Chemomechanics of Non-stoichiometric Oxide Films for Energy Conversion

by

Jessica G. Swallow

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Abstract

Electrochemical energy conversion and storage devices including solid oxide fuel cells (SOFCs) and lithium ion batteries (LIBs) are enabled by materials known as "non-stoichiometric oxides" that contain large concentrations of point defects such as oxygen or lithium vacancies. While this non-stoichiometry provides the essential functional properties of ionic conductivity or reactivity that make these materials useful, it also tends to couple to material volume through the effect of chemical expansion. Chemical expansion, or volume coupled to defect concentration, is in turn tied to mechanical variables including stress, strain, and elastic constants. This electrochemomechanical coupling, or interaction between functional properties, defect chemistry, and mechanical variables, can have important consequences for devices operated in extreme environments, where unexpected stress may lead to fracture, or well-engineered strain may enhance device efficiency. Such effects are particularly important in thin film devices, where strain engineering is within reach, undesired fracture can devastate performance, and defect chemistry and related properties can differ from bulk systems. In this thesis, we present a concerted investigation of chemomechanical coupling, including interactions between material chemistry, environmental conditions, stress, strain, and mechanical properties, for films of the model material Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO) that is a fluorite-structured oxide relevant to SOFC applications. PCO is an excellent model system because of its well-established defect chemistry model and known thermal and chemical expansion coefficients. The thesis begins by first characterizing key chemomechanical effects in PCO, including electrochemically induced high temperature actuation and non-stoichiometry-dependent mechanical properties that are modulated by environmental conditions including temperature and oxygen partial pressure. We then explore the mechanisms and microstructural contributions to these effects via computational modeling and high temperature transmission electron microscopy, identifying ways in which chemomechanical effects in thin film non-stoichiometric oxides differ from those in bulk. Finally, we extend the experimental and computational methods developed in the thesis to characterizing similar effects in Li-storage materials, demonstrating the broad applicability of results across the classes of non-stoichiometric oxides.

We first describe an experimental study in which we developed a novel method of detecting chemical expansion on short time scales in the model system PCO and characterized material deformation for a range of conditions of temperature and effective oxygen partial pressure ($pO_2$). In this method, electrically-stimulated chemical expansion caused mechanical deflection of a substrate, an effect that for PCO was enhanced for elevated temperatures...
or reducing conditions. We discuss the film and substrate properties that contributed to this high temperature oxide actuation, and consider methods of tuning this mechanical deflection. Additionally, we characterized the effect of high-temperature actuation for a perovskite-structured oxide (SrTi\(_{0.65}\)Fe\(_{0.35}\)O\(_{3-\delta}\), STF) also demonstrating the applicability of the methods used beyond the model system PCO. This first study constitutes a demonstration of how chemical expansion can directly generate stress or strain that can produce substantial deformation \textit{in situ} for layered devices based on non-stoichiometric oxide films.

Next, we explore the effect of thermal and chemical expansion on the mechanical stiffness of PCO films using high temperature, controlled atmosphere nanoindentation. We find that the Young’s elastic modulus \(E\) of PCO decreases with increased temperature or decreased \(pO_2\) as a result of thermal and chemical expansion. Furthermore, the decrease in \(E\) observed for PCO films \textit{in situ} is larger than would be expected based on bulk models or previous measurements of related oxides, demonstrating a new example of the ways in which chemomechanical coupling effects can differ between bulk and thin film forms of non-stoichiometric oxides \textit{operando}.

In conjunction with the experimental study of the relationship between chemical expansion and \(E\), we also applied density functional theory (DFT) to compute how changing defect chemistry and associated chemical expansion affect the elastic constants of PCO. Bulk computations reproduced the expected dependence of \(E\) on lattice parameter previously observed for bulk oxides in the literature. Additional simulations that directly compared bulk and membrane forms of PCO found that the biaxial stiffness of both forms should decrease with oxygen loss, but that this change was comparable for comparable changes in composition. These computational results provide additional evidence for understanding the mechanisms by which thin film and bulk mechanical properties differ \textit{in situ}, as described in previous experimental studies.

Having observed the effects of chemical expansion at length scales on the order of hundreds of nanometers, we then turn to characterizing chemical expansion in PCO films using atomic-resolution electron microscopy. By imaging cross-sections of PCO films grown on mechanically-constraining substrates, we characterized chemical expansion \textit{in situ}, including measuring anisotropic expansion, analyzing the interface structure and dynamics, and characterizing the film composition at different conditions and adjacent to the PCO-YSZ interface and threading defects that propagated from the interface toward the film free surface. From this high resolution characterization, we gained information about the atomic-scale changes that contribute to stress generation, changing elastic properties, and differences between thin film and bulk properties \textit{in situ}.

Finally, we show that the types of effects observed in the earlier parts of the thesis-including dynamic stress generation in response to electrochemical pumping of ions, volume change as a function of changing oxygen content, and non-stoichiometry dependent mechanical properties- are also present and important in Li storage materials. Specifically, we measured dynamic actuation for spinel-structured Li\(_x\)Mn\(_2\)O\(_4\) (LMO) films as a function of Li concentration, predicted computationally that LMO volume increases upon oxygen loss, and showed by nanoindentation that the Young’s elastic modulus \(E\), hardness \(H\), and fracture toughness \(K_{IC}\) of Li\(_x\)CoO\(_2\) (LCO) all decreased substantially upon Li loss. These results demonstrate the broad applicability of our methods and the chemomechanical coupling effects we have observed even in material systems with differing crystal structure,
composition, and mobile ions. The theme of this thesis is that chemical expansion, a natural consequence of changing defect chemistry in non-stoichiometric oxides, is connected intimately to mechanical variables including stress, strain, and elastic properties. These relationships are particularly important to understand for thin film electrochemical devices that regularly operate in extreme environments or far from equilibrium, where opportunities for strain engineering may enhance performance even as changing environmental conditions may restrict available choices for avoiding mechanical failure. Our results provide a comprehensive study of chemomechanical coupling in a model system, thus providing a framework for modeling similar effects in the diverse set of materials that undergo chemical expansion in operando environments. We also develop experimental tools that can be used to detect these effects in situ, enabling future development of devices based on chemomechanical coupling such as high temperature oxide actuators. Though often framed in the context of energy conversion, our methods and results may be extended to materials for applications that involve dynamic changes in composition or structure during operation, including resistive switches, electrolysis cells, and batteries.

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Chapter 1

Introduction

1.1 Context

In the last thirty years, global emissions of CO\textsubscript{2} and other greenhouse gases increased at the fastest rate in history, increasing by over 30% between 1990 and 2011 and continuing to increase today.[1] Simultaneously, over a billion people worldwide remain without access to modern electricity.[2] Greenhouse gas emissions have been linked closely with climate change, the effects of which are expected to most heavily impact low-income and developing regions that lack essential infrastructure or services.[1] These statistics highlight a progressing global paradox for technological and community development: the need to strike a sustainable balance between rising energy demands and a changing global climate.[1, 2] Included among the many solutions currently being explored to address these conflicting goals are technologies to enable electrified transport, portable or distributed power generation, and renewable or low-emission energy conversion and storage.[3] Such technologies will be heavily dependent on electrochemical devices that can mitigate the difficulties of intermittency in renewable resources or provide alternative, reliable, high-efficiency, and emission-reduced power generation.

Solid oxide fuel cells (SOFCs) and lithium ion batteries (LIBs) are among the devices that will play a crucial role in converting the vision of a sustainable energy infrastructure into a reality. Although these technologies share many parallels in terms of their operating principles and materials challenges, LIBs have seen widespread implementation in cell phones, laptops, and even electric cars, while SOFCs have struggled to capture a significant commercial market share. This is due to a number of technical challenges and limitations including the required high operating temperatures (above 600°C) that enable the charge transport and reactivity properties that are essential to SOFC operation, mechanical failures that limit durability and reliability, and cost competition with other technologies.[4, 3] Overcoming these challenges will only be possible with an improved understanding of the coupling that exists among the chemical composition, mechanics, and electronic properties of the oxides that support SOFC operation. Together, this set of interrelated properties is known as "electrochemomechanical coupling," an area of study that has been the subject of recent accelerated research.[5] The ultimate goal of this research area is to understand how such coupling may be harnessed to improve the performance, durability, and optimization of electrochemical energy conversion and storage technologies including SOFCs and LIBs. In
particular, this thesis will focus on electrochemomechanical coupling in oxide films relevant to SOFCs. By characterizing chemomechanical coupling effects in a model oxide material, including both directly observing chemical expansion under *operando* conditions and characterizing related changes in mechanical properties, we aim to provide tools necessary for designing devices that accurately manage dynamic stress and strain states *in situ*. Although primarily focused on a particular model SOFC oxide, results determined in this context are applicable to LIBs and other materials systems in which similar coupling is active.

Parts of the discussion below were previously published as part of a review paper on electrochemomechanical coupling in non-stoichiometric oxides for energy conversion and storage in the *Journal of Electroceramics*.[6]

### 1.2 Solid oxide fuel cells: operating principles

Solid oxide fuel cells are devices that convert chemical energy into electrical energy by oxidizing fuel electrochemically (rather than by combustion) and separating ionic and electronic transport. When operated in reverse, these devices may be used as electrolyzers, which are devices that catalyze, for example, electrochemical water splitting into oxygen and hydrogen, a process known as *electrolysis*.[7] SOFCs have many important advantages for distributed power generation, including low emissions, high energy conversion efficiency, quiet operation, and fuel flexibility.[3] Notably, the materials within these devices are operated far-from-equilibrium, particularly for rapid energy conversion, and are typically non-stoichiometric oxides, or materials that can sustain very large point defect concentrations.

As shown in Fig. 1-1, in a SOFC, gaseous oxygen is reduced at the cathode, and then transported through an electronically insulating, ionically conductive electrolyte. The oxygen typically diffuses via an oxygen vacancy mechanism to the anode, where it reacts with hydrogen or an alternative hydrocarbon fuel to produce water and release electrons back into the external circuit. Under open circuit conditions, a potential difference between cathode and anode is given by the Nernst potential (under ideal conditions). In the non-stoichiometric materials that comprise the cathode, anode, and/or electrolyte, spatial variations in oxygen vacancy concentration parallel corresponding variations in oxygen partial pressure. This gradient in vacancy concentration correlates with Vegard expansion in many non-stoichiometric oxides, an effect which is magnified at the high SOFC operating temperatures that are generally above 600°C and can produce significant stress *in situ*.[8, 9, 10]

The oxygen reduction reaction occurring at the cathode is given in Kröger-Vink notation by Equation 1.1:

\[
\frac{1}{2}O_2(g) + V_{\text{O}^{\bullet\bullet}} + 2e' \rightleftharpoons O_O^x
\]  

(1.1)

where \(V_{\text{O}^{\bullet\bullet}}\) is an oxygen vacancy with two net positive charges and \(e'\) is an electron. For SOFCs, electrode and electrolyte materials are commonly perovskite- or fluorite-structured oxides that can tolerate large oxygen vacancy concentrations (on the order of several percent) and many different atomic impurities (dopants) at high concentration. Mixed ionic-electronic conductors such as \(La_{1-x}Sr_xCoO_{3-\delta}\) (LSC), \(SrTi_{1-x}Fe_xO_{3-\delta}\) (STF), or \(Pr_{x}Ce_{1-x}O_{2-\delta}\) (PCO) are often selected as cathode materials because they can enhance oxygen reduction kinetics.
Figure 1-1: (a) Schematic of a solid oxide fuel cell (SOFC) showing electrochemical half reactions; (b) Inset of the SOFC cathode, showing the oxygen reduction reaction and oxide ion transport via the vacancy (open squares) mechanism across the cathode. The cathode shape is indicative of chemical expansion one might expect to see as a result of varied effective oxygen partial pressure. Figure from Ref. [6].

by extending active sites from triple phase boundaries (as for solely electronic conductors) to the full area of the electrode.[11, 12, 9] The electrolyte, on the other hand, must be both electronically insulating and highly conductive to oxide ions, and so materials such as yttria stabilized zirconia (YSZ) or Gd$_x$Ce$_{1-x}$O$_{2-δ}$ (GDC) are typically used. Lower valent dopants $A$ ($Y$ in YSZ and Gd in GDC) are added to the electrolyte material to fix vacancy concentrations at very high levels, as described in Equation 1.2: [13]

$$A_2O_3 \rightarrow 2A'_M + V'^*_O + 3O^x_O$$  \hspace{1cm} (1.2)

Device efficiency is optimized when ionic conductivity and oxygen exchange kinetics are maximized and when anode materials actively catalyze fuel oxidation. Therefore, SOFCs are often operated between 600 and 1000°C, and this operating environment confers the additional materials requirement of high thermal stability.

Despite the many advantages of SOFCs, their high operating temperatures and limited mechanical durability are two of the most significant challenges hindering their performance and practicality.[4, 3] Materials limitations, in particular those governed by electrochemomechanical coupling effects, are behind both of these obstacles, motivating an in depth exploration of such effects. Careful measurement and modeling of interrelated mechanical properties, functional performance, and defect chemistry in model material systems will allow for engineering that more completely accounts for these interrelated aspects of electrode and electrolyte materials. Not only that, but such measurement and modeling can enable the use of these materials in alternative applications including gas sensors, catalysis, resistive
switches, and high temperature oxide actuators.[14, 15, 16]

### 1.3 Chemical expansion in non-stoichiometric oxides

The chemomechanical effect that forms the backbone of this thesis is known as chemical expansion, which is coupling between material volume and point defect concentration. While chemical expansion can occur for many kinds of defects, for the context of this thesis we will consider that which occurs in association with oxygen vacancy formation as exemplified here for the oxygen vacancy formation reaction of $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ (PCO) shown in Eq. 1.3:

$$2\text{Pr}^\times_{\text{Ce}} + \text{O}_\times^\times \leftrightarrow 2\text{Pr}^\prime_{\text{Ce}} + \text{V}^\bullet\bullet_{\text{O}} + 1/2\text{O}_2(\text{g})$$  \hfill (1.3)

Here, $\text{Pr}^\times_{\text{Ce}}$ and $\text{Pr}^\prime_{\text{Ce}}$ denote $\text{Pr}^{4+}$ and $\text{Pr}^{3+}$, respectively, on Ce sites, $\text{O}_\times^\times$ denotes $\text{O}^{2-}$ on an oxygen site, and $\text{V}^\bullet\bullet_{\text{O}}$ denotes a vacancy on an oxygen site.

Chemical expansion has been observed in many oxide conductors, including doped and undoped $\text{CeO}_{2-\delta}$, $\text{Sr(Ti,Fe)}\text{O}_{3-\delta}$ (STF), $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ (LSCF), and $\text{LaMnO}_3$.[17, 18, 19, 20, 21, 22] In general, chemical expansion is defined using a chemical expansion coefficient $\alpha_c$ that relates chemical strain $\epsilon$ to a change in oxygen vacancy concentration $\Delta\delta$ according to equation 1.4:

$$\epsilon = \alpha_c \Delta\delta$$  \hfill (1.4)

This coefficient is generally assumed to be independent of temperature, but this is not always the case.[20] Additionally, the value of $\alpha_c$ can vary between bulk and thin film oxide forms of the same nominal material composition.[23, 24, 25]

Empirical observations and first principles calculations have demonstrated that chemical expansion arises from two competing factors: expansion from the increased diameter of reduced cations, and contraction around oxygen vacancies (see Eq. 1.3).[8, 26, 27, 28, 29] Marrocchelli et al. suggested that zero chemical expansion in a material could be obtained by choosing material compositions that balance these two effects. In later, related work, Marrocchelli et al. determined that charge localization at the cation increased chemical expansion relative to a structure with distributed charge.[30] With localized charge, the change in the cation radius upon reduction is greater than if charge is delocalized, increasing $\alpha_c$ for structures with greater charge localization. To a large extent, this effect also explains the difference between the chemical expansion coefficients of fluorite and perovskite oxides, as demonstrated in the same work.

Several researchers also found evidence for mechanical failure originating from fracture in SOFC electrodes and electrolytes due to thermochemical expansion mismatch of materials.[31, 32] Figure 1-2 highlights examples of delamination fractures that can increase area specific resistance and vertical electrolyte cracks that can lead to short circuiting. Sato et al. attributed this kind of failure to tensile stresses that arise in the SOFC cathode initiated from chemical expansion of the anode cell support, based on their analysis of bulk oxides that included acoustic emission analysis, post-mortem inspection, and finite element modeling.[33, 34] As we will see, mechanical strain resulting from chemical expansion is connected inherently to the functional and mechanical properties of non-stoichiometric oxides. This effect therefore has multiple, interrelated ramifications for design of robust,
high-efficiency non-stoichiometric oxide devices, especially those that include multilayer geometries and spatial gradients in oxygen partial pressure, or undergo dynamic changes in composition during operation.

Figure 1-2: (a) A delamination fracture between a Gd$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ electrolyte and a Pt$_{0.3}$Sr$_{0.7}$Co$_{0.3}$Fe$_{0.7}$O$_{3}$ cathode attributed to thermochemical expansion mismatch during long term cell operation. Adapted from [31]. (b) A vertical crack through an electrolyte in a solid oxide fuel cell subjected to redox cycling. Adapted from [32].

1.4 Electrochemomechanical coupling in non-stoichiometric oxides

Thermochemical expansion is expected to contribute to changes in mechanical and electrical properties and stability of materials.[13] For example, as shown in Fig. 1-3(a), increased lattice parameter due to thermal and chemical expansion is expected to cause decreased mechanical stiffness, which has been observed experimentally for bulk oxide materials including (Gd, Ce)O$_{2-\delta}$ (Gd-doped ceria, or GDC).[35, 36, 37] With increased lattice parameter, resistance to further bond stretching decreases in crystalline materials, resulting in decreased elastic modulus. This, of course, has the important consequence of changing the actual stress state present at oxide interfaces at elevated temperatures and under reducing conditions.[10] Not only does material volume change in situ, but the mechanical stiffness varies as well.

Operando stress and strain states, as well as composition-dependent mechanical properties, become particularly important when it is understood that mechanical strain can affect both the oxygen exchange reactivity and/or ionic conductivity of oxides including YSZ, GDC, (La,Sr)CoO$_3$ (LSC), and Nd$_2$NiO$_{4+\delta}$.[38, 39, 40, 41] Given the close association between chemistry and mechanics in ioniically conductive ceramics for SOFCs, it is reasonable to expect that strain may be used to influence chemistry just as chemical composition gradients produce strain in these materials. Multiple first principles studies of several non-stoichiometric oxides have found that both the oxygen vacancy formation energy and oxygen vacancy migration energy can significantly decrease upon application of tensile strain, poten-
Figure 1-3: (a) In bulk Gd$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$, increased lattice parameter due to chemical and thermal expansion are correlated with decreased Young’s elastic modulus. Adapted from [35]. (b) Tensile lattice strain can enhance the ionic conductivity $\sigma_{\text{tot}}$ of yttria stabilized zirconia (YSZ) relative to the bulk value $\sigma_{\text{vol}}$ when grown epitaxially on mismatched substrates. Adapted from [38].

Spatially increasing, respectively, oxygen reduction reactivity and oxygen diffusivity.[42, 43, 44] On the other hand, tensile strain was shown to simultaneously decrease the mobility of adsorbed oxygen atoms in the case of LaCoO$_3$.[43] This result indicates that lattice strain can cause competing effects on the oxygen reduction reaction (ORR) activity.

Related to the effect of strain on defect formation and migration energies is the important theory of the "activation volume."[45] Generally speaking, the rate constant $k$ of a typical process will show Arrhenius behavior of the type described by Eq. 1.5, where $\Delta G^\ddagger$ is the Gibb’s free energy of activation for the process, which can be broken into an entropic contribution, $-T\Delta S^\ddagger$, a contribution from the elastic strain energy of activation (where $\epsilon_{ij}^\ddagger$ is the activation strain of the process, and $\sigma_{ij}$ is the stress) and a contribution from the internal energy, $\Delta U^\ddagger$.

$$k = k_0 \exp \left( \frac{-\Delta G^\ddagger}{RT} \right) = k_0 \exp \left( \frac{\Delta S^\ddagger}{R} \right) \exp \left( \frac{\epsilon_{ij}^\ddagger \sigma_{ij}}{RT} \right) \exp \left( \frac{-\Delta U^\ddagger}{RT} \right)$$  \hspace{1cm} (1.5)

Such a rate law could be applied to the process of vacancy migration to a neighboring lattice site. In the simplified case of hydrostatic stress, the rate law then becomes Equation 1.6 where $P$ is the pressure and $\Omega^\ddagger$ is the activation volume.

$$k = k_0 \exp \left( \frac{\Delta S^\ddagger}{R} \right) \exp \left( \frac{-P\Omega^\ddagger}{RT} \right) \exp \left( \frac{-\Delta U^\ddagger}{RT} \right)$$  \hspace{1cm} (1.6)

If the activation entropy and internal energy remain insensitive to pressure, then the activation volume can be determined from the pressure dependence of the rate, according to Equation 1.7.
\[ \Omega^\dagger = -RT \left( \frac{\partial \log k}{\partial P} \right) \quad (1.7) \]

Thus, the application of a stress to the material will cause a change in the rate of vacancy migration corresponding to a change in the activation free energy of the process. In general it has been hypothesized that a tensile strain will lower the vacancy migration energy by decreasing the activation free energy, and therefore enhance the rate of vacancy migration, corresponding to an increase in ionic conductivity. The reverse effect is expected for a compressive strain. Multiple experimental studies have confirmed this predicted trend to varying degrees for a few non-stoichiometric oxides. [38, 46, 40] This effect is highlighted for yttria stabilized zirconia (YSZ) in Fig. 1-3(b). Such a result, if it is general beyond the few oxides for which it has been tested, could be used to lower SOFC operating temperatures by enhancing kinetics through mechanical cues.

These examples illustrate how lattice strain is closely coupled to both the composition (defect concentration) of non-stoichiometric oxides and their important functional properties including ionic conductivity and oxygen exchange reactivity. Defect concentrations are also highly dependent on environmental conditions including temperature and effective oxygen partial pressure, and are coupled to material volume via chemical expansion. As illustrated schematically in Fig. 1-4, not only can chemical expansion adjust in situ stress states in multilayer structures, but mechanical properties including mechanical stiffness depend on defect chemistry as well, adding further complication to the puzzle of how to predict stress, strain, activity, or conductivity operando.

1.5 Thin film oxides for low-temperature solid oxide fuel cells

An in-depth understanding of operando chemomechanical states becomes particularly important with the recent interest in thin film non-stoichiometric oxide devices. [15, 48, 49] Thin film SOFCs (micro-SOFCs) have the dual potential for decreased operating temperatures and improved portability, while also providing opportunity for "strain engineering" or the use of mechanical strain to improve functional properties. [15, 49, 48, 50] Examples of strain engineering include enhancing ionic conductivity or gas exchange reactivity through the application of tensile strain (as discussed above). In fact, non-stoichiometric oxides provide opportunity for strain engineering even outside of the realm of electrochemical energy conversion devices; mechanical strain has been used to engineer the magnetic states of oxide thin films, while mechanical stress has been used to alter the ionic transport characteristics of room temperature resistive-switching devices known as "memristors." [51, 52, 53]

Strain engineering is best implemented for thin film or low-dimensional structures, strongly motivating a detailed understanding of thin film electrochemomechanical coupling that moves beyond bulk models and measurements. There are several aspects to this challenge. First, it is essential to be able to predict operando stress and strain states (i.e., those relevant to device operating conditions) accurately in order to effectively use mechanical cues as engineering handles. Second, thin films and thin film devices will be particularly susceptible to mechanical failures including delamination fractures and cracks normal to these interfaces, meaning that understanding operando mechanical properties is particularly relevant.
Figure 1-4: Schematic of electrochemomechanical interactions in a layered non-stoichiometric oxide film-on-substrate system. A film (pink) on an oxide conducting substrate (white) undergoes chemical expansion when its oxygen vacancy concentration $\delta$ (dark holes) is adjusted either by applying electrical bias or by modulating oxygen partial pressure $pO_2$. The resulting chemical strain $\epsilon$ causes a mechanical stress $\sigma$ at the interface between the film and the substrate, along with film thickness change. Additionally, the film elastic modulus $E$ changes when the film undergoes chemical expansion. The mechanical stress at the interface is a function of both $\epsilon$ and $E$, and can lead to substrate deflection. Thus environmental conditions, mechanics, and defect chemistry are interrelated in the oxide film in ways that may differ from bulk counterparts. In turn, transport and reactivity properties are also coupled to $\epsilon$, $\delta$, and $\sigma$. Figure adapted from Ref. [47].

from a durability perspective. Third, thin films do not necessarily exhibit identical defect chemistry or charge transport to their bulk counterparts.[54, 55, 56, 57] For example, it has been observed that nominally equivalent compositions of several non-stoichiometric oxides can show significantly differing point defect concentrations in film forms as opposed to bulk under the same conditions of $pO_2$ and temperature.[54, 55, 56] Such discrepancies have been attributed to, for example, space charge layers at surfaces, interfaces, or grain boundaries that occupy a much larger volume fraction in thin films than they do in bulk.[57, 58, 59] Space charge is in turn expected to impact charge transport, causing, for example, grain-size dependent ionic conductivity that has been observed experimentally in nanocrystalline films.[57, 60, 61] Not only this, but films of nominally cubic perovskite or fluorite oxides may deform anisotropically due to biaxial stress states that could cause, for example, anisotropic chemical expansion.[25] In the case of highly strained ceria films, enhanced oxygen storage capacity has been observed and attributed to such anisotropic lattice distortion.[62]

These results highlight the key point that thin film and bulk oxides of theoretically identical composition can in practice have varied point defect concentrations which couple to functional and mechanical properties. Given the interrelated nature of defect chemistry,
stress, strain, mechanical stiffness, charge transport, and reactivity in these materials, it is crucial to be able to measure electrochemomechanical coupling of oxide films under \textit{operando} conditions including high temperatures and reducing oxygen partial pressures.

1.6 \textit{Operando} and \textit{in situ} characterization tools and the role of modelling

The study of electrochemomechanics in non-stoichiometric oxide films necessarily incorporates both computational and experimental methods, with an emphasis on \textit{in situ} characterization tools that can be used to observe the far-from-equilibrium processes that are fundamental to the operation of electrochemical devices. Temperature, oxygen partial pressure, and/or electrical control are the most important handles for a successful \textit{in situ} electrochemomechanical coupling measurement. While experimental techniques allow characterization of complex coupling effects under \textit{operando} conditions, additional insight into mechanistic aspects of these effects can be gained from computational methods. Therefore, this thesis uses a combination of \textit{in situ} experimental methods and \textit{ab initio} modeling to characterize chemical expansion in oxide films and its relation to mechanical deformation and elastic properties.

Pulsed laser deposition is the method of choice for preparing non-stoichiometric oxide films. As the name implies, PLD utilizes a high power pulsed laser beam to supply energy to target materials so that they are vaporized and transported to a substrate surface. The incident laser pulse penetrates only the outermost surface of the target material (typically about 10 nm depth), causing a rapid increase in surface temperature (up to about $10^3 \degree C$). One advantage of the PLD technique derives from this high heating (or evaporation) rate, which effectively enables all target constituents to be evaporated at the same time. As a result, PLD allows transfer of multi-component target materials onto a substrate with little change in chemical composition. In contrast, it is generally difficult to control the stoichiometry of the resulting thin film with other physical vapor deposition (PVD) techniques such as sputtering or electron beam evaporation. Another advantage of PLD is that it utilizes a highly confined plume of materials, which produces films with less contamination and high reproducibility. On the other hand, contamination of the source materials by the container is hardly avoidable in thermal and electron beam evaporation. In methods that use organic materials such as ink-jet printing, and metal organic chemical vapor deposition (MOCVD), the potential of leaving organic residues behind in the films exists. Additionally, PLD provides many accessible operating parameters that can be separately controlled, including laser power, pulse rate, background pressure, gas composition, substrate surface temperature, and crystallographic orientation of the substrate. Therefore, PLD provides a facile method for modifying the attributes of thin film microstructure, such as crystal orientation, grain size, and shape. Several members of the Crystal Physics and Electroceramics Laboratory of Professor Harry Tuller at MIT prepared thin film non-stoichiometric oxides characterized in this thesis by pulsed laser deposition.

Diverse methods exist for \textit{in situ} characterization of chemomechanical effects, most importantly those used to measure non-stoichiometry, those for characterizing chemical expansion, and those for detecting mechanical properties or deformation. Briefly reviewed
here are those of particular importance to this thesis including electrochemical impedance spectroscopy, nanoindentation, and atomic resolution electron microscopy.

1.6.1 Non-stoichiometry detection and impedance spectroscopy

For measuring non-stoichiometry, the most well-known technique is thermo-gravimetric analysis (TGA) which monitors mass change to determine oxygen content.\[65\] Because of the extremely small mass changes involved, TGA is not appropriate for detecting the oxygen content of thin films, and is superseded by electrochemical (i.e., measuring "chemical capacitance") or optical methods.\[54, 66\] Chemical capacitance $C_{\text{chem}}$ is defined as the chemical storage capacity of a material under a potential, and is generally measured using electrochemical impedance spectroscopy (EIS).\[56, 67, 68\] $C_{\text{chem}}$ will be discussed in more detail in the following chapter, but here we present a brief description of EIS as a method. EIS is a standard electrochemical method that can be used to measure the characteristics of electrochemical devices by deconvoluting resistive and capacitive contributions from the electrolyte and electrodes, bulk and interfacial effects, and equilibrium and kinetic processes. EIS also may be used to study electrode kinetics (exchange or diffusion limited, rate coefficients, etc.).\[69, 70, 71\] In potentiostatic impedance measurements, an oscillating electrical potential is applied to a sample while the resulting oscillating current is measured. Generally a range of frequencies are tested in such measurements, producing an impedance "spectrum" that can be used to separate reaction and migration steps in multistep processes by isolating individual time constants in the frequency domain.\[67\]

Impedance spectroscopy is also regularly used for \textit{in situ} testing, where conducting measurements at multiple temperatures is of interest for determining activation energies for reaction steps, and measurements at multiple $pO_2$ levels enable characterization of mixed ionic-electronic conducting behavior.\[67, 71\] Impedance spectroscopy in controlled gas and temperature environments also has been done to measure the rate constants of oxygen exchange reactions.\[71, 41\]

Often, impedance spectra are analyzed by constructing equivalent circuits with a minimal number of elements that plausibly represent the key steps in the electrochemical process being considered. The equivalent circuits and analysis procedures used for impedance spectra in this thesis were established previously and validated for sample designs equivalent to those used here.\[54, 71, 72\] Thus, impedance spectroscopy is a useful method for determining the oxygen content of thin films, as well as the charge transport and exchange characteristic of non-stoichiometric oxides.

1.6.2 Observing chemical expansion using microscopy

Previously available methods for detecting chemical expansion \textit{in situ} include optical approaches (e.g., interferometry \[73\] or multi-beam optical stress sensors \[57\]), diffraction-based methods based on X-rays \[22, 74, 75\] or neutrons \[76, 77\], and contact-based methods such as dilatometry \[23\] and scanning probe-based spectroscopy \[78, 79, 80\] methods that utilize the probe as an electrode.

Like TGA, dilatometry is generally only suited to studying bulk samples, while diffraction-based methods are generally limited in terms of spatial and temporal sensitivity unless conducted at a synchrotron facility.\[54, 81, 82, 75\] Chapter 2 discusses in detail a novel approach
for detecting chemical expansion on sub-second time scales in situ that can be done in a university lab setting without access to a synchrotron. Previous investigations of local electromechanical coupling in oxide bulk or thin films have employed scanning probe microscopy with nanoscale resolution. While such chemical expansion strain microscopy (ESM), as described by Kalinin et al., has enabled derivation of diffusion coefficients in cathode materials and provided insights into surface oxidation and evolution reactions, that approach employs the nanoscale probe tip itself as a moving electrode. As such, results reflect properties limited to regions within ~20 nm of the surface and due to the local perturbation near the nanoscale probe electrode. At present such ESM investigations are limited generally to temperatures < 200°C, and thereby requiring large electrical biases (>2 V) to obtain measurable displacement in response to polarization. The resulting mechanisms under exploration are thus also specific to the combination of probe and sample materials.

Extremely high resolution microscopy provides an interesting alternative means of characterizing chemical expansion in situ. There are two main types of atomic-resolution electron microscopy, each with diverse advantages, that are of interest for this purpose, specifically phase contrast transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM). The resolution of these techniques has been improving steadily, especially with recent developments in aberration-correction, and they are now readily able to resolve atomic columns. STEM is often available in combination with electron energy loss spectroscopy (EELS) that can be used to identify elemental composition as well as oxidation states. Atomic resolution images enable local lattice strain detection through a combination of selected area diffraction (SAD) and geometric phase analysis (GPA, a way of translating local fast Fourier transform (FFT) information throughout an image to identify strain states relative to a user-specified reference state). Because chemical expansion is characterized by both a change in lattice parameter and a change in oxidation state, high resolution microscopy with EELS provides a powerful method of characterizing this chemical expansion at the atomic level.

1.6.3 Environmental nanoindentation

Two operando experimental methods based on environmental nanoindentation were used extensively during the course of this thesis. Chapter 2 discusses in detail the development and application of one of these methods (dynamic chemical expansion detection) that was devised specifically in support of this thesis, but here we discuss the background behind environmental nanoindentation as a technique and describe the particular instrument used.

Traditionally, nanoindentation has been used to measure mechanical properties including elastic modulus $E$, hardness $H$, and fracture toughness $K_{IC}$. The general procedure is as follows: A hard, stiff probe of known geometry is pushed into a sample with a well-controlled loading and unloading profile. Simultaneously, the displacement of the probe is measured with sub-nm precision. The result is a load-depth hysteresis curve like the one shown in Fig. 1-5 that can be analyzed to determine mechanical properties including $E$ and $H$. As a contact-based approach, nanoindentation requires polished, flat samples that will
not react with the probe. For room temperature measurements, probes are generally made of diamond, but for elevated temperature (>500°C) cubic boron nitride must be substituted because of its chemical stability.[96, 97] The method has several advantages over other mechanical property measurement options such as tensile or acoustic testing; it requires a very small quantity of material, is relatively non-destructive, can measure a wide variety of mechanical properties (including, but not limited to $E$, $H$, $K_I$, creep compliance, and mechanical energy dissipation), is effective for most material classes (crystalline, amorphous, polymeric, etc.), and is one of the few ways to measure the mechanical properties of thin films.[93, 98] The instrument itself also has some key, useful features including instantaneous data collection and highly precise displacement and load measurement (nm and mN scale).

The instrument used most prominently in this thesis is the pendulum-based NanoTest Vantage designed by MicroMaterials (Wrexham, UK) and pictured schematically in Fig. 1-5, with temperature control up to 750°C and gas control to $pO_2 < 10^{-3}$ atm. A detailed description of this high-temperature indentation setup and documentation of its effectiveness for precise measurements at elevated temperatures can be found in Refs. [99, 100]. A key innovation of the NanoTest Vantage is the capability to heat both the probe and the sample, which minimizes signal drift due to temperature mismatch between the sample and the probe.[100] Samples for high temperature testing were generally attached to the stage using high temperature, water-based cement (Omega-bond 600); it is imperative that the cement chosen for this purpose produce no fumes or decomposition products at high temperature that could re-deposit on sample surfaces or the probe during measurement. Another important advantage of the NanoTest is its adaptability for research purposes. For example, for the work described in Chapter 2, we added electrical leads to the NanoTest to enable simultaneous electrical and mechanical measurements of samples at elevated temperatures.

Figure 1-5: (a) Example load-depth hysteresis produced by a standard indentation experiment. The unloading stiffness $S$ and the projected contact area of the probe (inset, scale bar 400 μm) at the plastic depth are the key parameters for determining elastic stiffness. (b) Schematic of the high temperature instrumented indentation apparatus. This pendulum-based machine can heat both the probe and the sample stage, minimizing error due to temperature mismatch during measurement.
High temperature nanoindentation has been demonstrated as a technique for measuring mechanical properties of bulk and thin film samples at temperatures up to 800°C for diverse material classes including oxides and alloys.\cite{101, 102, 103, 104, 105, 99} While the expected error of standard room temperature indentation measurements of $E$ and $H$ is below 5\%, high temperature indentation carries additional challenges that can increase the size of this error. These necessitate a statistical approach to data collection and analysis discussed in Chapter 3 and Appendix A.\cite{104} During the course of this thesis, we used the high temperature instrumented indenter for both the traditional purpose of detecting mechanical properties, and the non-traditional purpose of detecting chemical expansion in situ.

1.6.4 Atomistic simulations

These experimental methods, while essential to understanding the phenomena that occur in non-stoichiometric oxides, are time consuming and the information gained can be difficult to interpret as it stems from multiple coupled parameters. Computational methods enable complementary analysis of the wide and interdependent phase space of electrochemomechanically coupled, conductive ceramics, while allowing precise control of specific details such as strain state or defect concentration.

Density functional theory (DFT) is a type of atomistic modeling that can be used to investigate the electronic structure of materials and a wide range of related properties, such as the elastic constants\cite{106}, the energy barrier to vacancy migration\cite{107} and the diffusion coefficients of various point defects\cite{108} or, in combination with molecular dynamics (MD) simulations, the chemical expansion behavior of a given material.\cite{30} For example, the study by Marrocchelli et al. that identified the role of charge localization on the chemical expansion coefficient of CeO$_{2-\delta}$ and BaCeO$_{3-\delta}$ did this by systematically varying the value of the Hubbard $U$, a parameter that is used in DFT to enforce charge localization in systems like CeO$_2$.\cite{30} This study exemplifies one major advantage of computational techniques in that they can artificially isolate the contributions of individual variables in a given material system that would be unavoidably coupled to other variables in experimental systems. DFT + $U$ may also be used in a predictive capacity, as highlighted above for the studies that identified the influence of mechanical strain on the activation energy for vacancy formation or migration.\cite{42, 43, 44}

In the work presented in this thesis, we used DFT + $U$ primarily to compute how chemical expansion resulting from changes in point defect concentrations affects elastic properties. The results demonstrate from a more theoretical standpoint how elastic stiffness in bulk or thin film oxides can be affected by composition, and moreover how local lattice structure can be affected by introduction of point defects including reduced cations and oxygen vacancies.

1.7 Model non-stoichiometric oxide film: Pr$_x$Ce$_{1-x}$O$_{2-\delta}$

This thesis aims to present a unified study of the chemomechanical consequences of chemical expansion in non-stoichiometric oxide films by studying a model oxide material, Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO). This fluorite structured oxide undergoes large changes in non-stoichiometry $\delta$ and corresponding oxygen vacancy concentration in both cathodic and anodic SOFC conditions, along with significant chemical expansion, as shown in Fig. 1-6.\cite{23, 71, 109} Generally for
PCO, increased $\delta$ is correlated to increased Pr$_{Ce}$ and lattice parameter $a$. Large changes of $\delta$ in cathodic conditions are facilitated by the ease of Pr reduction according to Eq. 1.3, and thus larger volume fractions of Pr within the oxide generally increase electrochemical reducibility in these conditions.\[110]\ The thermal and chemical expansion coefficients of PCO have been measured at $1.2 \times 10^{-5}$ and $0.084-0.087 \Delta \varepsilon/\Delta \delta$.\[111, 23, 24\] The chemical expansion coefficient varies slightly between bulk and thin film forms of PCO.\[23, 24, 25\] Due to the mixed-valent nature of Pr, PCO is a mixed ionic-electronic conductor under relatively oxidizing conditions.\[9, 65\]

Because PCO has been extensively characterized by a detailed defect model relating temperature and effective $pO_2$ to $\delta$, it provides an excellent basis for studying in situ defect chemistry modulation and detection.\[65, 23, 110\] For example, PCO has been used previously to demonstrate that in thin films supported on ionically conducting substrates, the oxygen vacancy concentration $\delta$ can be controlled both by changing the surrounding atmosphere and by application of electrical bias.\[54, 112\] As shown in Fig. 1-6, these results showed that thin films of PCO exhibit larger $\delta$ than equivalent compositions of bulk PCO in the same environmental conditions. Additionally, PCO was studied by simultaneous optical and chemical capacitance measurements to demonstrate a non-contact way of detecting $\delta$ in thin films that exhibit an optically active impurity band coupled to $\delta$.\[66\] PCO has also been investigated in several computational studies, including computations of vacancy formation and migration energies estimated using DFT and Monte Carlo simulations.\[113, 114, 115\]

PCO is therefore an excellent model non-stoichiometric oxide film because of its easily controlled defect content under relatively easy-to-access experimental conditions, and the predictive power of the defect chemistry model.\[65, 23, 110\]

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**Figure 1-6:** (a) Thermochemical strain of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO) vs. temperature for several compositions $x$. Above 500°C, PCO undergoes chemical expansion with increased oxygen vacancy concentration correlated with increased dopant concentration $x$. Adapted from \[9\].
(b) The oxygen vacancy concentration $\delta$ of PCO depends on oxygen partial pressure $pO_2$ and temperature $T$, and is also different for thin film (solid lines, filled symbols) and bulk (dashed lines, open symbols) samples with equivalent $x$ under the same conditions of $T$ and $pO_2$. Adapted from \[54\].
1.8 Thesis goals and organization

Having established the background and general methods for this thesis, the following chapters will explore in detail a series of studies conducted with the overall goal of characterizing chemomechanical coupling effects for the model oxide material PCO under *operando* conditions. The aim is to present a unified understanding of how environmental conditions, defect chemistry, mechanical states (volume, stress and strain), and mechanical properties interact in an electrochemomechanically coupled model oxide film. This work will inform the design of micro-SOFCs and other thin film non-stoichiometric oxide devices to ensure that stress and strain can be effectively managed to enhance material performance without detrimentally impacting device durability. The thesis also presents a set of related studies on Li-storage materials to demonstrate the broad relevance of these chemomechanical coupling effects and characterization methods.

- **Chapter 2** describes an in depth study of dynamic chemical expansion of thin film non-stoichiometric oxides at extreme temperatures. This constitutes *in situ* detection of chemical expansion of PCO films using a novel, dynamic, probe-based approach. This study makes liberal use of the fact that oxygen content can be modulated in many non-stoichiometric oxides through electrochemical pumping of oxygen, and addresses a range of questions relating to dynamic chemical expansion in oxide films. Which conditions increase or decrease the volume change experienced by an oxide film in response to an applied electrochemical potential? Which processes control the rate and magnitude of mechanical deformation? Can we detect dynamic chemical expansion on short time scales without the aid of a synchrotron? This chapter also presents a novel, positive application of chemical expansion; that of the high temperature oxide actuator. Finally, the chapter concludes by showing the generality of these methods and results by applying the same approach to a perovskite structured non-stoichiometric oxide, SrTi$_{0.65}$Fe$_{0.35}$O$_3$ ($\delta$ (STF)).

