Surface Activity and Bulk Defect Chemistry of Solid Oxide Fuel Cell Cathodes

Thesis by

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In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2015

(Defended July 24, 2014)

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Acknowledgments

I owe thanks to a number of collaborators who made important contributions to this work. Shingo Maruyama prepared several initial samples for the scanning impedance probe. Chris Kucharczyk turned my Matlab data reduction routine from a functional tool into a tour de force. Tim Fister and Kee-Chul Chang at Argonne National Laboratory provided invaluable support for the synchrotron measurements. Richard Wang helped with the SCN measurements.

I'm grateful to the Resnick Sustainability Institute at Caltech for the fellowship they provided me and for the many interesting people they helped bring together. Additional funding was provided by the National Science Foundation, the California Institute of Technology Summer Undergraduate Research Fellowship program, and the National Central University of Taiwan.

Many thanks to my research advisor Sossina Haile for sharing her scientific talent and judgment and for being such an eminently reasonable advisor. Northwestern will be lucky to have you.

I dedicate this thesis to my parents, Zalman and Karen Usiskin. This work would never have happened without their devotion and support and the high value they placed on intellectual excellence. I love you, Mom and Dad.

Abstract

In the first half of this thesis, a new robotic instrument called a *scanning impedance probe* is presented that can acquire electrochemical impedance spectra in automated fashion from hundreds of thin film microelectrodes with systematically varied properties. Results from this instrument are presented for three catalyst compositions that are commonly considered for use in state-of-the-art solid oxide fuel cell cathodes. For $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3+\delta}$ (LSM), the impedance spectra are well fit by a through-the-film reaction pathway. Transport rates are extracted, and the surface activity towards oxygen reduction is found to be correlated with the number of exposed grain boundary sites, suggesting that grain boundaries are more surface-active than grains. For $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSC), the surface activity degrades ~50x initially and then stabilizes at a comparable activity to that of previously measured $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ films. For $Sr_{0.06}Nb_{0.06}Bi_{1.87}O_3$ (SNB), an example of a doped bismuth oxide, the activity of the metal-SNB boundary is measured.

In the second half of this thesis, $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ is selected as a case study of perovskites containing Sr and Co, which are the most active oxygen reduction catalysts known. Several bulk properties are measured, and synchrotron data are presented that provide strong evidence of substantial cobalt-oxygen covalency at high temperatures. This covalent bonding may be the underlying source of the high surface activity.

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CHAPTER 1 OVERVIEW

1.1 Summary

This thesis is divided into two halves. The first half describes a high throughput approach for characterizing the electrochemical activity of *thin film* samples of solid oxide fuel cell (SOFC) catalysts. The second half contains investigations of *bulk* samples that yield insight into the defect chemistry and electronic behavior of a model catalyst, $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCN). The two halves are linked by a common motivation to understand the electrochemical properties of the most important SOFC cathode materials. This motivation is explained below in more detail.

1.2 Why study solid oxide fuel cell (SOFC) materials?

Solid oxide fuel cells (SOFCs) are the most efficient devices yet invented for converting fuel into electricity. Industrial systems that cogenerate electricity and heat using SOFCs have projected efficiencies of up to ~75%, exceeding what is possible in combustion systems.[1] SOFC systems are also fuel flexible; they can generate electricity from natural gas, hydrogen, ethanol, propane, biofuels, and more. Furthermore, when operated in reverse, SOFCs are the most efficient electrolyzers known, i.e., when supplied with electricity, an SOFC can efficiently split water to generate hydrogen fuel. Despite the enormous promise of this technology, commercial SOFC development has been hampered by inadequate catalyst performance, coupled with a lack of understanding of how the catalyst can be improved. These technological capabilities and challenges are described in detail elsewhere.[1,2]

The study of SOFC electrodes is also intricately linked to a number of fundamental scientific questions in catalysis: What intrinsic material parameters determine the rate of electrochemical charge transfer at an interface? What are the reaction pathways? What chemical changes cause catalysts to improve or degrade with time? These questions have been discussed in recent reviews pertaining to SOFC cathode[3-5] and SOFC anode[5,6] materials. Among other conclusions, these reviews make clear the importance of electrochemical impedance measurements on dense patterned thin film electrodes for elucidating the redox activity and catalytic pathways at the surfaces of these materials.

1.3 Why study thin films of SOCF catalysts?

The motivation for measuring dense patterned thin films is that in porous catalyst microstructures, a consequence of porosity is that the intrinsic surface activity of the catalyst is convoluted with extrinsic factors like surface area, microstructure interconnectedness, tortuosity, length of the so-called "triple phase boundary" (the boundary between the catalyst, the electrolyte, and the gas phase, where the rate-limiting step is often thought to occur), and so on. It can be quite difficult to characterize and deconvolute these geometry-dependent factors. The task has been helped by recent advances in 3D characterization techniques like x-ray tomography and focused ion beam milling in combination with scanning electron microscopy. However, these methods remain fairly slow and expensive and often include significant uncertainty. On the other hand, by using dense samples with well-characterized geometries, it becomes easier to normalize by geometry (e.g., scaling catalytic activity by surface area) to obtain intrinsic material properties.

