NMR spectra at temperatures to 400 ˚C on ZrO_2 with 8% Sc_2O_3. Although the sample spinning rate obtainable with out high T NMR probe is not optimal to give completely narrowed spectra (spinning sidebands overlap with the central resonance), it is clear that the NMR peak becomes significantly broader at higher temperature as oxide ions begin to be mobilized, increasing the range of disorder in local Sc coordination shells. The center of gravity of the peak also moves to lower chemical shift, consistent with a slight increase in the average coordination number of the Sc as oxygen vacancies become more randomly distributed at higher temperature. We note that these structural changes apparently are rapidly reversible on cooling, highlighting the importance of these unique, *in situ* spectroscopic studies.

Sc-45 NMR, "doubly-doped" ZrO_2

To improve electrical and mechanical properties, and to allow higher total dopant levels in ZrO_2 while retaining the desired cubic crystal structure (maximum long-range disorder), systems with two aliovalent dopant ions have been explored. We have followed this approach by synthesizing a series of Sc-stabilized zirconias with added MgO, CaO, or Y_2O_3 and collecting ^{45}Sc NMR spectra to characterize the Sc environments. Preliminary results indicate that there are systematic effects of the size of the "third" cation on the mean chemical shift of the Sc, suggesting a higher mean coordination number and thus more disorder with the larger cations. Near-term future work will explore the effects of composition more systematically as well as characterizing effects on electrical conductivity.

Sc-45 NMR, other oxide-ion conductors

We have begun to apply our newly developed approach of high-resolution ^{45}Sc NMR to other Sc-doped oxide ionic conductors with structures related to ZrO_2. A number of oxides of $A^{3+}_2B^{4+}_2O_7$ stoichiometry form the "pyrochlore" structure with 8-coordinated A sites and 6-coordinated B sites. An example is $Y_2Ti_2O_7$, in which cation sizes are different enough to result in full ordering. In contrast, if cations are more similar in size, the disordered fluorite structure results, as in $Y_2Zr_2O_7$. Because of their relationship to cubic stabilized zirconias, the effects of other dopants on enhancing electrical properties have been explored.

As in other aspects of the structures of disordered oxides, a method that reveals the local, short-range structure can be a revealing complement to the long-range, average picture developed from diffraction studies. To test the utility of ^{45}Sc NMR, we have prepared Sc-doped samples of both $Y_2Ti_2O_7$ and $Y_2Zr_2O_7$, varying the compositions to

attempt to maximize Sc substitution on either the A or the B site. NMR data were collected at the "high" field of 14.1 T and the "very high" field of 18.8 T to determine the contributions to the Sc line shape from cation disorder (distribution of chemical shift) and from quadrupolar broadening (distortion from local cubic symmetry). Results for the two systems are quite different. In the fluorite-structured $Y_2Zr_2O_7$, the similarity of the peak shapes at the two fields indicates that we are detecting primarily the effects of Sc coordination on chemical shift. We clearly discern Sc in two types of site, one octahedral and one with higher coordination (about seven). The intensity of the latter increases somewhat in the sample with composition adjusted to favor Sc in the larger site, but a wide distribution remains. In contrast, in the pyrochlore-structured $Y_2Ti_2O_7$, the NMR peak shape is dominated by a well-defined quadrupolar line shape (whose width is a strong function of the external magnetic field) consistent with Sc occupancy primarily in a distorted octahedral (B) site, regardless of the composition of the starting material. Oxygen vacancies are therefore probably also introduced, but the apparent absence of Sc with only five oxygen neighbors suggests that vacancies are not ordered next to Sc^{3+} ions. These results are quite promising for applying this approach to disordered oxide ion conductors.

Perovskite-structured oxides, again doped with aliovalent cations, have been widely studied as possible protonic conductors for SOFC's and other applications, as their oxygen vacancies can allow considerable H^+ contents. In the case of Sc-doped $CaZrO_3$, our initial [45]Sc and ^{17}O NMR results are already revealing new details of the nature of disorder. [45]Sc MAS NMR spectra show the presence of only a single, narrow NMR peak whose shape and position are consistent only with Sc in symmetrical, octahedral sites. The oxygen vacancies in this structure thus cannot be preferentially associated with Sc, but are probably randomly distributed in the lattice. ^{17}O NMR shows the two oxygens expected from the known (non-cubic) long-range crystal structure, but, at higher Sc contents, also reveal an additional, low-intensity peak probably related to variation in coordination by the cations.