- **Chapter 3** presents an environmental nanoindentation study of *operando* reduction of elastic modulus in PCO thin films. The work is the first measurement of Young’s elastic modulus in a non-stoichiometric oxide film as a function of temperature and oxygen partial pressure, and relates the measured stiffness to predicted chemical and thermal expansion based on the defect model for PCO. How does chemical expansion impact elastic properties of oxide films, and how should this translate to *operando* stress states? Do oxide films behave the same way as bulk counterparts under the same environmental conditions? While conducted on the model system PCO, these results extend to any non-stoichiometric oxide material that may undergo chemical expansion or exhibit differing defect chemistry as a function of physical dimensions of the oxide.

- **Chapter 4** recounts a simulation study of Defect-mediated mechanics in non-stoichiometric oxide films. In this case, DFT + U is applied to computing composition-dependent elastic properties in PCO. We conducted two studies. The first computed the elastic stiffness tensor for several compositions of PCO, addressing the simple question: What is the predicted effect of chemical expansion on the elastic constants of non-stoichiometric oxides? That study was conducted in parallel with the indentation study of Chapter 3 and provided additional data for contrasting bulk and thin
film composition-dependent mechanical properties. The second study in this chapter describes a parallel DFT + U investigation of the composition-dependent biaxial stiffness of bulk and slab forms of PCO. That study addressed two important questions: Is non-stoichiometry or low-dimensionality a more important factor in determining composition-dependent mechanical properties in non-stoichiometric oxides? Is chemical expansion in non-stoichiometric oxides expected to happen in a uniform manner? How strongly do point defect configurations influence mechanical properties (i.e., do surface vacancies have the same influence on mechanical stiffness as interior vacancies?)? These computational results inform the previous chapter and also extend general understanding of the relationships among elastic moduli, defect chemistry, and local lattice structure.

- **Chapter 5** describes an in depth transmission electron microscopy investigation of nanoscale chemical expansion in PCO. Using a combination of conventional TEM, annular dark field scanning tunneling microscopy (ADF-STEM), and EELS, this study characterizes chemical expansion of PCO film cross sections as the atomic scale for various conditions of temperature and oxidation state. We address several considerations relating to inhomogenous chemical expansion in oxide films. Is chemical strain anisotropic, and over what length scale is this the case? Is there evidence for space charge layers that may produce different average non-stoichiometry than bulk samples? Is there evidence for inhomogeneity of oxidation state and associated chemical strain (e.g., at linear defects)? Can we directly image dynamic structural changes associated with oxygen "breathing?" These results provide important context for understanding why thin film non-stoichiometric oxides have often been observed to behave differently from bulk counterparts *operando*, in terms of actual defect chemistry, mechanical properties, and functional properties.

- **Chapter 6** examines electrochemomechanical coupling in Li-storage materials in a few example cases. Included in this section is a non-contact extension of the dynamic chemical expansion method described in Chapter 2 applied to films of \( \text{Li}_{1-y}\text{Mn}_2\text{O}_4 \) (LMO). Additionally, we leverage DFT + U to determine whether oxygen loss could cause chemical expansion in the same material system. Finally, we report composition-dependent elastic modulus, hardness, and fracture toughness measurements for the commercially significant Li-storage material \( \text{Li}_x\text{Co}_2\text{O}_2 \) (LCO). In this chapter, we demonstrate that the methods and effects described in the earlier thesis chapters are broadly relevant and applicable, even beyond the field of oxide-ion conductors. Chemical expansion and composition-dependent mechanical properties present an important technical challenge for many electrochemical devices that can be both useful and detrimental to performance, and must be managed accordingly.

Finally, the thesis concludes with a discussion of the most important findings of these studies, their relevance to our general picture of *operando* chemomechanical coupling in non-stoichiometric oxide films, their application to device design, and suggested future work.
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Chapter 2

Direct Measurement of Chemical Expansion in Thin Film Non-stoichiometric Oxides

As introduced in Chapter 1, the effect known as chemical expansion is at the heart of electrochemomechanical coupling effects in non-stoichiometric oxide films. In a layered structure, the volume change resulting from oxygen "breathing" can produce mechanical stresses that lead to fracture, and that must be well-understood in order to prevent such mechanical failure or enhance functional performance through strain-coupled effects. Characterizing thin film chemical expansion \textit{in situ}, especially on short time scales, is not always possible in a university or industrial laboratory setting. Furthermore, for the purposes of understanding our model system \( \text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta} \) (PCO), we require a strong understanding of which conditions will interact with the oxide film to enhance or suppress expansion effects.

Therefore, in this chapter we had a two-fold purpose: First, to identify conditions that enhance or impede chemical expansion effects in the model oxide material PCO, and second, to demonstrate a novel, accessible, and time-resolved \textit{in situ} measurement approach for characterizing conditions or materials that maximize or minimize thin film chemical expansion. During the course of this study, we also developed the concept of the high temperature oxide actuator, a positive application of electrically-activated chemical strain, and applied the approach developed for PCO to a perovskite-structured oxide, \( \text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\delta} \) (STF).

Much of the work described in this chapter was published in Nature Materials as the result of a collaboration between the Van Vliet Laboratory for Material Chemomechanics and the Crystal Physics and Electroceramics Laboratory of Professor Harry Tuller, both at MIT.[1] The section on STF and some additional exposition of the modeling and analysis that can be applied to this measurement approach are included in a follow-up manuscript currently in preparation.[2] Jae Jin Kim (Tuller group) prepared the samples for the portion of this work concerning PCO with the exception of the two samples involved in Sections 2.2.1-2.2.2 which were prepared by Chang Sub Kim (Tuller group). Jae Jin Kim also conducted impedance spectroscopy measurements and assisted with initial experiment design for the work concerning PCO. Professor Nicola Perry (Kyushu University) provided samples for Section 2.3. For those samples, Ting Chen (Perry group) grew the STF films and
Thomas Defferriere (Tuller group) prepared Pt electrodes. Dr. John M. Maloney (Van Vliet group) designed the LabView signal analysis code used for detecting expansion phase lag and amplitude. Dr. Sean Bishop (Tuller and Van Vliet groups) developed analysis methods linking impedance and mechanical results. Dr. Di Chen (Tuller group) contributed to sample design and application of the defect model. Finally, Dr. James F. Smith, founder of MicroMaterials Ltd. and longstanding Van Vliet group collaborator, contributed to the frequency-based measurement experimental design.

2.1 Introduction

Chemical expansion, as discussed in detail in Chapter 1, has significant potential for producing stress, fracture, and strain during high temperature electrochemical device operation.[3, 4, 5, 6] This may have a negative functional impact, leading to cracking or delamination in situ, or it may be turned to a more positive outcome by tuning material performance through mechanical cues including stress and strain. Being able to take advantage of chemical expansion operando while avoiding detrimental mechanical failures fundamentally requires the ability to detect such effects under in situ conditions. This includes characterizing oxides in both equilibrium conditions and dynamic conditions that might represent, for example, gas interruption or redox cycling. Additionally, given the differences known to exist between film and bulk forms of these oxides, thin film-specific characterization methods are required.[7, 8, 9, 10]

Section 1.6 described several ways to characterize chemical expansion, and among these the most prominent are diffraction-based techniques and dilatometry. Diffraction has many important advantages, including a diversity of in situ measurement possibilities and the flexibility to measure films, powders, or pellets and determine orientation-specific information.[11] However, most diffraction instruments require a minimum of ten seconds to achieve a usable signal-to-noise threshold, meaning that faster measurements are not possible without the aid of a synchrotron.[12, 13, 14] Furthermore, while diffraction is sensitive to lattice strain or phase changes, it will not detect new lattice site formation or volume change that is not periodic (e.g., that might be associated with grain boundaries, dislocations, or similar defects).[15] In contrast, dilatometry is a fairly straightforward type of measurement that is sensitive, on sub-second time scales, to all types of volume change. Unfortunately, dilatometry is unsuitable to detecting chemical expansion in thin films. Therefore, there is a need for a method that can combine the simplicity of dilatometry with the flexibility of diffraction in a standard laboratory setting. The method presented in this chapter aims to satisfy this need.

The method we present is substantially enabled by the ability to electrically pump oxygen into our PCO films through a construction called the "effective pO₂".[16] Returning to the defect formation reaction of PCO (Eq. 2.1), we are reminded that oxygen vacancy formation, which couples to lattice dilation, is favored by low oxygen partial pressure environments.

\[
2Pr^\times_{Ce} + O^\times_{O} \leftrightarrow 2Pr^\prime_{Ce} + V_{O}^{\bullet\bullet} + 1/2O_2(g)
\]  

(2.1)

This can be seen by writing out the mass action relation for the above equation, Eq. 2.2, where \(\Delta H_r,Pr\) is the enthalpy of reaction, \(k^s_{r,Pr}\) is a pre-exponential term, and \(K_{r,Pr}\) is the
equilibrium constant of this reaction:

$$\frac{[Pr'_{Ce}]^{2}[V_{O}^{\bullet\bullet}]pO_{2}^{1/2}}{[Pr'_{Ce}]^{2}[O_{O}^\circ]} = k_{r,p_r}^\circ \exp\left(\frac{-\Delta H_{r,Pr}}{kT}\right) = K_{r,P_r}$$ \hspace{1cm} (2.2)

In fact, in an electrochemical system, the oxygen vacancy concentration $[V_{O}^{\bullet\bullet}]$ is determined based on the effective chemical potential of oxygen $\mu_{O_{2},eff}$, which can be shifted away from the chemical potential of oxygen in the gas phase, $\mu_{O_{2},g}$ by an electrical bias $\Delta E$ according to the Nernst relation Eq. 2.3:

$$\mu_{O_{2},eff} = \mu_{O_{2},g} + 4e\Delta E$$ \hspace{1cm} (2.3)

Thus, for an oxide film that is electrically biased relative to a reference state in equilibrium with a gas phase, we can define an effective oxygen partial pressure $pO_{2,eff}$, as follows:

$$pO_{2,eff} = pO_{2,g}\exp\left(\frac{4e\Delta E}{kT}\right)$$ \hspace{1cm} (2.4)

Having established the concept of $pO_{2,eff}$, we now move on to chemical capacitance, which is defined as the chemical storage capacity of a material under a potential, and results from formation and annihilation of oxygen vacancies and Pr$_r'_{Ce}$ in PCO.[9, 17, 18, 16] Equation 2.5 relates chemical capacitance $C_{chem}$ to $pO_{2,eff}$, film volume $V_{film}$, and $[V_{O}^{\bullet\bullet}]$:

$$C_{chem} = -\frac{8e^2}{kT}(pO_{2,eff}\frac{\delta[V_{O}^{\bullet\bullet}]}{\delta pO_{2,eff}})$$ \hspace{1cm} (2.5)

This equation may be derived following Ref. [7]. By rearranging Eq. 2.5 and integrating with respect to $pO_{2,eff}$, $[V_{O}^{\bullet\bullet}]$ may be determined if a reference state $pO_{2,eff}^\circ$ is available for which $[V_{O}^{\bullet\bullet}]$ is known. This results in Eq. 2.6:

$$[V_{O}^{\bullet\bullet}](pO_{2,eff}) = \frac{kT}{8e^2V_{film}} \int C_{chem}d\ln pO_{2,eff} + [V_{O}^{\bullet\bullet}](pO_{2,eff}^\circ)$$ \hspace{1cm} (2.6)

In the high $pO_{2}$ regime, solving the above equation gives a linear relationship between chemical capacitance and $[V_{O}^{\bullet\bullet}]$. This result has been well-established through prior electrochemical measurements coupled to defect modeling for PCO.[7, 16]

An important consequence of the above result is that electrical bias can be used to "pump" oxygen into and out of a PCO film grown on an ionically conducting substrate. This "electrochemical breathing" enables instantaneous adjustment of an oxide’s equilibrium $[V_{O}^{\bullet\bullet}]$ or $\delta$, meaning that all coupled effects (including volume change through chemical expansion) may also be driven rapidly via electrical modulation. In principle the same approach can be used to pump oxygen or other mobile ionic species into or out of any conducting oxide so long as leakage currents (e.g., due to gas-phase reactions) are minimized.[19, 14]

To quantify film "breathing" and mechanical deflection due to reversible oxygen uptake within PCO thin films, we employed a distinct probe-based approach (Fig. 2-1) capable of nanometer-scale displacement and sub-second-scale temporal resolution at temperatures up to 650$^\circ$C. In this method, a film of up to micrometer-scale thickness is electrically biased with modest voltages ($\sim$100 mV) to drive oxygen content changes within the entire film by
adjusting the Nernst electrochemical potential.[16, 20] The corresponding strain \( \epsilon \) arising from the change in non-stoichiometry \( \Delta \delta \) follows the chemical expansion coefficient of PCO (0.087 [21]) defined in equation 2.7:

\[
\epsilon = \alpha_c \Delta \delta
\]

Figure 2-1: Dynamic chemical expansion upon oscillating electrical bias. (a) Films of \( \text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta} \) (PCO) with deposited thickness \( t_f \) ranging from 300-1000 nm were grown on yttria stabilized zirconia (YSZ) single crystal substrates (1 mm thickness) with porous Pt reference and counter electrodes. (b) The depth-sensing probe rests in contact with the PCO sample surface, with the sample maintained at a constant temperature ranging from 550 to 650\( ^\circ \)C. Alternating bias \( V_{WE} \) applied to the working electrode with respect to the reference electrode modulates the oxygen activity in the PCO film, causing oxygen vacancies (empty squares) to be pumped in and out of the film through the YSZ substrate. This in turn leads to mechanical response that is the result of a combination of film volume change and substrate deflection due to PCO chemical expansion, detectable through probe displacement. (c) Sinusoidal applied bias (blue) induces a corresponding and lagging change in probe position (red), from which phase lag \( \phi \) and amplitude \( A \) are detected. Positive probe displacement indicates increased film thickness (expansion) and positive substrate curvature and is driven by negative (reducing) bias, whereas negative displacement indicates decreased film thickness (contraction) and negative substrate curvature that is driven by positive (oxidizing) bias. From [1].

Film adherence to the yttria-stabilized zirconia (YSZ) substrate constrains in-plane chemical strain to produce interfacial stress that can be sufficient to induce detectable structural deflection. This coupling of electrical bias and mechanical displacement enabled demonstration of nanoscale electrochemomechanical spectroscopy (NECS) under conditions of extreme operating environments to quantify mechanisms controlling the extent and rate of film "breathing." Figure 2-1 summarizes the film configuration and measurement of NECS.
at constant elevated temperature. PCO films of varying thickness (∼300 to 1000 nm) and approximately 8 × 8 mm in plane dimensions on YSZ single crystal substrates were fabricated with a three-electrode configuration (Fig. 2-1(a); see Section 2.5). Control samples lacking only the PCO film were also prepared to decouple the response of the film from that of the substrate and Pt electrodes, and one PCO-YSZ sample with smaller in-plane film dimensions (3 mm diameter) was prepared to decouple out-of-plane strain from deflection.

During mechanical measurements, the position-sensing probe was placed in contact with the film surface as a sinusoidal electrical bias was applied to the working electrode with respect to the reference electrode (Fig. 2-1(b)), and the mechanical displacement was detected as a combination of film thickness change and substrate deflection. Figure 2-1(c) shows example traces, illustrating that positive applied bias causes negative probe displacement as the film contracts, while a reduction in bias produces concomitant, reversible film expansion and positive probe displacement. This oxide film contraction under positive bias is expected from the $pO_{2,\text{eff}}$ in the film given by Eq. 2.4. The asymmetry in magnitude of mechanical response apparent in Fig. 2-1(c) is reasonably explained by the asymmetry in defect concentration change with respect to applied bias: PCO tends toward stoichiometry ($\delta \to 0$) under more oxidizing conditions and toward $\delta = 0.05$ for more reducing conditions.

We detected such reversible, nanometer-scale mechanical response, using electrical biasing frequencies $\omega$ ranging from 1 to 0.01 Hz. Probe displacement on film-free YSZ/Pt electrode control samples exposed to oscillatory electrical bias was < 1 nm; we thus concluded that there was little to no detectable contribution to the measured mechanical response from dimensional changes in the substrate, counter-electrode, or current collector. Curvature of the film/substrate system was detected by acquiring measurements at multiple surface locations with mm-scale lateral spacing relative to the film center; see Section 2.2.2. Therefore, we attribute the dynamic actuation exemplified in Fig. 2-1(b) to concurrent increased PCO film thickness and positive substrate curvature due to interfacial stress.

This approach has several key advantages over existing techniques to measure film expansion, primarily in that it is more versatile and accessible than any one alternative approach. As we will see, unlike curvature-based methods, NECS can be applied to measure both strain-only displacement and displacements amplified by substrate deflection. Furthermore, unlike interferometry-based measurements, this method requires no particular knowledge of the optical properties of samples, nor does it require samples to have specific optical properties (e.g., reflectivity) as are required for many curvature-based techniques. Unlike diffraction-based chemical expansion measurements, this method can measure displacements and volumetric expansion resulting from mechanisms other than lattice strain (e.g., grain boundary mediated effects). Additionally, NECS can achieve second-scale temporal resolution for lattice-strain-based displacements without the aid of a synchrotron used in XRD or neutron diffraction (methods that can also include potentially damaging high energy radiation), and may be able to achieve faster temporal resolutions than those presented in this thesis with additional modification of instrumentation and software. Unlike dilatometry, this method can be applied to thin film samples, and has improved spatial resolution as compared to most dilatometers.

In the following sections, we first demonstrate the versatility of this approach to detecting both strain-only displacement and amplified, deflection-based displacement. We then characterize the PCO on YSZ model system via nanoscale electrochemomechanical spectroscopy,
focusing on the effect of temperature and shifted pO$_{2,\text{eff}}$. We compare these results with the defect model of PCO, and then shown to demonstrate the novel concept of high temperature oxide actuators, which is a possible positive application for electrochemically-driven chemical expansion. Finally, we describe the application of this measurement approach to another non-stoichiometric oxide of great technical significance, SrTi$_{0.65}$Fe$_{0.35}$O$_{3-\delta}$ (STF).

2.2 Results: Dynamic chemical expansion in PCO

2.2.1 Strain-only displacement

To confirm that we could measure displacements resulting from chemical strain alone, we designed a sample to minimize substrate deflection by using a thick substrate (1.5 mm) and small film footprint (3 mm diameter, $\sim$1 $\mu$m thickness as measured by profilometry). This prevented the film from developing enough interfacial stress under electrical-bias-stimulated chemical expansion to induce substrate deflection. Figure 2-2 shows that we measured 1 nm of displacement amplitude consistently across the width of the film, with no sign of curvature due to substrate deflection. The measured displacement is therefore attributed solely to PCO film thickness change, confirming that the method described in this work for detecting dynamic chemical expansion can be applied to measure film thickness changes as well as displacements resulting from combined film thickness change and substrate deflection.

![Figure 2-2](image-url)  
Figure 2-2: The measured displacement amplitude for a $\sim$ 1 $\mu$m film with reduced area (3 mm diameter) grown on a 1.5 mm-thick substrate is consistently 1 nm across the width of the film, indicating the absence of substrate deflection under electrically stimulated chemical expansion. The measured displacement is therefore attributed solely to PCO film thickness change, confirming that this method can be used to detect chemical strains as small as 1 nm. Figure from Supplementary Information to Ref. [1].
Figure 2-3: Samples deflect in response to applied bias. (a) Schematic of sample geometry and probe positions for testing deflection amplitude vs. position across the sample surface. A 600 nm film of Pr$_x$Ce$_{1-x}$O$_{2-δ}$ (PCO) was grown on a 1 mm-thick yttria stabilized zirconia (YSZ) substrate. The surface electrode is a sputtered layer of porous Pt. Pt paste was also added to improve connectivity of the surface electrode in regions where probe contact would not be necessary. Probe contact positions are not to scale. (b) Equilibrium deflection amplitude $D_0$ and (c) characteristic time constant $\tau$ vs. lateral probe position, indicating increased deflection near sample center as compared to sample edges, confirming curvature upon application of electrical bias signal. The time constant is unaffected by probe position, as deflection rate is controlled by oxide ion diffusion through the substrate. Figure from Supplementary Information to Ref. [1].

2.2.2 Deflection-based displacement

To confirm that samples were deflecting in response to applied electrical bias, we tested a sample with the surface geometry shown in Fig. 2-3(a) at positions near and far from the center or the clamped sample edges (as marked in the Fig.). For each test, we applied an oscillating bias of $\pm128$ mV for a frequency range of 1-0.025 Hz, and determined magnitudes of equilibrium displacement amplitude $D_0$ and characteristic time constant $\tau$ according to the model and fitting procedure outlined below. Figures 2-3(b)-(c) plot the results of this fit versus lateral probe position. $D_0$ is about a factor of 5 higher in the sample center than near the sample edges despite no apparent trend in the time constant $\tau$; this indicates sample curvature during the measurement and confirms that the substrate deflected as the film responded to the applied bias.
As a coarse estimate of expected deflection at the sample center, Stoney’s formula predicts a $D_0$ of 42 nm for a PCO film of 600 nm thickness at 650°C subjected to chemical strain amplitude of 0.13% leading to interfacial stress amplitude estimated at 0.29 GPa.[22] This estimate is based on the following assumed elastic properties for YSZ and PCO: Young’s modulus $E_{PCO} = 150$ GPa[23], Poisson’s ratio $\nu_{PCO} = 0.33$[24], $E_{YSZ} = 272$ GPa[25], $\nu_{YSZ} = 0.3$[26]. The difference from the actually measured $D_0$ of 7 nm is explained by the fact that the boundary conditions of Stoney’s formula are not met accurately by this experimental design (e.g., the sample is mounted to the heated stage with cement, the film only covers 64% of the substrate area, etc.).

2.2.3 Electrochemomechanical spectroscopy

The oscillatory mechanical response may be characterized by a phase lag $\phi$ and amplitude $A$ by fitting a sinusoidal function to the probe position (Fig. 2-1(c)). Given sufficient time to relax following a change in oxygen activity, the sample can equilibrate fully. Accordingly, with decreasing frequency, the amplitude approaches a maximum value ($\sim$10 nm), whereas the phase lag approaches zero (Figs. 2-5a, b). Further, at higher temperatures with concurrent reduction in oxygen transport barriers, the frequency at which the maximum amplitude is reached increases. As mentioned above, we refer to this mechanical characterization of the sample frequency response as nanoscale electrochemomechanical spectroscopy (NECS), in analogy to electrical admittance spectroscopy, and determine the complex function $Y$ describing the frequency response of the material relative to the applied signal. In the time domain, $Y$ is the ratio of displacement $D$ to applied bias $E$ described by Eq. 2.8:

$$Y[t] = \frac{D}{E} = \frac{A[\omega]\sin(\omega t + \varphi[\omega])}{E_0\sin(\omega t)} \quad (2.8)$$

Above, $\omega$ is the measurement frequency, and $E_0$ is the applied bias amplitude. This can also be expressed in the complex plane according to Eq. 2.9:

$$Y[\omega] = \frac{A[\omega]}{E_0}(\cos(\varphi[\omega]) + i\sin(\varphi[\omega])) \quad (2.9)$$

Figure 2-4 shows schematically how this function may be plotted on the complex plane using the frequency-dependent phase lag $\phi[\omega]$ and amplitude $A[\omega]$ defined by Eqs. 2.10 and 2.11:

$$A = \frac{D_0}{\sqrt{(\omega\tau)^2 + 1}} \quad (2.10)$$

$$\phi = -\varphi = \tan^{-1}(\omega\tau) \quad (2.11)$$

A detailed derivation of the transfer function relating $Y$ to Eqs. 2.10 and 2.11 can be found in the Supporting Information to Ref. [1] and Appendix A.1.

Figures 2-5(a)-(b) show that the measured deflection amplitudes and phase lags were well described by Eqs. 2.10-2.11, except at the highest frequencies ($\geq 0.5$ Hz) where phase lag is expected to asymptotically approach $\pi/2$ but exceeds this value experimentally. This discrepancy is explained by a slight internal signal collection delay. When these data are
Figure 2-4: Schematic plot of complex electrochemomechanical admittance $Y$. The x and y axes are the real and imaginary parts of $Y$ in nm/V. Each point on the plot can also be represented by its modulus $|Y| = A(\omega)$ (amplitude as a function of frequency) and phase lag $\phi[\omega]$, which is equal to the negative of the phase shift $\varphi$ (also known as the phase angle). The maximum $|Im(Y)|$ in the single semicircle indicates the point at which $\omega \tau = 1$. Figure from Supplementary Information to [1].

expressed on the complex plane for a given condition, as in Fig. 2-5(c), the displayed NEC spectrum shows a single characteristic maximum (e.g., $\sim 0.05$ Hz at 650°C) corresponding to the characteristic frequency of the sample (where $\omega \tau = 1$). As derived in Appendix A and the Supplementary Material to [1], the arc diameter in Fig. 2-5(c) corresponds to the maximum mechanical displacement $D_0$, normalized by applied bias amplitude $E_0$, and $\tau/D_0$ is the inverse rate of displacement. Note that the above relationships and following kinetics analysis are valid even for displacement attributed to concurrent film expansion and substrate curvature.

2.2.4 Temperature effects

The capacity to rapidly measure these breathing displacements over a wide range of temperatures and bias-modulated defect contents enables determination of the activation energies $E_a$ indicative of mechanisms by which oxygen moves in and out of functional oxides. Figure 2-5(a)-(b) show that for a fixed frequency, PCO generally exhibits increased displacement and decreased phase lag with increased $T$. In other words, the sample deflection is faster, or activated at higher temperatures. Figure 2-6(a) shows representative Arrhenius relations from which we determined the activation energies modulating the magnitude of mechanical response $D_0$ and inverse rate of displacement $\tau/D_0$ for a given sample and condition. These average $E_a$ values were $-1.05 \pm 0.13$ eV (for $\tau/D_0$), and $0.53 \pm 0.14$ eV (for $D_0$), reported as mean and standard deviation of at least six measurements across three samples. We also applied conventional in situ impedance spectroscopy (IS) to these same sample con-
Figure 2-5: Sample frequency response to expanding Pr$_{0.1}$Ce$_{0.9}$O$_2$-$\delta$ film. Amplitude $A$ (a) and phase lag $\phi$ (b) obtained at several different temperatures for PCO film thickness of 1 $\mu$m. For each temperature, $A$ and $\phi$ are fit to a first-order transfer function (solid lines) to estimate the characteristic time $\tau$ and equilibrium (zero-frequency) displacement amplitude $D_0$ of the mechanical response. With increasing temperature, the expansion response is more rapid, suggesting a temperature-activated process. (c) Electrochemomechanical admittance $Y$ shown on the complex plane for the same data indicates a single semicircle or process at each temperature. In analogy to electrical admittance spectroscopy, corresponding diameters are equivalent to $D_0/E_0$, while the frequency at the semicircle maximum marks $\omega\tau = 1$. For all data points, the standard deviation of fitted $A$ or $\phi$ over ten periods is smaller than the data points. Figure from [1].

Structs at 500-700°C, which allows for separate measurements of $E_a$ associated with electrical impedance between different working electrodes. We thus determined that the distinct activation energies measured mechanically were consistent with those attributable specifically
to the oxygen storage capacity, i.e., chemical capacitance, of the PCO film \( (E_a \text{ measured by IS at } 0.55 \pm 0.07 \text{ eV corresponds to displacement magnitude } D_0) \) and to resistance to oxide ion conduction through the YSZ \( (E_a \text{ measured by IS at } -0.99 \pm 0.06 \text{ eV corresponds to inverse displacement rate } \tau/D_0) \). These activation energies, measured via NECS and IS in our study, also agreed well with those reported previously for PCO chemical capacitance \((0.6 \text{ eV [27]})\) and YSZ diffusion \((1 \text{ eV [28]}\). We note that in the high pO\textsubscript{2} regime investigated here, chemical capacitance in PCO exhibits an activation energy that should correlate with the enthalpy of reaction from Eq. 2.1 and 2.2, shifted by a factor that is dependent on the average oxygen vacancy content \(\delta\)[27, 16] In accordance with the derivations given for \(D_0\) and \(\tau/D_0\), the good agreement with expected activation energies validated that the calculated maximum breathing displacements \(D_0\) of these oxide films are controlled by the chemical capacitance of the thin film PCO, and that the inverse displacement rate \(\tau/D_0\) is controlled by the rate of oxygen transport into and out of the PCO film through the YSZ substrate.

Figure 2-6(b) shows that \(D_0\) was approximately linear with film thickness \(t_f\), for different temperatures and applied bias amplitudes, with a vertical intercept at \(t_f = 0\) of \(D_0 \sim \pm 1\) nm similar to that detected for control samples (i.e., YSZ substrates with no PCO film). As expected, displacement amplitude increased with increasing temperature at a given applied bias, e.g., up to 12 nm at 128 mV and 650\(^\circ\)C for the 1018 nm film. Further, increasing the amplitude of the applied bias from 128 to 171 mV (increasing pO\textsubscript{2,eff} range by two orders of magnitude) at a constant temperature of 650\(^\circ\)C increased \(D_0\) of that sample to 16 nm. The observed mechanical response to rapid changes in electrical bias indicates dimensional oscillation in the PCO film that is driven by corresponding changes in oxide ion vacancy content.

### 2.2.5 Comparison with defect chemistry model

We next consider how chemical strain predicted for PCO films subjected to the conditions of this study relates to the displacement amplitude that was observed for all samples. Figure 2-6(c) shows that the expected equilibrium strain in these PCO films is 0.2 - 0.5\% (see Section 2.5.3) depending on applied bias and temperature; this estimate also includes a twofold increase in the strain of a constrained film as compared to a freestanding membrane.[16, 21, 7, 30] The above measurements are consistent with expectations shown in Fig. 2-6(c) from the PCO defect model: PCO is expected to contract upon a combination of decreased oxide ion vacancy and Pr\textsuperscript{3+} ion concentrations (oxidizing condition, positive bias), and expand for increased oxide ion vacancy and Pr\textsuperscript{3+} ion concentrations (reducing condition, negative bias).[21, 31] As the film is driven to expand in-plane, interfacial stress can drive substrate deflection at sufficient stress magnitudes and film lateral dimensions. Indeed, curvature was detectable (Section 2.2.2 and Fig. 2-3) for films of 8 mm in-plane dimensions as used in this study of PCO, while out-of-plane film expansion of \(~1\) nm (but not deflection) was detected for a PCO film of \(~1\) \(\mu\)m thickness but significantly smaller lateral dimensions at 650\(^\circ\)C (Section 2.2.1 and Fig. 2-2). Negative substrate curvature amplifies displacement due to film contraction, while positive substrate curvature amplifies film expansion. The observed increases in \(D_0\) caused by increased temperature or applied bias amplitude are also reasonable, in that these factors widen the equilibrium boundaries.
Figure 2-6: Factors controlling oxide film breathing. (a) Representative Arrhenius plots used to estimate the activation energy for YSZ diffusion and PCO chemical capacitance based on the values of $\tau/D_0$ (inverse deflection rate) and $D_0$ (deflection magnitude), respectively, identified from the mechanical measurements. These activation energies are comparable to those calculated based on in situ impedance spectroscopy. Data shown are for PCO film thickness $371 \pm 11$ nm. (b) Equilibrium magnitude $D_0$ of probe displacement increases with increasing temperature, applied bias amplitude $E_0$, and film thickness. Data correspond to $E_0$ of 128 mV unless otherwise noted. Where possible, error bars show the range of measured $D_0$ values for three replicate measurements. (All films at $E_0 = 128$ mV and $T = 650^\circ$C, highlighted by a red arrow, and all temperatures with $E_0 = 128$ mV for the film with thickness $1018 \pm 26$ nm, highlighted by black arrows.) This range is often smaller than the size of the data points. (c) Out-of-plane strain $\epsilon$ and non-stoichiometry change $\Delta \delta$ vs. applied bias at several temperatures for a constrained PCO thin film as predicted by the defect model for $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_2-\delta$. [20, 21, 29] (d) Measured deflection amplitude $D_0$ vs. predicted film thickness change based on chemical strains calculated in (c) for the set of measurements shown in (b). A consistent amplification of $5 \pm 0.5$ nm/nm ($\Delta D_0/\Delta \epsilon$) is observed across all samples, temperatures, and $E_0$ values, with error determined by bootstrapping as described in Appendix A.2. Figure from [1].
of accessed vacancy concentration and thus increase the mechanical response. Equilibrium or maximum displacement amplitude is thus proportional to film thickness.

2.2.6 High temperature oxide actuators

Materials that enable mechanical actuation and sensing in extreme environments are in high demand for applications including nuclear power control systems [32], jet turbine engines [33], and space exploration [34]. The artificial muscles required of these devices (e.g., electric motors and piezoelectrics) are often limited by material microstructural or compositional instability at high temperatures (> 200°C).[35, 36] The above work constitutes a demonstration of the functionality of non-stoichiometric oxide thin films as a new class of high-temperature, non-volatile, and low-voltage electromechanical actuators, using PCO as a model system.

To our knowledge, this is the first direct demonstration of such chemical-expansion-driven actuation at high temperatures by oxide films, with tens of nm cyclic actuation at hundreds of mV applied bias under sustained 650°C environments. Figure 2-6(d) shows that the detected displacement signal of the PCO film thickness change was consistently amplified over the expected breathing strains as computed in Fig. 2-6(c), by a factor of 5. This specific amplification factor is a function of the film lateral dimensions and substrate thickness, and could therefore be tuned accordingly. Additionally, the significant actuation amplitude observed under such extreme environments is repeatable for many cycles and on different samples, and can be tuned further by adjusting film thickness, operating temperature, or applied bias range. The effect described herein for PCO films at temperatures above 500°C is distinct from the electrostrictive effect described by Lubomirsky et al. for Gd-doped cerium oxide (GDC) at temperatures below 200°C.[37, 38] Those effects in GDC rely on oxygen vacancy ordering that would not be present at such high temperature, would require much larger electric fields than applied in the present study, and would not be polarity dependent.

The deflection profile of actuators based on PCO or other non-stoichiometric oxides can be tuned by shifting pO$_{2,\text{eff}}$, which can be accomplished either through changing gas environment or applying DC bias. Figure 2-7 shows this effect for the model system PCO. Referring to Fig. 2-6(c), we note that the relationship between $\Delta \delta$ and pO$_{2,\text{eff}}$ is nonlinear. However, for higher temperatures and slightly reducing conditions, this dependence can be reasonably approximated as linear. The displacement profiles collected for these conditions clearly reflect the asymmetry in $\Delta \delta$ vs. pO$_{2,\text{eff}}$. Figure 2-1(c) illustrates this effect, where the oxidizing (positive) bias condition exhibits less displacement than the reducing (negative) bias condition. This is a direct result of the fact that the PCO film’s oxygen content saturates in highly oxidizing conditions - at some point, the film cannot absorb additional oxygen, and ceases to contract. In contrast, on the reducing side of the plot, PCO is not limited in this way for the range of pO$_{2,\text{eff}}$ used during these experiments, and therefore doesn’t reach a plateau in $\delta$. (However, we note that eventually in the reducing direction, the oxygen content will again reach a plateau upon full reduction of the Pr cations.) This effect is particularly noticeable for low oscillation frequencies, which come nearest to the equilibrium extremes of $\delta$.

The Lissajous plot, which is a way to visually compare periodic signals, is a useful construction for understanding these kinds of effects. If two signals $A$ and $B$ of interest...
overlap and are completely in phase, then a Lissajous plot of $A$ vs. $B$ will appear as a straight line with a slope corresponding to the unit conversion (amplitude ratio) between $A$ and $B$. If $A$ and $B$ have the same symmetry and frequency (e.g., sine waves with a fixed frequency) but are out of phase, then the Lissajous plot will be an oval with an area correlating with the relative magnitude of the phase lag. If two signals have different symmetry and the same frequency, then these differences will be apparent in the Lissajous plot as peaks, plateaus, and other deviations from the ovoid symmetry. It is this third case that is most interesting for the current discussion.

Figure 2-7 displays a pair of Lissajous plots (averaged over ten cycles at 0.05 Hz) of displacement vs. voltage for a film subjected to two conditions of DC bias $V_{offset}$ ($V_{offset} \pm 128$ mV, where $V_{offset} = 0$ and -90 mV) at 650°C. Considering first the case of $V_{offset} = 0$ mV, there was a clear displacement plateau for positive (oxidizing) bias, indicative of the oxygen saturation described above. However, applying a constant DC bias of -90 mV (roughly two orders of magnitude $pO_{2,eff}$) produced a more symmetric profile, with a larger total displacement amplitude and a minimal displacement plateau at either extreme. Thus, we demonstrated a way to tune the deflection profile of a high-temperature oxide actuator - by shifting the effective $pO_2$ through applying DC bias or changing the operando gas environment. This has two important implications. First, the operando gas environment will be an important parameter when designing high temperature oxide actuators, because different materials will exhibit linear defect chemistry vs. applied voltage for different $pO_2$ conditions.
regimes, and low power operation conditions will favor those materials that require minimal DC potential. Second, these oxide materials are also useful as oxygen sensors. This last point is not new; gas composition sensors based on Nernst electrical potentials generated by difference in pO\textsubscript{2} have been around for years.\[39] However, here we add that gas composition can also produce a mechanical signal - with implications for non-electronic, non-contact sensor architectures. This concept would be similar to using the curvature of a bimetallic strip of two materials with differing thermal expansion coefficients to detect temperature changes.

The electrochemically driven breathing response of these specific non-stoichiometric oxide films presents advantages for high temperature actuation. The predicted strain of these oxides at temperatures above 550\degree C is \sim0.1-0.2\% for applied biases of \sim0.1 V. Thus, sensors or actuators based on these materials could operate at much lower voltages than a typical high temperature piezoelectric device that requires electric fields on the order of MV/cm to produce strains of the same scale. As an example, we can compare a 1 \mu m film of a piezoelectric material with strain coefficient \(d_{11}\) of 10 pC/N (about the highest currently available for piezoelectrics operating above 400\degree C \[36\]) to a PCO-YSZ device with the same film thickness. For the piezoelectric, 100 V of electrical potential are needed to achieve a strain of 0.1\%, while for the PCO device only 100 mV are needed. If both devices are subjected to the same 100 mV, then the achievable actuator "velocity" (frequency \times displacement) will be roughly the same when the piezoelectric is operated at 1 kHz and the PCO device is operated at 1 Hz. Finally, the interfacial stress generated in response to equal applied bias in these devices of comparable size will likewise differ by three orders of magnitude if elastic properties are held constant allowing enhanced deflection-based actuation.

2.3 Application to perovskite \(\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\delta}\) (STF)

In this section, we show how measurements of this type may be extended to an alternative oxide material, namely \(\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_{3-\delta}\) (STF), a model perovskite-structured oxide of interest for applications including gas sensors and solid oxide fuel cells.\[40, 41\] Like PCO, STF is a mixed ionic-electronic conducting oxide for which extensive bulk defect models are available to predict defect chemistry under a range of oxygen partial pressures and temperatures.\[41, 8, 42\] However, STF has several key distinctions from PCO including a tendency to exhibit compositional instability in the form of Sr segregation at high temperatures, a somewhat smaller chemical expansion coefficient (only \sim0.04 \[40\] instead of 0.087 \[21\]), and for thin films, a large pO\textsubscript{2}-independent capacitance identified by impedance spectroscopy that is not well-explained by a single defect model. \[8, 43\] Additionally, at ambient atmospheres, STF maintains a large enough oxygen vacancy concentration that it may be more readily oxidized than PCO, producing a more symmetric displacement response to applied bias. The goals in presenting this case study are two-fold: First, to demonstrate high-temperature oxide actuation in an alternative system to PCO, highlighting ways in which such electrochemically-induced actuation may be tuned, and second, to showcase features of dynamic chemical expansion that may be detected using this kind of measurement approach in a less well-behaved system than PCO.

For this study, 300 nm films of STF were grown by pulsed laser deposition on 0.5 mm-thick yttria stabilized zirconia (YSZ) substrates. The thinner substrate as compared to the
previously discussed PCO samples enabled appreciable displacement detection despite the lower chemical expansion coefficient and film thickness for STF. Additionally, the characteristic times measured for the mechanical response of the STF films were generally faster for the same reason. Figure 2-8 shows the electrochemomechanical admittance spectra obtained for STF under a few conditions of temperature and effective oxygen partial pressure. Like PCO, STF exhibited a single semi-circular arc, which is to be expected given the comparable sample construction. As for PCO, the diameter for this arc should correspond to the maximum predicted chemical expansion at 0 frequency, while the frequency located at the arc maximum is indicative of the characteristic mechanical response time at that condition. In the case of STF, it is clear that $pO_{2,eff}$ has a larger impact on the arc diameter than does the temperature. In fact, bulk models of STF predict slightly decreased chemical expansion for the same change in applied bias with increased temperature, a trend that is reproduced in these data. The time constant, in contrast, is significantly affected by temperature; this is because increased temperature activates the rate-limiting oxide ion diffusion step in the YSZ substrate.

![Electrochemomechanical admittance spectrum of SrTi$_{0.65}$Fe$_{0.35}$O$_{3-\delta}$ at different conditions of effective mean pO$_2$ and temperature. Applying a positive DC bias makes pO$_{2,eff}$ one order of magnitude more oxidizing, resulting in a substantial change in the total displacement magnitude. From Ref. [2].](image)

Figure 2-8: Electrochemomechanical admittance spectrum of SrTi$_{0.65}$Fe$_{0.35}$O$_{3-\delta}$ at different conditions of effective mean pO$_2$ and temperature. Applying a positive DC bias makes pO$_{2,eff}$ one order of magnitude more oxidizing, resulting in a substantial change in the total displacement magnitude. From Ref. [2].

Based on available defect models for STF, shifting to an oxidizing pO$_{2,eff}$ ought to enhance the amplitude of the mechanical displacement response.[8, 42] However, Figs. 2-8 and 2-9 shows that this is opposite to what is observed for the deflection data. There are a few possible explanations for this: (i) the defect model does not accurately predict defect chemistry in the high pO$_2$ regime, (ii) the chemical expansion coefficient in the high pO$_2$ regime is smaller than elsewhere for the same changes in defect content, or (iii) a leakage current present in the high pO$_2$ regime prevents the full reversible expansion effect from being realized. In principle, combinations of these three explanations are also possible. By comparing the displacement Lissajous profiles to the charge Lissajous profiles, we can begin to tease out the source of this discrepancy.
Figure 2-9: Lissajous plots of (a) displacement and (b) charge vs. applied bias for three $V_{\text{offset}}$ conditions. These experiments were conducted at 630°C, with an applied bias amplitudes of 128 mV centered around 0, 40, or -40 mV. When $V_{\text{offset}}$ is 40 mV (oxidizing condition), there is a slight plateau in the displacement signal for positive biases that is indicative of film saturation. However this effect is much less severe than was observed for the PCO films in Fig. 2-7. When pO$_{2,\text{eff}}$ is shifted in the reducing direction ($V_{\text{offset}} = -40$ mV), this plateau largely disappears and a more symmetric displacement vs. bias profile results, along with a slight increase in the total displacement amplitude. Comparing the charge and displacement Lissajous plots, we see that the plateau effect at positive biases is not apparent for the charge plots, or that the displacement is not necessarily proportional to charge flow. This indicates that there must be a charge storage mechanism in the STF sample that is not coupled to volume change.

