

### **II.1.6 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<sub>2</sub> 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 plan to use NMR to quantitatively characterize the structure of oxide ion conductors, in particular the nature of the order or disorder among dopant cations, that are difficult or impossible to obtain by other methods. We will study 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 also plan to use the unique capability of NMR to detect the dynamics of ion motion in *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 program is quite new, having started in mid-February with the hiring of an expert post-doc (Dr. Namjun Kim). This report will therefore focus on background material and then provide a summary of early program activities.

#### **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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

Most common types of fuel cells are designed around gas-impermeable solid barriers that separate the H<sub>2</sub>-rich fuel gas from the O<sub>2</sub>-rich oxidant, but which allow rapid transfer of either H<sup>+</sup> or O<sup>2-</sup> 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<sub>2</sub>, NO<sub>x</sub>, and particulate emissions), have led 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<sup>2-</sup> 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 valences that are reduced from that of the host phase. For example, in zirconia (ZrO<sub>2</sub>) “doped” with yttria (Y<sub>2</sub>O<sub>3</sub>, typically at the 9-10 mole % level), each mole of dopant introduces one mole of “missing” O<sup>2-</sup>. These vacancies provide abundant sites into which oxide ions can jump, enhancing conductivities by orders of magnitude.

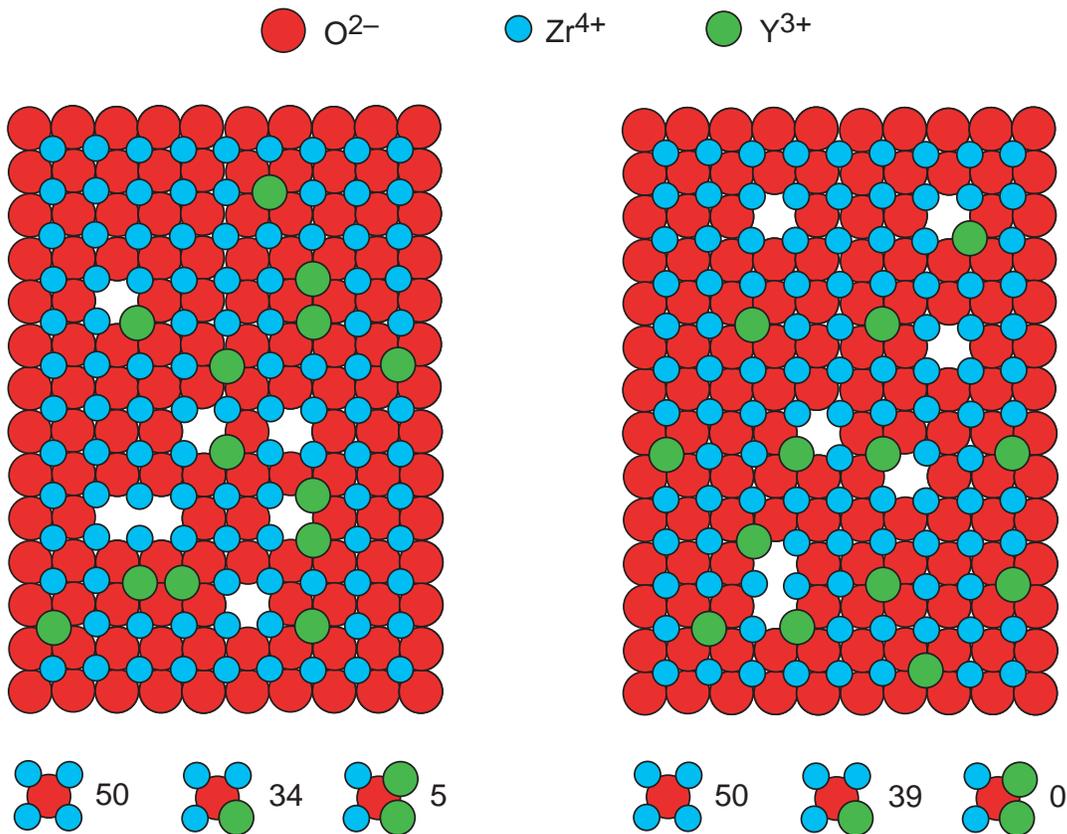
Despite good understanding of the general principles of oxide ion conduction, a lack of information about atomic-scale structure and dynamics of these materials has hindered full development of predictive models of their properties. In particular, most oxide conductors are solid solutions that have complex but poorly-characterized degrees of cation and/or vacancy disorder that may vary with composition, temperature, and even the partial pressure of O<sub>2</sub>. 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.

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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. An experimental approach potentially capable of determining such mechanisms directly is thus highly desirable for a more accurate view of these critical details.

An example of this type of problem is shown in Figure 1, which illustrates two of many possible variations in the atomic-scale structure of a fuel cell electrolyte material, focusing on the differences in the distributions of the major and dopant cations around the oxide ions. These differences are likely to exert critical control over the properties of the material, but have been very difficult to directly characterize.