Oxygen-17 NMR

In our previous GCEP report and in a manuscript being readied for publication, we describe in detail our results from ambient temperature and high-temperature ^{17}O MAS NMR studies of zirconias doped with Sc, Y, Ca and Mg, in both monoclinic and cubic phases. There we describe the progress made in using this approach to characterizing the ordering state and the oxide ion exchange dynamics, as functions of the charge and size of the dopant cations. The high T MAS NMR is made possible by the acquisition of a specially-built NMR probe from Doty Scientific, Inc., capable of remarkable performance to temperatures over 700 ˚C.

Recently we have extended these studies to other oxide systems of interest for electrolytes in SOFC's and related technologies. Yttria-doped bismuth oxide (Bi_2O_3) for example, has high oxide ion conductivity. Although volatility and Bi^{3+} reduction can be a problem at high temperatures as commonly used in SOFC's, these materials may become more important in thin film systems that can operate at lower T. We have synthesized a number of different Y-doped bismuth oxides and enriched them in [17]O. Initial NMR

experiments on four samples show a systematic shift in the peak position with composition as more oxide ions are coordinated by Y instead of Bi. This is seen particularly well in two-dimensional, triple-quantum MAS NMR, where effects of quadrupolar line broadening are eliminated.

Yttrium-doped cerium oxide, like stabilized zirconias, has a cubic, fluorite structure and excellent oxide ion conductivity. Although reduction of the Ce^{4+} by H_2 may be a problem in high-T SOFC's, ceria-based materials may again be important as lower operating temperatures are obtained. Y-doped ceria has been the subject of several ^{17}O NMR studies, including in-situ high T work, but all with low spectral resolution. Our first results using high-resolution ^{17}O NMR are thus quite dramatic. Pure CeO_2 has the very narrow, single peak expected for the cubic phase. As more Y_2O_3 is added, at least two other peaks appear at lower chemical shift, probably due to the development of oxygen sites with one or more Y neighbors. Analysis of these results should allow a detailed characterization of the short-range order/disorder in this system. Furthermore, these materials appear to be ideal candidates for further studies of oxide ion exchange dynamics using in-situ, high T MAS NMR: resolution among the various O sites is considerably better than we have seen for the zirconias.

Conductivity studies

In collaboration with the research group of Professor Prinz, we have begun to characterize the electrical conductivity of doped zirconia samples that we have synthesized as sintered ceramic pellets. High-temperature, complex impedance measurements made by Dr. Hong Huang over wide frequency ranges are quite encouraging to allow future direct comparisons between NMR measurements and the properties that are critical for SOFC performance.

Examples of the type of data collected show the complex impedance at 350 °C for two samples of Sc-stabilized zirconias annealed at 1000 °C and 1400 °C. In these plots, the loop towards the left (highest frequency region) corresponds to the bulk ionic conductivity, that in the mid-frequency range to the grain boundary conductivity, and that in the low frequency region (right) to a charge transfer reaction at the electrode/electrolyte interface. Derived conductivity data compare a laboratory standard sample of YSZ and literature values. Signs of a previously described phase transition (rhombohedral to cubic) in the 1400 °C SSZ are apparent. Observed activation energies are consistent with published data; bulk conductivities are similar or slightly lower, but indicate that the samples we are synthesizing for spectroscopic measurements are comparable to those produced for SOFC electrolytes.

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. We plan to continue 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. We will also continue our new work on other oxide ion conductors, such as doped bismuth and cerium oxides.

Our high T NMR studies have only just begun. Our new data on Y-doped ceria, showing well-resolved multiple ^{17}O NMR peaks, seems especially promising for such work. We intend to carry out more studies of oxygen site exchange rates with ^{17}O NMR peak shape analysis, and we will also continue 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 continue 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.

Publications, conference presentations, and reports
1. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Scandium coordination in solid oxides and stabilized zirconia: ^{45}Sc NMR. *Chem. Mat.* (in review)
2. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Oxygen site exchange and ionic conductivity in zirconias: a high-resolution, high-temperature NMR study. (in preparation)
3. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Studies of local structures and dynamics of stabilized zirconia solid electrolytes using solid state NMR (abstract). *Am. Ceram. Soc., 30th Int. Conf. Adv. Ceram. Mat.* (2006)
4. Kim, N., Hsieh, C.-H. & Stebbins, J.F. Local structure and motion in stabilized zirconia: ^{45}Sc and ^{17}O NMR studies (abstract). *47th Exp. NMR Conf.* (2006)
5. Hsieh, C.-H. Solid-state NMR and x-ray studies of local coordination environment in the ZrO_2-Sc_2O_3 system. *M.S. Report, Dept. of Materials Science and Engineering, Stanford University.*

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