Figure 2-9 presents this comparison for three conditions of pO$_{2,\text{eff}}$. Like for PCO, the STF displacement profile exhibited an oxygen-saturation plateau on the positive-bias side of the plot, which was mitigated mostly by a small DC bias of -40 mV. In contrast, the charge Lissajous plots showed a minimal plateau effect for the same regions. This means that for positive biases, charge continued to flow into the electrochemical cell without producing a mechanical signal. We note here that the charge and displacement Lissajous plots were both constructed from flattened data, meaning that leakage current and signal drift, respectively, were removed already. Therefore, this provides an example where charge storage (or capacitance) is not linearly coupled to chemical expansion. This could result from a change in the defect chemistry of the oxide at high pO$_{2,\text{eff}}$, or a different charge storage mechanism (such as an interfacial capacitance).[8] A more complete investigation of this effect is the subject of future work, combining displacement measurements, electrochemical measurements, and defect and kinetic modeling.

In this section, we demonstrated a second example of a high temperature oxide actuator, that of the perovskite STF. A comparison of Fig. 2-9(a) and Fig. 2-7 shows how this material selection impacts the high temperature oxide actuator’s linearity in different ranges of pO$_{2,\text{eff}}$. In oxidizing conditions, STF will produce a more linear displacement vs. $\Delta E$.
than PCO. However, PCO has a generally larger $\alpha_c$, meaning that it can produce larger strains as a function of changes in bias (or electric field). Additionally, this study of STF shows an important way in which NECS measurements can complement electrochemical measurements. NECS measurements are based on *mechanical signals only*, meaning that NECS can decouple charge storage or charge flow that couples to volume change (chemical expansion) from that which does not couple.

2.4 Conclusions and future work

Figure 2-10 summarizes this approach and the findings for PCO films at elevated temperature and dynamically oscillated oxygen content, driven by oscillating anodic and cathodic bias. The approach directly measures displacement, rather than lattice parameter changes as would be characterized by diffraction; it can be adapted depending on sample design to detect stress-amplified actuation or pure film strain on the scale of nm, including at *operando* high temperatures and gas environments. NECS can also be used to estimate changes in activation energy and breathing mechanisms in these or other functional oxide films (e.g., battery cathode materials) and multilayers as a function of composition or extreme environment, including the potential for spatially resolved mapping (Figs. 2-2 and 2-1). NECS also provides quantitative insights into the dynamic mechanical response of such materials to electrochemical driving forces, and should facilitate new understanding of materials and conditions that maximize or minimize stress, strain, and fracture under redox cycling or gas interruption for applications in fuel cells, electrolyzers, catalysis, or gas sensors, or in response to electrical signals or environmental stimuli for sensor or actuator applications. In the case of PCO, we found that reducing $pO_{2,eff}$ and elevating temperature enhanced chemical expansion effects. STF responded similarly to reducing $pO_{2,eff}$, but showed little (in fact, slightly opposite) dependence on temperature.

As with any experimental method, there exist some limitations to the NECS method implemented here. First, using NECS to acquire deflection-based measurements of quantitative chemical expansion (film strain as a function of applied bias) requires calibration of the relevant amplification factor for the sample geometry of interest. We suggest that PCO is an excellent model material for this purpose, due to the availability of accurate chemical expansion models for this material. For the geometry and attachment method of samples observed in this study (1 mm substrate thickness, 0.8 $\times$ 0.8 cm$^2$ film area) substrate deflection amplified the displacement signal by a factor of 5 relative to film thickness change alone, as highlighted in Fig. 2-6(d). The choice of electrode metal limits the temperature range for this method. For example, the use of silver paste to attach Pt wire to Pt electrodes set the maximum temperature for this study at $\sim$ 650°C. An alternative choice could raise that temperature. Additionally, samples that have very fast surface oxygen exchange (i.e. having exchange rates with characteristic times on the order of a few seconds) may experience oxygen leakage competing with electrochemical pumping; suggestions for mitigating this include use of blocking electrodes and designing samples where oxygen pumping is fast enough to overcome this limitation (e.g., by thinning the oxide ion conducting substrate).

In the context of these limitations, additional types of studies are possible, including those that probe the mechanical components of charge storage and transport in oxides separately from the electrochemical components. One important extension of the NECS
Figure 2-10: Schematic of processes occurring during direct chemical expansion measurement. The film (pink) on an oxide ion conducting substrate (white) is biased with respect to the reference electrode (gray circumscribed perimeter), oscillating between cathodic (negative, reducing) and anodic (positive, oxidizing) conditions. Under anodic bias, the film breathes oxygen in, producing an overall contraction and reduction in film thickness and corresponding negative substrate deflection. Under cathodic bias, oxygen is released from the film, resulting in increased oxide ion vacancy content (dark holes) and a corresponding increase in film thickness and positive substrate deflection. From [1].

Methodology involves an optical, non-contact approach to collecting similar types of data; we apply this adaptation to a Li-storage material (\(\text{Li}_{1-x}\text{Mn}_2\text{O}_4\)) in Chapter 6. In general, this is a useful, low cost way to quickly probe dynamic chemical expansion effects. For example, it might be of interest to observe whether capacity fade apparent in electrochemical measurements is also observable mechanically. If a film undergoes dopant segregation or similar compositional instability over time, does this impact its chemical expansion in a detectable way? How might the stress generated by a film undergoing electrochemical oxygen pumping vary when impurities or oxygen vacancies migrate preferentially toward grain boundaries, or when grain boundaries impede charge storage or transport? In this case, grain-size dependent measurements would be interesting. Along the same vein, how can nanostructuring be used to influence this stress generation? Furthermore, how do various types of impurities or dopants impact chemical expansion coefficients?[31] In systems with multivalent dopants, are there different regions of \(p\text{O}_{2,\text{eff}}\) (or equivalent Nernst electrochemical potential) that produce different expansion coefficients? This could be detected with a series of low bias-amplitude measurements conducted at multiple DC biases. These are just a few examples of the types of questions that might be answered through NECS, especially when combined with standard electrochemical testing and defect chemistry modeling.

Beyond this general methodology to directly measure nanoscale actuation under \textit{operando} conditions, the electrochemically driven breathing response of these specific non-stoichiometric oxide films presents advantages for high temperature actuation. For example, at a given material thickness of 1 \(\mu\text{m}\), the electrical bias required to produce 0.1% strain is effectively
reduced by three orders of magnitude for this PCO system as compared to state-of-the-art high temperature piezoelectric materials [36]; additionally, this actuation is accessible under sustained temperatures far exceeding those at which most piezoelectric actuators operate. Similar to a piezoelectric, the strain response of our system is reversibly proportional to the change in voltage, unlike other electrochemical devices that exhibit more step-wise behavior from multiple redox reactions. [44] The PCO actuator described herein acts as a model system; there are many chemomechanically coupled non-stoichiometric oxides that could operate according to the same principles, and even some that can combine the chemical expansion effect with a larger magnitude strain resulting from bias-induced phase change. [45, 14, 19] Furthermore, this actuator design has the advantage of non-volatile mechanical memory: if leakage is sufficiently limited (e.g., by blocking gas exchange), the device may be "frozen" in place upon disconnection of the circuit that permits ionic mobility. This opens up a new design space of high-temperature, low voltage micro-electromechanical systems based on a mechanism that couples electrical signals to mechanical stress and strain via material defect chemistry. Devices based on this alternative actuation mechanism are expected to be of interest to the design of robotics in extreme environments ranging from nuclear power plants to turbine engines to spacecraft.

These findings also highlight several key material properties that should be considered when designing any system that relies on an accurate understanding of deformation resulting from chemical expansion, including both actuators and strain engineered electrochemical devices. Firstly, the material’s chemical capacitance in the operando environment, as well as the chemical expansion coefficient, must be well-understood. Additionally, the elastic constants of the active film as a function of composition are relevant, as these will change the interfacial stress and film strain in situ. Finally, this kind of device requires an understanding of thin film specific chemical expansion, which may be anisotropic or result from defect chemistry different from that of bulk counterparts.

The operando chemical expansion for the model oxide film PCO and its relationship to chemical capacitance has been discussed in detail in this chapter, along with the first demonstration of high temperature oxide actuation, a positive potential application of chemical expansion in non-stoichiometric oxides. The following two chapters of this thesis describe experimental and computational modeling of elastic constants in the model film PCO as a function of operando environments and defect content. Chapter 5 reports a detailed high-temperature atomic resolution microscopy study of chemical expansion in a PCO film cross section, analyzing how interfaces, linear defects, oxidation state, and anisotropic chemical strain arise in this kind of structure. Understood collectively, these findings should present a complete picture of operando chemomechanical coupling in the model non-stoichiometric oxide, PCO.

2.5 Methods

2.5.1 Sample Design

Films of Pr$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ (PCO) with thicknesses of 371 ± 11, 600 ± 20, 883 ± 13, and 1018 ± 26 nm were grown by pulsed laser deposition (PLD) on single crystal (100) YSZ substrates (MTI Corporation, Richmond, CA) of dimensions 10 × 10 × 1.0 mm$^3$. Details of the PLD
film growth and characterization for thickness and crystal structure (by profilometry and X-ray diffraction) can be found in Ref. [1] and the associated Supplementary Material. Film surface roughness (root mean square) and grain size were 1.3 ± 0.2 nm and 2030 nm, respectively, obtained by atomic force microscopy (Digital Instruments Nanoscope IV, Veeco, Plainview, NY).

Films of SrTi$_{0.65}$Fe$_{0.35}$O$_{3-\delta}$ (STF) were prepared as described in Refs. [40] and [8].

Porous Pt layers, as the current collector for the PCO working electrode and as the counter electrode were prepared by a combination of Pt paste and reactive sputtering on the PCO film and the opposite PCO-free substrate surface, with thicknesses of 83 ± 4 nm and 159 ± 31 nm, respectively (as shown in Fig. 2-1). Porous Pt preparation procedures are described in detail in Ref. [46]. Pt paste was applied on the top of the sputtered PtO$_x$ layer except in the center area of the PCO working electrode, which was reserved for the mechanical response measurements (i.e., the region where the probe tip rested on the film surface). Pt paste was also applied to the outer perimeter of the YSZ substrate to serve as the reference electrode, with annealing procedures also described in Ref. [1]. The sputtered porous Pt layer was used to provide a thin layer with controlled thickness in the area for the mechanical measurement in addition to enhancing adhesion between the Pt paste and ceramic surfaces. There was no evidence of film delamination, as confirmed by subsequent FIB milling to expose the film/electrolyte interfaces for all samples investigated in this study.

2.5.2 Nanoscale electrochemomechanical spectroscopy measurement

Samples were mounted onto a high temperature stage (see Fig. 1-5(b)) by applying high temperature cement (Omega-bond 600) to the corners of the sample leaving a gap for gas flow to the counterelectrode. For the study of PCO, samples were heated at a rate of 1.6°C/min to temperatures 550, 575, 600, 625, and 650°C and allowed to reach equilibrium for at least 1 hour prior to testing. Samples were then brought into contact with a Berkovich-geometry, cubic boron nitride high-temperature probe using a MicroMaterials NanoTest Vantage instrumented indenter. Using the Modulab system (Solartron Analytical, Oak Ridge, TN) in conjunction with the Potentiostat (PSTAT 1Ms/s) and Frequency Response Analyzer (FRA 1MHz) module, sinusoidal electrical bias signals with amplitudes of 86, 128, and 171 mV were applied to the working electrode with respect to the reference electrode at frequencies of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, and 1 Hz. For $pO_2_{eff}$ testing, the following conditions of $V_{offset} \pm 128$ mV were tested at each condition: $V_{offset} = 0, -90$ mV. The mechanical response of the sample was measured by displacement of the probe detected by the instrumented indenter resting on the sample surface, with the minimum mechanical load necessary to maintain contact. Each driving frequency was run for a minimum of 35 periods to ensure that the fitting algorithm had measured the parameters of the response signal to suitable accuracy. Detailed discussion of the sensitivity of detected amplitudes and phase lags to experimental variation is available in Appendix A.2.

For the study of STF, films were heated to 685 and 630°C and tested for frequencies between 2 and 0.025 Hz. The following conditions of $V_{offset} \pm 128$ mV were tested at each condition: $V_{offset} = 0, 40, -40$ mV.
2.5.3 Chemical strain predictions

Chemical strain as predicted in Fig. 2-6 was computed based on the defect modeling information available for PCO in Refs. [16, 20] using a chemical expansion coefficient of 0.087 [21]. As discussed in Section 2.1, Eq. 2.2 describes the equilibrium of species for the oxygen vacancy formation reaction in PCO, Eq. 2.1. Enforcing charge neutrality, mass, and site conservation for the $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ composition after Ref. [16], (and using values of $H_{rP}$ and $k_r$ determined previously [21]), it is possible to determine vacancy concentration expected for this material at each temperature and $pO_{2,eff}$, where $pO_{2,eff}$ is determined according to Eq. 2.4. Based on these data, out-of-plane chemical expansion is predicted by assuming values based on a mechanically constrained film as compared to a freestanding membrane. More specifically, the out-of-plane strain $\epsilon_{c,z}$ is expected to be larger than the predicted strain $\Delta \epsilon$ of an unconstrained system under the same conditions by an amount described by Eq. 2.12, where $\nu$ is the Poisson’s ratio ($\sim 0.33$ [24]) and $\sigma_0$ is a reference stress:

$$\epsilon_{c,z} = \alpha \Delta \delta \frac{1 + \nu}{1 - \nu} - \frac{2\nu \sigma_0}{E} \tag{2.12}$$

To determine predicted chemical strain after assuming a reference stress of 0, Eqs. 2.7 and 2.12 combine to produce equation 2.13:

$$\epsilon_{c,z} = \alpha \Delta \delta \frac{1 + \nu}{1 - \nu} \tag{2.13}$$

Here, $\nu$ is the assumed PCO Poisson’s ratio of 0.33 and $\Delta \delta$ is the change in vacancy content $\delta$ with respect to a sample at the testing temperature and ambient $pO_2$ at 0 mV bias. Fig. 2-6(c) shows predicted $\epsilon_{c,z}$ and $\Delta \delta$ with single curves for each temperature and bias condition because these two factors are proportionally related. However, it should be noted that the $pO_{2,eff}$ values listed on the secondary x-axis are specific to 650°C.

2.5.4 Impedance testing

The asymmetrical cells used for the PCO mechanical measurement as illustrated in Fig. 2-1(a) were also investigated by electrochemical impedance spectroscopy (EIS) measurements conducted by Jae Jin Kim. The EIS measurements were conducted at temperatures between 500°C and 700°C in air and covered the frequency range from $\sim 1 - 10$ mHz to 1 MHz with an AC amplitude of 20 mV and no DC bias using the ModuLab system (Solartron Analytical) described above. The electrode impedance of both the PCO working electrode and the Pt counter electrode were separately investigated by using a three-electrode cell configuration including a reference electrode. ZView software (Scribner Associates) was used to fit and construct equivalent circuits to analyze the results. The equivalent circuit models used to analyze these samples have been validated previously on PCO-YSZ systems of the same configuration.[7] In addition to the activation energies reported above, impedance spectroscopy also showed that the PCO oxygen gas surface exchange reaction exhibited a considerably higher $E_a$ of $2.22 \pm 0.30$ eV, and that the area specific resistance at the counter electrode exhibited $E_a = 1.61 \pm 0.11$ eV.
2.5.5 Data processing and analysis

Input (driving) and output (displacement) signals were collected by USB-6009 DAQ (National Instruments) and a moving average across each driving cycle was subtracted to remove background noise.[48] Each of the two flattened signals was then fitted by linear least squares to a sum of sine and cosine waves according to Eqs. 2.14 and 2.15 to estimate the amplitude and phase lag of the displacement signal relative to the input signal:

\[ V_{\text{input}} = A \sin \omega t + B \cos \omega t \]

(2.14)

\[ V_{\text{output}} = C \sin \omega t + D \cos \omega t \]

(2.15)

where \( \omega \) is the known driving frequency.[49]

The transfer function magnitude and phase lag were calculated according to Eqs. 2.16 and 2.17 respectively:

\[ A = \sqrt{\frac{C^2 + D^2}{A^2 + B^2}} \]

(2.16)

\[ \phi = \tan^{-1} \frac{B}{A} - \tan^{-1} \frac{D}{C} \]

(2.17)

The fitting error was calculated according to equation 2.18:

\[ \frac{(MSE)}{D^TD}^{1/2} \]

(2.18)

where MSE is the mean squared error (the sum of squared residuals divided by the number of degrees of freedom) and \( D \) is the matrix of partial derivatives of the model evaluated at the final estimates.[48] These errors in A, B, C, and D were propagated with the equations above to determine the errors of the transfer function parameters.

At each experimental condition, oscillatory biasing (with real-time analysis) was conducted until the phase lag converged to within 0.1 radians and the amplitude to within 0.5 nm, typically exceeding 30 cycles. The measured phase lag \( \phi \) and amplitude \( A \) of the final 10 cycles of data were averaged for each frequency, and for a given condition (i.e., temperature and applied bias) the \( \phi \) vs. angular frequency \( \omega \) relationship was fit to Eq. 2.11 with one time constant \( \tau \) that was then used to fit the \( A \) vs. \( \omega \) results to Eq. 2.10 to determine an equilibrium amplitude \( D_0 \) at maximum applied bias. These steps were conducted using customized Matlab software available in Appendix E. These \( D_0 \) and \( \tau \) values were then used to estimate activation energies for the expansion signal as shown in Fig. 2-6(a), and the fitted value of \( D_0 \) was used to estimate equilibrium (zero frequency) mechanical response and determine the amplification factor. Reported activation energies are the average and standard deviation of at least six measurements across all three samples tested. Detailed discussion of the sensitivity of calculated \( D_0 \), \( \tau \), \( E_a \), and amplification factor values to experimental and sample-to-sample variation is available in Appendix A.2.

Lissajous plots of charge and displacement were produced using custom Matlab code available in Appendix E. Current was first integrated against time to produce charge vs. time data. Charge and displacement data were then flattened according to the moving
average procedure described above, and the output cyclic data vs. voltage were averaged over at least 10 cycles. Displacement and charge profiles were offset so that their minima match the minimum value for $V_{\text{offset}} = 0$ mV.
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Chapter 3

Operando Reduction of Young’s Elastic Modulus in (Pr,Ce)O$_{2-\delta}$ Thin Films

The previous chapter concluded by describing several key material properties required for accurate prediction of operando stress or strain in thin film non-stoichiometric oxides undergoing chemical expansion. This kind of prediction might be of interest to understand the most likely crack locations in multilayer devices subjected to extreme environments. Alternatively, it could be used to predict the strain state at an oxide interface, with the goal of understanding and perhaps engineering the attendant consequences for defect equilibria and charge transport kinetics. For any of these predictions, understanding of both chemical strain and elastic constants is essential. Additionally, these magnitudes must be determined for the operando conditions of the device, motivating the present study.

In this chapter, we explore electrochemomechanical coupling experimentally for the model non-stoichiometric oxide (Pr, Ce)O$_{2-\delta}$ (PCO). Using environmental nanoindentation, we quantified Young’s elastic modulus $E$ of PCO thin films in situ, at temperatures up to 600°C and oxygen partial pressures pO$_2$ as low as $10^{-3}$ atm. We used statistical analysis to assess the significance of observed changes in $E$. The observed significant reduction (up to 40%) in $E$ with increased temperature or decreased pO$_2$ correlated with changes in oxygen vacancy concentration $\delta$ and lattice parameter $a$ expected due to chemical expansion. However, the experimentally observed decrease in $E$ vs. pO$_2$ and temperature was more extreme than predicted by bulk computations (see Chapter 4) or available literature. This result is discussed in the context of operando differences between bulk and thin film non-stoichiometry and elastic and plastic properties. These results demonstrate that accurate models of deformation in thin-film devices comprising chemomechanically coupled non-stoichiometric oxides may differ markedly from bulk counterparts. To be predictive quantitatively, those models must reflect significant, reversible decreases in elastic moduli resulting from increased temperature and decreased pO$_2$.

Much of this work was published previously in Acta Materialia [1] and ECS Transactions [2]. Jae Jin Kim of the Crystal Physics and Electroceramics Laboratory of Professor Harry Tuller prepared samples for this study. This work was conducted concurrently with density
functional theory calculations of elastic modulus in PCO; the results of those calculations are presented and discussed in Chapter 4.

3.1 Introduction

As highlighted in detail in Chapter 1, mechanical durability has been a significant challenge impeding solid oxide fuel cells (SOFCs) from achieving widespread commercialization. A second important challenge, that of lowering SOFC cost by decreasing operating temperatures, has led researchers to develop μ-SOFCs that rely on thin film components, of μm-scale film thickness, and to attempt to use strain engineering, a strategy that relies on chemomechanical coupling, to improve device efficiency.[3, 4, 5, 6, 7] Before strain engineered materials can be incorporated effectively into active device architectures, however, it will be necessary to understand fundamental relationships between operando environments and material mechanical properties, specifically elastic constants, in order to prevent mechanical failures and optimize in situ strain or stress states. Thus, in the current chapter, we measure how Young’s elastic modulus $E$ responds to changes in temperature and pO$_2$ in our model system, PCO.

This project is also motivated from the more fundamental perspective of trying to understand chemomechanical coupling in thin film non-stoichiometric oxides. As noted in the previous chapter, electrical driving forces can stimulate chemical expansion in non-stoichiometric oxides, which in turn drives mechanical deformation that may or may not be desirable.[8] As electrochemical driving forces impact material stoichiometry, they also impact material volume. Simultaneously, composition changes modulate other functional properties including ionic conductivity and gas exchange coefficients.[9, 10] But how do these changes affect mechanical properties? Canonical intuition for mechanics in crystalline materials suggests that changes in point defect concentration will affect strength or toughness, while having relatively little impact on mechanical stiffness.[11, 12] While this intuition is accurate for many crystalline materials (e.g., metals, semiconductors) at room temperature, we shall see that this is not the case for non-stoichiometric oxides at elevated temperatures.[13, 14] Moreover, given observations from the literature about differences in non-stoichiometry and other properties between thin film and bulk oxides of the same nominal composition, are in situ mechanical properties, specifically elastic moduli, also impacted differently at these disparate length scales?

Section 1.4 introduced the general expectation that lattice dilation due to thermochemical expansion should lead to decreased Young’s elastic modulus. The reasoning for this essentially arises from the fact that increased lattice parameter tends to weaken atomic bonding, thus causing a decrease in Young’s elastic modulus $E$ and other types of elastic moduli that relate resistance to bond stretching. This result has been observed previously by both in situ and ex situ studies on bulk forms of certain non-stoichiometric oxides including (Gd,Ce)$_2$O$_{2-\delta}$, (La, Sr)(Co,Fe)$_3O_{3-\delta}$ (LSCF), and Y$_{0.15}$Zr$_{0.85}$O$_{2-\delta}$ (YSZ) that exhibit lattice expansion correlative with elastic properties.[15, 16, 17, 18] Amezawa et al. found by acoustic emission that an increase in lattice parameter, due to either chemical or thermal expansion, led to a decrease in the elastic modulus $E$ in bulk GDC, a result that was highlighted in Fig. 1-3.[15] This trend has also been replicated with molecular dynamics simulations using interatomic potentials.[19, 20] At the time of this work, the question of
whether Pr reduction results in detectable and significant changes in the elastic modulus of (Pr, Ce)O$_{2-\delta}$ had not yet been established. However, together, the above studies suggest that Pr reduction could lead to a decrease in $E$ of PCO, directly influencing how stress will increase with increasing strain in oxide components subjected to elevated temperatures or oxygen partial pressure gradients.[16, 21]

Few studies have explored how chemical expansion may impact mechanical properties of thin films, particularly in situ and in contrast to bulk counterparts.[22] As introduced in Section 1.5, thin films may differ from bulk oxides in the extent of coupling between electrochemical reduction and mechanical properties, due to the influence of strain at the film-substrate interface, the potential for differing point defect concentrations from bulk due to space charge effects or enhanced reducibility at surfaces and grain boundaries, and the possibility of anisotropic expansion resulting from a clamped geometry.[23, 24, 25, 26, 27] Methods for detecting elastic properties of thin films are limited: tensile tests and acoustic methods require bulk samples, while Raman spectroscopy can be substantially complicated by local strain or stress states in materials, or require extensive material modeling to understand the sources of individual features.[28, 29, 30, 31, 32] In contrast, nanoindentation is a widely used technique that includes relatively straightforward data interpretation and is now capable of data acquisition at high temperatures in controlled gas atmospheres.[33]

In the work presented in this chapter, we quantified the elastic modulus of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO) thin films via in situ nanoindentation under controlled temperature (24 - 600°C) and oxygen partial pressure (pO$_2$ of 0.2 - 7.6x10$^{-4}$ atm), to approximate operando conditions of SOFCs. We correlated these results with oxygen vacancy concentration via the point defect and chemical expansion model for bulk PCO.[34, 35, 9] Due to the challenges associated with nanoscale mechanical measurements at such elevated temperatures, we included statistical analysis to identify significant changes in $E$ as a function of composition, temperature, or pO$_2$.[2] These results demonstrated that $E$ decreased significantly with increasing lattice parameter $a$. This increase in $a$ was concurrent with increased oxygen vacancy concentrations quantified by the non-stoichiometry parameter $\delta$, which was modulated by increased temperature and decreased pO$_2$. The lattice expansion-associated reduction in $E$ of these Pr-doped CeO$_2$ thin films significantly exceeded that reported for bulk Gd-doped CeO$_2$[15], a result which we attributed to differences in film vs. bulk non-stoichiometry in situ.

### 3.2 Experimental results

#### 3.2.1 Film validation and room temperature Young’s modulus and hardness

CeO$_{2-\delta}$ and Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ thin films, deposited to $\sim$1 $\mu$m thickness on (001) YSZ substrates as described in Section 3.5.1, were highly (001) textured as evidenced by X-ray diffraction, and exhibited a root-mean-square surface roughness of <0.5 nm as measured via atomic force microscopy. This notation for PCO indicates Pr content of $x = 0.2$ or 0.1, and non-stoichiometry parameter $\delta$ that varies with the physical environment and resulting oxygen vacancy content.

At room temperature, we measured both Young’s elastic modulus $E$ and hardness $H$ for all three composition of PCO ($x = 0$, 0.1, and 0.2), but at high temperature we tested only
Table 3.1: Literature values of elastic modulus $E$ and nanoindentation hardness $H$ of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>$n$</th>
<th>$E$ (GPa)</th>
<th>$H$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\geq 49$</td>
<td>264.1 ± 2.2</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>0</td>
<td>$\geq 8$</td>
<td>263 ± 28</td>
<td>5.3 ± 0.6</td>
<td>[36]</td>
</tr>
<tr>
<td>0.1</td>
<td>$\geq 8$</td>
<td>288 ± 21</td>
<td>7.8 ± 0.3</td>
<td>[36]</td>
</tr>
<tr>
<td>0.2</td>
<td>$\geq 8$</td>
<td>274 ± 25</td>
<td>8.7 ± 0.5</td>
<td>[36]</td>
</tr>
</tbody>
</table>

the extremes of this composition range. Table 3.1 lists previously reported literature values for $E$ and $H$ of bulk CeO$_2$ and PCO at room temperature measured by nanoindentation, and Fig. 3-1 reports the values measured for our samples. We compared indentation sets using analysis of variance (ANOVA, as described in Appendix A.3) to assess statistical differences; no statistical difference in $E$ was detectable among the three compositions at room temperature.

This result is not unexpected for these oxidized PCO films. At room temperature, the vacancy concentrations of PCO are so low ($\delta < 10^{-2}$) that defect-induced chemical expansion effects would not be expected to impact $E$ detectably even at $x = 0.2$.\cite{35,10} The undoped CeO$_2$ film exhibited $E = 264.0 \pm 2.2$ GPa, and compared well with the $E$ reported by Wang et al. for bulk CeO$_2$ (264.1 ± 2.2 GPa) that was also measured at room temperature via nanoindentation.\cite{16} We measured $E$ for $x = 0.1$ and 0.2 at 265.0 ± 2.8 GPa and 276.5 ± 7.7 GPa, respectively, also comparing well with previously reported results for bulk samples of these compositions.\cite{36}

As shown in Fig. 3-1(b), $H$ (8.2 ± 0.1 GPa) of undoped CeO$_2$ was significantly different from that of the doped samples (10.2±0.1 GPa and 10.9±0.3 GPa for Pr-doping $x = 0.1$ and $x = 0.2$, respectively, tested via ANOVA). Hardness of both doped samples was statistically indistinguishable. These hardness magnitudes were consistently but slightly greater than previously reported values for bulk samples of these compositions at room temperature.\cite{36} In both these measurements and previously reported results for bulk samples, Pr-doping correlated with increased hardness as compared to undoped counterparts; although this is reminiscent of solid solution strengthening of metallic alloys, dislocation motion is not considered a predominant mode of plastic deformation in these comparably brittle systems, especially at room temperature.

We conducted Bonferroni-corrected Welch’s $t$-tests to compare measured $E$ and $H$ for thin films to values reported previously for bulk samples (Table 3.1) as mean ± standard deviation.\cite{16,36} The Bonferroni correction is applied when multiple $t$-tests are conducted to account for the increased chance of false positives. In this case, we conducted four $t$-tests for $E$ because two independent experiments were available for the undoped CeO$_2$ composition, and we conducted three $t$-tests for the $H$ results. The number of replicate measurements was estimated for prior reports of bulk samples at each composition, and considered to be the minimum number possible according to the description of experimental procedures in those works. For $E$, all thin film sample results at room temperature were statistically indistinguishable from bulk counterparts. For $H$, all values measured for thin film samples
Figure 3-1: Elastic and plastic properties of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ at room temperature and in air. (a) Young’s elastic modulus $E$ is not statistically different as a function of Pr content $x$ at a significance level $\alpha$ of 0.05. However, (b) nanoindentation hardness $H$ increases with addition of Pr to a statistically detectable degree. Error bars indicate standard error of the mean. From [2].

were significantly larger than those reported for bulk counterparts ($p < 0.005$).

Unlike the bulk samples that were reported to exhibit grain sizes on the scale of $\mu$m, our thin film samples were nanocrystalline (grain size $\sim$50 nm). The increased resistance to plastic deformation of the thin films could be attributable to grain boundary strengthening associated with grain size reduction, again with limited analogy to plasticity in polycrystalline metals that deform by line- and surface-defect motion. Further studies are needed to confirm these hypotheses.

Overall, our room temperature measurements for $E$ are in excellent agreement with other reported values of $E$ for bulk samples measured by nanoindentation at room temperature for bulk Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ ($x = 0, 0.1, 0.2$ [36]) and undoped ceria [16]. At room temperature, therefore, $E$ of our as-deposited thin films matched previously reported bulk values, validating this measurement technique for evaluating the mechanical properties of thin films.

3.2.2 Elastic moduli under operando temperature and oxygen environments

We conducted operando indentation tests on the samples with $x = 0$ and 0.2 in air at 300 and 600°C and at two additional $pO_2$ levels at 600°C. That is a sufficiently high temperature that oxygen exchange should be active in PCO, allowing non-stoichiometry equilibration in situ. When the temperature increased from 25 to 300°C, the measured Young’s modulus decreased to $228.1 \pm 4$ GPa for CeO$_2$ and $216.5 \pm 4.6$ GPa for Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$. This reduction is attributed to thermal expansion. When the oxygen partial pressure decreased from 0.2 to 7.6 x $10^{-4}$ atm at a constant temperature of 600°C, $E$ of Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ decreased significantly
from ~250 GPa to 150 GPa (Fig. 3-2(a)). In fact, this Pr-doped ceria also exhibited statistically significant decreases in $E$ at 600°C and an intermediate pO$_2$ of 7.5x10$^{-3}$ atm as compared to room temperature in air. No significant change was identified for CeO$_{2-\delta}$ over this change in atmospheric conditions at 600°C. According to the defect model of bulk Pr$_x$Ce$_{1-x}$O$_2-\delta$ described by Bishop et al., the above decrease in oxygen partial pressure at 600°C corresponds to a change in oxygen vacancy content $\Delta \delta$ of 0.04 for Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$, and $4 \times 10^{-7}$ for CeO$_{2-\delta}$.[9]

To facilitate comparison between the undoped and Pr-doped ceria, Fig. 3-2(b) shows the percentage change in $E$ at 600°C relative to that measured for the sample of the same composition at that temperature in air. The 38 ± 11% decrease in $E$ observed with reduced oxygen partial pressure for Pr-doped ceria was statistically significant, while the apparent decrease in $E$ observed for ceria upon this pO$_2$ excursion was not.

Figure 3-2: (a) Young’s elastic moduli $E$ of (Pr, Ce)O$_{2-\delta}$ thin films measured via environmental nanoindentation at 600°C. $E$ decreases with decreased oxygen partial pressure at 600°C. The decrease in $E$ observed for Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ at 7.6x10$^{-4}$ atm pO$_2$ with respect to air (0.21 atm) is statistically significant with $\alpha < 0.05$ (denoted by bracket marked ()), while no significant change in $E$ is observed with decreased pO$_2$ for undoped ceria. Non-bracketed points for the same sample are statistically indistinguishable. (b) The % decrease in $E$ for (Pr, Ce)O$_{2-\delta}$ thin films relative to the value measured for the same composition at 600°C in air is larger for Pr-doped ceria when the oxygen partial pressure decreases from 0.2 atm to 7.6x10$^{-4}$ atm. For both (a) and (b), error bars are standard error of the mean. Figure adapted from [1].

3.2.3 Relation of elastic properties to oxygen vacancy concentration and lattice parameter

This reduction in $E$ of Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ with decreasing pO$_2$ at constant temperature of 600°C can be expressed in terms of increasing non-stoichiometry or oxygen vacancy content $\delta$, where
δ is derived from the established defect model for PCO.[9] Figure 3-3(a) illustrates this reduction in mechanical stiffness with increasing vacancy concentration in Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$. Here, open symbols indicate $E$ measured at room temperature in air, for reference. Note that $\delta$ is several orders of magnitude lower in undoped CeO$_{2-\delta}$ than in Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$; thus, increases in $\delta$ associated with decreased pO$_2$ are more apparent on this scale for Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$. In contrast to the marked reduction in $E$ as a function of pO$_2$ at 600°C, undoped ceria did not exhibit statistically distinguishable changes in $E$ upon reduced pO$_2$. In other words, a significant decrease in the magnitude of $E$ was found only when the oxygen vacancy content $\delta$ was also altered significantly via the environmental conditions, as afforded by the greater reducibility of Pr. This relatively stronger response of PCO to elevated temperature and reduced oxygen partial pressure is not wholly unexpected, in that Pr reduction facilitates a greater increase in vacancy concentration relative to undoped ceria.

This decrease in $E$ can also be considered in terms of the lattice parameter $a$, which can increase due to thermal and/or chemical expansion and is determined as a function of coefficients of thermal and chemical expansion and $\delta$ (see Section 3.5.4). Lattice parameter changes with respect to room temperature in air were estimated from a combination of the predicted vacancy content change $\Delta \delta$ coupled to the chemical expansion coefficient of (Pr, Ce)O$_{2-\delta}$ reported in Ref. [34] and the thermal expansion coefficient of CeO$_{2-\delta}$ reported in Ref. [37]. Fig. 3-3(b) shows that, over the range of lattice parameters resulting from change in temperature and/or oxygen partial pressure, $E$ generally decreased with increasing $a$ for both ceria and Pr-doped ceria thin films. The effective slope of this $E(a)$ correlation, in terms of percentage decrease in $E$ per 1% increase in lattice parameter, was 42±10% for undoped ceria and 36±8% for Pr-doped ceria. Figure 3-3(b) also includes, for comparison, the relatively weaker trend of decreased $E$ with increased $a$ that was reported previously for bulk samples of CeO$_{2-\delta}$ and Gd$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ [16]. Note that those prior measurements of bulk samples were ex situ, in that samples were quenched to retain vacancy concentrations and then tested via nanoindentation at room temperature in air.[16] As discussed below, the greater apparent uncertainty in $E$ at larger lattice parameters for results in the present study as compared to Ref. [16] arises in part from experimental design differences and from the practical challenges of conducting in situ nanoindentation at elevated temperature, though the same trend of decreasing $E$ with increasing $a$ is apparent.

3.3 Discussion

We sought to determine whether and to what extent the elastic properties of PCO thin films may be altered under operando conditions known to promote chemical expansion, and found that indeed the elastic moduli of Pr-doped ceria decreased significantly at the high temperatures and low oxygen partial pressures typical of solid oxide fuel cell conditions. In fact, these in situ nanoindentation measurements demonstrated that $E$ of undoped ceria and PCO thin films decreased with increasing lattice parameter, driven by both thermal and chemical expansive effects. The decrease in $E$ has been observed previously in bulk samples of ceria-based materials and has been attributed to the weakening of resistance to bond stretching, as bond length increases upon thermochemical expansion.[21, 38] The reduction in $E$ per unit increase in lattice parameter was larger for our in situ experiments as compared to previous measurements of $E$ for other functional oxides in bulk form, and
Figure 3-3: (a) In situ nanoindentation measurements of Young’s elastic modulus $E$ vs. non-stoichiometry $\delta$ of $(\text{Pr}, \text{Ce})O_{2-\delta}$ thin films at $600^\circ\text{C}$, where $\delta$ is increased by decreasing oxygen partial pressure $p_{\text{O}_2}$. Open symbols indicate for reference room temperature measurements from Ref. [2] and Fig. 3-1. Increases in $\delta$ associated with decreased $p_{\text{O}_2}$ are more apparent on this scale for $\text{Pr}_{0.2}\text{Ce}_{0.8}O_{2-\delta}$ and correlate with decreasing $E$ because $\delta$ is orders of magnitude larger in $\text{Pr}_{0.2}\text{Ce}_{0.8}O_{2-\delta}$ than in $\text{CeO}_{2-\delta}$. (b) $E$ decreases with increasing lattice parameter $a$. For $\text{CeO}_{2-\delta}$, the change in $E$ observed is attributed to thermal expansion as temperature increases. $\delta$ is estimated according to the defect model in Ref. [9] and $a$ is calculated as described in Section 3.5.4. For both (a) and (b), error bars are standard error of the mean, and may appear smaller than data points. Shown for comparison (open symbols) are the values of $E$ ($\pm$ standard deviation) reported in Ref. [16] for bulk $\text{CeO}_{2-\delta}$ and $\text{Gd}_{0.1}\text{Ce}_{0.9}O_{2-\delta}$ measured at room temperature in air (ex situ conditions) for samples with oxygen vacancy concentration varied by quenching from high temperature. Figure adapted from [1].

as compared to our own DFT predictions which will be discussed in the following chapter. These differences may be attributable to several possible factors, relating to both technical aspects of the measurement and unique characteristics of these chemomechanically coupled oxides in thin-film form.

3.3.1 Technical challenges of high temperature nanoindentation

First, we note that in situ nanoindentation measurements of thin films at such elevated temperatures and controlled atmospheres include certain technical challenges [39, 40, 41]. The uncertainty in measured $E$ was greater at elevated temperatures than at room temperature, as indicated by the standard error of the mean denoted in Fig. 3-3(a). For this reason, statistical analysis of calculated elastic moduli for each set of samples and conditions was employed to identify significant changes in $E$ as a function of elevated temperature, reduced oxygen partial pressure, and initial composition. The relatively higher variance at extreme
temperatures is attributed chiefly to uncertainty in the accuracy of the probe geometric area function (contact area calibrated as a function of contact depth, as discussed below), and to slight differences in absolute temperature at the probe-sample interface for each replicate indentation site acquired over a span of 16-24 hr on a given sample surface.[39, 41] Further discussion of sources of variance in high temperature indentation measurements can be found in Section A.3.2. Results presented herein include only thermally well-matched experiments, meaning that temperature stability was achieved for both the probe and sample in contact, as described in Reference [42].

Over the extended durations at elevated temperatures required of such experiments that systematically varied pO$_2$ for a given sample, the boron nitride probe geometry was not invariant. This probe material was selected for its stability at high temperatures [43, 44], but repeated experiments on standard samples (fused silica after cooling to room temperature, or inconel at elevated temperatures) indicated detectable variations in the contact area relation $A(h_c)$ employed in Eq. 3.2. Accurate measurement of $E$ does not require that $A(h_c)$ is constant among all sample sets, only that it is known. We determined this function experimentally before and after acquiring each set of indentations at each condition, to minimize contributions to variance in $E$ from changes in probe geometry. However, this variance in measured $E$ motivated detailed statistical analysis to objectively identify significant changes in film stiffness with either temperature or pO$_2$ (see Section 3.5.3, Appendix A.3 and Ref. [2]). Further, although there is potential for degradation of the sample (via cracking or surface contamination upon heating) to affect measured $E$ in such films, these factors did not measurably contribute to the recorded changes in $E$. Films were deliberately heated and cooled at the slow rate of 1.6°C/min to avoid thermal and/or chemical expansion-induced shock, and no evidence of significant crack concentrations or delamination was observed on post-tested samples by optical microscopy. Additionally, we identified no correlation between changes in elastic moduli and the duration that a sample was exposed to high temperature and/or specific pO$_2$, as would be consistent with surface contamination. We also did not detect changes in loading curvature or pop-in events that would be indicative of cracking, delamination, or contributions from a surface contaminant in the load-depth hystereses analyzed herein. Thus, such possible contributions to marked reduction in $E$ of PCO at high temperature and low pO$_2$ appeared minimal. In summary, notwithstanding the technical challenges associated with heating and indenting these ceria-based films that could lead to appreciable variance in mean elastic modulus, the above calibration and control experiments support the primary finding: operando elastic modulus of PCO films decreased significantly with increasing non-stoichiometry $\delta$, from ~250 GPa in air at room temperature to ~150 GPa in ~10$^{-3}$ atm pO$_2$ at 600°C.

