

Nuclear Magnetic Resonance Studies of Ceramic Materials for Fuel Cells

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Objective: 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 (SOFCs), 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, SOFCs may eventually play an important part in the GCEP mission of reducing total CO₂ emissions to the atmosphere.

Background: The general principles of oxide ion conduction in ceramics have long been understood: O²⁻ 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 (ZrO₂) “doped” with yttria (Y₂O₃, typically at the 9-10 mole % level), each mole of dopant introduces one mole of “missing” O²⁻. 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 with the partial pressure of O₂. 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 a 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, 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.

Figure 1 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.

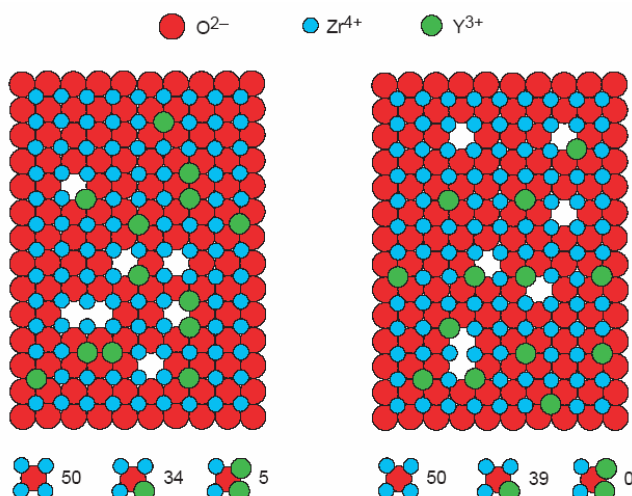


Figure 1: Atomic Scale Structure—Two-dimensional illustration of possible atomic-scale structures of an oxide ion conducting ceramic such as yttrium-stabilized zirconia (YSZ). Two different states of cation disorder are illustrated, with the different types of oxide ion (red) coordination shells shown.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

Approach: 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. 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.

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 content. We will exchange much of the isotopically normal oxygen in the samples with oxygen highly enriched in ^{17}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.

We will then carry out a number of different high-resolution solid-state NMR experiments on the materials, particularly emphasizing ^{17}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 about effects of composition and heat treatment on such structural details. As appropriate, we will observe other NMR-active nuclides as well, such as ^{89}Y , ^{45}Sc , and ^{25}Mg . 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. This work will be complemented by in situ, high temperature NMR measurements to determine the dynamics of anion hopping from one site to another, which is the fundamental step controlling the conductivity. These results will be interpreted in light of electrical impedance spectroscopy made in collaboration with the group of Professor Prinz.

In this way, we will develop a 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.

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