Massachusetts Institute of Technology
Department of Nuclear Science and Engineering

Thesis Prospectus
for the
Bachelor of Science Degree in
Nuclear Science and Engineering

Effect of Lattice Strain on Stoichiometry and Ionic Transport in Oxide Materials ($Nd_2NiO_{4+\delta}$ and ZrO_2)

Contents

1 Introduction

Oxide materials are well-known for having an outstanding variety of electronic and ionic phenomena. In fact, there is much interest in studying of ion transport and defect properties in oxides materials for many different purposes. The two main situations where these two properties become crucial are oxygen transport in fuel cell and metal corrosion. Two notable materials that can represent these two situations are, respectively, Neodymium Nickel Oxide and Zirconium Dioxide

1 Neodymium Nickel Oxide

The main performance bottleneck in current state-of-the-art solid oxide fuel cells (SOFCs) is the high value of cathode resistance, resulting from slow electronic or ionic transport [2]. This effect can be mitigated by the presence of elastic strains, which were shown to have a dramatic effect on ionic mobility and surface oxygen reduction reactivity in perovskite thin films. Currently, there is great scientific interest on a new family of phases, called Ruddlesden-Popper (RP) phases for applications in intermediate-temperature SOFCs due to their highly anisotropic diffusivities leading to very rapid oxygen transport along certain directions in the crystal [1].

Lattice strain effects are expected to play an important role in determining the performance of these systems, similar to the case of perovskites. However, due to the presence of anisotropic diffusion directions, the relationship between ionic diffusivity and lattice strain is yet to be fully understood. Prior experiments on RP phase thin film samples of Nd2NiO4 (NNO) demonstrate a correlation between surface activity and tensile strain along the c-axis [3]. This large variation in surface activity is currently attributed to the

higher number of oxygen interstitials thought to be present in tensile-strained samples. This hypothesis will benefit from accurate calculations of defect concentrations and ionic diffusivities in RP phases in different strain states.

2 Zirconium Dioxide

Zirconium alloys, Zircaloys, which consist of zirconium and other metals are well-known for their exceptionally low absorption cross-section of thermal neutrons along with their great mechanical properties: high hardness, ductility and corrosion resistance. For this reason, zircaloy is usually used in nuclear engineering as cladding of fuel rods in nuclear reactors.

Since these alloys are pushed to endure harsher operation environment in the nuclear reactor, there is an absolutely need to understand the fundamental of their metal corrosion process. In other words, it is crucial to be able to predict the performance of zirconium alloys under these demanding conditions, ultimately to ensure the safety of a nuclear reactor. The major player that controls the performance of a zirconium alloy cladding is the protective, electrically insulating layer of zirconium oxide (ZrO_2) which natively covers zirconium alloy. Thus understanding and prediction of point defects and ion transport properties in this metal oxide will be a major help in develop a framework to solve problems of relevance to the corrosion of zirconium alloys.

In this thesis, the two materials, NNO and ZrO_2, will have some aspects of their ion transport and defect properties studied. While the applications of the two materials are vastly different, a single method, which will be described in Chapter 3, will be using for both.

2 Objectives

The application of strain can influence two factors of direct importance to the ionic diffusion process, namely the oxygen interstitial concentration and the oxygen ion mobility. The former can be quantified through a calculation of formation energies of oxygen interstitials and the latter through a calculation of diffusion barriers along the ionic diffusion pathway. These two metrics are quantified on model systems that are strained similar to the experimental thin film samples of NNO and ZrO_2 to understand the effect of each factor on the kinetics of the overall oxygen reduction reaction.

The main objective of this study is to determine whether and how the strains applied on a pre-determined system affect its oxygen defects formation energies and the defects' diffusion barriers. From this results, the mechanism and the extent of increase in the oxygen anion diffusivity under lattice strain in the two materials can be possibly understood. These insights gained here will be helpful for optimizing the ionic transport properties in solid-state conducting material applications, in the NNO case, and for tuning the corrosion protection properties in structural materials, in the ZrO_2 case.

3 Method

1 Computational Modeling and Simulation

Density Functional Theory (DFT) is a powerful atomistic modeling technique widely used in condensed-matter physics, computational physics, and computational chemistry. In general, DFT is extremely helpful at interpreting and predicting of complex system behavior at an atomic scale. In fact, DFT is specifically used in understanding materials that are highly sensitive to synthesis and processing parameters. For this reason, DFT is chosen to be the main atomistic modeling technique that would be used to model and simulate the two material structures, NNO and ZrO_2, computationally.