3.3.2 Comparison of experimental results to bulk non-stoichiometric oxides

Second, we can compare these results for PCO thin films to those of related functional oxides in bulk form. As highlighted in Fig. 3-3(b), via nanoindentation Wang et al. reported decreasing $E$ for increasing lattice parameter, for bulk CeO$_{2-\delta}$ and Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-\delta}$ (Gd-doped ceria, often termed GDC rather than GCO) at room temperature; in those studies, vacancy concentrations within the room temperature samples were varied by quenching
from higher temperatures with correspondingly varying oxidation states.[16] The reported magnitude of $E$ is comparable for the most oxidized of these bulk samples (smallest $a$) to our own measured $E$ for thin films at room temperature; however, the rate of decrease in $E$ per increase in $a$ ($\sim 23\%$ decrease in $E$ per 1% increase in $a$) was weaker than that observed for our thin film samples. This weaker dependence of $\Delta E$ as a function of $\Delta a$ in bulk samples was also reported for GDC under *operando* conditions by Amezawa et al.[15] Those authors quantified $E$ for bulk GDC via acoustic measurements, over a range of temperature and $pO_2$ that correlated with changes in lattice parameter $a$ [15]. For that bulk oxide, they found that $E$ decreased from 190 GPa to 150 GPa as $a$ increased from $\sim 5.42-5.48$ Å. In that sense, undoped (bulk and thin film), Gd-doped (bulk) and Pr-doped ceria (thin films analyzed herein) showed decreased stiffness with increased lattice parameter brought on by changes in external physical environment. However, we note that the severity of this change was less pronounced in the bulk GDC over this change in $a$, with only $\sim 13\%$ reduction in $E$ for a 1% increase in lattice parameter. This comparison simply shows that it is reasonable that $E$ decreases with increasing lattice parameter in such functional oxides by 10s of GPa in *operando* conditions, and does not resolve whether the extent of this reduction is attributable chiefly to differences in composition (dopant species) or sample geometry (bulk or thin film). In principle, both factors can affect the vacancy concentration as a function of physical variables, which in turn affect $a$ and $E$. We discuss these factors in more detail in Chapter 5, which concerns atomic resolution transmission electron microscopy imaging of thin PCO film cross-sections during chemical expansion.

![Figure 3-4: Vacancy content $\delta$ varies in Pr-doped ceria as a function of oxygen partial pressure $pO_2$ at 600°C. The vacancy content of thin films is consistently higher than in bulk counterparts of the same volume-averaged composition. Optical data are from Ref. [45], thin film chemical capacitance ($C_{chem}$) and thin film model data are from Ref. [23], and bulk thermogravimetric analysis (TGA) data and model are from Ref. [34]. Figure from [1].](image)

Indeed, the vacancy concentration of PCO thin films typically exceeds bulk counterparts, as has been demonstrated previously and is highlighted in Fig. 1-6(b).[23] Fig. 3-4 illustrates this in terms of the non-stoichiometry parameter $\delta$ for Pr-doped ceria ($\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$, a different composition than measured here) as a function of oxygen partial pressure at
600°C. The vacancy content was consistently greater in thin films of <1 μm thickness as compared to bulk PCO with the same average Pr-content.[34, 23, 45] Although the full quantification of why such differences in point defect concentrations in non-stoichiometric oxide films and bulk exist is beyond the scope of the current study, it is attributed plausibly to relatively greater contributions of regions such as the film surface and film-substrate interface that could cause space charge depletion/accumulation or exhibit higher levels of reducibility.[26, 27, 46, 47, 48] Additionally, as PCO is cubic and elastically anisotropic, in these (100) textured films, together the elastic anisotropy and strong texturing of this material may serve as additional sources of variation between indentation-extracted elastic moduli of the bulk and thin film forms.

Finally, we note that thin films may also exhibit lower $E$ relative to bulk counterparts of similar composition due to constrained chemical expansion of the film upon increasing oxygen vacancy content. This idea of anisotropic chemical expansion for constrained films was also introduced in the previous chapter. As in-plane expansion of the adherent thin film is constrained, theoretically, by the substrate, the chemical expansion coefficient $\alpha_c$ is amplified out-of-plane (normal to the film-substrate interface) by a factor of $(\nu + 1)/(\nu - 1)$, where $\nu$ is the Poisson’s ratio of the film.[49, 27] A typical estimate of $\nu$ from bulk measurements of other oxides is $\sim 0.33$ [15], providing an estimated amplification of out-of-plane chemical expansion in PCO that could range up to twofold. The fact that the films in Chapter 2 were able to drive substrate actuation supports the expectation of anisotropic chemical expansion in films equilibrating their composition by simple gas exchange, because stress will only be generated at the interface if there is a mechanical constraint. Although this anisotropic expansion cannot be related directly to changes in $a$ and $E$ measured via indentation, we note the tendency for effective $a$ to increase upon such constrained expansion and that $E(a)$ did increase approximately twice as much in experiments on thin films as was reported from previous experiments or predicted via our DFT calculations for bulk PCO discussed in the next Chapter. This suggests an alternative and perhaps additional mechanism by which $E$ of thin films decreases to a greater extent than predicted or measured for bulk counterparts.

Taken together, these experiments and calculations demonstrate that thin films of functional oxides such as Pr-doped ceria exhibit significant reduction in mechanical stiffness with increasing oxygen vacancy content, mediated by changes in the lattice parameter $a$ under operando conditions. This change is more pronounced in Pr-doped ceria thin films than in previous reports for bulk Gd-doped ceria under similar conditions, and we attribute this chiefly to the relatively greater vacancy content (sample reduction) and effective lattice parameter of thin films as compared with bulk functional oxides of similar dopant content $x$. Such deviation would cause the predicted lattice parameter and oxygen vacancy content $\delta$ to be underestimated, meaning that the change in $E$ vs. $\Delta T$ or $\Delta pO_2$ would be underestimated as well based on bulk models or available data. However, additional factors may also play a role in the apparent differences between film and bulk oxides; these include anisotropy and higher densities of other types of defects such as interfaces, grain boundaries, and surface regions.
3.4 Conclusions and future work

The Young’s elastic modulus $E$ of thin films of (Pr, Ce)O$_{2-\delta}$ was measured by nanindentation at temperatures up to 600°C, and at 600°C at oxygen partial pressures between 0.2 and 7.6 x 10$^{-4}$ atm. Per 1% increased lattice parameter, caused by a combination of thermal and chemical expansion, a decrease in $E$ of 36%±8% was observed for PCO. This was, to our knowledge, the first experimental measurement of the operando Young’s modulus of non-stoichiometric oxide films, and we observed that the $E$ for films decreased more substantially than bulk measurements on related oxides would have suggested. The more pronounced decrease in $E$ observed for PCO thin films may be attributable to differences between thin films and bulk samples, including increased vacancy concentrations in films, increased sample reduction (and associated increased lattice volume) at grain boundaries or in space charge regions, or increased lattice parameter in the out-of-plane direction due to constrained expansion. An understanding of how mechanical properties such as elastic modulus of non-stoichiometric oxides are affected by changes in non-stoichiometry caused by temperature or oxygen partial pressure change is highly relevant to predicting where stresses or strains will arise in actual devices comprised of such chemomechanically coupled materials, and thereby facilitate mechanically robust designs. Following this consideration, we present a short thought experiment based on the results of this study.

3.4.1 Accounting for elastic constant changes in operating devices

Consider a film of PCO grown on a rigid substrate to be stress-free at 25°C and subjected to a change in temperature. To first approximation, there will be a stress $\sigma$ at the interface that can be predicted according to Equation 3.1, where $T_0$ is a reference or initial temperature, $\varepsilon_T$ is thermal strain, and $\varepsilon_c$ is chemical strain:

$$\sigma = E \ast (\varepsilon_T + \varepsilon_c) = E(T, pO_2) \ast (\alpha_T \ast [T - T_0] + \alpha_c \ast [\Delta \delta]) \tag{3.1}$$

Depending on the orientations and symmetries of the film and substrate, this equation may be modified to use more appropriate elastic constants (e.g., biaxial elastic constants), but for the current discussion, this simplified model will suffice. Now, allow the temperature to change from room temperature (298 K) to an elevated temperature of 650°C, or 923 K, with a constant pO$_2$ of 0.2 atm (air). Then, if we assume a rigid substrate, the interfacial stress will develop as shown in Fig. 3-5(a). This plot shows three cases; constant $E_{RT}$ equal to the room temperature value, $E$ as a function of temperature as predicted by bulk models ($E(T, bulk)$), and $E$ as a function of temperature as predicted by our own thin film measurements ($E(T, film)$). The deviation between the three models increases with increased temperature, and at 650°C, the deviation between the predicted stress for $E(T, film)$ and $E_{RT}$ is 30% (about 20% for the $E(T, bulk)$ vs. $E_{RT}$).

Of course, substrates do undergo thermal expansion, so this assumption of a rigid substrate is simplified, and some of the predicted stress would be mitigated by the concurrent thermal expansion of the substrate. Therefore, now consider a model where we assume that the film is stress-free in air at 650°C (a typical cathode operating condition). What happens when there is a change in pO$_{2,eff}$? This could be important in a few possible scenarios: redox cycling, local variations in pO$_{2,eff}$ due to gradients through a film’s thickness.
Figure 3-5: (a) Predicted film stress vs. temperature for a rigid-substrate model when the elastic modulus $E$ of the film is modeled in three possible ways. At 650°C, there is a 30% difference in the predicted film stress when the operando $T$-dependent values (based on the above measurements) are used as opposed to a constant value $E_{RT}$ equivalent to the value of $E$ at room temperature. The dashed line represents the onset of chemical expansion for $T >550^\circ$C. (b) Predicted film stress vs. effective oxygen partial pressure $pO_{2,eff}$ at 650°C assuming a stress-free film when $pO_{2,eff} = 0.2$. The film model of $E$ predicts a substantial deviation in film stress that is not captured by the bulk model. In general, the actual stress in the film is less than predicted by bulk models because the Young’s modulus is smaller.

or local polarizations, or gas interruption or leakage. This last is more important in reverse (starting in a reducing environment and having the gas line interrupted by a leak to air) but the same general principles would govern that scenario. Figure 3-5(b) shows again a comparison of three predicted stress states vs. $\log(pO_{2,eff})$: constant $E$ at the bulk 650°C value ($E_{650}$), $E$ as a function of oxygen partial pressure as predicted for bulk ($E(pO_2, bulk)$), and $E$ as a function of oxygen partial pressure based on our own thin film measurements ($E(pO_2, film)$). Here, the bulk model only differs from the prediction with $E_{650}$ by about 5% when $\log(pO_{2,eff}) = -4$, as compared to a 20% deviation predicted by $E(pO_2, film)$. It should be noted that the above discussion accounts for differences in film and bulk oxide mechanics in the elastic modulus only. A similar kind of prediction could be made by assuming that $E(\delta)$ is the same for bulk and thin films, and instead accounting for differences in $\delta$ between the two cases. However, given our own operando experimental measurements, the present model better reflects the implications of our results.

This discussion illustrates the kinds of errors that can be expected when elastic constants’ dependence on operating conditions are ignored in mechanical calculations for non-stoichiometric oxides in multilayered electrochemical devices. Beyond that, substantial additional error is introduced when bulk models are used in lieu of thin film models. In general, the actual film stress is less than predicted when a constant Young’s modulus is assumed. Thus, whenever the stress or strain state of a non-stoichiometric oxide film is important in device design (either for preventing mechanical failure or taking advantage of strain en-
gineering), thin film specific elastic constants should be used for predictive calculations. This is relevant even for devices that undergo electrochemical oxygen pumping, including the actuators described in Chapter 2, because the elastic constants depend strongly on the lattice volume, which is ultimately a function of temperature and oxygen content.

3.4.2 Future work and connection to the rest of the thesis

We conducted this experimental study concurrently with density functional theory calculations discussed in Chapter 4. However, there are several recommendations for additional experimental work that would be of interest. While this was the first experimental measurement of thin film elastic constants in a non-stoichiometric oxide film under operando conditions, and PCO is an excellent model system, it will certainly be worthwhile to conduct a similar study of operando elastic constants for other important crystal structures, including perovskites and Ruddlesden-Popper phases. This is particularly relevant for any system that undergoes a voltage-induced phase change (such as SrCoO$_x$), as such systems exhibit substantially larger changes in lattice parameter that are anticipated to correlate with changes in elastic moduli.[50]

Another important consideration based on the above results is that of anisotropy. Nanindentation analysis generally assumes that the material being probed is mechanically isotropic, but as we mentioned this is not necessarily the case for a constrained film undergoing chemical expansion, particularly when the film is very thin (<100 nm). Indeed, later chapters will discuss the question of anisotropically expansion in thin film non-stoichiometric oxides, but here we propose a few ways to experimentally explore the role of anisotropy in understanding film elastic constants specifically. One of these ideas is to probe different film orientations by comparing elastic constants measured for films grown on different substrates (including polycrystalline films and at least two texture orientations).[51] Another way to potentially resolve the symmetrized elastic tensor is to conduct in situ Raman spectroscopy on these samples, using the vibrational modes detected to infer elastic constants.[52, 32] Of course this last method would require some additional modeling to understand the meaning of each feature in the Raman spectrum, but this is in principle possible.[29, 32] The density functional theory modeling presented in the next chapter provides a useful starting point for trying to understand orientation-dependent elastic constants in thin films as a function of non-stoichiometry.

For general in situ elastic constant detection, the use of electrochemical methods should also be considered. For example, in the previous chapter we saw that changing defect chemistry through applied electrical bias could induce substrate deflection because of interfacial stress. If the substrate in question is a very thin cantilever with well-controlled geometry, then the curvature of that substrate at different conditions (including electrically-induced changes in $\delta$) could in principle be used to infer an interfacial stress. Coupled with defect modeling, this kind of measurement could help determine $E$ as a function of $\delta$ for many types of non-stoichiometric oxides. Reference [49] includes some modeling to this effect using multi-beam optical stress sensors to detect curvature. Cantilever stiffness (and associated film stiffness) can also be measured using a nanoindenter or an atomic force microscope, as described in Ref. [53]. Of course, in situ measurements of fracture properties are also of particular importance when concerned with preventing delamination or vertical fractures.
Furthermore, an important takeaway from the above results is the variability observed in the high temperature nanoindentation measurements. While much of this variability is related to measurement error resulting from the challenges of high temperature indentation, some of the error is intrinsic to the sample. Indeed, trying to distill these contributions was part of the goal of the ANOVA methods applied to these data. Therefore, it appears that thin film non-stoichiometric oxides, despite their well-controlled geometry, can still exhibit substantial variability in their elastic constants that may be the result of, for example, differences in defect concentration near grain boundaries or other kinds of defects. Further discussion of this consideration can be found in Chapter 5.

Finally, we note here the important tradeoff for low temperature SOFCs between chemical strain and mechanics. We saw in Chapter 2 that for PCO, lower temperature operation implies a smaller amount of chemical expansion *operando*. However, this is coupled to an increase in elastic modulus, that will mean that *operando* stresses are higher for the same chemical strains than they would be at elevated temperatures. This effect may also couple to changes in fracture properties at lower temperatures. Especially for devices involving thin film components, predicting strain arising due to such coupling is highly relevant to using strain to enhance gas reactivity, ionic conductivity, or other functional properties. These findings suggest that elastic properties of thin films change markedly *operando*, and may deviate significantly from bulk counterparts even under the same environmental conditions. Together, these results motivate further in situ experimentation and computational modeling for this and other material classes (e.g., perovskites), to refine these predictions for design of non-stoichiometric materials and devices for SOFCs, gas sensors, permeation membranes, and other oxide-enabled applications.

### 3.5 Methods

#### 3.5.1 Sample preparation

Films of undoped CeO$_2$, and Pr$_x$Ce$_{1-x}$O$_2$$_{2-\delta}$ ($x = 0.1, 0.2$) were deposited by pulsed laser deposition (PLD) onto (001) oriented single crystal YSZ (8 mol% Y$_2$O$_3$ stabilized zirconia) substrates (10x5x0.5 mm$^3$; MTI Corporation, Richmond, CA) using dense targets, prepared by sintering the corresponding powders above 1400$^\circ$C under N$_2$ atmosphere [54]. Details of the PLD film growth can be found in Ref. [1].

Film thickness was determined via surface profilometry (KLA- Tencor P-16+ stylus profiler) as 1.09 ± 0.03 µm for the CeO$_2$ film, 1.04 ± 0.06 µm for the Pr$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ film, and 1.11 ± 0.06 µm for the Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ film. X-ray diffraction patterns (XRD; X’Pert PRO MPD, PANalytical) obtained from 2$\theta$–$\omega$ coupled scans of the films exhibited highly (001)-oriented texture. Surface topographic analysis by atomic force microscopy (AFM; Digital Instruments Nanoscope IV) demonstrated dense and smooth films with root-mean-square surface roughness of approximately 0.4 nm, sufficiently smooth for instrumented indentation.
3.5.2 Elastic modulus measurement via *operando* nanoindentation

Elastic moduli for the samples with $x = 0$ and 0.2 were measured at each condition *in situ*, at temperatures ranging from 25-600°C and under oxygen partial pressures ranging from 0.21 - 7.6x10$^{-4}$ atm at 600°C, using the instrumented indenter (MicroMaterials NanoTest Vantage; Wrexham, UK) capable of elevated temperatures and controlled gas environments shown in Fig. 1-5(b). Both the sample and the cubic boron-nitride indenter of Berkovich pyramidal geometry were heated to the same temperature to minimize thermal drift. See Ref. [55] for additional information on high-temperature measurements with this specific indentation instrument. The loading rate was between 0.1 and 0.5 mN/s, with a maximum depth of 100 nm. Depth-dependent trends in elastic moduli were not detectable for indentations below this depth, and thus no finite-thickness correction was applied to account for mechanical contributions from the substrate.

For all conditions, at least four indentation arrays, each of which comprised of at least 25 indentations, were acquired; each array was located at a distinct location on the sample surface spaced at least 60 μm from the nearest adjacent array. A schematic of this data collection design can be found in Appendix A.3. Indentations with sufficiently low signal-to-noise ratio, poor indenter contact, excessive (>100 nm) plastic depth, or pop-ins during loading were excluded from further analysis, resulting in at least four arrays of at least ten indentations for each condition (i.e., four distinct locations with ten replicate experiments at that location, for a total of approximately 40 indentations per sample per condition defined by temperature and pO$_2$). One condition had fewer total indentations: CeO$_2$ at 600°C in 7.6x10$^{-3}$ atm oxygen comprised three arrays of at least 10 indentations each. Indentation center-to-center spacing within each array of 25 was 30 μm to minimize mechanical interactions among indentations.

Gas concentration was controlled by flowing nitrogen and oxygen at a fixed ratio through the indenter chamber, and oxygen partial pressures of the exhaust gas were measured using a custom-built Nernst-type YSZ-based oxygen sensor operated at 620°C. Heating and cooling rates were 1.6°C/min to prevent thermal shocking of samples, and a minimum of 12 hours were provided for samples and the measurement apparatus to equilibrate at the target temperature and oxygen partial pressure. This was necessary primarily for gas flow equilibration inside the instrumented indenter enclosure that holds roughly 0.5 m$^3$ of gas.

Young’s elastic modulus $E$ was calculated according to the method of Oliver and Pharr via Eq. 3.2, where $A$ is the projected contact area of the probe at a given plastic depth $h_c$ that we calculated according to an area function calibrated based on a standard sample of inconel or fused silica $A(h_c)$, and $S$ is the measured unloading stiffness [56].

$$E = \frac{1 - \nu^2}{\frac{2\sqrt{A}}{S\sqrt{\pi}} - \frac{1-\nu^2}{E_i}}$$  

(3.2)

The elastic modulus $E_i$ and Poisson’s ratio $\nu_i$ of the indenter as reported by the manufacturer were 800 GPa and 0.12, respectively; the Poisson’s ratio $\nu$ of the CeO$_2$ and Pr-doped CeO$_2$ samples was assumed as 0.33, within the range reported previously for acoustic emission measurements of Gd-doped CeO$_2$ at elevated temperatures.[15] A standard operating procedure for conducting high temperature nanoindentation using the NanoTest Vantage instrument available in the Van Vliet Laboratory for Material Chemomechanics is available.
in Appendix B.

At room temperature the hardness $H$ of the films was also calculated according to Eq. 3.3, where $P_{\text{max}}$ is the maximum load:

$$H = \frac{P_{\text{max}}}{A}$$

(3.3)

Hardness relies more strongly on a highly accurate area function $A(h_c)$; as this was a particular challenge at high temperature, requiring re-calibration before and after every experiment, we focused on Young’s elastic modulus $E$ for \textit{in situ} results because it has a weaker dependence on this function.

A few improvements in available instrumentation have been made since the conclusion of this project. Firstly, the methods of attaching cBN crystals into their support (usually done by brazing) have improved, making indenters less susceptible to failures related to repeated freeze-thaw cycles at this joining point. Secondly, high temperature probes with ceramic shafts are now available that are more resistant to oxidation at high temperatures. Both of these improvements can extend the life of a probe and potentially allow for a more stable apparent geometry over repeated use. It should be noted, however, that ceramic-supported probes are somewhat more fragile than metal-supported versions, and should be treated with care.

### 3.5.3 Statistical analysis of indentation data

One-way analysis of variance (ANOVA) based on Sokal and Rohlf was conducted on the multiple indentation arrays acquired on each sample at each condition, to determine whether these data acquired at four different sample locations could be considered to come from the same population of data, or if there was detectable variance among the arrays acquired under ostensibly identical conditions.[57] Detailed discussion of the statistical method used to analyze nanoindentation results has been published previously [2], and is summarized briefly here. Appendix A.3 provides a more in-depth description of this process. Three metrics of statistical comparison were computed ($p$-value $< 0.05$, Tukey-Kramer minimum significant difference, and Gabriel’s comparison interval); if at least two of these three showed that there was significant variance among indentation arrays for a given sample and condition, then the grand mean of the arrays was reported with standard error for $n$ representing the number of arrays. Otherwise, the arithmetic mean of all indentations for a given sample condition was reported, with standard error reported for $n$ as the number of indentations. Such array-to-array variance could be attributable to variations in sample topography or composition at different locations on the sample surface, variations in temperature of the contacting probe and sample at different sample locations, or variations in indenter geometry acquired during indentation among multiple arrays. The function describing probe geometry $A(h_c)$ was calibrated immediately prior to and following data acquisition for each condition, to minimize contributions from this latter source of variance. Further discussion of sources of variance can be found in Appendix A.3.2, and Table A.1 reports the values of $n$ and $N$ for each condition as well as whether data were pooled for all conditions shown in Fig. 3-3.
3.5.4 Calculation of non-stoichiometry parameter and lattice parameter

Oxygen non-stoichiometry parameters \( \delta \) for (Pr, Ce)O\(_{2-\delta} \) were calculated based on the defect model for bulk PCO outlined by Bishop et al.[9] Lattice parameters \( a \) were estimated according to Eq. 3.4 based on the value of the lattice parameter \( a_o \) of undoped CeO\(_2 \) and Pr\(_{0.2}\)Ce\(_{0.8}\)O\(_{2-\delta} \) reported at room temperature (5.41 Å [58, 59]), the thermal expansion coefficient of ceria \( \alpha_T \) (1.2x10\(^{-5}\) K\(^{-1}\) [37]), and the chemical expansion coefficient of PCO \( \alpha_C \) (0.087 [34]). The chemical expansion coefficient \( \alpha_c \), analogous to \( \alpha_T \), relates \( \Delta \delta \) to chemical strain \( \epsilon_c \). This approach assumes that in the oxidized case the PCO lattice parameter can be approximated by that of CeO\(_2 \), since Pr\(^{+4} \) and Ce\(^{+4} \) are nearly the same size (0.96 and 0.97 Å radii, respectively).[60] Our own density functional theory calculations reported in the next chapter support this assumption. The reference vacancy concentrations \( \delta_{ref} \) were values calculated by the defect model [9] at room temperature (10\(^{-16}\) for CeO\(_2 \) and 10\(^{-7}\) for Pr\(_{0.2}\)Ce\(_{0.8}\)O\(_{2-\delta} \)).

\[
a = a_o(1 + \alpha_T(T - 298 K) + \alpha_C(\delta - \delta_{ref}))
\]  

(3.4)
Bibliography


Chapter 4

Density Functional Theory
Computations of Coupled Mechanics and Chemical Expansion in \( \text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta} \)

Chapter 3 presented experimental evidence that the Young’s modulus of \( \text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta} \) (PCO) films decreases with increased lattice parameter resulting from thermal and chemical expansion. In this chapter we consider the same question (How does chemical expansion affect elastic constants in non-stoichiometric oxides?) from a computational perspective. Using density functional theory (DFT), we calculate how changes in defect concentration (that cause chemical expansion) change the elastic constants of ceria and PCO. Two separate investigations were conducted. The first study, contained in Section 4.2 comprised DFT + U computation of the stiffness tensor for bulk PCO and was conducted alongside the experimental study presented in Chapter 3. The results of this first study were previously published in *Acta Materialia*.\[1\] The second study, contained in Section 4.3, was undertaken to provide a more direct comparison than the one afforded by the *Acta* paper by computing the effect of changes in defect density on the biaxial elastic constant of equivalent compositions of PCO in bulk and membrane forms. This second study, which considered equivalent compositions in parallel, was aimed more at clarifying which of the possible factors discussed in the *Acta* paper (Sections 4.2 and 3.3.2) were most important in explaining the differences between film and bulk elastic constants. The second study is the subject of a manuscript currently in preparation.\[2\]

Collaborators for the work presented in this chapter include Dr. Mukul Kabir and Dr. Mostafa Youssef, two Van Vliet group alumni and colleagues that trained me to apply DFT and provided useful discussion for determining both the limitations and implications of the results.
4.1 Introduction

Computational methods provide an important avenue for probing chemomechanical effects by precisely controlling defect chemistry and eliminating complicating factors that are difficult to avoid in experiments. While PCO makes an excellent model system because of its well-known defect chemistry, the interrelated factors of mechanical constraint, environmental conditions, measurement error, and technical limitations mean that the exact defect concentrations for the films discussed in Chapter 3 were inferred from available models, rather than known with complete certainty. In contrast, with computational methods, we can choose the quantity and location of point defects, precisely adjust strain states, and avoid the time-consuming task of taking a statistically useful number of measurements. Furthermore, unlike nanoindentation, computation has the potential to determine the entire stiffness tensor and/or more readily manage orientation-dependent information. In this way, computation allows us to consider more carefully which contributions (e.g., defect concentration change, film vs. bulk dimensions, anisotropy) cause changes in the elastic constants of our model non-stoichiometric oxide. We can also take a first step toward characterizing the local nature of chemical expansion by studying how the presence of point defects changes lattice configurations on the atomic scale.

In this chapter we employ the computational method of density functional theory with inclusion of the Hubbard U term (DFT + U). DFT is a first principles method for computing the electronic structure of materials that may be extended to predicting elastic constants, defect formation energies, and many other material properties. In these studies, we included the Hubbard U term in order to account for the on-site Coulomb repulsion of f-electrons in the transition metal cations (Ce and/or Pr). This is an important detail, as the degree of charge localization directly impacts the chemical expansion coefficient of non-stoichiometric oxide materials (increased charge localization, controlled by increasing U, increases the chemical expansion coefficient). While the inclusion of U is not an ab initio decision, it is made so that the computed structures reflect the experimentally well-known electronic structure of ceria (a small-polaron conductor), rather than the charge-delocalized structure that would result without it. The value of U also systematically affects the magnitude of the elastic constants and the lattice parameter, meaning that it is not possible to achieve exact agreement between the computed moduli, lattice parameter, and chemical expansion coefficient $\alpha_c$ and the corresponding experimentally measured values. With this in mind, we selected U to reflect the known $\alpha_c$ of PCO, with the expectation that resulting changes in stiffness with changes in defect concentration should be readily comparable to experiments.

Several previously published DFT and computational studies of mechanics and chemomechanical coupling in ceria provide a foundation and basis of comparison for the work presented here. Kanchana et al. used multiple DFT methods to compute the elastic constants of vacancy-free ceria and a few other fluorite-structured oxides and achieved reasonable agreement with experimental results. Molecular dynamics simulations with interatomic potentials have replicated the trend that chemical expansion should correlate with decreased mechanical stiffness, but those calculations did not include Pr among the dopants investigated and moreover did not simulate electronic structure. For Pr-doped CeO$_2$, vacancy formation and migration energies were estimated via DFT and kinetic Monte Carlo
simulations, identifying optimal migration pathways and finding that the energy barrier to migration increased for $x > 0.15$. DFT+U was also used to show that the activation barrier for oxygen vacancy formation and migration in ceria decreases with application of tensile strain, potentially explaining some of the experimental findings mentioned in Chapter 1. Additionally, a study of rutile TiO$_2$ surfaces found that elastic strain could tune the type of energetically favored oxygen vacancy, influencing not only defect formation energies but also mechanical stiffness for oxide surfaces. This last result is particularly interesting in light of recent experimental results that showed that biaxial strain could increase the oxygen storage capacity of very thin films of CeO$_2$. Thus, DFT + U has been applied to understanding several chemomechanical effects in CeO$_2$ and related oxides, and can now be applied to understanding the effect of chemical expansion on elastic constants.

The experimental results of Chapter 3 demonstrated that the Young’s elastic modulus of PCO films decreases with increased temperature or oxygen partial pressure more strongly than expected based on measurements of related oxide materials in bulk form. In Section 4.2, we confirm through computation that the trends observed in the literature on related bulk oxides are quantitatively consistent with expectations for bulk PCO. In Section 4.3, we extend the consideration to include additional computations that compare directly the bulk and membrane forms of equivalent composition of PCO, with the aim to understand which factors most strongly influence the stiffness of thin films. The discussion begins in Section 4.2 with computation of the stiffness tensor for bulk PCO as a function of $\delta$ and $x$ that was conducted concurrently with the experimental study of Chapter 3, and then turns to directly comparing computed biaxial stiffness for thin film and bulk PCO as a function of defect chemistry in Section 4.3.

4.2 Density functional theory calculations of bulk lattice parameters and elastic constant tensor (Acta Materialia study)

4.2.1 Methods

The generalized gradient approximation (GGA) to density functional theory (DFT) with incorporation of the Hubbard U term was used to calculate the lattice parameters and elastic constants of CeO$_2$ and Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ with varying vacancy concentrations $\delta$, using the Vienna ab-initio simulation package (VASP). Inclusion of the Hubbard U term accounted for the on-site Coulomb repulsion of the localized 4f electrons in Ce. A magnitude of U = 5.0 eV was used for Ce, which has been shown previously to reproduce the chemical expansion coefficient of CeO$_{2-\delta}$. This U overestimates the lattice constant $a$ and Young’s modulus of CeO$_2$ by $\sim 1\%$ and $\sim 14\%$, respectively. However, because the chemical expansion coefficient is accurately reproduced by this U, it is expected that trends in $\Delta E$ vs. $\Delta a$ and $\Delta \delta$ will be accurately reproduced for bulk PCO, while the magnitudes of $E$ and $a$ will be systematically overestimated. No U term was included for Pr. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used with a basis set composed of projected augmented wave (PAW) pseudopotentials, with an energy cutoff of 500 eV. A 2x2x2 (96 atoms) supercell was constructed from conventional unit cells of CeO$_2$, and Pr and oxygen vacancies were substituted in as needed. Before calculating elastic constants, the lattice parameter and atomic positions of the supercell at
each composition were permitted to relax with a 2x2x2 Monkhorst-Pack k-point grid applied to CeO$_2$. Elastic constants $C_{ij}$ were then calculated on the relaxed structure. This choice of energy cutoff and k-point grid were found to converge lattice parameter to $<0.002$ Å and elastic constants to $<2$ GPa. Oxygen vacancy positions were chosen, as shown in Fig. 4-1, to be maximally distant because such systems were of minimum system energy at that vacancy concentration. Pr positioning was varied depending on target Pr concentration, and variation of the relative spacing between Pr atoms did not significantly affect lattice parameter or elastic constants ($<0.002$ Å and $<1$ GPa).

![Figure 4-1: Schematic of the 2x2x2 supercell of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ used for elastic constant calculation by density functional theory. Cerium atoms (Ce) are large spheres shown in yellow, praseodymium atoms (Pr) are large spheres in green, oxygen atoms (O) are small spheres in red, and oxygen vacancies (V$_o$) are small spheres in blue. For $\delta = 0.03125$ calculations, only one of the vacancies was present, while for the $\delta = 0.0625$ calculation, the supercell contained two vacancies. The Pr configuration shown is for the $x = 0.09325$ calculations; for other values of $x$, these sites were occupied by Ce and Pr was substituted for Ce elsewhere in the supercell. Species radii are not to scale. Figure from Ref. [1]. The Young’s modulus $E$ was determined based on the computed stiffness tensor $C$ by first inverting $C$ to determine the compliance tensor $S$ and then using the following relationships: $S_{11} = 1/E$ and $S_{12} = -\nu/E$, where the subscripts used here are from Voigt notation. This is possible because of the cubic symmetry of PCO. The magnitude of $\nu$ was assumed to be 0.33.[24]

4.2.2 Results and Discussion: Chemical expansion decreases the elastic constants of bulk PCO

First principles calculations of elastic constants $C_{ij}$ for bulk ceria and Pr-doped ceria with finite vacancy content demonstrated a significant reduction in stiffness with increasing lattice parameter associated with increasing $\delta$. Table 4.1 summarizes computed $C_{ij}$ and $E$ for three compositions of CeO$_{2-\delta}$ with either zero or finite oxygen vacancy concentration denoted by $\delta$. The results for $C_{11}$ and $E$ are shown graphically in Fig. 4-2. Generally, a larger $\delta$ correlated with increased lattice parameter and decreased $E$ and $C_{11}$. While the magnitudes of $E$ calculated via density functional theory (DFT + U) exceeded those determined experimen-
Table 4.1: Structural and elastic constants for bulk Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ calculated by density functional theory

<table>
<thead>
<tr>
<th>Pr content $x$</th>
<th>Nonstoichiometry $\delta$</th>
<th>Lattice constant $a$ (Å)</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>5.48</td>
<td>343</td>
<td>93</td>
<td>54</td>
<td>303</td>
</tr>
<tr>
<td>0</td>
<td>0.03125</td>
<td>5.49</td>
<td>332</td>
<td>97</td>
<td>52</td>
<td>288</td>
</tr>
<tr>
<td>0</td>
<td>0.0625</td>
<td>5.51</td>
<td>326</td>
<td>100</td>
<td>55</td>
<td>279</td>
</tr>
<tr>
<td>0.03125</td>
<td>0</td>
<td>5.48</td>
<td>343</td>
<td>94</td>
<td>51</td>
<td>302</td>
</tr>
<tr>
<td>0.0625</td>
<td>0</td>
<td>5.48</td>
<td>341</td>
<td>92</td>
<td>52</td>
<td>301</td>
</tr>
<tr>
<td>0.09375</td>
<td>0</td>
<td>5.48</td>
<td>372</td>
<td>122</td>
<td>35</td>
<td>312</td>
</tr>
<tr>
<td>0.09375</td>
<td>0.03125</td>
<td>5.49</td>
<td>336</td>
<td>97</td>
<td>55</td>
<td>292</td>
</tr>
</tbody>
</table>

Totally (Chapter 3), the calculated chemical expansion coefficient of 0.088 (unitless) matched well with the reported experimental value (0.087 [25]); this correlation is expected because the magnitude of the Hubbard U term was optimized for this parameter. The magnitudes of stiffness constants $C_{11}$, $C_{12}$, and $C_{44}$ for undoped, vacancy-free CeO$_{2-\delta}$ agreed well with those reported previously by Kanchana et al. for the same system with the GGA exchange functional (354, 99, and 51 GPa, respectively).[3] Addition of Pr to the supercell minimally altered the lattice parameter or elastic constants as compared to undoped CeO$_{2-\delta}$ in this vacancy-free case. This is expected given that the Shannon ionic radii of Pr with +3 and +4 charge (1.126 and 0.96 Å, respectively) are comparable to those of Ce (1.143 and 0.97 Å, respectively).[26] Therefore, it is expected that the effect of chemical expansion on the elastic constants of Pr-doped and undoped ceria should be comparable.

Figure 4-2 shows that both the stiffness constant $C_{11}$ and the computed Young’s elastic modulus $E$ decreased with increasing lattice parameter $a$. This reduction in mechanical stiffness can be expressed in terms of the slope of an approximately linear correlation $E(a)$ (with least-squares regression $R^2 = 0.95$). Overall, the reduction in $E$ per increase in $a$ for all simulated compositions was -1128 GPa/Å, or 20% reduction in $E$ for a 1% increase in $a$. This dependence was on the same order and slightly more pronounced for the Pr-doped ceria case shown in Fig. 4-2 ($x = 0.09375$). Here, the inclusion of a vacancy within the Pr-doped ceria supercell resulted in an increase in $\delta$ from 0 to 0.031. This increase in $\delta$ resulted in an increase in $a$ and corresponding decrease in $E$, summarized as -1706 GPa/Å or a 32% decrease in $E$ per 1% increase in $a$. However, the composition with $x = 0.09375$ is an oddity among the structures investigated; it had an apparently larger value of $C_{11}$ (372 GPa) compared to other vacancy-free configurations (341–343 GPa), and was also artificially symmetric as shown in Fig. 4-1. This face-centered arrangement of Pr atoms was necessary in order to achieve computational convergence. However, without a symmetry-breaking oxygen vacancy, it appears that the computed stiffness increased beyond the expectation suggested by the rest of the computed values. $C_{12}$ and $C_{44}$ for this composition also seemed unusual when compared with the other vacancy-free simulation results. Therefore, although it may appear that PCO has a slightly larger dependence on $a$ than CeO$_2$, consideration of the data as a whole suggest that the trend of 20% reduction in $E$ for a 1% increase in $a$ is a better descriptor for the effect of chemical expansion on the elastic constants of bulk PCO.
This is further supported by the fact that the magnitude of computed elastic moduli varied only weakly with atomic configuration in all other cases, even when Pr was substituted for Ce up to a composition of $x = 0.0625$. When the position of a Pr atom or an oxygen vacancy was shifted to distinct locations within the unit cell of a given composition (Pr-content $x$ or non-stoichiometry $\delta$), the computed elastic constants varied by only a few GPa, and the lattice parameter changed by less than 0.002 Å.

When considered together with the experimental results presented in Chapter 3, our DFT calculations indicated that differences between bulk and thin film stiffness can be expected for appreciable Pr-content $x$ in such oxides, as a function of vacancy content $\delta$ (Table 4.1 and Fig. 4-2). Specifically, these DFT results demonstrated that $E$ decreased in these functional oxides with increasing oxygen vacancy content $\delta$, which in turn increased $a$. For undoped ceria ($x = 0$), the lattice parameter increased by 0.5% as $\delta$ increased from zero (perfect crystal) to 0.06 (comparable to our experimental $\delta$ at the lowest $pO_2$). The effective elastic modulus $E$ decreased by nearly 10% as a result of this vacancy-mediated increase in lattice parameter. In the absence of vacancies and at lower Pr-doping of $x = 0.03$ or 0.06, $E$ was approximately the same as for vacancy-free, undoped ceria. For a fixed Pr-content ($x = 0.09$) but increased vacancy content $\delta$ (from 0 to 0.03), however, $E$ decreased from 312 to 292 GPa. Altogether the dependence was $\sim 20\%$ reduction in $E$ per $1\%$ increase in lattice parameter as compared to undoped ceria without vacancies. For the Pr-containing compositions, the correlation was slightly more pronounced, but we attribute this to the artificially increased value of $E$ for the very symmetric vacancy-free case when $x = 0.09375$. These dependences were less than the relative decrease in $E$ measured for our thin films.

Figure 4-2: (a) Elastic constant $C_{11}$ and (b) Young’s elastic modulus $E$ calculated by DFT $+ U$, as a function of lattice parameter $a$. Circular symbols indicate that $x = 0$ (undoped ceria), while diamond symbols indicate that $x > 0$. Open symbols indicate that $\delta = 0$ (no vacancies), while filled symbols indicate the presence of vacancies. For the open diamonds (Pr-doped ceria without vacancies), Pr concentration increases from right to left. For the closed circles (undoped ceria with vacancies), vacancy concentration increases from left to right. Figure from Supporting Information to Ref. [1].
(~40%, Fig. 3-3), but agreed well with the ~23% decrease in $E$ for ~1% increase in $a$ reported by Wang et al. for bulk undoped ceria via ex situ indentation measurements.[27] Therefore, the trends reported here for DFT computations on PCO are consistent with experimental results on bulk counterparts, and deviations from the experimental results of the previous chapter may be attributable to microstructural and in situ non-stoichiometry differences between bulk and thin film counterparts.

Specifically, this similar but relatively lower dependence of mechanical stiffness on lattice strain in such predictions may be attributed reasonably to a higher average vacancy content in thin films as compared to bulk oxides with similar Pr-content $x$. If thin films have a higher operando vacancy content than bulk models predict, then they should also have a larger lattice volume that, in addition to the other thin film factors described in Chapter 3, decreases the operando $E$. That expectation is supported by the calculations in which we varied $\delta$ for an otherwise constant average composition: even for constant $x$, an increase in vacancy content defined by $\delta$ resulted in an increase in $a$ and corresponding decrease in $E$. Therefore, our DFT results predict trends for $E$ vs. $a$ for doped ceria that compare well with previously reported experimental results for bulk samples, and highlight the role of chemical expansion due to increased $\delta$ in modulating $E$ that become even more pronounced in thin films under operando conditions.

4.3 Biaxial elastic constants for bulk and membrane PCO

The results of the Acta Materialia paper discussed in Section 4.2 and Chapter 3 provided indirect comparisons of bulk and film elastic constants in PCO, specifically between computed bulk values, measured thin film values, and literature values measured for bulk ceria and Gd$_x$Ce$_{1-x}$O$_2$-$\delta$. The results showed that PCO’s elastic modulus decreased more in situ than bulk predictions or bulk measurements would anticipate as a function of temperature and oxygen partial pressure, and we offered a few possible explanations for this including the possibility of larger in situ vacancy concentrations in films and the contributions of anisotropic effects that are not present in the bulk. Missing from that study was a direct comparison of bulk to thin film elastic constants determined in the same way. The present study attempts to bridge that gap.

What makes the elastic constant of films depend more on $T$ and pO$_2$ than they do for bulk samples? Is it solely the effect of increased $\delta$ in situ, or could there be additional contributions, perhaps related anisotropy effects or which type of oxygen vacancy is favored under certain conditions? Others have already shown that mechanical strain can tune the type of energetically favored oxygen vacancy in rutile TiO$_2$, as well as the formation energies of oxygen vacancies at CeO$_2$ surfaces - couldn’t a similar effect happen in Pr-doped, fluorite ceria?[16, 7] Given the inherent chemomechanical coupling of non-stoichiometric oxides such as PCO and the potential for surface layers to show differing non-stoichiometry and mechanical responses than bulk forms of the oxide, we sought to compare the elastic response of bulk and membrane forms of this material with equivalent compositions. In this section, we report a parallel study of bulk and membrane forms of PCO of equivalent composition, specifically considering the effect of composition on biaxial stiffness that is the most relevant for thin film applications. The unsupported membranes simulated here provide a first step towards understanding the composition-dependence of elastic constants in low-dimensional
structures. Simulations containing a film-substrate interface could build on these results, but would require far greater computational resources than were available for this study.