Over the last twenty years, solid state nuclear magnetic resonance (NMR) has



**Figure 1:** Two-dimensional “cartoon” of possible atomic-scale structures of an oxide ion conducting ceramic such as yttrium-stabilized zirconia (YSZ). Two different states of cation disorder are illustrated, with the different types of oxide ion (red) coordination shells shown. The two states give measurably different distributions of oxygen coordinations, as shown by totals in lower part of figure.

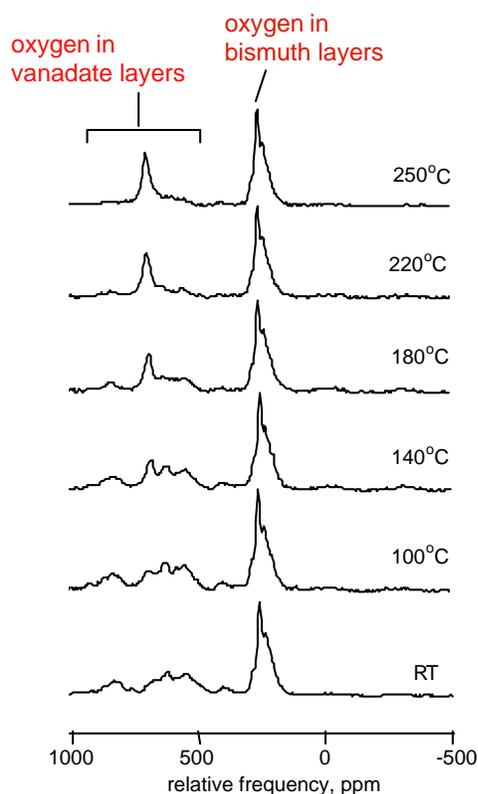
developed into a powerful new method for elucidating the short-range structure of disordered oxide materials. Even more uniquely, NMR can often directly sample ion dynamics at the microsecond to second time scales required to characterize diffusion in disordered crystalline systems.

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 (symmetry) 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,  $^{17}\text{O}$ , has a natural abundance of only 0.035% and a moderately low resonant frequency (which contributes to lower sensitivity and increased quadrupolar line broadening). Isotopic enrichment by up to  $>1,000$  times is usually needed to observe high-quality spectra, especially where disorder and local site distortion produce relatively broad peaks. Such enrichment is not inexpensive, but is feasible. In recent years, applications of  $^{17}\text{O}$  NMR to the structure of disordered oxide materials has burgeoned with the development of synthesis methods, new high-resolution techniques (for example, “triple-quantum magic-angle spinning” or “3QMAS”), and correlations of observables with structural variables. In many cases, spectral sensitivity and resolution have been greatly enhanced by the availability of higher field NMR magnets (e.g. 14.1 and 18.8 Tesla, and even higher). Oxygen-17 NMR on oxide ion conducting ceramics has been demonstrated to be feasible and interesting, but applications have so far been limited. 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. For example, in at least some types of doped zirconia-based oxide ion conductors, we expect to be able to use this method to actually count the different types of oxygen sites as illustrated in Figure 1, providing for the first time a direct view of this critical aspect of the structure.

Two types of NMR methods can be used to elucidate diffusive time scale dynamics in solids. The approach that has been and continues to be most widely applicable is the measurement of spin-lattice relaxation times (“ $T_1$ ”), which characterize the rate of transfer of nuclear spin energy to random thermal energy of the host material (“lattice”) after perturbation by NMR excitation. Because this transfer generally must be stimulated by fluctuations in the local magnetic field or electric field gradient at the Larmor frequency,  $T_1$  measurements are sensitive to dynamics in the 10’s to 100’s of MHz range or at time scales of micro- to nanoseconds, which are often in the range of ion hopping frequencies in conductive solids at high temperature. Although such data can in principle be collected for any observable NMR signal on any nuclide, in practice it can be quite complex to relate such data to details of dynamics, as relaxation can be caused by local ion motions (e.g. the “rattling” of a cation in its “cage” of coordinating anions), by the motions of other ions in the structure, as well as by the through-going, site-to-site

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**Figure 2:** Oxygen-17 NMR spectra of a bismuth vanadate oxide ion conductor (1) collected at the temperatures shown. At higher temperatures, the multiple peaks for oxygen in various sites in the vanadate layers merge together, indicating ion hopping among those sites only, thus helping to define the mechanism of conduction.

hopping of greatest relevance to conductivity. Nonetheless, a number of studies spin-lattice relaxation of solid cationic conductors have proven to be useful.