2 Formation Energies of Oxygen Defects

Oxygen defects referred in this case consist of oxygen interstitials and oxygen vacancies. In order to calculate the formation energy of the oxygen defect, we monitor the change in computational energies when introducing one oxygen defect into a non-defect material structure. Since most of the errors due to the nature of simulating are canceling each other out in this case, the result of formation energy should approximately resemble any experimental data conducted at the same physical conditions.

3 Diffusion Barriers Along the Ionic Diffusion Pathway

In order to calculate the barrier for the oxygen defect diffusion, we instead monitor the change in computational energies when moving one oxygen defect along the ionic diffusion pathway. Similarly, most of the errors will also be canceling each other out which makes it possible to compare the computational results to any experimental data conducted at the same physical conditions.

4 Strain-Dependence Characterization

To find the influence of strain on the ionic diffusion process, strain-dependence characterization of oxygen interstitial concentration and the oxygen ion mobility are needed to be done. By examining the oxygen interstitials' formation energies over a range of applied strains, the relationship between oxygen interstitial concentration and the application of strain can be found. Similarly, by looking at the oxygen defects' diffusion barriers over a range of applied strains, the dependence of oxygen ion mobility on the lattice strain will also be characterized.

4 Task Descriptions and Schedule

The following tasks have been outlined as critical for the completion of this project and my thesis:

1 Literature research

There will be mostly gathering related results from the literatures, to not only fully understand the materials but also avoid duplicating work that other people have done previously.

2 Modeling and Simulating $Nd_2NiO_{4+\delta}$

The NNO system will be modeled computationally using the results from previous studies. Simulations and computational calculations will be done in order to determine oxygen defects position in the modeled system. At the end, more calculations will also be done in order to find out quantitatively the effect of strain on stoichiometry, oxygen defects concentration, oxygen diffusivity and vice versa.

3 Modeling and Simulating ZrO_2

Same procedures described in modeling and simulating $Nd_2NiO_{4+\delta}$ applies to the case of modeling and simulating ZrO_2.

4 Analysis of results

The results found in the simulations and computational calculations of the two materials will be analyzed to find out the effect of lattice strain on stoichiometry and ionic transport in these two materials.

This task should be proceeded alongside with simulating the materials.

5 Writing up Thesis

Finally, the project results will be compiled into a thesis report.

6 Thesis Revision and Submission

Drafts of Thesis will be submitted to undergraduate chair, thesis advisor and communication instructor for recommendations and approvals.

The final version of the Thesis draft will be submitted to the Thesis Committee for final review.

Schedule

In order to complete the thesis by May 2015, the work has been and will be completed according to the schedule below:

Task	No	Start	End
Literature research	1	09/03/2014	03/16/2015
Modeling and Simulating $Nd_2NiO_{4+\delta}$	2	10/01/2014	03/16/2015
Modeling and Simulating ZrO_2	3	01/05/2015	09/03/2015
Analysis of results	4	09/03/2015	05/04/2015
Writing up Thesis	5	03/16/2015	04/13/2015
First Draft of Thesis	6.1	04/13/2015	
Second Draft of Thesis (content revision)	6.2	04/20/2015	
Third Draft of Thesis (language revision)	6.3	04/27/2015	
Final Draft of Thesis for Review	6.4	05/04/2015	

Bibliography

[1] E. Boehm, J.-M. Bassat, P. Dordor, F. Mauvy, J.-C. Grenier, and P. Stevens. Oxygen diffusion and transport properties in non-stoichiometric ln 2- x nio 4+ δ oxides. *Solid State Ionics*, 176(37):2717–2725, 2005.

[2] S. Singhal. *High-temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications: Fundamentals, Design and Applications.* Elsevier, 2003.

[3] N. Tsvetkov, Q. Lu, Y. Chen, and B. Yildiz. Surface chemistry and non-stoichiometry of nd2nio4+ δ epitaxial thin films with different orientation and strain. *ECS Transactions*, 57 (1):1743–1752, 2013.

22.THT Undergraduate Thesis Tutorial

Fall 2015