4.3.1 Methods

Bulk and membrane supercells of (111) oriented Pr\textsubscript{x}Ce\textsubscript{1-x}O\textsubscript{2-δ} containing 108 and 216 atoms, respectively, were simulated using the Vienna ab initio Simulation Package (VASP, [20]) with compositions of x = 0 and 0.056 and δ = 0 and 0.028. We use the term membrane to denote a structure that is much thinner in one dimension (in this case, the z or sample-thickness dimension) than in the other two. All calculations were implemented in the generalized gradient approximation formalism of density functional theory with an on-site Coulomb interaction term (GGA + U). The Perdew-Burke-Ernzerhof (PBE) variant of the GGA exchange-correlation functional was employed together with projector augmented wave (PAW) pseudopotentials.[20, 18, 19, 21] All the computational details were similar to our previous work presented in Section 4.2 [1] with the exception that in the case of Ce, a "harder" pseudopotential was used for a more accurate representation of Ce valence electrons. Additionally, for both Pr and Ce, a U of 5.0 eV was used to ensure 4f-electron localization in the case of the 3+ oxidation state.[5, 6] This U for Ce and a slightly lesser value for Pr (4 eV) were shown previously to be sufficient to ensure localization of f-electrons to the appropriate number of cations in defective ceria, and this correct localization was also confirmed in this work for both Pr and Ce using U = 5 eV.[28, 13, 29]

To localize an electron on a particular cation (that is, to create a small polaron on a specific site) we initiated the ionic relaxation by representing this cation with a pseudopotential that treats one of the f-electrons as a core electron. This created the needed distortion to ensure electron localization. This step was followed by subsequent ionic relaxation after restoring the usual pseudopotential of this cation in which the f-electron is treated as a valence electron. This recipe has been used previously to model electron localization in CeO\textsubscript{2}.[30] We chose the (111) surface orientation because this is the lowest energy choice for ceria.[31] As shown in Fig. 4-3, membranes containing six trilayers were simulated with fixed x-y dimensions at each biaxial strain state, while planes were permitted to relax in the z-axis direction. Thus, although the nominal vacuum thickness was 11 Å, the exact membrane height differed depending on the composition and biaxial strain state. This vacuum was determined to be sufficient to prevent membrane polarization due to interaction with the periodic images along the z-axis.

To calculate the biaxial stiffness \(C_{\text{biax}}\) of each supercell, bulk supercells of each composition were relaxed to identify the equilibrium in-plane area. At least seven biaxial strains \(\epsilon_{\text{biax}}\) were applied to each supercell based on this equilibrium area, allowing relaxation with fixed in-plane supercell dimensions to produce a strain-energy curve for biaxial strains ranging to roughly ±0.6%. This strain range has been shown previously to be within the elastic regime for CeO\textsubscript{2}.[4] A quadratic fit was applied to each strain-energy curve in order to calculate \(C_{\text{biax}}\) according to Eq. 4.1, where \(V_0\) is the membrane equilibrium volume and \(U\) is the internal energy of the membrane:

\[
C_{\text{biax}} = \frac{1}{2} \frac{1}{V_0} \frac{\partial^2 U}{\partial \epsilon_{\text{biax}}^2}
\]  

(4.1)
Figure 4-3: Membrane structure for DFT calculations. (111)-oriented, 6-trilayer membranes of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ were simulated at distinct magnitudes of biaxial strain to determine the biaxial elastic constant $C_{biax}$ for different compositions of $x$ and $\delta$. Shown in the schematic are the positions of Pr dopants (dark blue spheres) for compositions with $x = 0.056$ and oxygen vacancies for compositions with $\delta = 0.028$. Three vacancy-containing configurations were investigated: one with surface oxygen vacancies (light blue spheres) and two with subsurface oxygen vacancies with Pr cations at the first (gray spheres) and second nearest neighbor positions, respectively. For clarity, the second nearest-neighbor configuration is not shown in this schematic. Mirroring (111) crystallographic planes are labeled alphabetically starting at the surface and moving toward the membrane interior. Bulk supercells were simulated with the same orientation and set of compositions, but with only three trilayers. Figure from Ref. [2].
Figure 4-4: Example strain energy curve. At least seven distinct biaxial strains were applied to the Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ structures. A quadratic fit to the resulting strain-energy curve was used to determine the elastic constant $C_{\text{biax}}$. Shown here are the data for Pr-content $x = 0.056$ and non-stoichiometry $\delta = 0.028$ (vacancies in plane A). Figure from Ref. [2].

The factor of $1/2$ in this equation arises from the orthorhombic symmetry of the applied strain, $\epsilon_{\text{biax}}$.[32, 33] Figure 4-4 shows an example of this quadratic fit as applied to the bulk supercell with composition $x = 0.056$, $\delta = 0.028$ (vacancies in plane A). For membranes, elastic constant calculation required a consistent definition of membrane height. Thus, the equilibrium volume $V_0$ used for membranes was computed as the product of the equilibrium area of the bulk supercell for that composition and the maximum $z$-direction atom-to-atom distance for the membrane at that area. The error of the quadratic fitting approach was estimated as described in the Appendix A.4 by comparing the elastic constants computed when using subsets of a total of 15 data points for the bulk supercell with $x = \delta = 0$. Based on that result, an error of $\pm 5\%$ is assumed for all computed elastic constants in this study.

4.3.2 Results and discussion

Bulk structures containing oxygen vacancies (both $x = 0$ and $x = 0.056$) relaxed to larger volumes than corresponding stoichiometric cells. When we introduced an oxygen vacancy into the structure, two cations simultaneously reduced, leading to charge localization that increased supercell volume.[9] Pr cations reduced preferentially to Ce when Pr was present ($x = 0.056$). The chemical expansion coefficient $\alpha_c$ for both compositions was 0.06 ($\Delta \epsilon / \Delta \delta$), which agrees reasonably well with the experimentally measured chemical expansion coefficient of PCO (0.087).[25]

Membrane optimization

In order to run these simulations efficiently and effectively, we needed to optimize the membrane dimensions, including both the membrane thickness (number of trilayers) and the vacuum height. We optimized these parameters by first simulating undoped CeO$_2$ membranes.
with 5, 6, and 7 trilayers and a vacuum height of 13 Å, choosing the optimal membrane thickness, and then simulating several vacuum heights at that thickness. Fig. 4-5(a) shows that a membrane thickness of 6 tri-layers achieved the optimal compromise between computational (CPU) time and surface energy - the surface energy for this membrane was within 0.001 J/m$^2$ of the membrane with 7 trilayers. Fig. 4-5(b) shows that decreasing the vacuum height to 11 Å slightly increased the surface energy (by < 0.001 J/m$^2$), but also improved the computational time by about 25%.

We next confirmed that this membrane configuration (6 tri-layers and 11 Å vacuum) resisted polarization when it contained point defects. Figure 4-6 shows the local potential function for relaxed CeO$_2$ membranes containing oxygen vacancies with vacuum heights of 11 and 15 Å, and for 15 Å with and without a dipole correction applied. The local potential function oscillated upon traversing the membrane thickness as it crossed through the six trilayers of atomic planes. Based on these results, we determined that the dipole correction was on the order of 0.1 eV, and that the expected error in defect formation energy vs. the membrane with a 15 Å vacuum was < 0.1 eV/defect. The computed surface energy for our defect-free CeO$_2$ membrane was 0.72 eV/Å$^2$, which agrees well with literature reports for the same system that range from 0.6 to 0.7 eV/Å$^2$. Therefore, all subsequent calculations used a membrane with six atomic tri-layers (216 atoms when there are no vacancies) and 11 Å of vacuum height because that configuration achieved the best compromise between computational time and surface energy. These results also validated our approach prior to advancing to more complicated systems with non-zero $x$ and $\delta$. 

Figure 4-5: (a) Computational time (blue diamonds) and surface energy (green circles) for CeO$_2$ membranes with 13 Å vacuum vs. number of layers of atoms. The optimal compromise between computational time and accuracy was achieved for six tri-layers. This also allowed for exact compositional correspondence between bulk and membrane systems. (b) Computational time and surface energy vs. vacuum height in the $z$-direction for CeO$_2$ membranes with six tri-layers. 11 Å of vacuum provided a slight improvement in computational time with minimal impact on surface energy.
Figure 4-6: Local potential vs. position across the simulation cell (z-direction, normal to the surface) for membranes of two different thicknesses. No significant electric field traverses the membrane for either a 15 or 11 Å vacuum.

Biaxial elastic constants of PCO in the presence of point defects

As shown in Fig. 4-7, we computed $C_{b\text{iax}}$ for four compositions of PCO and found in general that it decreased with increasing oxygen vacancy content for both bulk and membrane forms. Across the range of structures considered (doped and undoped, membrane and bulk), excepting the membranes with subsurface (plane C) vacancies, we calculated an 8-10% decrease in the biaxial stiffness for an increase in oxygen vacancy content of $\Delta \delta = 0.028$. When vacancies were present in the subsurface plane (plane C), $C_{b\text{iax}}$ was 14-16% less than the value calculated for doped, vacancy free PCO. The membrane with Pr cations at second nearest neighbor positions relative to the subsurface oxygen vacancies was the most energetically favored configuration for that composition ($x = 0.056, \delta = 0.028$), and exhibited a 14% decrease in $C_{b\text{iax}}$ relative to the vacancy-free case. That configuration is marked by an asterisk in Fig. 4-7. We also note that previous computational work has shown that the second-nearest neighbor (2NN) position is energetically favored for reduced ceria, consistent with our own findings for PCO.[35] Given the expected $\pm 5\%$ error of these calculations, the change vs. $\Delta \delta$ is considered significant. For the case of surface vacancies, we identified no significant difference between the bulk and membrane forms for the proportional change in stiffness as a function of chemical expansion. In fact, the bulk and membrane forms of PCO behaved quite similarly. Although membrane PCO appeared to show a larger relative change in stiffness (10%) than was computed for CeO$_2$ (8%), this is not beyond the precision of the method, and it is therefore unclear whether this 2% difference is real. Additionally, although Fig. 4-7 appeared to show an overall increase in stiffness for membranes as compared to bulk, we note here that membrane volume is defined differently than bulk volume, so such a difference may not be meaningful. In fact, a slight over-estimate is expected for all membrane elastic constants due to the definition of $V_0$ for the membrane that is likely a slight underestimate. Thus, the relative changes in elastic constants vs. composition
are more meaningful than direct comparisons of bulk and membrane values at equivalent compositions.

![Graph showing biaxial stiffness vs. non-stoichiometry](image_url)

Figure 4-7: Biaxial elastic constant computed for different compositions of $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ (PCO). The biaxial elastic constant $C_{biax}$ of PCO decreased by 8-16% when oxygen vacancy concentration $\delta$ increased to 0.028 for doped ($x > 0$) and undoped ($x = 0$) compositions. The relative change in $C_{biax}$ was of similar magnitude for both bulk (8-9%) and membrane structures with surface oxygen vacancies (8-10%), and larger (14-16%) when the oxygen vacancies were subsurface. The most energetically favorable oxygen vacancy configuration for the Pr-containing membrane is highlighted by an asterisk. Fig. from Ref. [2].

We also considered the effect of varying vacancy position on the computed $C_{biax}$. For the bulk case, changing the position of oxygen vacancies relative to Pr dopants (first nearest neighbor vs. second nearest neighbor) only affected $C_{biax}$ by a few GPa, which is well below the error of our method. In contrast, when vacancies were positioned in the subsurface plane (layer C), there was an additional decrease in stiffness that was not present for vacancies in the surface plane (layer A). This apparently resulted from the fact that subsurface vacancies removed a larger number of bonds from the crystal than their surface counterparts, an effect that was apparently more relevant near the broken symmetry at the surface than it was in the PCO interior region. Our calculations also showed that strain affected the formation energies of the different types of oxygen vacancies in the membrane. While the subsurface vacancy with Pr cations at the 2NN position was energetically favored against the other two configurations for all strains (by $\sim$0.1 eV/vacancy), the other configurations exhibited differing relative favorability depending on the strain state. For tensile strain, the surface vacancy was the next most energetically favored, while for compressive strain, the subsurface vacancy with first-nearest neighbor (1NN) Pr cations was second to the 2NN subsurface vacancy configuration. However, the energetic difference of the surface and 1NN subsurface positions was quite small ($\sim$0.05 eV/vacancy), and the difference in energy of both relative to the 2NN subsurface configuration was only $\sim$0.1-0.15 eV/vacancy. These relative magnitudes imply that a mix of these vacancy types should be expected, especially at elevated temperatures typical of solid oxide fuel cell (SOFC) operation. Averaging the
change in $C_{biax}$ for the three types of vacancy gives a change of about 13% (compare to 10% for bulk PCO). Therefore, we conclude that certain types of near-surface vacancy can have a larger impact on biaxial stiffness than bulk vacancies, but that this effect is relatively small and does not fully account for experimentally observed differences for film vs. bulk elastic constants. An additional factor, such as higher in situ vacancy concentrations, is necessary to explain the experimentally observed effect.

Out-of-plane relaxation and lattice plane rearrangement under biaxial strain

In addition to considering the overall change in stiffness for these materials, we analyzed the local changes in material structure to identify any differences between the bulk and membrane response to biaxial strain. In particular, we computed the relative z-direction membrane thickness relaxation per biaxial strain, as well as the changes in the spacing between atomic planes with biaxial strain. While the ratio between z-direction strain and biaxial strain was relatively constant regardless of composition in both the bulk and membrane cases, the spacing between individual lattice planes did show variation.

The (111) oriented supercells studied in this work are constructed from a series of O-Ce-O trilayers. With reference to Fig. 4-3, the atomic planes may be labeled alphabetically moving from the surface toward the membrane interior. Accordingly, the surface planes, which consist of O atoms, are labeled "A," with the subsurface Ce planes labeled "B," followed by the first subsurface planes of O atoms labeled "C," and so on.

Considering first the bulk relaxation vs. biaxial strain, the spacing between adjacent O and Ce lattice planes was nearly uniform for stoichiometric structures regardless of Pr content. In contrast, introduction of oxygen vacancies (and corresponding cation reduction) led to clear stratification of O-Ce plane spacing. As expected, the distances between lattice planes containing vacancies and/or reduced cations and their neighbors were affected most.

The case of the membrane provides some additional insight. Figure 4-8 shows how the A-B and C-D distances both increased with introduction of surface oxygen vacancies (in plane A), while the B-C distance decreased. In other words, the cation plane B moved farther from the surface oxygen plane A when that plane contained an oxygen vacancy, instead being more strongly attracted to the fully intact subsurface oxygen plane C. The explanation for this arises from Coulomb repulsion. The oxygen planes A, C, and D are composed of anions and therefore negatively charged, while the cation plane B is positively charged. When plane A contained an oxygen vacancy, it was more weakly negative than plane C, meaning that plane B was pulled closer to plane C. The change in the C-D distance follows from this effect, as the cation plane B was more weakly positive than the subsurface cation planes, allowing planes B and D to spread out more than they would in a stoichiometric structure.

When the oxygen vacancies were instead added to plane C (still keeping the reduced cations in plane B), the interplane distances changed in an opposite manner (A-B and C-D decreased, while B-C increased), confirming this explanation. When plane C contained an oxygen vacancy, plane B was attracted more strongly to plane A, and plane D was repulsed more weakly from plane C, so plane B moved closer to plane A. We note that for the 2NN subsurface configuration, the same trends occurred except for the C-D distance, which was not affected relative to the vacancy-free membranes. The explanation for this arises from the fact that in the 2NN configuration, reduced cations were located on both sides of the
Figure 4-8: Near-surface crystallographic plane spacing in biaxially strained Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO). Local z-direction relaxation was not uniform for biaxially strained PCO membranes of varying composition. When an oxygen vacancy was present in the surface plane A, with corresponding reduced cations present in the subsurface cation plane B, plane B moved (a) away from plane A and (b) closer to the subsurface O layer C. (c) The distance between the first two subsurface oxygen planes also increased when an oxygen vacancy was added to plane A. The opposite trend occurred when the oxygen vacancies were instead located in plane C. Subscripts and parenthetical labels A-D denote the atomic layer as shown in Fig. 4-3. Overall, interplane distances were affected more strongly by oxygen vacancy formation than by simple cation substitution or biaxial strain. Figure from Ref. [2].
oxygen planes C and D, mitigating the Coulomb repulsion effects observed for the surface and 1NN configurations.

The broken symmetry at the membrane surface reflects the role of Coulomb repulsion in the framework of total charge, as opposed to the relative charge for point defects when defined in Kröger-Vink notation. Additionally, we note here that neither biaxial strain nor cation substitution impacted atomic plane rearrangements as significantly as the presence or absence of oxygen vacancies and associated reduced cations. This non-uniform rearrangement of lattice planes is of interest whenever the local surface structure is particularly important for charge transfer or gas reactivity, for example when an oxide is used to catalyze oxygen reduction in an SOFC cathode or H2O reduction during electrolysis. In fact, Feng et al. have found that for H2O reduction on CeO2 surfaces, the electron transfer step is rate limiting, while oxygen transfer into vacancies is relatively facile.[36] Our work supports this result in the following way: We found that when plane A contained an oxygen vacancy (necessary for a mass transfer step in a surface reaction), plane B, containing the reduced cations and associated spare electrons, moved away from the surface, impeding electron transfer to any adsorbed surface species. Although we observed the opposite trends of interplane distance changes when vacancies were in the subsurface layer C, for mass transfer to occur the vacancies need to be at the surface, so the case of vacancies in plane A is more relevant to the present discussion. Also, we note that tensile strain promoted surface vacancy formation, suggesting that tensile strain could also promote oxygen mass transfer when PCO participates in gas exchange (as it would in a fuel cell).

This study showed that membrane and bulk forms of PCO exhibited comparable changes in biaxial stiffness for comparable changes in oxygen vacancy concentration. Vacancies located at the membrane surface, a condition that was promoted by tensile biaxial strain, elicited no detectable differences between the bulk and membrane dependence of C_biax on Δδ. Subsurface vacancies (promoted by compressive strain) actually break the nearest-neighbor bonding symmetry at the free surface, and thus may affect the stiffness of films more than they would in the bulk because of the film’s relatively greater surface area to volume ratio. When considered in the context of previous experimental results measuring the elastic modulus of PCO films grown on YSZ under in situ conditions of temperature and pO2, these results support the hypothesis that film effects are more strongly related to differences in the in situ defect content than finite thickness effects. Additionally, this study demonstrated at least one local structural effect associated with biaxial strain- that of non-uniform z-axis lattice relaxation. In the presence of surface oxygen vacancies, the subsurface cation plane moved away from the membrane surface, potentially impeding electron transfer steps during electrolysis or similar gas-surface reactions. For very thin films, or those that contain high concentrations of grain boundaries or other defects that may produce a space-charge layer, such differences could contribute to producing non-uniform strain, elastic moduli, or charge transfer. The combination of this kind of local effect and differences in operando defect content are expected to produce experimentally observable differences between nominally equivalent compositions of bulk and thin film non-stoichiometric oxides. However, we note that these inferences neglect the potential additional implications of a film-substrate interface, which we did not include in membrane simulations.
4.4 Conclusions

This chapter presented two DFT + U investigations of how changes in composition in the model non-stoichiometric oxide material PCO modulate mechanical stiffness. Both studies found that increased oxygen vacancy concentration, which causes chemical expansion, led to decreased elastic moduli. The first study, which focused on computing the stiffness tensor for bulk PCO, found that the Young's modulus $E$ decreased by 10% per 1% increase in lattice parameter $a$, which compares well with literature results for bulk measurements of $E$ as a function of chemical expansion in Gd$_x$Ce$_{1-x}$O$_{2-\delta}$ (GDC), a related oxide to PCO. Although these bulk simulations agree well with bulk data from the literature, the experimental results of Chapter 3 found larger decreases in $E$ as a function of temperature and oxygen partial pressure than would have been expected given predicted changes in $a$ according to the chemical and thermal expansion coefficients of PCO. Possible explanations for this experimentally measured stronger dependence of $E$ for thin films on $T$ and $pO_2$ than bulk models, measurements, or calculations predict include larger \textit{in situ} point defect concentrations (causing larger than predicted changes in $a$), anisotropy effects, or finite thickness effects. Therefore, we sought a more direct comparison of thin film and bulk elastic constants in order to elucidate the source of this difference between thin film and bulk oxide mechanical stiffness.

With that in mind, we undertook a parallel DFT + U computation of the biaxial elastic constant $C_{b\text{ia}x}$ of bulk and membrane forms of the model non-stoichiometric oxide material Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO). $C_{b\text{ia}x}$ is the most technologically relevant stiffness for this application, as it governs the stress or strain state thin films will experience when constrained in a multilayer device. Understanding stress and strain states at interfaces such as those that exist between cathode materials and electrolytes is helpful both in predicting sites of mechanical failure, and in engineering materials to take advantage of mechanical strain. For PCO, we found an overall decrease in $C_{b\text{ia}x}$ with increasing oxygen vacancy content $\delta$ that corresponds to increased lattice volume due to chemical expansion. The relative change in $C_{b\text{ia}x}$ per increase in $\delta$ was comparable for bulk and membrane forms of PCO, particularly when vacancies were present on membrane surfaces. Those findings support the hypothesis that experimentally observed differences between bulk and film elastic properties are not attributable solely to finite thickness effects such as artifacts of indentation-measured elastic moduli, and are more likely related to differences in \textit{in situ} oxygen vacancy content. We also found that biaxial strain could modulate the energetics of oxygen vacancy formation in PCO. Of the three configurations investigated, the 2NN subsurface vacancy configuration was energetically most favored. However, for fixed cation positions, tensile strain favored surface vacancies, while compressive strain favored subsurface vacancies. Given that subsurface vacancies appeared to have a stronger influence on $C_{b\text{ia}x}$ than surface vacancies, it is possible that films grown with compressive as opposed to tensile strain might also have slightly stronger dependencies of elastic constants on $T$ and $pO_2$. However, this effect would likely not extend beyond the first few nm of the film surface. Future simulations including a film-substrate interface would be able to provide a more complete picture of the chemomechanical factors influencing thin film biaxial stiffness.

Additionally, inhomogeneous strain effects were evident in this work, as atomic planes adjusted their spacing local to oxygen vacancies or reduced cations. In particular, significant
non-uniform rearrangement of z-direction atomic plane spacing occurred when oxygen vacancies were located at the surface of the PCO membranes, apparently resulting from changing local electrostatic forces with surface reduction. This result has important implications for surface reaction kinetics such as H₂O reduction during electrolysis. Although PCO was used as a model system in this study, the comparison of composition-dependent bulk and thin film mechanics is expected to have general applicability for other non-stoichiometric oxide systems that also undergo chemical expansion with oxygen vacancy formation.

Although beyond the scope of the above work, during the course of the calculations determining $C_{\text{biax}}$, it became clear that the magnetic state of the reduced cations had a fairly significant effect on the total energy of the bulk and membrane forms of PCO, with the ground state being the one with maximum magnetization (this difference between the fully magnetized and demagnetized states for the 108-atom bulk simulation cell was on the order of 1 eV) that might also interact with $C_{\text{biax}}$. Literature results have indicated that doping CeO₂ with Pr can produce a dilute magnetic oxide at room temperature, while undoped CeO₂ films do not exhibit this property.[37, 38] An interesting potential area for future study would be to investigate the phase diagram relating the magnetic cation states to biaxial strain, potentially determining whether there is a way to use mechanical strain to favor certain magnetic states in this model oxide.

In the broader context of this thesis, these results indicate that there are anisotropic factors in thin film non-stoichiometric oxides that can cause local lattice structure to distort non-uniformly. Additionally, local mechanical strain may adjust the energetics of preferred point defects. Given these observations, it seems probable that non-stoichiometric oxide films will respond to mechanical constraints when they undergo chemical expansion. It also seems probable that regions of broken symmetry, including not only surfaces but also interfaces, grain boundaries, or linear defects, can be expected to influence the energetics of point defect formation. This could happen, for example, as a result of strain fields near these types of linear or planar defects, or, in the case of the surface, the relaxation of mechanical constraints. Not only should films expand differently when they are subjected to a mechanical constraint, but coupling between volume and composition will lead to non-uniform composition local to structures that produce such strain fields. Given that elastic properties directly respond to changes in lattice volume, variation in elastic moduli will also follow these patterns. Thus, the large scale deformations that were observed in Chapter 2 actually resulted from complex interactions between stress, volume, defect chemistry, and mechanical properties that are not uniform on the atomic scale. The next chapter seeks to characterize these complex interactions by using in situ electron microscopy to observe chemical expansion in PCO cross sections grown on the commonly used electrolyte material yttria stabilized zirconia. This characterization analyzes both film-level structural deformation and nm-scale composition redistribution and interface structure. With a deeper understanding of how chemomechanical coupling manifests on the atomic scale, we hope to further explain the unusually large changes in elastic constants observed for thin films experimentally while also providing a more detailed description of the mechanisms that triggered large-scale structural deflection in Chapter 2. These results can inform the design of non-stoichiometric oxide devices that aim to harness interfacial stress to achieve either mechanical deformation or strain engineered functionality.
Bibliography


Chapter 5

Transmission Electron Microscopy Investigation of Nanoscale Chemical Expansion in $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$

The preceding thesis chapters explored chemical expansion and its effects on mechanical properties in films of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO) through measurements that probed the material on the scale of hundreds of nm. Nanoscale electrochemomechanical spectroscopy (NECS) measurements recorded mechanical actuation resulting from interfacial stress generated by electrochemical oxygen pumping (and associated chemical expansion) into the PCO film. Nanoindentation measurements showed that chemical expansion decreases the elastic modulus of PCO thin films more than expected for bulk samples of the same material. Computational simulations confirmed that trend and also showed that the magnitude of displacements can vary within the crystal, dependent on features such as the number and crystallographic location of oxygen vacancies. These observations demonstrated the mechanical consequences of chemical expansion in terms of both structural deflections and changes in mechanical properties, while also highlighting an additional way in which non-stoichiometric oxide films differ from their bulk counterparts in situ. In the present chapter, we characterize chemical expansion of PCO through direct visualization of the atomic scale structure, including interactions among defect chemistry, chemical strain, interfaces, and threading defects. The goals of this work included determining and visualizing the nanoscale mechanisms of chemical expansion and stress accommodation in situ, and identifying possible sources of differences between film and bulk properties including extent of chemical expansion.

Through a combination of high-temperature scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and phase contrast transmission electron microscopy (TEM), we characterized chemical strains and composition variations in cross-sections of PCO films grown on yttria stabilized zirconia (YSZ) at temperatures exceeding 600°C. We quantified, both statically and dynamically, the nanoscale chemical expansion as a function of position and direction relative to the film-substrate interface. We also characterized the in situ PCO-YSZ interface structure and composition and observed periodic structures that varied in position as a function of temperature and redox condition. Ad-
ditionally, we observed reduced cation localization to threading defects within PCO films. These results illustrate several key aspects of structure and mechanical deformation in non-stoichiometric oxide films that clarify distinctions between films and bulk counterparts, and that hold several implications for operando chemical expansion of such oxide films.

This study represents a collaboration among the laboratories of Professors Krystyn J. Van Vliet (MIT), Harry L. Tuller (MIT), and Jamie H. Warner (Oxford University). Films for this study were grown by Thomas Defferriere (Tuller group), and FIB cross-sections were prepared by Prof. Jamie Warner and Dr. Gareth Hughes of the David Cockayne Centre for Electron Microscopy at Oxford University. TEM, STEM, and EELS data were collected by Prof. Jamie Warner and Dr. Jakyung Lee (Warner Group) at Oxford University for analysis conducted by the thesis author primarily at MIT. Dr. Shilpa Raja assisted with image analysis for Section 5.3.3. Dr. Hidetaka Sawada (visiting scientist at Oxford University) assisted with microscope operation and image collection, and Profs. Brian W. Sheldon and Sharvan Kumar (Brown University) provided useful discussion. Parts of this chapter are also included within a manuscript in preparation for publication.[1]

5.1 Introduction

Throughout this thesis, we have discussed in detail the effect known as chemical expansion, and demonstrated that such a driving force can lead to mechanical stress and strain in situ as a function of temperature, oxygen partial pressure, or electrical stimulation that modulate the defect chemistry of non-stoichiometric oxide films. While chemical expansion has been characterized most often by diffraction or dilatometry, it has rarely been observed directly on the atomic scale, especially at elevated temperatures characteristic of solid oxide fuel cell (SOFC) operation.[2, 3, 4, 5] Instead, computational results such as those presented in Chapter 4 and by Marrocchelli et al. have provided insights into the mechanisms contributing locally to chemical expansion. Those computational predictions included increased ionic radii for reduced cations associated with oxygen vacancy formation.[6, 7] However, leveraging or engineering such chemical expansion effects in situ, particularly for applications including strain engineered SOFC cathodes or high-temperature oxide actuators, requires detailed understanding of how stress and strain develop near constrained interfaces in situ. Both the uniformity and magnitude of such effects are important, especially at length scales <100 nm, where line defect contributions to deformation are described, and where the elementary steps of charge or mass transfer take place. Here we characterized in situ the atomic-scale response of a model non-stoichiometric oxide film to elevated temperature up to 650°C and distinct oxidation states, through high resolution transmission electron microscopy and electron energy loss spectroscopy.

Thin films exhibit two important differences from bulk counterparts of the same material: (1) relatively higher densities of crystallographic defects, and (2) influence of mechanical constraints at the film-substrate interface. These differences hold particular importance in non-stoichiometric oxide films such as Pr-doped CeO$_2$ considered herein. The potential for higher defect density in thin films is attributed generally to the relative contribution of surfaces and interfaces, which naturally comprise a larger proportion of material volume in thin film specimens, to the total film volume. For example, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) experiments have shown that CeO$_2$
films and nanoparticles can exhibit especially large oxygen vacancy concentrations near free surfaces, or exhibit regions enriched in reduced cations in space charge layers at grain boundaries or interfaces. [5, 8, 9] Furthermore, additional capacity for inducible film stress due to thermal or chemical stimuli is attributed to the fact that films adhered to substrates are constrained from lateral displacement and strain at the film-substrate interface. At the atomic scale, this constraint can also include strain associated with film deposition, including atomic lattice mismatch between the two materials. In the context of thermal and chemical expansion, this constraint of lateral displacement with respect to bulk forms of the same material induces additional film strain (or stress) that depends on relative magnitude of thermal or chemical expansion coefficients describing lattice parameter changes as a function of temperature or point defect content, respectively.

Non-stoichiometric oxide films can also exhibit lattice strain as the point defect content changes in situ, including changes in concentrations of reduced cations and corresponding oxygen vacancies. Interfacial constraint may cause most of this environment-dependent lattice strain to occur perpendicular to the interface. This anisotropy in lattice parameter as a function of distance from the film-substrate interface could result plausibly in anisotropic physical and mechanical properties including charge transport and elastoplastic properties. Particularly in the context of the high-temperature oxide actuators discussed in Chapter 2, it is of interest to determine to what extent stress-relief mechanisms, such as anisotropic chemical strain, line defect motion, or phase separation, occur and contribute to non-stoichiometric oxide films at high temperatures. Such direct observations are important particularly to discern whether linear defects, phase changes, or spatially anisotropic strains may also couple to other important functional properties of these oxides.

Several previous studies of undoped and Pr-doped CeO₂ at room temperature have been conducted by TEM, STEM, and EELS. Sheth et al. reported that PCO films grown by pulsed laser deposition (PLD) on YSZ substrates exhibited partial epitaxy with threading dislocations observable via TEM that propagated from the interface to the (100) oriented film surface.[10] Those authors also reported irreversible stress relaxation observed by multi-beam optical stress sensors at high temperature for which the mechanisms were not elucidated.[10] Several groups have reported misfit dislocations in CeO₂ films grown epitaxially on YSZ.[11, 8, 12] Sinclair et al. also noted that substantial electron beam exposure for very thin (∼ 11 nm) CeO₂ membranes induced vacancy ordering and sample reduction that could be recovered readily with re-oxidation of the sample.[11] Vacancy ordering can also be induced in CeO₂ films at room temperature by application of volt-scale electrical bias, a type of in situ TEM that recently has been applied to the study of resistive switching effects in non-stoichiometric oxide materials at room temperature.[13, 14, 15]

Others have also reported non-uniform composition or oxidation state in close proximity to grain boundaries, interfaces, and surfaces in doped and undoped CeO₂ at room temperature. CeO₂ nanoparticles exhibited large vacancy concentrations, surface rearrangements, and lattice expansion on the order of 7% after sample reduction in hydrogen at high temperatures, an effect that may be enhanced by doping.[16, 17] Room temperature STEM imaging of CeO₂ films grown on YSZ with EELS has shown substantial Ce cation reduction within a 5 nm distance from the interface, consistent with the concept of interfacial space charge existing at room temperature. [8] Enhanced cation reduction has also been observed within grain boundary cores in sintered Gd/Pr co-doped ceria powders, along with Gd and
Figure 5-1: Schematic of *in situ* TEM experiments on non-stoichiometric oxide film cross-sections. Epitaxial Pr$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ (PCO) films grown on yttria stabilized zirconia (YSZ) substrates subject to mechanical constraint at the interface. Upon heating inside the microscope, the PCO film undergoes anisotropic thermal and chemical expansion and associated sample reduction (indicated by lighter film color) through oxygen loss. Defects at the interface between the film and substrate and threading throughout the film thickness may contain higher concentrations of reduced cations. PCO strain was determined through Fourier transform analysis of electron microscopy images, and oxidation state change was identified by electron energy loss spectroscopy.

Pr enrichment at grain boundaries. This observation was correlated with reduced migration energies for oxygen vacancies, representing an important way in which local microstructural features may be used to enhance functional properties (e.g., ionic conductivity) by providing fast-conduction pathways.[18] In that case, cation reduction at the grain boundary was concurrent with depleted oxygen content, indicating that this was not a space-charge effect. Opposite effects might exist proximal to dislocations in doped or undoped CeO$_2$; computational results have indicated that edge dislocations could retard oxide ion diffusion by causing segregation of charged defects.[19] While those prior studies observed or predicted many types of non-uniform composition or oxidation states in CeO$_2$ at room temperature, little direct evidence of these effects at high temperatures has been gathered. Further, the correlation of these defect distributions with chemical expansion has been explored only minimally. In fact, while volume-averaged chemical expansion has been observed by diffraction, stress measurements, or probe-based approaches (Chapter 2), there exist few reports of defect distribution or chemical expansion at film-substrate interfaces.[20]

Here we present analysis of defects and displacements in a model PCO-YSZ system, using high-temperature TEM, STEM, and EELS to quantify chemical expansion, composition, and oxidation state of a film-substrate cross-section. As shown schematically in Fig. 5-1, we focused particular attention to the role of the interfacial constraint, modes of chemical expansion accommodation within the defective lattice, and the nature of linear defects that emerged upon film oxidation. These results confer important implications for understanding
how epitaxial non-stoichiometric oxide films may respond to interfacial stresses arising from thermal or chemical expansion operando, including potential impact on charge transport or reactivity relevant to high-temperature actuation or electrochemical energy conversion.

5.2 Methods

5.2.1 Sample preparation

Pr$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ (PCO) films were prepared by pulsed laser deposition (PLD) from oxide targets. The films were deposited onto (001)-oriented single crystal yttria stabilized zirconia (YSZ, 8 mol% Y$_2$O$_3$ stabilized) substrates (10 × 10 × 0.5 mm$^3$; MTI Corporation, Richmond, CA). The 2.5 cm diameter oxide target was fabricated according to the methods of Refs. [21] and [22].

The PLD system (Neocera Inc., Beltsville, MD) was operated with a KrF excimer laser (Coherent COMPex Pro 205) emitting at 248 nm, with 400 mJ/pulse and repetition rate of 8 Hz. The substrates were heated to 600°C during deposition, while the oxygen pressure was maintained at 10 mTorr after pumping the background pressure to less than $8.56 \times 10^{-6}$ Torr. The film was deposited with 45000 shots after 2000 pre-ablation shots with a substrate to target distance set to 7 cm. Following deposition and prior to cooling, the oxygen pressure in the chamber was increased to approximately 6-7 Torr to facilitate complete oxidation of the film. Film thickness was determined to be 196 nm via surface profilometry (KLA-Tencor P-16+ stylus profiler) of the film deposition edge.

Two PCO-YSZ cross-sections were prepared by focused ion beam (FIB) milling by J. Warner and G. Hughes of Oxford University. The thickness of the final cross-sections was 50-100 nm. Throughout the chapter, the cross-sections imaged at room temperature and high temperature are referred to as Samples A and B, respectively. Figure 5-2(a-c) shows Sample B attached to a heating chip, including false coloring to denote different materials both before and after additional milling to extend the slit in the Si$_3$N$_4$ for improved image resolution.

5.2.2 Imaging and EELS

Three microscopes were used to acquire images and spectroscopic analysis described below. Initial room temperature imaging of as-grown PCO films on YSZ (Sample A) was conducted using an aberration corrected JEOL JEM-2200MCO field emission gun TEM/STEM operated at 200 keV, equipped with CEOS image/probe correctors. In situ imaging at high temperatures up to 650°C was conducted using a commercially available in situ heating holder from DENS Solutions (SH30-4M-FS). The resistance of the platinum coil in the heating chip (DENS Solutions DENS-C-30) is monitored in a four-point configuration, and the temperature is calculated using the Callendar-Van Dusen equation (with calibration constants provided by the manufacturer). Slits were produced into the Si$_3$N$_4$ membrane by focused ion beam milling. Phase contrast transmission electron microscopy of samples at elevated temperatures was conducted with a standard JEM-2100 (JEOL) transmission electron microscope operated at 200 kV, with a LaB$_6$ filament, while both high temperature and room temperature annular dark field - scanning transmission electron microscopy (ADF-
Figure 5-2: Scanning electron microscope image of the Pr$_{1}$Ce$_{0.9}$O$_{2-\delta}$ (PCO) on yttria stabilized zirconia (YSZ) cross-sections prepared by focused ion beam (FIB) milling. (a) After milling, Sample B was placed on a high temperature heating chip that uses Pt heating elements (spirals) to raise the sample temperature up to 650°C. (b) Higher magnification image with false color shows the different regions of the FIB cross-section and heating chip. Colors indicate: YSZ substrate (pink), PCO film (green), Pt capping layer (yellow), Si$_3$N$_4$ window (turquoise) and thicker Si$_3$N$_4$ (purple). (c) A slit expanded by FIB-milling into the Si$_3$N$_4$ window after cross-section placement. Image prepared by J. Warner.

STEM) of Sample B was conducted using a JEOL ARM-200F microscope operated at 200 kV.

An initial annealing study was conducted using the JEM-2100 while heating Sample B from room temperature to a maximum temperature of 650°C in increments of 50-100°C and imaging along the film and interface cross-section. This resulted in substantial electrochemical reduction of PCO while inside the TEM column at $T > 500^\circ$C. The sample was rapidly cooled to room temperature to maintain this reduced state and then imaged and analyzed via EELS using the ARM-200F microscope at 300°C and 650°C. Sample B was then heated to 650°C for 30 min outside of the TEM column to enable re-oxidation of the PCO film. To observe sample reduction in situ, Sample B was cooled rapidly to room temperature and heated to 200°C with image focusing adjustments at each temperature, before rapidly heating the sample to 650°C within 2 min inside the JEM2100. For the next 7 min, sample equilibration to the column vacuum was observed by continuous imaging along the film near the interface; images were recorded every 10-30 sec, with the imaging location translated every 0.5-2 min. The sample was then re-oxidized again at 650°C in air and placed in the ARM200 at room temperature. Imaging and EELS analysis were conducted at room temperature, followed by 300°C (a temperature sufficient to prevent significant oxygen loss despite the TEM vacuum), followed by 650°C. This last condition following intentional oxidation of the PCO is labeled "post-oxidation" or "postox" in the figures, to distinguish from image acquisition at 650°C prior to forced oxidation.

EELS data were gathered using the ARM-200F microscope for an energy range of 300-2350 eV. To mitigate sample reduction by electron beam dosage, the imaging location was frequently adjusted for all imaging conditions. However, little evidence of beam-induced sample reduction was observed during imaging, due to the larger cross-section thickness compared to the reports of Sinclair et al.[11]

Images below reference the x-y plane as the imaged cross-section plane of the PCO
lattice, with the image z-axis oriented along columns of atoms extending into the milled cross-section. We thus refer to the displacements normal to the film-substrate interface as "out-of-plane" and select a y-axis orientation normal to the interface. Thus, displacements normal to the film-substrate interface are denoted as those extending in the y-direction normal to the interface, or "out-of-plane" because such displacements would indeed represent film thickness increased or decreased in a direction perpendicular to the film plane and free surface of the film in plan view (i.e., rotated 90° from the cross-sectional view of the TEM image plane). Displacements parallel to the interface are denoted as those observed in the x-direction, or "in-plane." Clearly, the z-axis in this orthogonal axis set is normal to the cross-section surface, and any misorientation of the lattice displacements with respect to the x-y axes refer to those offset from the film-substrate interface normal.

5.2.3 Data analysis

Images were analyzed using Digital Micrograph version 3. To determine lattice spacing in PCO and YSZ, Fast Fourier transforms (FFT) of TEM and STEM images were analyzed for peak positions using the Measure Spacings and Angles script in the DiffTools package available from D.R.G. Mitchell.[23] To determine the x- and y-components of PCO lattice spacing for ADF-STEM data at each condition, four to eight square regions of 10 × 10 nm were selected adjacent to the interface, and the FFT peak positions and angles were measured. Because FFT representations of the ADF-STEM images produced a hexagonal pattern, the y-direction projection of the out-of-plane spots (θ ~ 72°) were used to determine the "y-component" lattice spacing normal to the interface. The resulting magnitudes of x- and y-component spacing were averaged for each condition and compared to the spacings measured in the same imaging conditions for the YSZ substrate. In the case of rectangular lattice projections (Sample A room temperature images and parts of Sample B images during re-oxidation), this analysis did not require the additional step of accounting for angles θ.

Strain maps were produced by Geometric Phase Analysis (GPA) of x-component or in-plane strain parallel to the film-substrate interface, using the FRWRTools plugin for Digital Micrograph written by C. Koch.[24] The following parameters were used for GPA: 3 nm resolution, 1 nm smoothing.