A second approach has become more feasible with the improvements in the resolution of solid NMR spectra brought by “magic angle spinning” (where the sample is rapidly rotated at an angle of  $54.7^\circ$  with respect to the external field) and high magnetic fields (which reduce the quadrupolar effects that often broaden spectra for nuclides such as  $^{17}\text{O}$ ). If NMR spectral peaks for different types of local structural environments can be resolved, then exchange of an ion among those sites can be detected when the exchange frequency becomes similar to the frequency separation of the peaks. In favorable cases, the exchange frequencies over a range in temperatures can be quantified by computer simulations of the resulting partially to fully averaged peak shapes. Because peak separations in typical spectra are on the order of about 100 Hz to 100,000 Hz, this approach can sample dynamics at much slower time scales than relaxation measurements ( $10^3$ 's of milliseconds to  $10^3$ 's of microseconds) and thus can be used to study diffusion mechanisms at much lower temperatures. By using two-dimensional exchange spectroscopy, site exchange at even slower rates (on the order of seconds) can be detected. Very recently, the possibilities of using this approach for oxide ion conducting

ceramics has been beautifully demonstrated for a series of bismuth vanadates and related materials, with high resolution 1-D and 2-D  $^{17}\text{O}$  spectra collected up to 250 °C (Figure 2). Here, multiple peaks in the spectra, and the averaging among some of them that takes place even at this relatively low temperature, allowed site-specific exchange to be detected for the first time in such materials. The first author of this landmark study, Dr. Namjun Kim, has joined our program at Stanford to continue such studies and expand them into materials more applicable to fuel cell electrolyte membranes.

### Results

We have spent the first several months of this project laying the groundwork for our planned studies. The lead post-doc, Namjun Kim has been hired. Two graduate students have been recruited: Cheng-Han Shieh is working closely with Dr. Kim and Professor Stebbins on beginning to synthesize zirconia-based ceramics and to become trained in NMR methods; Hong Huang is working with the group of Professor Prinz on thin film materials.

We have made good beginnings at several of the key aspects of the project. Design specifications have been completed and an order placed for a unique, state-of-the-art high temperature magic-angle spinning NMR probe, being built by Doty Scientific, Inc., and capable of *in situ* observations of oxide ion site exchange to temperatures as high as 700 °C. A special vacuum line system for exchanging  $^{17}\text{O}_2$  gas into ceramic materials has been designed and largely completed, and an initial supply of this valuable gas has been purchased. Initial tests of sol-gel methods for the synthesis of homogeneous, nano-sized particles of doped zirconia have been made and methods are being refined; components for pressing samples into compact ceramic materials have been ordered or designed.

### Progress

It is too early in this project to predict in detail its specific consequences for reduction in global  $\text{CO}_2$  emissions. However, its most important overall goal is to provide the detailed, 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- $\text{CO}_2$  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 plan to synthesize a number of different zirconia-based ceramic materials, selected both for their technological interest and the likelihood that they will yield NMR spectra with high information contents. For example, scandium-doped zirconia is a good candidate in both categories, and is thus a high priority. We are exploring several published methods of synthesis, the most promising of which relies on aqueous precursors to produce extremely fine-grained materials with homogeneous distributions of dopant cations. After high-temperature sintering (under a variety of conditions and thermal histories), we will exchange much of the isotopically normal oxygen in the samples with oxygen highly enriched in  $^{17}\text{O}$  above its normal, 0.04% natural abundance, using in most cases a gas source and relying on the inherently rapid oxide ion diffusion of these materials to facilitate the exchange.

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We will then carry out a number of different high-resolution solid-state NMR experiments on the materials, particularly emphasizing  $^{17}\text{O}$  spectra, which we expect to provide unique new information about the extent of order/disorder among dopant ions, whether or not defects and vacancies are clustered, and effects of composition and heat treatment on such structural details. As appropriate, we will observe other NMR-active nuclides as well, such as  $^{89}\text{Y}$ ,  $^{45}\text{Sc}$ , and  $^{25}\text{Mg}$ . For “quadrupolar” nuclides, particularly  $^{17}\text{O}$ , we will employ advanced two-dimensional techniques including “multiple quantum” NMR to maximize spectral resolution, and, for the same reason, will collect data at very high external magnetic fields (14.1 and 18.8 Tesla, on “600 MHz” and “800 MHz” spectrometers). Quantitative analysis of these data should allow us to make new energetic models of cation and vacancy distributions, analogous to studies that we have made of highly disordered amorphous oxides (2-5). These results will be interpreted in light of electrical impedance spectroscopy made in collaboration with the group of Professor Prinz. Also working with that group, we will perform similar studies on thin film materials.

Somewhat later in the project we will begin *in situ*, high temperature NMR studies, again emphasizing  $^{17}\text{O}$ , to characterize the atomic-scale mechanisms of ionic transport. We will apply two approaches. In systems where we find multiple, well-resolved spectral peaks (e.g. Fig. 2), we expect to be able to observe exchange among sites directly, measure its average rate, and use this to test and constrain models of conductivity, as we have previously done on several cationic conducting oxide materials (6-8). In less well-resolved systems (for example, yttrium-stabilized zirconia), we will use measurements of “spin-lattice” relaxation times to elucidate ion transport. Again, impedance spectroscopy is planned on the same samples, to allow us to relate observed atomic-scale mechanisms to desired electrical engineering properties.

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