A second common difficulty is that in typical electrochemical methods for measuring activity (which involve current and voltage measurements and which go by various names, including a.c. impedance spectroscopy and d.c. voltammetry), it is challenging to decoupling the rates of the anode and cathode reactions, since they occur simultaneously and both contribute to the overall measurement. In electrochemical systems with a *liquid* electrolyte, this common problem is usually resolved by using a reference electrode, i.e., a third electrode that is placed in the liquid electrolyte to help decouple the potential changes at the two electrodes.

Numerous workers have also tried to use a reference electrode to decouple the anode and cathode overpotentials in systems with a *solid* electrolyte. However, papers by Adler and others have shown quantitatively that "minor errors in the alignment of the anode and cathode can create significant errors in the measured half-cell overpotential... [including] cross-contamination of anode and cathode frequency response... [and] even if electrodes are perfectly aligned, differences [in kinetics]... may cause inherent distortion of the impedance, including frequency dispersion and inductive artifacts."[7] For this reason, reference electrodes have largely fallen out of favor in studies of the activity of SOFC catalysts.

As an alternative, microelectrodes have emerged over the last fifteen years as a reference-less way to decouple the anode and cathode behavior. In this approach, the two electrodes are fabricated with vastly different surface areas: a small area working electrode (~ 10^{-4} cm^2) is dwarfed by a large area counter electrode (~ 1 cm^2). In such a configuration, the measured electrochemical response can often be attributed entirely to the small area electrode, a.k.a. the microelectrode, with negligible error. The conditions under which this attribution is sufficiently accurate have been estimated previously.[8]

These sample requirements --- dense, geometrically well-defined, and having tiny area --- motivate the use of patterned thin film microelectrodes. First reported in 2000,[9] such films are typically grown by physical vapor deposition (usually pulsed laser deposition or sputtering) and then patterned into the desired shapes by photolithography and subsequent dry etching (milling with argon ions) or wet etching (dissolution in acid). The area/perimeter of the microelectrodes can be systematically varied within a single pattern, which helps to identify scaling relations and interpret the electrochemical results. Roughly 25 papers using this approach have been published since 2000.

Despite its success, a number of issues have constrained the microelectrode approach. First, sample preparation is slowed by the need to synthesize a different target for each composition prior to physical vapor deposition. Studying tens or hundreds of compositions can thus be quite cumbersome. (This constraint is not unique to the microelectrode approach.) Varying other parameters besides composition --- film thickness, surface decoration, growth conditions, substrate orientation, and so on --- has also required growing numerous films one at a time, in series. Acquiring impedance spectra from these samples also had to be done in series, further adding to the experiment time. This time constraint likely explains why studies typically report results for only two or three film thicknesses, even in cases where film thickness appears to be a critical parameter.[10,11] Another issue is that subtle differences between samples prepared or characterized in series can introduce experimental errors that mask trends of interest. Surface activity may be sensitive to small changes in impurity content, for example. Also, prior to this work, the acquisition of each of hundreds or potentially thousands of impedance spectra required the cumbersome operator task of manually contacting each microelectrode with a tiny metal probe tip every few minutes. Perhaps in part because of the repetitive nature of this task, the stability and repeatability of impedance measurements from microelectrodes are not always clearly reported in the literature. Indeed, sometimes the stability is not mentioned at all,[10,11] leaving the reader to assume(perhaps incorrectly) that the material properties are entirely stable over time.

1.4 Why study bulk defect chemistry?

The surface activity is arguably the single most important property of a catalyst, but there are many reasons why understanding the bulk defect chemistry may also be extremely useful:

First, bulk thermodynamic instability of a material can explain why its surface properties change with time. Second, correlations between surface and bulk transport rates (specifically, the oxygen tracer surface exchange coefficient k* and the oxygen tracer bulk diffusion coefficient D*) have been observed over a wide range of oxygen-conducting materials,[12,13] suggesting that the surface and bulk properties are closely linked. Third, in $SrTi_{1-x}Fe_xO_{3-\delta}$ a strong correlation has been observed between the surface activity and the Fermi level in bulk samples, again suggesting that the surface catalystis and the bulk electronic structure can be closely linked.[14] Fourth, a knowledge of bulk properties helps with experimental design. For example, the results of thin film studies of surface activity can be distorted if electronic sheet resistance contributes significantly to the measured impedance, and knowing the electronic conductivity helps in predicting and avoiding this distortion.[15] Fifth, a knowledge of bulk properties also helps with device fabrication. For example, a nearly ubiquitous concern in developing practical solid oxide fuel cell devices is that if the thermochemical expansivities of the cathode and electrolyte are not well-matched, mechanical stresses can crack the electrolyte and ruin the device.

1.5 Why focus on the bulk defect chemistry of $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$?

As described further in Section 3.2, a large number of state-of-the-art SOFC cathode catalysts are materials with the perovskite structure that contain the elements Sr and Co. This category of materials includes such compositions as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), $La_{1-x}SrCoO_{3-\delta}$ (LSC), $Sm_xSr_{1-x}CoO_3$ (SSC), and others. The composition $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCN)[16] also exhibits extraordinary performance as a fuel cell cathode,[17] yet its defect chemistry is likely simpler than many of the above compositions, since it contains only three cations, and the niobium cation is in relatively low concentration and is fixed-valent (as shown in Chapter 6).[18] For these reasons SCN is a reasonable choice as a "model material" for fundamental studies of persovskites containing Sr and Co; thus SCN is the focus of the bulk defect chemistry investigations in Chapter 5 and Chapter 6.