Observed strains were computed with reference to the YSZ sample, specifically by determining the ratio of PCO lattice spacing to YSZ lattice spacing at the same imaging condition (T, oxidized or reduced sample) for each FFT peak of interest, and then comparing the difference in this ratio between oxidized and reduced states. For example, to compute the chemical strain perpendicular to the interface at 300°C for the reduced sample, the change in this ratio ([PCO y-spacing/YSZ y-spacing in reduced state] - [PCO y-spacing /YSZ y-spacing in oxidized state]) was computed and then divided by the ratio in the oxidized case, which gave the chemical strain perpendicular to the interface. This calculation assumed, consistent with expectations, that only PCO, and not YSZ, responded to oxidation or reduction conditions at high temperature. Changes in defect chemistry based on observed strains were estimated by applying the chemical expansion coefficient of PCO (α_c = 0.087) and Eq. 1.4.[3]

To improve image signal to noise ratio, images from the annealing study were stitched together using the pairwise stitching toolbox in Fiji.[25, 26] Using ImageJ, the widths W of
the interfacial periodic contrast fringes were analyzed by drawing lines across the interfacial width regions to obtain widths in pixels. Between 10 and 15 such data points were collected per image. Reported values for $W$ at a given temperature represent mean and standard deviation of these measurements. Higher temperatures generated more high-quality fringe images, so it was generally possible to obtain, analyze, and average together more images for higher temperatures. For example, 19 images were used to obtain averages for $400^\circ C$, while only five were used for $100^\circ C$. Periodic spacing $\lambda$ between adjacent fringes was obtained by drawing a line of width of $\sim 50 - 300$ pixels (depending on temperature and array width) parallel to the interface such that the entire array was covered. The resulting periodic line profiles were obtained in Image-J. To determine spacing, the average trough-to-trough and peak-to-peak distances in the images were measured and averaged. Depending on how much of the interface was clearly visible in each image, 10-20 peak-peak distances were analyzed and averaged per image. This quantification of $W$ and $d$ as a function of $T$ was conducted by Dr. S. Raja.

EELS data were analyzed following the background subtraction procedure described in Ref. [18] and briefly summarized here. Background subtraction for the Ce peaks was conducted by fitting an exponential loss function to a 50 eV window that was positioned to end 5 eV below the Ce M5 peak. For the Pr peaks, background subtraction was done by a two-window procedure available in Digital Micrograph version 2, with a 5 eV window below the Pr M5 peak and a second window from 1120-1165 eV; that window was well beyond the high energy loss tail of Pr. The Ce M5 and M4 peak areas were measured based on integrating 20 and 25 eV fitting windows after background subtraction, respectively, spaced by 1 eV and starting at $\sim 871$ eV. The Pr M5 and M4 peaks were similarly characterized starting at 920 eV, and the full-width half-maximum (FWHM) of the Pr M5 peak was determined after applying a double-gaussian fit to the peak (after background subtraction) between 900 and 938 eV. This peak fitting was conducted using the curve-fitting toolbox in Matlab. The Cornell Spectrum Imager plugin for ImageJ was also used to handle, view and compare EELS spectrum image files and maps.[27, 28]

Time series data were fitted by linear regression. For the $x$-component lattice spacing, sufficient data density and range were available to apply a bootstrapping procedure to determine errors in fitting coefficients.[29] Using a custom Matlab code (Appendix E), the slope and intercept of the linear fit of $x$-component lattice spacing vs. time was recomputed from 1000 resampled data sets to identify 95% confidence intervals for these parameters.

5.3 Results and discussion

5.3.1 Structural characterization of as-grown PCO

We first characterized samples at room temperature to assess as-deposited PCO microstructure. Figure 5-3(a) shows a low magnification image of the PCO-YSZ cross-section. The film exhibited apparently columnar microstructure. However, upon closer inspection, the threading defects propagating from the interface to the surface of the film (highlighted by white arrows) were discerned to be disordered regions and not grain boundaries separating grains of distinct orientations. Distinct grain orientations would appear as rotated or distorted FFT patterns, while doubled spots at the same orientation but slightly differing spacing $d$
indicate epitaxy. We found no evidence of grain rotation or mismatch on either side of these defects; instead the film was oriented in a consistently epitaxial manner extending along the y-axis from the interface toward the free surface of the deposited films. The doubled spots in the FFT at the PCO-YSZ interface shown in Fig. 5-3(b) support this conclusion; this doubling is typical of the interface. Sheth et al.[10] observed similar defects in PCO films grown by PLD on YSZ; those authors attributed such image contrast features to threading dislocations. While our microstructure is consistent with those authors' results, the region at the PCO-YSZ interface at room temperature was in general too disordered in our own images of Sample A to resolve specific dislocation cores or Burgers vectors. However, the film lattice was otherwise possible to resolve with atomic resolution, as exemplified by Fig. 5-3(c).

Figure 5-3(c) also denotes the notation we use throughout the Chapter: "x-component" corresponds to the direction parallel to the film-substrate interface, along which PCO displacement is constrained by the substrate, while "y-component" refers to the direction normal to the film-substrate interface and unconstrained in displacement toward the film free surface. We also note here that there existed a layer of atomic disorder (~10 nm thickness) at the film free surface in Sample A. Figure 5-3(a) denotes that region by a dashed line, and our FFT and EELS analysis indicated a larger proportion of reduced cations and larger lattice volume in that region relative to the rest of the film. Those features were indicative of significant film reduction and associated chemical expansion in that area, and thus we attributed the features of that region to damage during sample preparation by FIB milling.

We quantified the as-prepared lattice spacing in the PCO film relative to the YSZ substrate as a function of distance from the interface, as shown in Fig. 5-3(d). Near the interface, strain normal to the interface (y-component) was significantly larger than that parallel to the interface (x-component). This difference decreased with increasing distance from the interface and was approximately equal at a distance of ~40 nm. This result is expected in that YSZ exhibits a smaller lattice parameter than PCO, such that the PCO x-component lattice parameter near the film-substrate interface is smaller than that of unconstrained bulk PCO. The PCO film strained normal to the interface under this constraint, and this anisotropic lattice distortion was reduced with increasing distance from the interface. We report this PCO lattice parameter change as a ratio with respect to the YSZ lattice parameter, both because the ~6% lattice mismatch between these materials is well-established, and because the YSZ lattice parameter at room temperature is a useful reference length in our subsequent experiments that incurred thermal expansion in both the film and substrate lattices but chemical expansion in only the PCO film lattice. We note here that the as-grown PCO film exhibited relatively invariant composition as a function of distance from the interface, as quantified by EELS. Except for the FIB-damaged region at the film free surface (i.e., maximum distance in y-direction from the interface), neither the cation oxidation state nor the dopant distribution varied significantly throughout the film or near the linear defects. This result is also consistent with the room temperature results of Ref. [10].
Figure 5-3: (a) Low magnification image of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO) film on yttria stabilized zirconia (YSZ) substrate cross-section at room temperature. Threading features propagating from the YSZ interface to the surface (highlighted by white arrows) were not grain boundaries, but instead disordered regions. The FIB preparation resulted in a disordered and reduced "surface layer" separated by a dashed line. (b) Fast Fourier Transform (FFT) of PCO-YSZ interface (inset, 5 nm scale bar) showing doubled reflections indicative of epitaxy. Red arrows denote PCO spots, and white arrows denote YSZ spots. Sample tilt accounts for slight asymmetry in the FFT pattern. (c) High resolution image of PCO film showing atomic resolution and coordinate system (inset, FFT of this region). Lattice spacing parallel to ($x$) and normal to ($y$) the film-substrate interface are labeled by blue and orange arrows, respectively. (d) The ratio of PCO lattice spacing to YSZ as a function of distance from the interface. In general the PCO had a larger lattice parameter than YSZ, leading to an expected $\sim 6\%$ mismatch. However, within 30 nm of the interface anisotropic strain was observed - strain normal to the interface was larger than that parallel to the interface and constrained by the substrate. The region near the film free surface had slightly larger than average volume due to reduction during FIB preparation and associated chemical expansion.
5.3.2 Thermochemical strain anisotropy

Having established the initial PCO film structure, we next characterized film response to a change in temperature or oxidation state. Using the spatial and chemical resolution afforded by ADF-STEM imaging coupled to EELS analysis, we imaged a cross-section loaded on a high temperature TEM holder at four conditions of temperature and oxidation state. Figure 5-4 shows the lattice spacings of PCO and YSZ measured at these conditions parallel to \((x)\) and normal to \((y)\) the interface, as well as the ratio of PCO lattice spacing normalized against the corresponding values for the YSZ substrate. We note that because we conducted high temperature imaging on a different specimen than the specimen analyzed at room temperature in Fig. 5-3, with a different FIB-cut orientation and imaging conditions, the lattice spacings observed for sample A in Fig. 5-3(b) are not identical to those observed in Fig. 5-4(a-b). Both the PCO and YSZ crystals exhibited thermal expansion; however, the PCO film also exhibited chemical expansion. This additional capacity of the PCO film to exhibit expansion due to cation valence and oxygen vacancy concentrations that vary with temperature can be recognized through comparison of the "reduced" and "oxidized" lattice spacing ratios. Note that PCO at temperatures \(> 500^\circ\text{C}\) is capable of fast oxygen exchange and is expected to equilibrate to the vacuum (low \(p_{O_2}\)) in the TEM column within minutes by releasing oxygen (i.e., undergoing electrochemical reduction).[30, 31] Thus, at \(650^\circ\text{C}\), PCO was reduced significantly within the 15-20 min required to focus the electron probe. However, at a lower temperature of \(300^\circ\text{C}\), comparison of pre-oxidized and pre-reduced samples was possible, allowing direct observation of thermal and chemical expansion.

The EELS spectra in Fig. 5-5 confirmed the electrochemical reduction of PCO at elevated temperature. We recorded these spectra at a distance of 10 nm from the interface at each condition. The spectra shown in Fig. 5-5 exemplify the features used to characterize cation composition and oxidation state. The key features in these images are the Ce M5/M4 peak ratio (quantified in Fig. 5-5(b)) and the shape of the Pr M5 peak; the EELS signature of PCO at different oxidation states was characterized previously and reported elsewhere.[18, 32] Pr reduces preferentially to Ce, and when this occurs the Pr M5 peak narrows and shifts to lower energy. This shape change was apparent for the reduced spectra in Fig. 5-5, including the "post-oxidized" spectrum that we recorded upon heating the oxidized sample to \(650^\circ\text{C}\). We quantified the change in peak shape using the peak full width half maximum (FWHM) reported in Fig. 5-5(c). The Pr M5 peak width did not change appreciably when we heated the reduced sample from 300 to \(650^\circ\text{C}\). In contrast, the peak narrowed with increased temperature (from 300 to \(650^\circ\text{C}\)) for the oxidized sample. Elevated temperature of \(650^\circ\text{C}\) should be sufficient to elicit oxygen loss (sample reduction) inside the TEM column. Thus, Pr contained in reduced samples or in samples above the oxygen exchange threshold temperature of \(\sim 500^\circ\text{C}\) should be assumed to be chiefly in the +3 state.

The EELS signature for Ce oxidation state, as characterized by a change in the relative heights of the Ce M5 and M4 peaks (and associated areas), was remarkable. For Ce, increased M5/M4 ratio and associated left-shifted M5 and M4 peaks (with appropriate peak referencing) indicate \(\text{Ce}^{+4} \rightarrow \text{Ce}^{+3}\) cation reduction [32]. Thus, it is clear that the "reduced" samples in Fig. 5-4 were reduced to the point of Ce reduction, an effect that was most pronounced for sample reduction at \(650^\circ\text{C}\) (orange, dashed line, Fig. 5-5). Changes in the EELS signature for Pr reduction were quantifiable but less pronounced than those of
Figure 5-4: (a) Lattice spacing parallel to the interface (x-component) and (b) normal to the interface (y-component) in PCO and YSZ at four conditions of temperature and oxidation state imaged by ADF-STEM. We conducted sample imaging for the electrochemically reduced state of PCO (300°C followed by 650°C), followed by re-oxidation of PCO and imaging (25°C followed by 300°C). We normalized PCO lattice spacing normal to the interface (y) with respect to the expected YSZ lattice spacing resulting from thermal expansion, to account for varying tilt angles during different imaging sessions. We determined the y-component lattice spacing from the out-of-plane diffraction spots produced by the hexagonal fast Fourier transform (FFT) diffraction patterns from the images. This hexagonal FFT pattern also means that the x and y component lattice spacings differ in magnitude. We report PCO lattice spacings as mean and standard deviation measured at multiple locations within 10 nm of the interface. (c) Ratios of PCO lattice spacing normalized by YSZ lattice spacing in the same conditions. The effect of chemical expansion, present for reduced samples (open symbols) was greater normal to the interface (y) than parallel to the interface (x, constrained by the YSZ).
Ce oxidation. We further note that the "post-oxidized" sample at 650°C did not achieve complete reduction; this suggests that inside the TEM chamber the process of oxygen loss associated with cation reduction was relatively slow (on the scale of 10-30 min) despite the small sample thickness (<100 nm). Note that we did not ascribe physical interpretation to the apparent peak shifts in Fig. 5-5, as no standard peaks were available to calibrate spectra recorded at different times and under distinct in situ conditions.

Figure 5-4(c) illustrates that the strain variation with distance from the film-substrate interface that we observed in the as-grown film at room temperature (Sample A, Fig. 5-3(d)) was absent upon re-oxidation of PCO at high temperature (Sample B). This contrast in the magnitude of strain within 10 nm of the film-substrate interface in the as-prepared and post-annealed specimens at room temperature suggests that the annealing process relieved interfacial stress sufficiently to relax the film lattice upon re-oxidation at elevated temperature. If we refer to the distinct PCO lattice spacing in the $x$ and $y$ directions as "strain anisotropy," then Fig. 5-4 shows that such strain anisotropy was evident for all conditions except PCO oxidized at room temperature. Thermal expansion in PCO and YSZ was comparable, such that PCO lattice strain (relative to YSZ) parallel to the interface was changed minimally under conditions allowing only thermal expansion. Even so, PCO expansion normal to the interface ($y$-component) increased slightly with increased temperature for the oxidized or reduced cases. In contrast, chemical expansion affected strain both along and normal to the interface (both $x$ and $y$-components) though strain normal to the interface was modulated more strongly. At 300°C, PCO in the reduced state exhibited out-of-plane strain ($y$) of 1.4% as referenced to the oxidized state, whereas in-plane strain along the interface ($x$) was only 0.9% upon reduction. We estimate the measurement error for strain along the interface as ±0.15%, given that this in-plane strain was 0.6% for PCO reduced at 650°C. Even with this level of measurement uncertainty, the strain normal to the interface was ~50% greater than that parallel to the interface, indicating clearly that chemical expansion resulted chiefly in increased atomic spacing normal to the interface (and therefore increased film thickness) due to the film-substrate interface constraint. As measurable expansion was also quantified parallel to the interface, we assert that the chemical expansion coefficient can be understood to be both thickness-dependent and anisotropic with respect to distance from the interface.

By considering Fig. 5-4 and the chemical expansion coefficient of PCO, we can infer differences in point defect concentration, as quantified by the change in non-stoichiometric parameter $\Delta\delta$ that existed in the PCO films in the oxidized and reduced states in situ. Using the strain parallel to the film-substrate interface resulting from partial reduction of PCO at 300°C, $\Delta\delta$ is approximately 0.1 according to Eq. 1.4. Using the strain measured for the fully reduced sample at 650°C, this estimate of $\Delta\delta$ is 0.06-0.1. Assuming that mechanical constraint of the substrate amplified the film strain normal to the interface ($y$-component) by approximately a factor of two [10], we can also estimate $\Delta\delta$ independently at 0.08. Since we observed measurable and repeatable strain parallel to the film-substrate interface, a slightly larger value of $\Delta\delta$ of about 0.1 appears plausible. Given that these films have a Pr concentration of $x = 0.1$, the reduction of Pr can contribute a change in $\delta$ of only 0.05. Therefore, the remaining strain must be attributed to that arising from Ce reduction, an assertion that is further supported by our EELS data in Fig. 5-5. Given these results, we infer that either the effective partial pressure of oxygen $pO_2$ within the TEM chamber
Figure 5-5: (a) Electron energy loss spectroscopy (EELS) at different temperatures at several imaging conditions of temperature and oxidation state. These spectra were shifted against the Ce satellite peak at 1163 eV which is not necessarily an immovable reference, and were collected at a distance of 10 nm from the YSZ interface, which should be sufficient to avoid space-charge effects. Inset shows Pr M5 and M4 peaks after separate Pr background subtraction. (b) Spectra for pre-reduced samples or samples at high enough temperature to evolve oxygen in situ exhibited an increased Ce M5/M4 peak ratio and a leftward shift of the Ce M4 peak, indicative of Ce cation reduction. Additionally, the Pr M5 peak (highlighted by the black arrow) narrowed with Pr cation reduction. (c) The full width half maximum (FWHM) of the Pr M5 peak decreased as Pr reduced. At temperatures of 300°C and below, Pr resisted in situ reduction, although it was fully reduced when exposed to the microscope’s vacuum at high temperature (650°C) for > 10 minutes.

was < 10^{-18} \text{ atm} (the point of Ce reduction in PCO at 650°C [33, 34]), and/or the reduced PCO film cross-section was significantly more reduced than expected based on available defect models. Since the TEM vacuum was at about 10^{-11} \text{ atm} for the results reported herein, a reducing gaseous species such as H₂ or CO would need to have been present to achieve such a low pO₂, making this explanation unlikely. The electron beam dosage may have induced some reduction of PCO, but we intentionally varied the imaging location to minimize such effects, and similar beam dosages applied to oxidized samples did not cause detectable Pr or Ce reduction (see Fig. 5-5). Therefore, we attribute the observed lattice expansion to a combination of low pO₂ and enhanced sample reduction in these very thin (<100 nm) PCO cross-sections.

5.3.3 Interface structure

The variation of chemical expansion exhibited by the PCO films as a function of orientation with respect to the film-substrate interface results directly from the mechanical constraint
of the interface. Figure 5-6 shows that image contrast features existed normal to and near (if not transecting) this interface, and translated parallel to the interface upon sample annealing. These features were visible upon initial annealing, and appeared to translate during sample annealing, even as the samples lattice resolved more clearly and inclusions with dissimilar orientation realigned with the rest of the PCO lattice. Figure 5-6(e-f) shows that the thickness $W$ of these fringes increased with increased temperature even as the interfringe spacing $\lambda$ changed non-monotonically with changes in temperature. In fact, $\lambda$ decreased from about 4 nm at 300° C to about 3 nm at 600° C, then increased again to 4 nm at 650° C to remain constant upon sample cooling to room temperature.

When we imaged the same sample by STEM subsequently, the interface continued to exhibit a periodic array of defects, as shown in Fig. 5-7(a) and (c). Geometric phase analysis (GPA) of these images produced strain maps such as those shown in Figs. 5-7(b) and (d), which feature periodic hourglass-shaped strain features along the interface with a characteristic spacing of $\sim 4$ nm. This spacing agrees well with that of $\lambda$ reported in Fig. 5-6, and the strain profiles in the GPA images are consistent with GPA contrast expected of edge dislocations. High resolution imaging of these interfacial defects (Fig. 5-7(e)) also indicated a mismatched lattice at this interface, and inverse Fourier transform analysis resolved the position of an apparent extra lattice half-plane, (Fig. 5-7(f), arrow). We also note that the width $W$ of the disordered or strained region produced by these interfacial defects also increased with increased temperature, as can be seen by comparing Fig. 5-7(c) and (e); this temperature-dependent increase in the strained zone width was consistent with observations in Fig. 5-6.

Several previous TEM studies have reported observation of edge dislocations at the interface between epitaxial ceria (both undoped and doped with Sm) and YSZ substrates.[11, 12, 8] Generally imaged at room temperature, these dislocations were present in both oxidized and highly reduced films for which sample reduction (even to an ordered structure with $\delta = 0.3$) was induced by high energy irradiation with the electron beam.[8, 10, 11] The spacing of CeO$_2$-YSZ misfit dislocations reported previously for the (100) orientation ranges from 3.7-4.8 nm, and is understood generally to relieve misfit stress at the interface.[11, 12, 10] In molecular dynamics simulations of CeO$_2$ recrystallization from an amorphous phase adjacent to crystalline YSZ, arrays of misfit edge dislocations appeared spontaneously, along with other mixed screw-edge dislocations that extended into the film.[35] Sheth et al. also observed by TEM the existence of threading dislocations for PCO films grown on YSZ.[10]

Others have also posited possible mechanisms of dynamic stress relief in ceria with sufficient energetic excitation (e.g., via temperature or electron beam irradiation). Ding et al. observed dislocation annihilation in CeO$_2$ particles by glide of Shockley partials when samples underwent beam-induced reduction.[36] Those authors attributed this effect to the stress of chemical expansion inducing dislocation motion that was further enabled by the greater mobility of Shockley partials relative to perfect dislocations.[36] Additionally, Sheth et al. observed (by multi-beam optical stress sensors) that thin films of PCO grown on YSZ exhibited irreversible stress relaxation during redox cycling at a temperature of 750° C.[10] Those authors suggested that this stress relaxation resulted from a mechanism similar to surface adatom diffusion and incorporation into grain boundaries, but were not able to confirm this suggestion.[10] Sinclair et al. observed surface adatom mobility directly for CeO$_2$ films irradiated to an equivalent temperature of 350° C.[11] Given that the cross-section im-
Figure 5-6: (a-d) TEM images at the same resolution of the PCO-YSZ interface at different temperatures T and locations showed interfacial contrast fringes that refined with increased T. With increased T, lattice imaging resolution improved and hexagonal lattice domains (shown in (a)) disappeared. (e) Interfacial fringe width $W$ reversibly increased with increased T. (e) Interface fringe periodicity $\lambda$ irreversibly changed with increased temperature. Comparison of (a) and (d) illustrates the irreversible change in the interface structure. The periodic contrast at the interface is attributed to lattice mismatch dislocations that relieved stress when they became mobile at elevated temperature. PCO chemical expansion at high T induced interfacial stress beyond what was present during sample fabrication. Error bars are standard error of the mean of multiple measurements of multiple images. Scale bars are 5 nm.
Figure 5-7: (a) Scanning transmission electron microscope (STEM) image of pre-oxidized Pr$_x$Ce$_{1-x}$O$_{2-\delta}$(PCO)- yttria stabilized zirconia (YSZ) interface with a threading defect at room temperature. (b) Geometric phase analysis of (a) showing interfacial periodic strain field and linear defect (indicated by black arrow) propagating away from interface. Scale bars for (a) and (b) are 10 nm. (c) STEM image of fully reduced PCO-YSZ interface at 300$^\circ$C and (d) corresponding geometric phase analysis. The distance between strain-field cores is 4.1 and 4.3 nm in (b) and (d), respectively, agreeing well with results for \( \lambda \) values in Fig. 5-6. Scale bars for (c) and (d) are 5 nm. (e) High resolution image of a misfit dislocation at the PCO-YSZ interface with Burgers circuit (black, dashed line); (f) inverse Fourier transform analysis of this defect highlighting the position of the extra half plane of atoms. The distance between dislocation cores in this image is 4.3 nm. Scale bars for (e) and (f) are 2 nm.
aged at high temperature in the present study was quite thin (∼50 nm), it is plausible that a combination of these effects (dislocation annihilation during chemical expansion at high temperature and defect-mediated lattice motion) were active at ∼600°C.

Periodic contrast fringes similar to those in Fig. 5-6 have been observed by TEM in interfaces such as heteroepitaxial GaSb/GaAs and grain boundaries in Bi0.5Sb1.5Te3. In prior work, those features were attributed by the authors as resulting from periodic arrays of misfit dislocations. In our own images, the disordered nature of the lattice in this interfacial region precluded direct, lattice-resolved observation of these features during the initial annealing cycle, although later analysis via STEM showed stress and lattice features consistent with edge dislocations with comparable interfringe periodic spacing \( \lambda \). However, we note that interfacial strain can also induce periodic phase separation when that phase separation is coupled to changing lattice volume, as Cao et al. observed for the insulating and metallic phases of VO2. In fact, Hu et al. showed using phase field simulations that the combined effects of periodic dislocations, substrate constraint, and compositional strain promote spinodal decomposition at interfaces that resulted in interphase spacing comparable to interdislocation spacing.

The phase diagram of ceria exhibits a miscibility gap below 650°C between the compositions of \( \delta \approx 0.05 \) and \( \delta \approx 0.2 \); this miscibility gap persists when ceria is doped with Gd, although at higher values of \( \delta \). The highly reduced phase of \( \delta = 0.2 - 0.3 \) is an ordered structure, and has been observed by TEM after beam-induced reduction and/or high concentration fixed-valent doping (with Gd or Sm, e.g.). In fact, neutron powder diffraction at 1273 K and Monte Carlo simulations of ceria found that vacancy ordering began for \( \delta \) as low as 0.06 with vacancies ordering along the \( <111> \) cubic lattice directions. As vacancies may localize to dopant positions, ordering is more likely when vacancies are not tightly bound to dopants. Our own samples exhibited some superlattice ordering after sample reduction at high temperatures inside the TEM column, as can be seen in Fig. 5-6(c), and the lattice strain observed for reduced samples indicated a \( \delta \) of ∼0.1, which is within the miscibility gap for ceria. Thus, once samples can achieve oxygen exchange, they may reduce and phase separate into an ordered, low oxygen phase, and a disordered, high oxygen phase. Therefore it is possible that the periodic contrast observed in the TEM images was in fact a combination of dislocation arrays and associated phase separation. However, our EELS mapping did not resolve a periodic oxidation state parallel to the interface between PCO and YSZ. Additionally, we observed the periodic contrast to appear first at a temperature of 250°C, which was too low a temperature to reduce these samples in situ, as shown in Fig. 5-5. Therefore, our findings suggest that the periodic contrast and the periodic line defects observed by TEM and STEM, respectively, were both due to misfit dislocations and associated strain fields.

Based on the above discussion, we now offer an explanation for the dynamic contrast changes observed at the PCO-YSZ interface during sample annealing. Firstly, we observed some recrystallization after the damaging FIB preparation of these samples; this recrystallization, consistent with the computational results of Maicaneanu et al., appears to have included misfit dislocations that then exerted a periodic strain field along the interface. This strain field extended from the interface over a width \( W \) that varied with the degree of lattice mismatch (and associated stress, e.g., due to dissimilar thermal expansion) between the substrate and the film. Upon continual heating, the sample eventually reached a temperature
(of approximately 500°C, but possibly lower in this extremely low pO\textsubscript{2} environment for these samples of <100 nm thickness) at which the PCO film also exhibited chemical expansion and released oxygen to the vacuum. While thermal expansion would have altered the interfacial stress of these films (with the interfacial region of PCO film becoming increasingly compressive, as \( \alpha_{T,PCO} > \alpha_{T,YSZ} \)), chemical expansion would have more significantly modulated the interfacial stress. This is because the corresponding chemical strain reached as much as 1.4%, including both Ce and Pr cation reduction. The stress resulting from chemical strain of 1% with an assumed Young’s modulus of \( \sim 220 \text{ GPa} \),\textsuperscript{[45, 46]} is about \( \sim 2.2 \text{ GPa} \). Since films were deposited in a higher pO\textsubscript{2} environment than existed in the TEM chamber, the addition of chemical strain would induce significant stresses in excess of those induced during film deposition. Upon initial induction of chemical strain, the film interface was compressed and \( \lambda \) decreased. At some point, the temperature was high enough and the strain-energy large enough to drive dislocation motion and annihilation along with overall oxygen loss, possibly by a mechanism similar to that described by Ding et al.\textsuperscript{[36]} This mechanism, which may have been assisted by adatom diffusion like that described by Sheth et al. and observed by Sinclair et al., allowed stress relief and resulted in a final dislocation periodicity of 4 nm.\textsuperscript{[10, 11]} Upon cooling, the sample was unable to recover oxygen from the vacuum, remaining trapped at this higher volume and dislocation spacing. The overall effect of this process would have been an irreversible stress change. Re-oxidized samples maintained the periodic dislocation array at the interface and appeared to nucleate new defects (discussed in Section 5.3.4) at high temperature.

The discussion of PCO-YSZ interface evolution during annealing inside the TEM illustrates a key observation about these cross-sectional samples. Namely, the interfacial defect structure is not static \textit{i n s i t u}, such that defects such as dislocations may exhibit substantial mobility at sufficient stress and/or temperature. Additionally, chemical expansion of films on constrained interfaces is known to be capable of causing structural substrate deflection; such a deflection may have occurred inside the TEM column as PCO underwent chemical expansion.\textsuperscript{[10, 47]} While we do not claim that such dislocation mobility is anticipated necessarily in thicker cross-sectional samples, we find such observations important illustrations of the role of chemical expansion – whether initiated by changes in temperature or pO\textsubscript{2} – in establishing mechanical driving forces for defect motion in constrained thin films of ionic conductors such as PCO.

After this annealing process, we also imaged and analyzed the PCO-YSZ interface via STEM with EELS to consider measurable features of space charge. Notably absent from the highly reduced samples was evidence of space charge, either in the case of Ce cations or Pr cations. Song et al. observed space charge previously in ceria at room temperature within about 5 nm of an epitaxial interface with YSZ.\textsuperscript{[8]} For these relatively thick, tilted cross-sections, resolving space charge regions local to the interface was not necessarily straightforward; however we did detect changes in the Ce M\textsubscript{5}/M\textsubscript{4} peak ratio (indicative of Ce reduction) elsewhere in the films (see Section 5.3.4), meaning that interfacial space charge may have been truly absent in the highly reduced film cross-sections at elevated temperature.

In contrast, at 300°C, with re-oxidized samples, we resolved a gradient in the Pr\textsuperscript{+3}/Pr\textsuperscript{+4} ratio within 10 nm of the interface, as shown in Fig. 5-8. At a distance of about 7 nm from the interface, most of the Pr was oxidized, while somewhat more Pr was reduced within
Figure 5-8: (a) Series of EELS spectra showing Pr reduction near the interface at 300°C in the pre-oxidized condition. (b) The decreased full width half maximum (FWHM) of the Pr M5 peak indicated Pr reduction at the interface. Spectra are for 1 nm wide strips, labeled by distance from the interface and normalized to the Ce M5 peak height at ∼882 eV. The inset compares the spectra that were farthest from (red) and closest to (black) the interface.

a few nm of the interface. While a complete reduction of Pr at the interface could have been present, this was difficult to resolve due to the distance-averaging effect and poor Pr signal-to-noise at the interface, which was not atomically sharp. However, we observed no change in the Ce M5/M4 peak ratio with proximity to the interface, indicating that Ce was not participating in any space charge layer that may have been present. This modest enrichment of Pr$^{+3}$ may be indicative of a space-charge layer at the PCO-YSZ interface for oxidized PCO. The alternative explanation would be enhanced sample reduction at the interface, a possibility that will be further discussed in Section 5.3.5.

Taken together, we conclude that the PCO films grown on YSZ exhibited periodic arrays of dislocations that did not appear to correlate with concurrent phase separation or periodic oxidation state modulation. At sufficiently high temperatures and at chemical-expansion induced stresses, these defects appeared mobile enough to relieve interfacial stress. Upon sample cooling and re-oxidation, those defect features remained immobile in position and some Pr$^{+3}$ enrichment appeared at the PCO-YSZ interface accompanied by emergence of longer range, threading defects. Section 5.3.4 concerns analysis of these new defects.

### 5.3.4 Linear defects

After sample re-oxidation, we observed defects extending from the film-substrate interface that were not visible previously. Figures 5-7(a) and 5-9 show one such defect, along with an EELS map of the associated Ce M5/M4 peak area ratio ratio. The EELS map exhibited a maximum at the position of the linear defect, shown also in the inset to Fig. 5-9(c) that
compares spectra within and far from the defect. We detected this signature, which indicates increased sample reduction at the position of the defect, to a lesser degree for the same defect at room temperature (Fig. 5-10), and also for a similar defect imaged for the oxidized sample at 300°C (Fig. 5-11). We consistently observed sample reduction relative to the lattice at these defects, both at low temperature, oxidized conditions (when the rest of the sample should contain minimal Pr\(^{+3}\), or Ce\(^{+3}\) content) and at high temperature, reduced conditions. This localized reduction implies that these defects acted as traps for reduced cations and/or oxygen vacancies relative to the rest of the lattice, establishing spatial heterogeneity of such defects within the lattice.

Figure 5-9: (a) ADF-STEM image of a linear defect (white arrows) propagating from the PCO-YSZ interface through the PCO film at 650°C toward the PCO free surface with selection region for EELS data collection highlighted. (b) Map of the Ce M5/M4 EELS peak area ratio from the highlighted region in (a). Increased M5/M4 ratio indicated sample reduction, and occurred local to the linear defect. (c) A comparison of EELS spectra within and outside the linear defect confirmed Ce reduction inside the defect through both changing peak height and peak shift. The inset plots the average Ce M5/M4 ratio moving left to right across the EELS map in (b), showing a maximum at the linear defect. We also observed the same trends in pre-oxidized samples for threading defects at room temperature and 300°C. Scale bars are 5 nm.

Linear defects that appeared in re-oxidized (redox cycled) samples thus may have acted as sinks for Ce\(^{+3}\) cations, and possibly also for corresponding oxygen vacancies. Because the cation oxidation state change requires only small polaron hopping, oxygen vacancy diffusion (and associated volume change) could be a mechanism of stress relief during re-oxidation at 650°C. Not only should reduced cations correlate with increased sample volume (which is difficult to resolve given the disordered nature of these regions), but they would also potentially affect charge transport and gas reactivity properties.[19, 48] For example, Sun et al. determined that edge dislocations in CeO\(_2\) could cause charged defect localization
Figure 5-10: (a) ADF-STEM image of a linear defect (white arrows) propagating from the YSZ interface through the PCO film at room temperature with selection region for EELS data collection highlighted. (b) Map of the Ce M5/M4 EELS peak area ratio from the highlighted region in (a). Increased M5/M4 ratio indicates sample reduction, and occurred local to the linear defect. (c) A comparison of EELS spectra within and outside the threading defect confirmed Ce reduction inside the defect through changing peak height. The inset plots the average Ce M5/M4 ratio moving left to right across the EELS map in (b), showing a maximum at the linear defect. Scale bars are 5 nm.

Appearance of such defects in redox cycled, mechanically constrained films could explain several observed differences between film and bulk PCO in situ, including enhanced oxygen vacancy concentrations,[30] and the results of Chapter 3 including relatively lower elastic modulus than expected for defect models of bulk PCO and a high degree of variability in the measured Young’s modulus by nanoindentation.[45] Space charge regions of reduced cations distributed inhomogeneously throughout a film would be expected to have larger volume than the surrounding lattice, causing associated, inhomogeneous decreases in
elastic modulus. Furthermore, there is the potential that propagation of such defects to the film free surface catalyze oxygen vacancy formation, even as they may impede charge transport.[19, 48] These defects appeared in our samples after re-oxidation that corresponded to a change in stress state (in the tensile direction); if this is a general effect in other non-stoichiometric oxides, this mechanism could also mediate effects of tensile strain on oxygen exchange reactivity and diffusivity.

5.3.5 Dynamic imaging of \textit{in situ} oxygen breathing

We conclude our discussion by considering the \textit{in situ} re-reduction of the PCO film at 650°C inside the TEM vacuum after oxidation outside of the TEM. While others reduced CeO\textsubscript{2} \textit{in situ} by electron-beam irradiation previously [11, 36], those studies did not analyze in detail the anisotropic or localized chemical expansion during the re-oxidation process. After focusing on a fully oxidized film at room temperature and 200°C, we rapidly heated the film (within 2 minutes) to 650°C inside the TEM column. We then collected a time series of images such as the one shown in Fig. 5-12(a) while the sample reduced (and underwent chemical expansion) inside the TEM vacuum. We collected images of many regions in the PCO film in order to prevent any sample reduction \textit{in situ} by the electron beam. As shown in Fig. 5-12, for each image we analyzed two regions: one adjacent to the interface, and one far (> 20 nm) from the interface. These images exhibited two characteristic types of fast Fourier transform (FFT): a hexagonal (72°, Fig. 5-12(b)) pattern and a rectangular (90°, Fig. 5-12(c)) pattern. These patterns sometimes coexisted within an analyzed image region, indicating slightly different lattice projections as dominant features in different parts of the
film during re-reduction. We observed no such lattice variability in the previously discussed STEM images for either oxidized or reduced samples, suggesting that the redox process may have involved some local nucleation phenomena or lattice distortion.

We reported the lattice spacing both parallel to the interface ($x$) and normal to the interface ($y$) based on the FFT patterns as a function of time in Figs. 5-12(d)-(e). Both data sets showed a positive slope with time, reflecting lattice dilation as the sample actively released oxygen from its structure. We were able to resolve the $x$-component lattice planes more easily than the $y$-component planes, and also more consistently between the two lattice projections. This enabled a statistical analysis of the linear fits applied to the $x$-component data. This analysis produced 95% confidence intervals (CI) for the intercept and slope of the linear fit (Fig. 5-12 shaded regions), from which we determined that the mean PCO lattice spacing along the direction parallel to the interface ($x$) was smaller near the interface (0.277 nm) as compared to that located more than 20 nm from the interface (0.279 nm). We did not find the differences in slope to be statistically significant, in that the 95% CIs for the slopes of the linear fits overlapped. However, these data are consistent with the concept that the region nearest the interface existed in a state of compression relative to the bulk, prior to chemical expansion excursions. We further found that this relative (though statistically insignificant) difference in this lattice parameter near and far from the interface was also retained during film expansion.

The PCO film also exhibited positive strain with time in the direction normal to the interface, which was larger for the region closest to the interface. The overall apparent slope of this lattice strain direction with time was statistically larger than that observed for the strain parallel to the interface, indicating (consistent with Fig. 5-4(c)) that chemical expansion was more pronounced in the direction normal to interface ($y$) than parallel to the interface ($x$). However, we note that the $y$-component data in Fig. 5-12(e) are too sparse, with too large of an uncertainty range, to identify statistical differences between the interface and film regions for the intercepts or slopes.

Our observation of multiple lattice projections during this in situ sample reduction suggests that this transformation occurred in a spatially heterogeneous manner. Some phase separation consistent with a miscibility gap may have occurred, but it is unclear to what degree such phase separation involved ordered and disordered phases. However, we did resolve superlattice reflections, at least in the direction parallel to the interface ($x$), in many image FFTs. Additionally, the apparently percent-scale change in $y$-component lattice strain would be consistent with formation of highly reduced, ordered phases.[42] However, note that when we later imaged the cross-section by STEM, we observed only one lattice projection.

Near the interface, the lattice spacing normal to the interface was larger on average than it was far from the interface. Even accounting for the decreased lattice spacing parallel to the interface, this suggests that the interface region has an overall larger volume than the film region. Along with the enhanced Pr$^{+3}$ concentration near the interface suggested by Fig. 5-8, this indicates increased chemical expansion near the interface. This effect would be enhanced for a reduced-cation-enriched space charge layer as opposed to a locally charge-neutral reduced region. However, we note that a space charge layer is only expected to occupy a few nm relative to the interface, in contrast to the 20 nm box analyzed here.[49, 8] Therefore, this apparent increased volume near the interface is not well-explained by a space charge layer.
Figure 5-12: (a) Example TEM image from time series collected during sample reduction in situ, showing regions selected near and far from the PCO-YSZ interface for lattice spacing analysis. (b) FFT resulting from the film region with the 72° and 90° y-component (normal to the interface) lattice reflections highlighted by white arrows. (c) FFT from the interface region in (a). (d) Measured x-component (parallel to the interface, with shaded 95% confidence intervals for the linear fit) and (e) y-component lattice spacing vs. time as the cross-section equilibrated with the TEM vacuum (i.e., reduced). All components exhibited lattice expansion with increased time in the TEM as the sample "breathed" oxygen from its structure. Relative to the y-component trend, the trend observed for the x-component was shallower in terms of strain vs. time. However, the x-component spacing far from the interface was statistically larger than that adjacent to the interface.
The time series images therefore demonstrated the PCO exhibiting chemical expansion *in situ* that was both anisotropic and position- (relative to the interface) dependent as the structure breathed oxygen out of the lattice. Additional images with a different zone axis might be able to resolve the $y$-component lattice spacing with more accuracy. The present data suggest, at least qualitatively, that the $y$-component strained more than the $x$-component during chemical expansion.

5.4 Conclusions

This Chapter reported *in situ* TEM, STEM, and EELS analysis of chemical expansion in the model non-stoichiometric oxide thin film $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (PCO) grown on yttria stabilized zirconia (YSZ) substrates. We found that PCO films grown on YSZ exhibited anisotropic chemical expansion that was more pronounced in the direction normal to the interface ($y$-component) relative to the direction parallel to the interface ($x$-component). This lattice expansion also varied with distance from the interface: near the interface the $x$-component was smaller than it was far from the interface, and the reverse was true for the $y$-component. PCO films exhibited periodic arrays of misfit dislocations that appeared to move enough to relieve interfacial stress when the sample was highly reduced at elevated temperature inside the TEM vacuum; these defects also exhibited strain fields imaged by ADF-STEM that changed width during thermochemical expansion. Upon sample re-oxidation, threading defects appeared in the PCO cross-sections. These defects trapped reduced cations for both oxidized, low temperature conditions and reduced, high temperature conditions, possibly impeding charge transport or affecting local oxygen vacancy formation energies. Finally, we directly observed the PCO film undergoing chemical expansion as it released oxygen, dynamically imaging this anisotropic, position-dependent chemical expansion *in situ*.

Extensions of this work would include measuring local lattice expansion while precisely controlling changes in oxidation state, either through electrical pumping with a solid-state oxygen source or changing $pO_2$ inside an environmental TEM. Especially interesting would be the ability to visualize the interface structure during electrochemical oxygen pumping, as this could clarify to what extent threading defects are mobile *in situ* vs. simply acting as sinks for certain types of point defects.

In the context of Chapter 2, these results inform the mechanisms of high-temperature oxide actuation. By observing anisotropic chemical expansion, we both confirmed that *in situ* changes in interfacial stress affect the structure of the film (which likely also impacts elastic properties) and found that some expansion still happened in the $x$-component (in-plane) direction. Despite the interface with the non-expanding YSZ substrate, films were not constrained completely parallel to the interface, which will be reflected in the *operando* deflection of high-temperature oxide actuators or multilayer micro-SOFCs. Furthermore, our results indicating stress relaxation under forced reduction at high temperature suggest that, depending on time scale and structure geometry, some stress relaxation may be observable using the dynamic chemical expansion measurements reported in Chapter 2. This question of scaling effects represents an interesting avenue for future research into high temperature oxide actuation.

The *in situ* observations of oxidation state and structure change also help explain the results of Chapters 3 and 4 indicating that the Young’s elastic modulus $E$ decreases sub-
stantially more *operando* than predicted based on bulk measurements or models. Firstly, our observations of chemical strain *in situ* indicated a higher degree of PCO reduction than modeling predicts for the conditions of the TEM chamber. Unless an unexpected reducing agent (e.g., CO or H\textsubscript{2}) was present in the column, this result shows, consistent with previous literature results [30, 9, 50], that for very thin PCO cross-sections, there was increased oxygen vacancy concentration and chemical strain than expected, which should also correlate with larger decreases in Young’s elastic modulus *in situ*. A second important observation was that of especially reduced zones surrounding threading defects in these films. These defects appeared after sample re-oxidation, emanated from the YSZ interface towards the film surface, and would not necessarily be expected in non-constrained, bulk forms of PCO. Regions of increased +3 cation concentration will correlate to lattice expansion, again decreasing $E$ beyond expectations. This second observation is particularly important, because these reduced zones are localized and therefore would cause inhomogeneity in the value of $E$ throughout the film. Finally, we note that the chemical expansion observed was *anisotropic*, and more specifically, larger normal to the interface ($y$-component) than parallel to the interface ($x$-component), especially near the interface. This means that the value of the uniaxial elastic modulus in the $y$-component direction should decrease more rapidly with increased temperature or decreased pO\textsubscript{2} than a bulk $E$ responding to isotropic expansion. Although the films probed by nanoindentation were somewhat thicker than the cross-section analyzed for this study, the actual indentation depth was less than 100 nm, a comparable scale to that of the cross-sections, and, given the observed film surface structure and Fig. 5-3(a), certainly full of defects that could correlate to enhanced reduced cation concentration. Furthermore, because of the large-area format of the films, the mechanical constraint created by the PCO-YSZ interface would be more restrictive than it is in the FIB cross-sections, possibly causing both anisotropic expansion and threading defects to reach the surface *in situ*. Thus, the combination of these three effects: increased *in situ* chemical strain, localized regions of reduced cations near threading defects, and anisotropic chemical strain, could contribute to the larger than expected (for bulk) changes in $E$ observed for PCO films *operando*.

With respect to the broader literature, these results demonstrated several mechanisms facilitating chemical expansion in thin film non-stoichiometric oxides, including strain anisotropy, long range defect dynamics, and spatially inhomogeneous strain and composition. Films can be expected to exhibit significant strain normal to the film-substrate interface, and, at high enough temperatures, large magnitudes of interfacial stress caused by thermochemical strain may be released by defect mobility or adatom diffusion. These effects may be enhanced for structures that are also thin in the orthogonal dimension, such as the cross-sections considered in this study, with longer time scales or larger driving forces required to see similar stress-relief in large-area films. However, the observed anisotropic chemical expansion and lattice strain showed that interfacial stress persists *in situ* despite such effects. Furthermore, threading defects that appear during redox cycling may localize charged cations *in situ*, potentially impacting total oxygen vacancy content, lattice stiffness, and transport properties. These results provide direct and detailed analysis of chemical expansion in a model thin film non-stoichiometric oxide that will inform the design of high temperature oxide actuators or strain engineered functional oxides for applications involving gas exchange, storage, or ionic conductivity.
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Chapter 6

Electrochemomechanical Coupling in Li-storage Materials

The main focus of this thesis has been electrochemomechanical coupling effects as these apply to oxide films for solid oxide fuel cell (SOFC) applications. However, the kinds of effects described in the previous chapters are relevant for materials and applications beyond SOFCs, thin films, and oxide-ion conductors. Rather, this coupling extends to non-stoichiometric oxides in general, including Li-intercalation compounds relevant to Li-ion battery (LIB) applications. This chapter details a set of studies on Li-storage materials that apply much of the same methodology as was used in the previous chapters to understanding electrochemomechanical coupling in LIBs.

This chapter includes three sections, following a short introduction describing the context in which electrochemomechanical coupling manifests in batteries. Section 6.2 describes a non-contact, optical stress measurement approach, analogous to that used in Chapter 2 for studying chemical expansion in PCO, applied to detecting chemical expansion effects in Li$_{y}$Mn$_2$O$_4$ (LMO) resulting from Li intercalation and de-intercalation. The experimental data for that study was collected by Jay Sheth and Leah Nation in the group of Prof. Brian Sheldon at Brown University (Providence, RI). The results of that work will be included in a manuscript currently in preparation.[1] Section 6.3 reports a short density functional theory study conducted to assess whether chemical expansion could be attributed to oxygen loss in a specific electrode material, Li$_{1+x}$Mn$_{2-x}$O$_{4-\delta}$ spinel. That study was conducted at the request of Sheldon et al. to address experimental results observed in Ref. [2]. Finally, Section 6.4 reports a study of how compositional change, particularly Li-content change, can affect the mechanical properties of a technologically relevant, model Li-intercalation compound, Li$_2$CoO$_2$ (LCO). Portions of Section 6.4 were published in Ref. [3]. Collaborators in that published study included William H. Woodford (Chiang and Carter groups, MIT), who fabricated samples and electrochemically charged the examined cells; Frank P. McGrogan (Van Vliet Group), who conducted image analysis and X-ray diffraction; and Dr. Nicola Ferralis (Grossman Group, MIT), who conducted Raman spectroscopy.

The chapter concludes with a discussion of the parallels of electrochemomechanical coupling in non-stoichiometric oxides for SOFCs and LIBs, with a focus on methodology and results that are broadly applicable within this material class.
6.1 Context

Lithium ion batteries are energy storage devices that have achieved widespread usage in recent years as lightweight portable batteries in consumer technologies ranging from cell phones to electric vehicles. These batteries work by shuttling Li ions between electrodes with different chemical potentials comprising materials that can accommodate large changes in Li content. Typically, these electrodes comprise a graphitic negative electrode and a positive electrode that consists of densely packed particles of a non-stoichiometric oxide such as Li$_x$CoO$_2$ (LCO).[4, 5] Like the oxides used for electrodes and electrolytes in SOFCs, the electrodes in LIBs often undergo chemical expansion as a result changes in stoichiometry. In the case of LIBs, however, the mobile ion is Li rather than oxygen. Significant extents of Li-content-dependent chemical expansion have been imaged for SnO$_2$ nanowire anodes using in situ TEM, but more modest chemical expansion in LCO and other Li-intercalation oxides is well documented, primarily by X-ray diffraction.[6, 7, 8, 9, 10] Li-intercalation oxides can also exhibit charge-dependent phase changes that can in turn modify crystal symmetry, volume, and other properties including charge and mass transport properties.[11, 10, 12]

Understanding chemical expansion in Li-intercalation materials has become particularly important as research efforts have turned toward development of LIBs that comprise both electrodes and electrolytes made of solid-state materials. The appeal of all solid-state LIBs arises primarily from the anticipated improvements in long-term stability and power density.[13] Understanding how electrochemomechanical coupling affects mechanical properties, including those that govern fracture and stress in electrodes and electrolytes for solid-state LIBs, will be essential in preventing electrochemomechanically-mediated performance degradation.[14, 15, 16, 17, 18] For example, stress arising as a result of composition-dependent volume changes can lead to mechanical damage to active cathode particles in the form of fracture or so-called "electrochemical shock," an effect similar to thermal shock that can manifest in charge rate dependent and charge rate independent forms. Electrochemical shock has been observed in a number of commonly used cathode materials including Li$_x$CoO$_2$ (LCO) and Li$_y$Mn$_2$O$_4$. [19, 20, 21] Transport properties of such materials can depend on Li content, just as changes in oxygen content affect oxide ion conductivity and oxygen reduction reactivity in oxides for SOFCs such as Pr$_x$Ce$_{1-x}$O$_2$ (PCO) and SrTi$_{0.65}$Fe$_{0.35}$O$_{3-δ}$ (STF). [11, 22, 23, 24] For example, LCO exhibits electrical conductivity ranging from that of a semiconductor to that of a metal for the composition range $1 > x > 0.75$ where $x$ denotes Li content.[25] Thus, electrochemomechanical coupling is of concern for electrochemical performance related to mechanical stability in Li-storage materials as it has been shown to be in oxides for SOFC applications. That is, similar expectations are anticipated for composition-dependent mechanical properties and dynamic volume changes in these materials. Likewise, similar experimental and computational methods may be applied to Li-storage oxides to understand how such effects manifest, and how best to account for them.

6.2 Dynamic chemical expansion in Li$_y$Mn$_2$O$_4$

LIBs are generally operated at ambient temperatures and are repeatedly cycled through the full range of reversible Li-storage capacity such that the Li density also varies temporally and spatially operando. In contrast, SOFCs are operated at temperatures in excess
of 500°C and exhibit steady-state composition gradients due to the range of oxygen partial pressures experienced on either side of the electrolyte *operando*. Although there may be local fluctuations in composition and electrochemical potential within SOFC electrodes and electrolytes during normal operation, larger-scale, more persistent changes in these values would only occur in more unusual applications or circumstances, such as redox cycling or fuel interruption. Therefore, *rate dependence* and *cyclability* are of particular interest in understanding electrochemomechanical coupling in Li-storage compounds, as these materials regularly and continuously undergo changes in composition and therefore associated composition-dependent properties during normal operation.

As noted in Chapter 2, the method of choice for detecting structural changes of ionic conductors *in situ*, X-ray diffraction, has limited temporal resolution without access to a synchrotron. Because the *operando* conditions for Li-ion batteries tend to be far from equilibrium, it is of interest to demonstrate the ability to detect chemical expansion in Li-storage materials *operando* in order to elucidate any useful information about rate-dependent chemical expansion. Such techniques could also be used to characterize solid-state actuator devices based on room temperature intercalation compounds like LMO.[26] Here, we apply a non-contact, optical approach to study chemical expansion in LMO, drawing from the same principles of dynamic chemical expansion detection outlined in Chapter 2.

Li$_y$Mn$_2$O$_4$ (LMO) serves as the model material for this study. This spinel oxide is a low cost, environmentally benign Li-intercalation material with a large initial energy storage capacity. LMO is typically cycled in the range 0 < $y$ < 1 because of severe capacity fade that occurs for $y$ > 1.[2] The crystal structure of LMO is within the $Fd\bar{3}m$ space group, with Li located at 8a tetrahedral sites and Mn at 16d octahedral sites within the oxygen (32e) sublattice.[27, 28, 29] While the stoichiometric structure ($y = 1$) is cubic, Jahn-Teller distortions and orthorhombic crystal distortion have been observed for off-stoichiometric Li compositions and at low temperatures.[30, 12] Several experimental and computational studies have characterized the phase diagram of LMO, and together can be summarized by the statement that delithiation decreases material volume for $y < 1$, and increases material volume for $y > 1$.[12, 31, 32, 33] Therefore, if we consider a film of LMO of $y < 1$ adhered to a substrate of significantly higher stiffness (effectively rigid), we would predict that delithiation would increase tensile stress within the film due to contraction under the film-substrate constraint.

A typical charge-discharge hysteresis for LMO proceeds between 3.5 and 4.3 V and exhibits two plateaus in the voltage profile at ~4.05 and 4.16 V, indicative of phase changes initiated at these electrical potentials.[32] The exact positions of these plateaus depend on the oxygen non-stoichiometry, a subject that we consider in more detail in Section 6.3. We here first restrict our consideration to the effects of charge and discharge rate on the stress development within LMO films. In contrast to the consideration in Chapter 2 of a PCO solid film adhered to a yttrium-stabilized zirconia substrate that served as a solid electrolyte, the LMO film under consideration here is adhered to a substrate that does not participate in charge storage or transfer, and the electrolyte is a liquid. Therefore, the rate of chemical expansion of LMO will not be controlled by diffusion through a supporting substrate.
6.2.1 Methods

Sample fabrication and multi-beam optical stress sensor (MOSS) method

Samples for this study were prepared by Jay Sheth and Leah Nation using the same methods described in detail in Ref. [2], with solution-deposited LMO films (∼80-100 nm thickness) and spin-coated Pt electrodes on quartz substrates. Beaker cells were constructed as described in Ref. [2], with a Li foil anode and non-aqueous liquid electrolyte of 1M LiPF$_6$.

Sinusoidal electrical bias was applied to the films using a Biologic VMP3 potentiostat at seven frequencies ranging from $10^{-4}$ to $10^{-1}$ for 10-15 cycles at each frequency. A set of frequencies with an amplitude of 0.3 V was applied for three different mean applied biases (3.8, 3.9, and 4.0 V) to explore the effect of the applied voltage window on the stress-thickness response of the film.

Operando stress-evolution measurements were acquired by measuring changes in the curvature of the elastic substrate during electrochemical cycling. A description of the multi-beam optical stress sensor (MOSS) technique used for this purpose can be found elsewhere and is briefly described here.[34, 35, 36] An array of parallel laser beams incident on the back of the quartz substrate were reflected toward a CCD camera, which recorded changes in spacing between adjacent beams. This spacing $d$ was related directly to substrate curvature $\kappa$ by Equation 6.1:

$$\kappa = \frac{d - d_0}{d_0 A_m}$$

(6.1)

where $d_0$ is the initial distance between adjacent beams, $A_m$ is the mirror constant that is dependent on three parameters: the optical path length of the laser from the reflective substrate to the CCD camera, the refractive index of the electrolyte through which the laser travels, and the incident angle of the laser upon the substrate. Changes in curvature were then directly related to the product of stress and film thickness $<\sigma > h_f$ using Stoney’s formula (Eq. 6.2):

$$<\sigma > h_f = \frac{M_s h_s^2 \kappa}{6}$$

(6.2)

where $<\sigma >$ is the thickness-averaged stress in the film, $h_f$ is the film thickness, $M_s$ is the biaxial elastic modulus of the substrate, $h_s$ is the substrate thickness, and $\kappa$ is the curvature of the film-substrate system.[37] Stress measurements were made relative to the initial curvature of the substrate, which was non-zero indicating the presence of some residual stress in the as-prepared films.

Data analysis

The phase lag and amplitude of detected stress-thickness response data were determined according to the same procedure described in Chapter 2, with some modification for phase lag determination. For this study, two different computers were used to acquire the current-voltage (I-V) data and the $<\sigma > h_f$ data, with an unknown time delay between the start of data collection on each computer. This time delay $\tau_d$ was on the scale of ∼2 seconds, and arose from the need of the operator to initiate data collection on the $<\sigma > h_f$ computer as...
soon as possible after starting the experiment on the IV computer. This effect is negligible unless determining phase lag for frequencies with a period length on the order of <10\(\tau_d\) (e.g., 0.1 Hz and 0.05 Hz). To account for the error in estimated phase lag introduced by this time offset, the fitting form applied to the phase lag vs. frequency data to determine the time constant \(\tau\) was modified to include an additional fitting parameter \(\tau_d\) according to Eq. 6.3:

\[
\Phi = \tan^{-1} \omega \tau + \tan^{-1} \omega \tau_d
\] (6.3)

In addition to considering the magnitudes of equilibrium displacement amplitude \(D_0\) (See Eq. 2.10) and \(\tau\) for the different applied bias ranges, Lissajous plots for these data were produced to allow comparison of the asymmetry of the \(<\sigma> h_f\) signals in these different ranges, as well as any other interesting rate-dependent features. This type of plot displays the \(<\sigma> h_f\) output vs. the input voltage averaged over all cycles at each frequency. In general, if the output and input overlap with no phase lag, then the Lissajous plot will appear linear and the slope will be related to the amplitude ratio of the two signals. If there is a phase lag, the Lissajous plot will appear as a loop with an internal area that increases with increased phase lag. Asymmetry in the output with respect to the input (e.g., differences in positive and negative amplitude) will be apparent in the shape of the Lissajous plot as well (see Section 2.2.6 for further discussion of Lissajous plot interpretation). Lissajous plots were acquired using a custom Matlab code (see Appendix E).

### 6.2.2 Results

Figure 6-1(a) shows Lissajous plots for stress-thickness and charge vs. voltage for an LMO sample at four different frequencies. To determine charge \(Q\) as a function of time \(t\), we integrated the oscillatory current \(I(t)\) to determine cumulative \(Q(t)\). We then flattened \(Q(t)\) by subtracting a moving average from the data resulting in data centered at zero charge in Fig. 6-1(a). This should be interpreted as "charge relative to the average at 4 V" in Fig. 6-1(a). Additionally, we note that this procedure effectively removed the contribution of leakage current to the reported data. However, such leakage is present and can be considered in future studies over repeated cycling.

First considering the stress results, we note that ranging the frequency \(\nu\) over four orders of magnitude of frequency produced a variation in the measured stress thickness \(S\) spanning over one order of magnitude. This comparison of magnitudes of effect highlights the sensitivity of the MOSS approach, even for a film as thin as 80-100 nm. The plot shows clearly the onset of asymmetry at the slowest frequency (10^{-4} Hz) that is absent for the other tests. In fact, at the slowest frequency features (highlighted by black arrows) appear in the Lissajous plots that relate to the phase-change plateaus for LMO mentioned above. It is apparent that for faster charging, the magnitude of stress-thickness decreases, as well as the degree of asymmetry, at the cost of decreased accessible capacity.

Turning now to the \(Q(V)\) Lissajous plots (dashed lines), these trends were clearly reproduced. While \(Q(V)\) and \(S(V)\) overlapped almost completely when \(\nu \geq 10^{-3}\) Hz, this overlap disappeared at the slowest frequency. Instead, a phase lag arose along with the asymmetry in the data. This suggests that the detected stress thickness values were not necessarily directly correlated with charge storage, or, in other words, that the chemical expansion co-
efficient was non-uniform in this sample. This important result reflects the ways in which this measurement approach is complementary to standard electrochemical techniques. This approach allows us to decouple electrochemical and mechanical effects, using the frequency domain to probe the material at different depths or compositions.

Figures 6-1(b)-(c) show the electrochemomechanical admittance spectra and current Lissajous plots at 4.0 ± 0.3 V obtained for LMO. Like STF and PCO, the spectra are individual semi-circles. However, the mechanism controlling charge transport and the rate of mechanical response is quite different for LMO, as charge moves through a liquid electrolyte that provides no mechanical constraints for sample deflection.

The time constants of these measurements were on the order of ~100 seconds, indicative of the much slower charging rate for LMO at room temperature as compared to STF and PCO at high temperature. For the three voltage ranges investigated, the mechanical response rate (ratio of amplitude to time constant) increased with increased average mean voltage, suggesting that charge transport was faster in the higher mean voltage regimes. As for PCO and STF, shifting the mean applied bias also changed both the shape and amplitude of the mechanical deflection profile, in this case because the mean Li content shifted as a result.

In general, phase changes can be expected to produce asymmetry in the cyclic profiles at slow frequencies. Comparing the $I(V)$ plots in Fig. 6-1(c) to the $S(V)$ and $Q(V)$ plots in Fig. 6-1(a), we observe that features correlated with redox processes of Li insertion/extraction (inflection points in $S(V)$ and $Q(V)$), maxima or minima in $I(V)$ do not necessarily occur at the same voltages.[32] This may be related to the kinetics of the insertion and extraction process, and how these translate to mechanical effects. For example, if a phase has a relatively low nucleation energy barrier, it should grow via a phase change front that propagates uniformly across the film. However, if nucleation and growth kinetics favor multiple small domains nucleating and then growing, a different set of mechanical compatibility conditions will be active. The rate-dependent stress signal provides complementary information based on a different signal-generation mechanism than electrochemical results, potentially providing an additional way to probe phase change kinetics in Li-storage materials.

6.2.3 Conclusions

We established here that the same dynamic method used to detect electrochemical actuation (or chemical expansion) in non-stoichiometric oxides like STF and PCO (Chapter 2) can be applied to a Li-storage material via a non-contact approach. This case study demonstrated the flexibility of this technique while also exploring the role of C-rate in producing stress in an example thin film Li-storage material. There are many possible extensions of this measurement approach to the LMO system and other charge-storage systems. For example, if the sample deflection rate is controlled by ion diffusion within the active oxide film, then thickness-dependent measurements would be of interest to probe rate or charge-state dependent diffusivities. A grain-size dependent study of equivalent film thicknesses could provide information about (a) charge transport characteristics as a function of grain size and (b) chemical expansion as a function of grain size. This is particularly interesting if it is expected that grain boundaries and grain interiors exhibit significantly different contributions to the chemical expansion coefficient. Overall, the potential to simultaneously probe the kinetics, mechanics, and electrochemistry of non-equilibrium phase changes in charge
Figure 6-1: (a) Lissajous plot of stress-thickness amplitude and charge vs. voltage for four frequencies applied to Li$_x$Mn$_2$O$_4$ (LMO). Asymmetry appeared in the data at the slowest frequency, along with a clear deviation between the two Lissajous plots indicative of phase lag and non-uniform translation between stress and charge storage. (b) Electrochemomechanical admittance spectra for dynamic MOSS measurement of LMO. Shifting the mean voltage changed the overall capacity accessed during each individual charge-discharge period. (c) Lissajous plot of current vs. voltage for dynamic measurement of LMO. From Ref. [1].
6.3 DFT + U calculation of chemical expansion due to oxygen vacancy formation in Li$_{1+x}$Mn$_{2-x}$O$_{4-\delta}$

The previous section demonstrated that chemical expansion in LMO films can generate stress reversibly upon electrochemical cycling of Li for $x < 0$ (Note the change in $x$ notation from Section 6.2). For many Li-ion intercalation oxides, the volume changes induced by Li content changes have been characterized in detail.[7, 10, 8, 9] In contrast, chemical expansion due to oxygen evolution (and concurrent oxygen vacancy formation) has rarely been explored for this class of materials. This arises in part from the difficulty of decoupling oxygen and lithium content in such materials experimentally, and in part because Li content change is the dominant and repeated mechanism of volume change in this application. In contrast, oxygen loss, if it occurs, is generally irreversible in such systems, and therefore not expected to continuously affect material properties throughout the life of a battery.

Understanding oxygen loss in Li-ion batteries is nonetheless relevant for several reasons. Firstly, oxygen loss necessarily changes the defect chemistry of the oxide, potentially impacting Li-storage capacity.[38, 39, 40] Additionally, unexpected oxygen evolution can lead to undesired chemical reactions and thermal runaway.[41] Finally, oxygen vacancy formation and concurrent cation reduction, as has been seen throughout the thesis from the known behavior of non-stoichiometric oxides for SOFCs, can lead to volume change through the mechanism of chemical expansion. As a result, mechanical stress or mechanical property changes may arise upon oxygen evolution.

A study published in 2016 by the Sheldon group at Brown University tracked stress evolution in LMO spinel films during repeated electrochemical cycling using a multi-beam optical stress sensor (MOSS) like the one described in Section 6.2. Those authors observed an irreversible compressive shift in the mean film stress during the first electrochemical cycle, indicative of an increase in the average sample volume during that time. This irreversible "stress drop" was attributed to the combination of loss of crystallinity during the first cycle and formation of oxygen vacancies. Oxygen vacancy formation could be expected to cause increased lattice parameter in LMO due to the increased Mn$^{+3}$ content relative to Mn$^{+4}$.[2]

Some experimental evidence exists to suggest, consistent with the above observation, that oxygen vacancy formation can cause increased volume in LMO.[39, 30] However, it is very difficult to precisely control Li and oxygen content independently in LMO samples. In contrast, computation provides exact control over these compositional variables. Therefore, computation is the ideal tool to determine whether oxygen loss could lead to significant volume change (chemical expansion) in such oxides, and to assess the expected sign of the chemical expansion coefficient. The study described here seeks to address this question using a density functional theory + U (DFT+U) computational framework.

6.3.1 Methods

A 56-atom (8 formula-unit) unit cell of Li$_{1+x}$Mn$_{2-x}$O$_{4-\delta}$ was simulated using the generalized gradient approximation (GGA) to density functional theory (DFT) with inclusion of
Figure 6-2: Schematic of the Li$_{1+x}$Mn$_{2-x}$O$_4-\delta$ (LMO) simulation cell. Li, Mn, and O atoms are shown in green, purple, and red, respectively. Position (i) denotes the location of Li substitution onto a Mn site ($Li_{Mn}$) for compositions with $x = 0.125$. Positions (ii) and (iii) denote the locations of oxygen vacancies ($V^{\bullet}_O$) when $\delta = 0.25$. The oxygen vacancy was positioned at either position (iii) or position (iv) for the two simulations with $x = \delta = 0.125$. Positions (iii) and (iv) are, respectively, first and second nearest neighbors to the $Li_{Mn}$ at position (i). Cation radii not to scale.

the Hubbard U term to account for on-site Coulomb repulsion of Mn 3d electrons. Cell volume and lattice parameter were computed for compositions with oxygen non-stoichiometry $\delta$ ranging from 0 to 0.25 and Li content $x$ ranging from 0 to 0.125. Calculations were implemented in the Vienna ab-initio simulation package (VASP) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and a basis set composed of projected augmented wave (PAW) pseudopotentials, with an energy cutoff of 520 eV. All calculations used a 3x3x3 Monkhorst-Pack k-point grid. Lattice parameter for these calculations was converged to within 0.01 Å and total energy was converged to within 5 meV/atom. Figure 6-2 shows the simulation cell and relative $Li_{Mn}$ substitution and oxygen vacancy positions. Where applicable, Li was substituted directly onto the Mn site (i). For stoichiometric LMO, all oxygen vacancy sites are chemically equivalent; however, in the presence of excess Li it is possible to have multiple chemically dissimilar oxygen vacancy sites. Therefore, structures were relaxed with the oxygen vacancy located at the first or second nearest neighbor positions from the Li substitution site, as shown in Fig. 6-2.

**Hubbard U selection**

Figure 6-3(a) shows that increasing the value of the Hubbard U term leads to increased simulation cell volume. $U = 5.0$ eV was selected to replicate the known chemical expansion of LMO (linear: -0.03 to -0.05 $\Delta \varepsilon/\Delta x$ or volumetric: -0.09 to -0.14 $\Delta \varepsilon_V/\Delta x$) upon lithium
6.3.2 Results

As mentioned above, these simulations produced a half-metallic electronic structure for $U = 5$ eV. This result has been noted previously for DFT+U simulations of this and other Li spinels, and corresponds to partial electron localization in the structure.[28, 29, 43] As shown in Fig. 6-3, the onset of this half-metallic structure corresponds to a significant increase in overall cell volume and a reversal in the sign of the chemical expansion coefficient vs. Li content. It is not unexpected that the value of $U$ could affect the chemical expansion coefficients for either Li or oxygen content change; for perovskite and fluorite structured Ce-based oxides DFT+U simulations showed that increased charge localization caused by increasing the value of $U$ led to increased chemical expansion coefficients with respect to
Figure 6-4: The volume of Li$_{1+x}$Mn$_{2-x}$O$_{4-\delta}$ (LMO) increased with increased oxygen non-stoichiometry $\delta$ for both stoichiometric ($x = 0$) and non-stoichiometric ($x = 0.125$) compositions. Although two oxygen vacancy positions were simulated for the composition $x = \delta = 0.125$, only one data point is visible because the simulation cell volume was insensitive to this change.

Oxygen vacancy formation.[44] However, in the simulations reported here for LMO, when $U$ was sufficiently large to induce half-metallic electronic structure (3 or 5 eV), the computed chemical expansion coefficients were consistent in sign and within 30% in magnitude.

Fig. 6-4 shows that compositions with increased oxygen vacancy content $\delta$ exhibited increased volume for both Li-stoichiometric ($x = 0$) and Li-excess ($x = 0.125$) compositions. Note that this expansion happened in an anisotropic manner, with the $a$ and $b$ axis lengths of the simulation cell increasing with increased $\delta$ while the $c$-axis length decreased. Based on the simulations, we estimate the volumetric expansion coefficient $\alpha_V$ at 0.09 $\Delta V / \Delta \delta$. Considering the average lattice parameter ($\bar{a} = \sqrt[3]{V}$), this is a linear expansion coefficient $\alpha_C$ of 0.03. This positive change in volume $V$ upon oxygen loss is consistent with the hypothesis of Sheth et al. that the observed decrease in mean tensile stress in their films during the first electrochemical cycle was caused at least in part by increased sample volume due to oxygen evolution.[2] The result is also consistent with literature experimental results showing that oxygen-deficient samples of LMO have larger unit cell volume than their more stoichiometric counterparts.[30] In fact, the expansion coefficient is within the range (0.01-0.09) that can be estimated based on the sparse available data from the literature for a few compositions of LMO, indicating that it would be detectable if measured during a comprehensive experimental study.[30]

We also tested two oxygen vacancy positions for the composition $x = \delta = 0.125$. These were, respectively, the first and second nearest neighbor positions to the $Li_{Mn}$ substitution site (position (i)), labeled as positions (iii) and (iv) in Fig. 6-2. The total volume of the simulation cell was insensitive to this change in oxygen vacancy position, and neither position was energetically favored. However, placing the oxygen vacancy at position (iii) resulted in
smaller magnitudes of change in the \( a \), \( b \), and \( c \) lattice parameters. That is, for position (iii), \( a \) and \( b \) increased less and \( c \) decreased less than they did for position (iv). Therefore, the oxygen vacancy position did not strongly influence total volume change, although it did slightly affect the directions of unit cell distortions. Although this study was by no means an exhaustive investigation of oxygen vacancy and \( Li_{Mn} \) substitutional defect configurations, the lack of energetic preference between the configurations that were investigated suggests that a randomized oxygen vacancy arrangement may be reasonably expected, and therefore that overall volume change may not be anisotropic in nature. Simulations with larger cell sizes might be able to further clarify this aspect of the results while also exploring a greater number of specific compositions defined by \( x \) and \( \delta \).

6.3.3 Conclusions

This section demonstrated the application of DFT+U to the problem of chemical expansion due to oxygen loss in a Li-ion battery cathode material, \( Li_{1+x}Mn_{2-x}O_{4-\delta} \). Using similar methods to those used in Chapter 4 for the fluorite-structured SOFC cathode material PCO, we showed here that oxygen loss in LMO could lead to increased unit cell volume for both Li-stoichiometric (\( x = 0 \)) and Li-excess (\( x = 0.125 \)) compositions. This result supports the hypothesis of Sheth et al. that oxygen loss caused in part the observed irreversible decrease of the mean tensile stress in LMO thin films after the first electrochemical cycle.\[2\] Recommendations for future work include a more detailed investigation of defect configurations, including randomization of defect position, in this material, as well as assessment of chemical expansion for a greater number of specific compositions defined by \( x \) and \( \delta \). Finally, given the results of Chapters 3 and 4 above and the upcoming section studying LCO with respect to the effect of chemical expansion on the mechanical properties of non-stoichiometric oxides, experimental and computational determination of the Young’s modulus, hardness, and/or fracture toughness of LMO as a function of oxygen and Li content could be of interest. In fact, a few authors already measured \( E \), \( H \), and \( K_{IC} \) in LMO as a function of Li content, finding that upon Li removal and associated decreased lattice parameter, Young’s modulus and hardness increased, while fracture toughness decreased.\[45, 46\] We shall see that these results are consistent with our own indentation results on LCO, presented in Section 6.4.

6.4 Effect of electrochemical charging on the elastoplastic properties and fracture toughness of \( Li_xCoO_2 \)

This section describes a study of how Li-content change can affect the mechanical properties of a technologically relevant, model Li-intercalation compound, \( Li_xCoO_2 \). Although conducted at room temperature with a completely different material than the model system PCO, this study demonstrates the broad applicability of one of the most important conclusions from Chapters 3 and 4: that oxides that undergo chemical expansion can exhibit composition-dependent mechanical properties. While the previous work focused on elastic constants, here we discuss both elastic and plastic properties including Young’s modulus \( E \), hardness \( H \), and fracture toughness \( K_{IC} \). The results of this work have important implications for the design of fracture-resistant batteries.
6.4.1 Introduction

Microstructural damage has been observed directly in numerous electrode materials subjected to electrochemical cycling, both within single crystals (or grains) and among polycrystalline aggregates.\[47, 48, 49, 50, 51, 52\] Structural changes can also lead to mechanical stresses that degrade battery performance metrics including power, achievable storage capacity, and lifetime.\[48, 47, 53, 54, 55\] In particular, for some materials, such mechanical damage has been correlated with capacity loss.\[49, 40\] There are a few hypotheses about how particle fracture can contribute to capacity loss, including separation between charge storage material and the conductive binder, increased path lengths for Li diffusion, and the formation of additional surface area that accelerates capacity loss either through Mn dissolution (in the case of LMO or Li\(_x\)(Ni\(_{0.5}\)Mn\(_{0.3}\)Co\(_{0.2}\))O\(_2\), NMC) or Li depletion when new solid-electrolyte interphase forms.\[40, 53, 54, 55\] In the case where fracture is indeed linked to capacity fade, being able to predict and prevent fracture will be key to improving material performance. This goal requires knowledge of the mechanical properties, most importantly fracture toughness, of the Li-intercalation material of interest. As highlighted in the introduction to this chapter, the field of solid-state Li-ion batteries also requires such information in order to prevent mechanical failures that could cause short-circuiting or increased area specific resistance for layered battery designs.\[14, 16, 13\]

While the relationships among electrode microstructure, electrochemical cycling conditions, crystallographic changes in the active materials, and resulting mechanical stresses have been elucidated, at the time of this work, relatively little was known about the composition-dependence of the key physical properties. Numerous models had been developed to predict mechanical deformation in ion-storage materials during electrochemical cycling, but the quantitative utility of such models is dependent on measured elastoplastic properties, particularly the fracture toughness \(K_{IC}\) of these materials.\[56, 57, 16\] Prior to the date of this work, little experimental data were available for \(K_{IC}\) of battery materials.\[58, 15, 59, 60\] Similarly, few measurements of composition-dependent mechanical properties had been reported, with the exception of lithiated silicon for which both fracture toughness \[59\] and elastic constants \[61, 62, 63, 64\] were reported as functions of composition. Thus, the extent to which \(K_{IC}\) and other elastoplastic properties of ion-storage materials vary with lithium concentration, was understood poorly.\[59, 17\] Identifying any such correlations facilitates realistic application of mechanical failure models as a function of state-of-charge, and allows prediction and extension of the durability and lifetime of electrode materials and devices.

Here, we investigated the mechanical properties of the model lithium intercalation compound, Li\(_x\)CoO\(_2\) (LCO), as a function of electrochemical delithiation. Of particular interest was whether and to what extent the fracture toughness \(K_{IC}\), which quantifies resistance to fracture, depends on electrochemical history and instantaneous composition. The availability of dense polycrystalline sintered LCO, an air-stable compound, facilitated direct measurement of the mechanical properties of individual crystallites (grains) via instrumented nanoindentation.\[58\] The phase behavior of LCO within the cycling range has been studied thoroughly and is well understood.\[10, 11, 65\] The fracture toughness of the uncycled, as prepared LCO, which was assumed to be well-annealed and relatively defect-free, was measured previously via the nanoindentation-based pop-in method, described extensively elsewhere.\[58, 66, 67, 68, 69\] This experimental approach relates \(K_{IC}\) to so-called "pop-in"
events (see Fig. 6-5 and Section 6.4.2) that manifest when cracking is induced during nanoindentation loading. Briefly, the resulting crack length $c$ was determined from displacement bursts at a given applied load; the calculated $K_{IC}$ depends on $c$ as well as the Young’s elastic modulus $E$ and hardness $H$ of the uncracked material. This provided a means to determine $K_{IC}$ of small, brittle material volumes without direct imaging of indentations or optical measurement of $c$. While Qu et al. established previously that this approach could be used to quantify $K_{IC}$ at the level of individual LCO grains or crystals, the effect of electrochemical charging on fracture toughness or other mechanical properties had not previously been investigated.

In this section, $E$, $H$, and $K_{IC}$ of individual grains within sintered pellets of LCO were measured via instrumented nanoindentation for several samples charged (delithiated) to varying degrees. The values of all three mechanical properties decreased significantly upon a single electrochemical half-cycle. The same properties were also measured for thermally shocked LCO, to distinguish changes in the measured properties due to microstructural damage, namely intergranular and transgranular fracture of the polycrystalline microstructure, from those due to compositional changes in electrochemically delithiated LCO.

6.4.2 Methods

Sample fabrication

Dense, polycrystalline LCO pellets were prepared from commercial, battery-grade LiCoO$_2$ powder (AGC Seimi Chemical Co. Ltd, Kanagawa, Japan) by pressing ~1.8 g of powder into a 1.3 cm-diameter die under an applied uniaxial compressive stress of 100 MPa. Pellets were sintered at 1060°C for 8 h with a heating rate of 9°C/min and furnace cooled, yielding an average grain diameter of ~10 μm. To coarsen the grains further to obtain single crystallites that were large compared to the indentation volumes, the samples were fired a second time at 1090°C for 12 h with the same heating and cooling rates. The density of the pellets was found to be 4.80 g cm$^{-3}$ (96% relative density), as determined by Archimedes’ method in isopropanol. The grain size of the polished pellets was determined by a method similar to the lineal intercept procedure in ASTM Standard E112, but with fewer than 50 grains per line.

Coarsened samples were polished using silicon carbide sandpaper of decreasing grits (500, 800, 1200, 2400 and 4000) and diamond polishing pads (UltraPrep, Buehler Limited, Lake Bluff, IL); grit sizes of 3 μm, 1 μm, and 0.5 μm were used for the final polishing steps to achieve a mirror-like finish on the LCO surface. Samples were cleaned with water between each polishing step.

The polished pellets were used as the positive electrode in a Swagelok$^T_M$-type half-cell, with the polished face of the sample against the separator and the opposite side of the pellet against the current collector. The electrolyte was a blend of alkyl carbonates with 1.2 M LiPF$_6$ salt, and all cells used 2 pieces of Tonen E20MMS separator and a Li metal (Alfa Aesar) negative electrode. To reduce contact resistance between the electrodes and the current collectors, the current collectors were coated with a compliant conductive binder that was a mixture of polyvinylidene fluoride (PVDF), carbon black (Ketjenblack ECP), and vapor grown carbon fiber (VGCF) in $n$-methyl-2-pyrrolidone (NMP). This binder was cured overnight at 120°C in a vacuum oven before transferring the current collectors to a glovebox.
for cell assembly. Four pellets were charged on a MACCOR 4000 tester at a constant rate of 0.135 mA/g (equal to a charge-rate or C-rate of C/1000 assuming uniform charging of the entire sample and 135 mAh/g specific capacity) for durations of 50 (two pellets), 100, and 500 h. These samples will be referred to in the text by the duration of the charging process in units of hours (e.g., the pellet charged for 500 hours at the C/1000 charge rate will be denoted LCO-500). Samples were not re-polished after this electrochemical cycling, prior to indentation analysis (except in the case of cross sections discussed in Section 6.4.5), but were cleaned by sonication in acetone prior to indentation.

An identically prepared and polished LCO pellet was thermally shocked as a control; this sample is referred to hereafter as LCO-TS. A tube furnace (Lindberg/Blue M) was pre-heated to 950°C in air. The pellet was placed upon a bed of LCO powder in a high-alumina boat, and this boat was inserted to the center of the tube furnace and heated for 30 min. The boat was withdrawn and the pellet was observed to be glowing orange-red hot; it was immediately quenched in a hydraulic oil bath (~3.8 L) held at room temperature (~22°C). The sample was allowed to cool for 10 min in the bath, after which it was ultrasonically cleaned in acetone.

Materials characterization

Optical images of sample surfaces were collected using differential interference contrast (DIC, Nikon Eclipse L150). The DIC images were analyzed to quantify microstructural surface damage using open-source image analysis software ImageJ.[70] As intergranular cracking (i.e., along grain boundaries) was evident in charged samples and in LCO-TS, the extent of microstructural damage was quantified by measuring the lengths of cracked and uncracked grain boundaries. Intragranular cracking (i.e., emanating from a grain boundary to the grain interior) was also present, but due to the high variability of these features the quantification of intragranular crack lengths and numbers was much less precise. Grain orientation with respect to the indentation loading direction and relative misorientation among adjacent grains were not assessed.

The atomic force microscopy (AFM) height image in the inset of Fig. 6-5 was acquired in contact mode (Asylum Research MFP-3D, with Olympus AC160TS silicon cantilever of ~25 nm tip radius), with pixel width of 19.4 nm.

X-ray diffraction (XRD) patterns were collected over a range of 2θ = 15° to 80° using copper Kα tube-source radiation (PANalytical X’Pert Pro). Micro-Raman characterization was conducted using a Horiba LabRAM 800HR spectrometer with a 514 nm excitation wavelength source, 100X objective lens, and 80 s collection times.

Nanomechanical characterization

E, H, and K_{IC} were measured in air via instrumented nanoindentation (Hysitron, Inc. Triboindenter, Minneapolis, MN) for 27-30 individual grains per sample within each sintered LCO pellet. Within each grain, sixteen load-depth hystereses were acquired to measure E and H up to a maximum load of 1.2 mN (below loads that would induce detectable cracking) and another sixteen indentations were acquired at a maximum load of 9 mN to measure K_{IC}. Via an integrated optical microscope, all indentation grids were intentionally placed far from grain boundaries, such that the nearest indentation was ~5 μm from the nearest visible grain.
Figure 6-5: Indentation load-depth response, showing pop-ins and parameters $h_x$, $h_m$, and $P$ used to calculate fracture toughness $K_{IC}$. Inset shows an atomic force microscopy (AFM) contact mode image of an individual indent exhibiting radial cracks highlighted by black arrows. The scale bar is 1 \( \mu \)m. Figure from Reference [3].

boundary; this minimized potential for mechanical contributions from the grain boundaries to affect the measured properties.[58] The resulting indentation depths (~100-350 nm) were significantly less than the average grain diameter of ~80 \( \mu \)m. Following Qu et al. [58], a diamond Berkovich indenter was used, with loading and unloading times of 10 s and a dwell period of 10 s at maximum load. Center-to-center indentation spacing for $E$ and $H$ indentations was 10 \( \mu \)m, while for $K_{IC}$ indentations the spacing was 20 \( \mu \)m. Reduced elastic moduli $E_r$ were calculated from the load-depth hystereses using the method of Oliver and Pharr [71, 72], from which $E$ was calculated using Eq. 6.4 with an assumed Poisson’s ratio $\nu$ of 0.3 for LCO, and the $E_i$ and $\nu_i$ of the diamond probe at 1070 GPa and 0.07, respectively: [58, 67, 68, 69, 66, 73]

$$E = \frac{1 - \nu^2}{\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}}$$

(6.4)

Hardness $H$ was calculated according to Eq. 6.5, where $A$ is the projected indentation contact area at the maximum load $p_{max}$:

$$H = \frac{p_{max}}{A}$$

(6.5)

Figure 6-5 illustrates the parameters used to calculate the fracture toughness of brittle materials from nanoindentation hystereses, according to the pop-in method of Field et al.[66] The crack length $c$ was determined according to Eq. 6.6, where $E$ and $H$ were measured as described above for indentations at lower loads, and pop-in depth $h_m$ and length $h_x$ as defined in Fig. 6-5 were determined for each indentation according to a Hertzian fitting procedure using a custom Mathematica 7.0 (Wolfram) code:

$$c = \sqrt{2}h_m + (Q\frac{E}{H} - \sqrt{2})h_x$$

(6.6)

The unitless prefactor $Q$ was 4.55, following Refs. [58] and [66]. Qu et al. previously
confirmed that crack lengths calculated using Equation 6.6 were comparable to crack lengths measured using AFM imaging post-indentation, for uncharged LiCoO$_2$.[58] Figure 6-5 inset shows an example AFM height image of an indentation, with radial cracks indicated by arrows and confirmed via additional AFM, SEM, and focused ion beam (FIB)/SEM imaging. Additional characterization confirming the presence of cracks at indentation corners was conducted primarily by Frank McGrogan and can be found in the Supporting Information to Ref. [3]. Load-depth hystereses that did not exhibit detectable pop-in displacements up to the maximum load of 9 mN were excluded from further analysis, such that there were 5 to 16 replicate indentations used to determine $K_{Ic}$ in each grain according to Eq. 6.7:

$$K_{Ic} = k(Q E H)^{1/2} \frac{P}{e^{3/2}}$$

where $P$ is defined in Fig. 6-5 and the unitless prefactor $k$ was 0.036 [58, 66]. The assumed magnitude of $k$ can range from 0.036 for a cube-corner indenter to 0.018 for a Vickers indenter, with various possible adjustments as a function of equivalent cone angle, number of sides, etc.[67, 68, 69, 66]

Data for $E$, $H$, and $K_{Ic}$ for each sample are reported as the mean ± the standard error of the mean measured for the 27-30 individual grains for each sample. Although the statistical distribution of $K_{Ic}$ was consistently right-skewed (Appendix A.5), even non-parametric assessments of error and sample centering (quartiles and medians) have no effect on the trends reported below. Significant differences among samples’ mean mechanical properties were determined according to $p$-values derived from Student’s t-test; see Appendix A.5.

6.4.3 Results and Discussion

Mechanical property results

Upon electrochemical delithiation, the measured values of $E$ and $H$ decreased significantly, as shown in Fig. 6-6(a)-(b). $E$ decreased by over 40%, while $H$ decreased by over 50% for all charged samples. Interestingly, $E$ and $H$ did not decrease significantly with further charging; LCO-500 exhibited similar mechanical properties to LCO-50 despite being charged for ten times as long. These same trends are apparent in Fig. 6-6(c), which shows that $K_{Ic}$ decreased by more than 60% at the minimum level of electrochemical charging, and also remained nearly constant for all longer charge durations (lower Li content). From the results described below, we propose that this dramatic reduction in these mechanical property values can be attributed to a combination of chemical expansion and phase changes due to Li depletion within the near-surface volume sampled by nanoindentation.

$E$ for the uncharged LCO grains was 177 ± 4 GPa and $H$ was 8.3 ± 0.5 GPa. The mean $K_{Ic}$ of these LCO grains was 0.9±0.1 MPa-m$^{1/2}$, with a median magnitude of 0.8 MPa-m$^{1/2}$. The present results for $E$, $H$, and $K_{Ic}$ of the uncharged LCO sample are in good agreement with the previously reported results of Qu et al.[58]

The reduction in $K_{Ic}$ observed for electrochemically charged samples correlated with extensive microstructural damage of LCO surfaces. Figure 6-7 displays both quantitatively and qualitatively the significant grain boundary cracking near the free surface of all the electrochemically charged samples. This microstructural damage is quantified in Fig. 6-
Figure 6-6: (a) Young’s modulus and (b) hardness are each plotted against charge duration in the first charge-cycle of Li$_x$CoO$_2$ samples. After even the smallest charge duration (50 hours at rate C/1000), a significant decrease was observed for both properties. (c) Fracture toughness $K_{IC}$ as a function of first-cycle charge duration as determined by the pop-in method. After the smallest charge duration, the fracture toughness decreased by about 70%. Error bars are standard error of the mean. Figure adapted from Ref. [3].

7(a) as the percentage of grain boundary length exhibiting intergranular cracking (for a fixed image surface area), determined from DIC images of sample surfaces as shown in Fig. 6-7(b)-(e). Intergranular cracking was evident for 50% of grain boundary length in LCO charged for 50 h (LCO-50), as compared to only 10% of grain boundary length in uncharged LCO (LCO-0) but further increases in charge duration caused only modest increases in this observed microstructural damage. Figure 6-7(f) shows a cross-section of LCO-500, in which cracking occurred only over a depth of $\sim 70 \mu m$ from the free surface; the interior of the sample displayed no identifiable intergranular cracking. This trend was also observed in cross-sectional imaging of LCO-50. Because surface cracking and delithiation occurred concurrently, an additional experiment was conducted to decouple the contribution of each to the observed decreases in mechanical properties.

6.4.4 Thermal shock control

In this additional experiment, we considered the possibility that intergranular (or the less pervasive intragranular) cracking could alter the far-field boundary conditions on the indentations, due to either extension of such cracks in the charged samples under indentation loading or to indentation-induced grain sliding. Accordingly, to isolate the effect of microstructural damage in the absence of Li depletion, we conducted nanoindentation testing on the thermally shocked sample of LCO (LCO-TS). The idea here was to induce fracture in the LCO samples comparable to that caused during electrochemical charging, but without changing the Li composition. Figure 6-7(a),(e) shows that the surface of LCO-TS displayed intergranular cracking comparable to the electrochemically charged samples. However, $E$ of LCO-TS decreased by less than 10% relative to the uncharged sample (see Table 6.1). This decrease had a $p$-value of 0.027 and was much less than the reduction in $E$ of 40-55% found for all charged samples. Similarly, $H$ upon thermal shock decreased modestly (by 17%, $p$
Figure 6-7: Grain boundary cracking appeared on sintered pellet surfaces after electrochemical cycling in Li$_x$CoO$_2$ (LCO). (a) Electrochemically charged samples show increased grain boundary (gb) cracking as compared to uncharged LiCoO$_2$. Differential interference contrast (DIC) images of the indented surface of (b) LiCoO$_2$ (LCO-0) (c) LCO-50 (pellet charged at C/1000 for 50 h), (d) LCO-500, and (e) thermally shocked LiCoO$_2$ (LCO-TS). (f) DIC image of a cross section of LCO-500, showing grain boundary cracks near the polished surface. Red arrows highlight cracking between grains. Scale bars are 100 $\mu$m. Figure from Ref. [3], with data acquired and analyzed by F. P. McGrogan.
Table 6.1: Mechanical properties of electrochemically charged and thermal shocked Li$_x$CoO$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic Modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Fracture Toughness (MPa-m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCO-0</td>
<td>178 ± 5</td>
<td>8.3 ± 0.5</td>
<td>0.94 ± 0.09</td>
</tr>
<tr>
<td>LCO-50</td>
<td>100 ± 3</td>
<td>3.1 ± 0.2</td>
<td>0.29 ± 0.03</td>
</tr>
<tr>
<td>LCO-50 (2)</td>
<td>92 ± 3</td>
<td>3.8 ± 0.1</td>
<td>0.35 ± 0.07</td>
</tr>
<tr>
<td>LCO-100</td>
<td>85 ± 3</td>
<td>3.3 ± 0.1</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>LCO-500</td>
<td>89 ± 3</td>
<td>3.5 ± 0.1</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>LCO-TS</td>
<td>161 ± 5</td>
<td>6.9 ± 0.5</td>
<td>1.04 ± 0.01</td>
</tr>
</tbody>
</table>

Reported values are mean ± standard error of the mean.

= 0.071) relative to the uncharged LCO, while $H$ in response to electrochemical charging decreased by 45-70%. $K_{Ic}$ of the thermally shocked sample did not differ significantly from the uncharged sample, retaining a mean value of 1.0 MPa-m$^{1/2}$ ($p = 0.60$). Note that thermal shock produced similar levels of grain boundary cracking and microstructural damage (Fig. 6-7(a), (e)) in the absence of any electrochemical shock. Thus, microstructural damage alone cannot account for the degraded stiffness, hardness, and fracture toughness observed in the electrochemically charged grains. Therefore, both the observed decreases in $E$, $H$, and $K_{Ic}$ and the observed intergranular cracking in charged samples can be attributed to the electrochemically induced change in Li nonstoichiometry.

6.4.5 Non-uniform pellet composition

As mentioned above, $E$, $H$, and $K_{Ic}$ were sensitive to whether the LCO was uncharged or charged, but insensitive to the duration of electrochemical charging. This apparent insensitivity to charge duration can be understood as the result of a similar composition near the free surfaces of all charged samples. Electrochemical charging of polycrystalline samples of mm-scale thickness presents the possibility of non-uniform composition across the total sample thickness. Because lithium removal occurred preferentially through a single external surface - the free surface facing the separator during electrochemical cycling, which was subsequently indented - the structure and composition of the samples had the potential to be non-uniform through the thickness. In fact, Fig. 6-8 summarizes characterization of the sample surfaces via XRD and Raman spectroscopy, which together indicated that the sample surfaces were all overcharged (i.e., Li-poor) compared to the volume-averaged or bulk composition. This was true particularly beyond the first 50 hours of charging; one of the two pellets charged for this duration had not fully crossed the phase transition at $x = 0.71$. The inset of Fig. 6-8(a) also shows a representative optical micrograph of the sintered polycrystalline samples, for which we quantified an average grain diameter of 70-85 $\mu$m.

The crystal structure of all LCO samples was confirmed by XRD to be that expected from established phase diagrams. Lattice parameter variation upon electrochemical charging was also confirmed from the XRD patterns, as illustrated by the downshift in the position of the (104) Bragg peak ($2\theta \sim 45^\circ$) in Fig. 6-8(a).[10] Quantification of these peak shifts for LCO-50 and LCO-500 indicated compositions of Li$_x$CoO$_2$ at $x = 0.71$ and $x = 0.6$, respectively, over the X-ray sampling depths of $\sim 9$ $\mu$m; this sampling depth was estimated via the
automated mass attenuation coefficient calculator (PANalytical HighScore Plus). These compositions are within the range \(1.0 \leq x \leq 0.5\) accessed during normal electrochemical cycling of practical LCO-based electrodes.

The local Li content at the free surfaces of LCO-50 and LCO-500 was assessed at \(0.6 \leq x \leq 1\) and \(x \leq 0.6\), respectively, by Raman spectroscopy. Stoichiometric \((x = 1)\) LCO has two Raman-active modes \(A_{1g}\) and \(E_g\) at 596 and 486 cm\(^{-1}\), respectively. Upon lithium deintercalation, both Raman peaks decreased in amplitude, and near \(x = 0.6\) they shifted discontinuously to lower wavenumber.\([25, 74, 75]\) This behavior can be attributed to decreased laser penetration depth as a result of the first-order Mott transition between trigonal phases at \(x = 0.95\) and \(x = 0.75\), and/or to the emergence of the monoclinic phase via a second-order phase transformation at approximately \(x = 0.6\).\([11, 65, 75]\) Figure 6-8(b) shows the Raman spectra for LCO-0, LCO-50, and LCO-500, indicating a decrease in peak intensity with increasing charge duration. The observed peak shift occurred in all spectra collected for LCO-500, and both the shifted and unshifted spectra were observed for LCO-50, as highlighted in the inset of Fig. 6-8(b). This interpretation of Raman spectra suggests, consistent with the XRD results, that within the Raman sampling depth of \(\sim 1\) \(\mu m\), the surface of LCO-500 had a Li content of \(x \leq 0.6\), and that LCO-50 had a composition between \(x = 0.6\) and \(x = 1\). The indentation plastic zones were estimated at several \(\mu m\) for the indentation depths and indenter geometries employed herein, and were com-
parable to the sampling depths of Raman spectroscopy and XRD. Thus, nanoindentation measurements made on sample surfaces reflect the mechanical properties of LCO compositions that are more Li-deficient than the nominal (i.e., uniform bulk) compositions expected from electrochemical charging at C/1000 for the different durations. Further discussion of sample characterization (conducted primarily by Frank McGrogan) by XRD, Raman, and scanning electron microscopy of sample surfaces and imaging of radial cracks at individual indentations can be found in the Supporting information to Ref. [3].

Cross-section results

After completing all mechanical and microstructural characterization of the sample free surfaces, we cross-sectioned the samples denoted as LCO-0, LCO-50, and LCO-500 through the diameter of the cylinders with a diamond wire saw and hot-mounted them in Bakelite at 155°C for 10 min; this exposed the sample interiors along the cylinder height axis for further testing. We then polished these samples as described in Section 6.4.2. We then collected measurements of $E$ and $H$ for twenty grains along the cylinder height using the same procedure as described in 6.4.2 for free surfaces. We did not also measure $K_{IC}$ due to spatial constraints in the sample cross-section. Figure 6-9 shows that $E$ and $H$ measured in the interior of LCO-0 compared well with values measured for the polished surface. This is expected, as this sample was never subjected to electrochemical charging and therefore should have uniform composition and properties throughout its bulk. In comparison, electrochemically charged samples exhibited decreased $E$ and $H$ on their surfaces relative to the sample interiors; for LCO-50, $E$ was 20% lower near the charged surface as compared to the interior, whereas for LCO-500, $E$ was 30% lower near the charged surface as compared to the interior. The measured values of $H$ followed a similar trend: for LCO-50, $H$ near the surface was 40% less than the interior value, while for LCO-500 this difference was closer to 50%. This relative trend was consistent with the results of X-ray diffraction (XRD) and Raman spectroscopy (Fig. 6-8), which showed that the surfaces of the charged samples contain less Li than the average bulk composition. Given this information, and as we observed, mechanical properties affected by Li-dependent chemical expansion should differ near the surface (of relatively lower Li content) and within the interior for these electrochemically charged samples.

Figure 6-9 also shows a small decrease in $E$ and $H$ of the interior volume of the charged samples, relative to that of LCO-0. For the LCO-50 interior grains, we detected a modest decrease for both $E$ ($p < 10^{-2}$) and $H$ ($p < 10^{-5}$) as compared to the interior grains of the uncharged sample. We detected a moderate decrease of $E$ ($p < 10^{-5}$) for interior LCO-500 grains compared to LCO-0 interior grains; this decrease was larger than that seen for LCO-50 interior grains compared to LCO-0 interior grains. The decrease in $H$ for LCO-500 interior grains compared to LCO-0 interior grains was about the same ($p < 10^{-4}$) as that seen for LCO-50; however the associated error was larger.

Chemical expansion and phase changes lead to composition-dependent mechanical properties

Together, these results suggest that electrochemical charging of LCO resulted in significant reduction in $E$, $H$, and $K_{IC}$ that is attributable to severe depletion of Li at the grain surface,
Figure 6-9: (a) Young's modulus $E$ and (b) hardness $H$ at the surface (adjacent to the separator) and in the interior of Li$_x$CoO$_2$ sintered pellets at several durations of first-cycle charging. "Interior" values are based on measurements of $E$ and $H$ over a cross-section, for twenty individual grains at least 0.25 mm from the original free surface. The comparably greater reduction in $E$ and $H$ observed at the free sample surfaces is attributed to severe Li depletion near the charged electrode surfaces. Error bars are standard error of the mean and are smaller than the data points. Figure from Supporting Information to Ref. [3].

Associated with chemical expansion and phase transitions. Li deintercalation from LCO leads to expansion of the layered structure along the c-axis crystallographic direction (normal to the layers) and contraction within the a-b plane (within the layers), resulting in an overall volume increase of 1.9% when charging to the composition Li$_{0.5}$CoO$_2$.[10] Additionally, the trigonal-to-monoclinic phase transition may result in differing mechanical properties of the material after significant charging, as compared to uncharged LCO. Further, in non-stoichiometric materials, increased bond lengths are correlated to decreased Young’s elastic moduli.[76] Additionally, residual stresses could plausibly develop due to coherency stresses at the interfaces between Li-rich and Li-poor phases, or due to compatibility stresses at the grain boundaries; LiCoO$_2$ grains undergo anisotropic shape changes.[20] Although we did not assess relative grain misorientation or residual stress, tensile residual stress would be expected to exhibit lower fracture toughness. Furthermore, computational results have shown that Li-deficient compositions of LCO can have decreased surface energy, which could also contribute to decreased fracture toughness.[77] Ultimately, these atomic-scale modifications as a function of Li content $x$ also manifested as intergranular fracture at the electrochemically charged surfaces of the polycrystals. However, comparison to thermally shocked LCO of similar microcracking extent but unchanged fracture toughness showed that microcracking alone was not the source of the decreased mechanical property values within the LCO grains.

The dense monolithic electrodes used in the present work are not intended to serve as practical battery electrodes, but to enable measurement of mechanical properties at the level of individual grains with high precision. Nevertheless, the observed dependence of
mechanical properties on Li content informs the design of practical electrodes. The unique electrode architecture that enabled our nanomechanical analysis also exacerbated the observed surface overcharging, which we expect to be less pronounced in practical electrodes comprised of active material particles (single or polycrystalline) of 10s of μms in diameter. Surface overcharging of the dense polycrystalline pellets of mm-scale thickness could have resulted from ion transport limitations that would be eased in smaller volumes with similar electrochemical histories.

![Diagram](image)

Figure 6-10: (a) Li$_x$CoO$_2$ particles before and after electrochemical charging will exhibit an overall decrease in average composition (indicated by color change), and a larger decrease in Li content close to the particle surface. The surface is a phase-changed region, which has significantly reduced fracture toughness. Grain-boundary cracking can be expected to develop after electrochemical charging within the severely Li-depleted region. The required characteristic length (particle or grain size) to avoid fracture due to electrochemical shock at a given C-rate and fracture toughness $K_{IC}$ is shown in the electrochemical shock map (b). The length scale required when one takes into account the as-cycled fracture toughness is smaller than that predicted based on uncharged material properties. Figure from Ref. [3].

Concentration gradients in these samples can be more severe because of the highly-composition dependent ionic and electronic transport properties of LCO, particularly with this dense monolithic microstructure that requires all ionic transport to occur through LCO. Additionally, the first-order phase-transformation that occurs between compositions $0.95 \leq x \leq 0.75$ may exacerbate composition gradients; due to the nearly one-dimensional cell geometry used herein, this phase transformation would nucleate on the sample surface with a phase boundary separating Li-rich and Li-poor LCO phases. This is consistent with the fact that the LCO-50 pellet appeared to be at the transition point for surface overcharging, with parts of the sample surface showing a Raman signature indicative of this phase change that was absent elsewhere (Fig. 6-8). While the sintered compacts exhibited high conductivity, they could charge relatively uniformly. However, after crossing the transition, their conductivity sharply decreased, forcing a diffusion-limited kinetic regime that caused the surface of the pellets (adjacent to the electrolyte, later indented) to charge first.
This surface overcharging also explains why the mechanical properties of the cross-section exhibited a gradient between the original surfaces and the interior.

In normal battery electrodes, uniform electrochemical reactivity throughout the thickness of the electrode is facilitated by limiting electrode thickness to $<100 \mu m$, adding conductive materials to form composite electrodes, and having open porosity infiltrated with liquid electrolyte. Well-engineered composite electrodes would not experience the same solid-phase concentration gradients we observed. However, the total range of compositions over which we characterized the mechanical properties ($0.6 \leq x \leq 1$) is representative of normal cycling limits for LCO and other layered compounds. Therefore, the measured changes in mechanical properties between the discharged and charged states expand our understanding of the behavior of practical electrodes. Given the marked reduction in elastoplastic and fracture properties that we report, these variations should be taken into account in the design of mechanically robust electrodes.

Anisotropic chemical expansion and phase transformations in LCO and other intercalation compounds can generate stresses sufficient to drive electrochemical shock, often manifested as grain boundary fracture in layered materials such as LCO.[47, 52, 51, 20] This process is depicted schematically in Fig. 6-10(a). Design criteria for mechanically robust electrodes have been developed, but typically under the assumption of composition-independent mechanical properties. Figure 6-10(b) shows a schematic electrochemical shock map prepared by William Woodford [20, 21, 19, 78], which is a graphical summary of such design criteria. The horizontal axis of the electrochemical shock map is a representative microstructural length scale (particle size or grain size) and the vertical axis is the electrochemical cycling rate (C-rate); for convenience both axes are logarithmic. The lines on the map are drawn for constant $K_{IC}$ and serve to visually separate the conditions for which catastrophic fracture due to electrochemical shock is possible or not possible. Above and to the right of a failure line, fracture is possible; below and to the left of the failure line, it is not. The sloping portion of the failure line corresponds to fracture due to concentration gradient stresses, which are C-rate dependent [21, 19, 79]; the vertical segments correspond to C-rate independent electrochemical shock mechanisms, for example the failure of a polycrystalline aggregate due to anisotropic shape changes of the individual grains [20] or coherency stresses accompanying a first-order phase transformation.[21, 78] For each of the latter mechanisms, stresses develop in response to the overall composition change, not in response to the rate of cycling. The failure lines for two different magnitudes of $K_{IC}$ -1.0 MPa-m$^{1/2}$ and 0.3 MPa-m$^{1/2}$- are shown in Fig. 6-10(b). These values are representative of the decrease in $K_{IC}$ that we observed in LCO upon charging over a single half-cycle, and illustrate how the observed reduction in $K_{IC}$ changes the predicted critical length scale below which fracture is averted. This schematic takes into account the composition-dependence of $K_{IC}$, but additional effects will arise due to more complex stress states in materials with composition-dependent elastoplastic properties.[16]

6.4.6 Conclusions

We observed decreases in $E$, $H$, and $K_{IC}$ of 40, 50, and 60%, respectively, after electrochemical charging of Li$_x$CoO$_2$ surfaces to $x \leq 0.71$. Comparison to a thermally shocked sample, along with XRD and Raman analyses, showed that this change is related primarily
to chemical expansion and phase changes occurring upon lithium content reduction, and
is not exclusively the result of microstructural damage which occurred concurrently in the
dolomite samples. These dramatic changes in elastoplastic and fracture properties
occur within the normal electrochemical cycling window of Li$_x$CoO$_2$, and therefore the de-
sign of mechanically robust electrodes should consider that the mechanical properties of the
active compound can deviate significantly from those reported for uncharged compounds
upon even a single electrochemical charge cycle.

We note here that the trend reported for LCO (decreased $E$, $H$, and $K_{IC}$ with Li removal)
was specific to this material. Given that mechanical stiffness tends to decrease with increased
specific volume (and associated bond lengths), this trend was expected for LCO. However,
in a material that undergoes a decrease in volume upon Li removal (e.g., LMO), the opposite
trend would be anticipated for elastic modulus. Indeed, in the years following publication of
the above results several additional studies of composition-dependent mechanical properties
in Li-storage materials were published [46, 80, 45], including one that showed this exact
trend for LMO.[45] That study showed that for LMO, which contracts with Li removal, Li
deintercalation led to increased $E$ and $H$ and decreased fracture toughness $K_{IC}$ attributed
to changes in volume, increased defect density, and diffusion-induced stresses.[45] That result
also suggests that the decreased $K_{IC}$ observed in our own work may be more related to
non-elastic effects such as decreased surface energies for non-stoichiometric samples, than
to changes in elastic strain energy. In fact, computational work has suggested that LiCoO$_2$
ehibits decreased surface energy for Li-deficient compositions, an effect that could decrease
fracture toughness.[77] These effects are not exclusive to Li deintercalation; McGrogan et al.
also later showed that doping LMO with Ni and/or Fe, which also decrease material volume,
correlated with increased $E$ and $H$.[80] These results further emphasize our conclusion that
the chemomechanical effect of composition-dependent mechanical properties presented above
for LCO is broadly relevant to Li-storage materials as a class. Not only that, but this result
is further evidence of the parallels that exist between oxygen ion conductors relevant to
SOFCs, including the model system PCO discussed in previous chapters, and Li-storage
materials like LCO and LMO. Indeed, although it was beyond the scope of the investigation
presented in Chapters 2 and 3, our results for LCO suggest that the fracture toughness of
PCO is a function of oxygen content, a potentially interesting area for further study in oxide
ion conductors. Because these materials undergo chemical expansion, mechanical properties
are coupled to composition, meaning that in situ experimental data and computational
modeling should be utilized in robust device design.

Further work in this area should therefore focus on measuring and modeling mechanical
properties in the most promising ion-intercalation materials, including both positive and neg-
ative electrode materials, and materials for emerging battery chemistries such as Li-sulfur,
Li-air, or Na-ion.[81, 82] In particular, mechanical properties will be important to measure
for solid-state battery materials (including electrolytes). In this case not only the Mode I
fracture toughness $K_{IC}$ will be of interest, but also the Mode II fracture toughness $K_{IIC}$.
Any time a technologically relevant material is likely to undergo chemical expansion such
that stress, strain, or fracture could either enhance or impede performance operando, it will
be important to anticipate and design for the associated impact on mechanical properties.
6.5 Chapter Conclusions

In this chapter, we demonstrated how the methods used to study the in situ electrochemomechanics of non-stoichiometric oxides for solid oxide fuel cell applications can be applied to Li-storage materials. Many of the effects present in oxides for SOFCs can also be expected to exist in Li intercalation materials, including actuation [26] or volume change upon changing Li or oxygen composition, and concurrent, composition-dependent changes in mechanical properties including Young’s modulus, hardness, and fracture toughness $K_{IC}$. Li-storage materials regularly undergo rapid and continuous changes in composition, meaning that they are likely to exhibit fluctuations in material volume, mechanical properties, and associated stress during normal operation.

As we have seen, these effects depend not only on the extent to which the composition changes, but also on the rate at which this occurs. Thus, it is essential to develop in situ, dynamic characterization methods that can rapidly identify changes in stress state or volume under non-equilibrium conditions. For example, the non-contact approach to detecting dynamic chemical expansion discussed in Section 6.2 could be useful for characterizing high temperature oxide actuators like those discussed in Chapter 2. Beyond this, tools that help battery designers account for different coupling effects within the available material space will enable improved mechanical performance. Electrochemical shock maps are a good example of one such tool, showing how C-rate and particle size are handles that may be used to prevent electrochemical shock when dealing with electrochemomechanically coupled cathode materials.

Computation also plays a major role in understanding electrochemomechanics of battery materials. Although widely used as a tool for identifying potential new Li-storage compounds (a technique that could also be helpful in identifying improved SOFC cathode materials) [29], atomistic calculations can also explore the detailed mechanisms behind effects such as chemical expansion or strain-dependent transport properties. The effect of mechanical strain on the transport and reactivity properties of battery materials, especially in the context of solid-state batteries, is certainly a worthwhile area of study. From a more macroscopic perspective, computation can also be applied to modeling device structures to account for dynamic changes in volume, mechanical properties, and transport properties and thereby better predict how devices will respond to various simulated load cycles.

Lessons learned from LIB research for how to study and account for electrochemomechanical coupling in non-stoichiometric materials can and should be applied to the field of SOFC research, and vice versa. Just as electrochemical methods like impedance spectroscopy have been used to study both classes of materials, so too must the methodology of in situ experimentation be adapted between these two seemingly disjointed fields. Temperature, environmental, and electrical control each have their place in both contexts, allowing us to understand important details including activation energies, reaction chemistry, and rate-dependent effects. Probe-based techniques that can acquire local information with high resolution are particularly interesting, as these help bridge the gap between atomistic modeling and macroscopic observations. In sum, electrochemomechanical coupling is pervasive in electrochemical energy conversion and storage technology, and the study of each specific material may provide clues for broader effects that apply to non-stoichiometric oxide materials in general.
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Chapter 7

Conclusions

This thesis characterized chemomechanical coupling in the model oxide Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ (PCO) under operando conditions, presenting a multi-component study of how environmental conditions, defect chemistry, mechanical states (including volume, stress, and strain) and mechanical properties interact in an electrochemomechanically coupled non-stoichiometric oxide. Using both novel experimental approaches and computational modeling, we characterized the conditions that enhance chemical expansion for our model system and demonstrated that chemical expansion could be harnessed to produce mechanical actuation or changes in elastic properties in situ. Those results also delineated ways in which thin film chemomechanical coupling in non-stoichiometric oxides differs from bulk effects operando. We then characterized this chemomechanical coupling on the atomic scale using high temperature electron microscopy, highlighting several key details that contribute to the effects observed earlier in the thesis. Finally, we demonstrated that many of the chemomechanical coupling effects we observed for the model system PCO were relevant to the broad class of non-stoichiometric oxides, including Li-storage compounds, and applied the methods used earlier in the thesis to measuring rate-dependent stress profiles during electrochemical charging in Li$_x$Mn$_2$O$_4$ (LMO), predicting chemical expansion as a result of oxygen loss in the same system, and quantifying composition dependent mechanical properties in Li$_x$CoO$_2$ (LCO).

7.1 Contributions

With reference to the concluding sections of Chapters 2-6, we list here the key results and scientific questions addressed throughout this thesis.

How can we detect chemical expansion in non-stoichiometric oxide films on short time scales, and which conditions enhance or suppress this effect? Chemical expansion in non-stoichiometric oxides such as the model system PCO happens as a result of increased lattice volume when cations reduce in association with oxygen vacancy formation. We developed a novel method to stimulate and detect chemical expansion in thin film oxides by electrochemically pumping oxide ions into and out of a film grown on an ionically conducting substrate, and measuring the resulting film thickness change and/or substrate deflection using a probe with sub-nanometer displacement resolution and sub-second temporal resolution.[1] Applying this method to the model system PCO, we found
that mechanical displacement followed expected trends based on the defect model of PCO, and that the magnitude of displacement was controlled by the film’s chemical capacitance, while the rate of displacement was controlled by oxide ion diffusion through the zirconia substrate. Increased temperature or reducing $pO_{2,eff}$ increased chemical expansion in PCO for the same applied bias range, and shifting to more reducing conditions also caused sample deflection to be more linear as a function of applied bias. We also applied this method of detecting dynamic chemical expansion to two alternative material systems: perovskite oxide ion conductor $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_2\text{O}^\delta$ (STF) and Li-ion storage material $\text{Li}_x\text{Mn}_2\text{O}_4$ (LMO), and identified rate- or $pO_{2,eff}$- dependent deflection (and stress) in these systems.[2] This general approach can be used to identify conditions or materials that maximize or minimize chemical expansion effects for non-stoichiometric ion conductors in situ, can be adapted to many types of materials and sample designs, and is accessible in a typical university lab setting, without need of a synchrotron. Furthermore, these results demonstrated that chemical expansion of non-stoichiometric oxide films could be electrically driven to produce high temperature oxide actuators, a novel and positive use for the chemical expansion effect with applications in robotics for extreme environments.

How does the mechanical stiffness of non-stoichiometric oxide films depend on chemical expansion? We addressed this question from both an experimental perspective, with high temperature, controlled atmosphere nanoindentation experiments, and a computational perspective using density functional theory.[3, 4] In general, the increase in bond length associated with either chemical or thermal expansion can be expected to include a weakening of atomic bonds within a crystalline material and a concurrent decrease in Young’s elastic modulus. High temperature, controlled atmosphere nanoindentation showed that the Young’s modulus of PCO films decreased by about 36% per estimated 1% increase in lattice parameter $a$ resulting from either thermal or chemical expansion. However, this decrease was larger than that predicted by density functional theory for bulk samples (20% decrease in $E$ per 1% increase in $a$) or previous literature results for bulk doped and undoped $\text{CeO}_2$ (23% decrease in $E$ per 1% increase in $a$). Several factors are expected to contribute to the discrepancy between bulk and film forms of $\text{CeO}_2$, including larger-than-predicted oxygen vacancy concentrations in films (and therefore underestimated $a$), anisotropic effects, and a significant proportion of film volume contained in grain boundaries or linear defects that may include space charge regions with larger lattice parameter. Computational results showed that the biaxial stiffness of (111)-oriented PCO likewise decreased with increasing oxygen vacancy concentration, but that this effect was quite similar for bulk and membrane forms of PCO.[5] Therefore, finite thickness effects alone cannot account for the discrepancy between bulk and thin film samples, and instead composition differences in situ (either through greater film reducibility or space charge layers) and mechanical constraint must also play a role. The consequences of these results are two-fold; firstly, designers of $\mu$-SOFCs for intermediate temperatures will need to measure the in situ, thin film specific elastic constants in order to accurately predict stresses operando, and secondly, designers of strain engineered devices will need to account for composition and temperature-dependent elastic constants in order to achieve desired strain states.

How does biaxial strain or interfacial stress impact chemical expansion in non-
Simulations of biaxially strained PCO membranes showed out-of-plane relaxation that depended on defect content and the oxygen vacancy type. Local defect chemistry affected atomic plane rearrangement more strongly than did biaxial strain. However, biaxial strain affected the energetics of oxygen vacancy formation; for vacancies of fixed distance relative to reduced cations, surface vacancies were more favored for tensile strain, while subsurface vacancies were more favored by compressive strain. Since the type of oxygen vacancies available near an oxide surface and resulting local lattice rearrangement are essential components of gas exchange kinetics, this provides a possible mechanism by which biaxial strain could impact gas exchange reactivity. Furthermore, transmission electron microscopy (TEM) imaging of PCO cross-sections grown on yttria stabilized zirconia (YSZ) substrates confirmed the presence of anisotropic chemical expansion local to the PCO-YSZ interface, and also identified periodic arrays of misfit dislocations with strain fields that changed dynamically with environmental conditions. Therefore, non-stoichiometric oxide films can be expected to chemically strain anisotropically in situ, especially adjacent to mechanically constraining interfaces, and this could cause anisotropic transport and mechanical properties including ionic conductivity and elastic moduli. However, with sufficiently large interfacial stress at high enough temperature (e.g., \( \sigma_{\text{int}} \sim \text{GPa at } T > 650\,^\circ\text{C} \)), films may be able to dynamically relieve stress through defect mobility.

**Are composition and chemical expansion uniform in non-stoichiometric oxide films at the nanoscale?** TEM analysis of PCO-YSZ cross-sections showed that films underwent anisotropic chemical expansion in situ, with more chemical strain occurring in the direction perpendicular to the interface than in the direction parallel to the interface, and with the degree of anisotropy decreasing with distance from the interface. Additionally, threading defects in PCO films were observed to trap reduced cations in situ, meaning that even in oxidizing conditions PCO films may have regions of increased lattice volume and decreased lattice stiffness. These threading defects may also impact oxygen exchange and transport kinetics. We observed a weakly enhanced Pr\(^{3+} \) concentration at the PCO-YSZ interface in oxidized, intermediate temperature conditions, but did not observe evidence of interfacial space charge otherwise. Therefore, we conclude that non-stoichiometric oxide films can exhibit non-uniform oxidation state local to threading defects in situ, as well as anisotropic chemical expansion that varies as a function of distance from the mechanically constraining interface.

**What chemomechanical effects contribute to differences between bulk and thin film non-stoichiometric oxide properties under operando conditions?** The main differences between thin film and bulk forms of non-stoichiometric oxides are the mechanical constraint applied to the films, the degree of reducibility, and the volumetric proportion of imperfect lattice including interface regions, surface regions, grain boundaries, or linear defects. These effects are interrelated; films may reduce more easily because of their increased surface or grain boundary volumetric proportions, and they may exhibit increased linear defect densities because of their mechanical constraint. Nonetheless, the presence of these factors changes the manner in which oxide films undergo chemical expansion. Firstly, film lattices can be expected to strain anisotropically adjacent to a constraining interface, producing both anisotropic elastic moduli and transport properties. Because of their greater
reducibility, films may also strain more under less reducing conditions than bulk, causing correspondingly decreased mechanical stiffness. This effect can be expected to extend to any other non-stoichiometry-dependent property, such as oxygen storage capacity or oxide ion conductivity. The regions of local, concentrated differences in oxidation state will contribute to non-uniformity in composition-dependent properties such as elastic moduli, and may also impact diffusion or gas exchange kinetics. When thin films are used to generate stress, the degree of mechanical constraint and the presence of microstructural features such as grain boundaries or threading defects may affect the magnitude of stress generated in situ.

In what ways do the chemomechanical coupling effects observed for oxygen-deficient oxides extend to Li-storage materials? Li storage materials undergo chemical expansion as a function of Li content, and so should be expected to also exhibit the other chemomechanical coupling effects, including stress generation and composition-dependent mechanical properties, that we observed for PCO. In three separate studies, we showed that lithium storage materials do follow this prediction. For example, we showed that Li$_3$Mn$_2$O$_4$ (LMO) could generate mechanical stress and dynamic actuation through electrochemical charging and discharging with Li.[2] The same material system, which was known to have Li-content dependent volume, was also predicted by density functional theory to undergo volume change upon oxygen loss, explaining an operando change in stress that had been previously observed experimentally. Finally, we quantified composition-dependent mechanical properties including Young’s elastic modulus $E$, hardness $H$, and fracture toughness $K_{IC}$ for the widely used battery material Li$_x$CoO$_2$ (LCO).[7] These results emphasize the key conclusion that there are many parallels in terms of chemomechanical effects present in non-stoichiometric oxides regardless of the type of mobile ion (non-stoichiometry), and researchers of electrochemomechanical coupling should remain cognizant of results that cross between specific material compositions and classes, as well as end-use applications.[8]

7.2 Outlook and Perspectives

This thesis was focused primarily on understanding how chemical expansion, mechanical properties, mechanical stress, and mechanical strain interacted in a model system under extreme in situ conditions including elevated temperatures and reducing environments. In pursuit of this goal, we developed operando experimental techniques that blended electrical stimulation, temperature control, and mechanical detection to measure chemomechanical coupling effects in environments relevant to devices such as solid oxide fuel cells, gas separation membranes, or catalysts for oxygen storage or exchange. However, the problem at hand is complicated by the fact that experimental results arise from the very coupled contributions being investigated (environmental conditions, stress, strain, chemistry, etc.) as well as experimental error. An important way to manage this complexity was the application of statistical approaches where possible (e.g., analysis of indentation results), while a second way was simulation of simplified, carefully controlled structures. Therefore, while many of the results predicted or measured here for PCO are general for materials undergoing chemical expansion in situ, we caution that individual material systems with differing crystal structures and/or additional deformation mechanisms (e.g., anisotropic chemical expansion or concurrent phase changes) may incorporate interesting additional or alternative results.
that were not captured by our own study of PCO. Furthermore, we caution that the TEM environment by which we analyzed chemical expansion on the atomic scale is naturally highly reducing, and recommend that environmental (pO$_{2,\text{eff}}$-controlled) TEM experiments would be a very interesting way in which to precisely quantify, on the atomic scale, changes in mechanical strain or interface structure as a function of changes in defect chemistry. In general, predicting *operando* stress or strain in layered electrochemical devices will require knowledge of both *in situ* elastic constants and chemical expansion coefficients.

We anticipate that the composition-dependent mechanical properties measured and predicted here for PCO and LCO will serve as a useful model for simulations of composition-dependent mechanics in non-stoichiometric oxides of these diverse classes. However, we also hope that these results will inspire further measurement of composition-dependent mechanics in other technologically relevant chemistries, including perovskite and Ruddlesden-Popper systems. In Chapter 3 we suggested several alternative experimental methods by which these measurements might be conducted. Additionally, although not considered here, we anticipate that an investigation of the effect of *operando* conditions and chemical expansion on the fracture or delamination properties of non-stoichiometric oxide films for SOFCs would produce insights into the sources of mechanical failures for operating devices. An important innovation from this thesis, that of stimulating and controlling rapid chemical expansion *in situ* by applying electrical signals, may be an attractive way to enable certain types of composition-dependent mechanical property measurements moving forward. For example, a study of composition-dependent fracture properties might be accomplished by combining *in situ* microscopy with electrochemical pumping of oxygen into and out of these materials. Given an initial flaw, perhaps produced through prior indentation with a sharp probe, can we visualize crack propagation in (or delamination of) non-stoichiometric oxide films during electrically-induced chemical expansion? More simply, electrical bias could be used in place of gas control to hold materials at a fixed composition during mechanical property measurements (e.g. measuring fracture toughness using the pop-in method of Section 6.4), potentially mitigating some of the challenges of environmental nanoindentation. Of course, variations and improvements to the NECS approach of Chapter 2, for example the non-contact optical methods used in Section 6.2, may be particularly useful for characterizing reactive or very thin materials. Given the variety of chemomechanically coupled oxides available, we anticipate that material chemistry (including composition-dependent mechanical properties) and device geometry will be tailored in the development of optimized high temperature oxide actuators for various *operando* environments.

We note that an important additional coupling effect, that between chemistry and functional properties such as ionic conductivity or gas exchange kinetics, was considered mostly in a contextual fashion throughout the thesis. Although not measured here, it is important to recognize that these functional properties are coupled to material mechanics through their relationships with defect chemistry. While investigations of the relationship between mechanical strain and ionic conductivity or gas exchange reactivity have been a subject of recent interest, the related impact of *mechanical stress* and *changing elastic properties* has rarely been a focus of such research, and there is still a large amount of debate about to what extent, by what mechanism, and for which materials mechanical strain can impact these properties. Further experimental work to address the challenge of strain engineered functional properties provides an important avenue towards lowering the operating
temperatures of SOFCs and other non-stoichiometric oxide devices. One potential way to address the question of coupling between ionic conductivity and mechanical strain could employ a cantilever-based approach. In such an experiment, the oxide film of interest could be grown on an insulating substrate, with patterned electrodes attached. Then, electrochemical transport or reactivity properties could be measured (e.g., using impedance spectroscopy) while mechanical strain was applied by bending the cantilever. Ideally, such an experiment would be conducted inside of a temperature and/or pO\textsubscript{2} controlled chamber. Some further questions for work on electrochemomechanical coupling in oxide films include: Does mechanical stress (as opposed to strain) affect oxide composition and functional properties? How do ionic currents affect mechanical properties \textit{in situ}\? To what degree can we transduce between mechanical effects (volume, stress, strain) and electrochemical properties (composition, ionic conductivity, reactivity) \textit{in situ} for various material systems?

In the context of developing research, we point to the topics of resistive switches and solid-state batteries as areas that will benefit (and are already benefiting) from serious consideration of electrochemomechanical coupling. Just as they are in SOFCs, delamination and vertical fracture present important mechanical failure mechanisms that must be considered and overcome in order to produce durable devices that will last over many usage cycles. Composition-dependent mechanics (including for films of <100 nm thickness) will be just as relevant in the non-stoichiometric materials used for these devices as they are in batteries and SOFCs. Furthermore, although these devices are largely intended to function at room temperature, we point out here that temperature-dependent measurements are an important tool for learning about fundamental kinetic processes that should be widely applied wherever device mechanisms are still a topic of debate. The opportunity to produce various novel types of integrated switches, not only between resistive states but also between optical, mechanical, magnetic, or volumetric states, is an exciting area of research for future sensors and actuators that will draw heavily on the field of electrochemomechanical coupling.

Finally, we comment on \textit{in situ} materials characterization. In recent years, there have been many developments in tools for \textit{in situ} experimentation that integrate temperature, gas, and electrical control, sometimes also with imaging capabilities. These tools, which exist for probe-based systems, within microscopes and spectrometers, and along beamlines, are great enablers to the investigation of electrochemomechanical coupling. Beyond this, such tools continue to broaden the time and length scales over which chemomechanical coupling effects can be observed and measured, and will facilitate many advances in understanding not only chemical expansion or ionic conductivity, but also the mechanisms of these effects and how they interact with microstructure and complex defects including dislocations and grain boundaries. We are humbled to have made even a small contribution to the many available types of \textit{in situ} characterization methods available, and look forward to new and interesting uses for our methods that are identified in time, beyond the field of oxides for energy conversion and storage. Even so, we expect that the utility of computation will continue to grow as more advanced computers facilitate simulation of increasingly complex microstructures and answer questions about materials behavior through precise, artificial control of factors that are inextricably coupled experimentally. This kind of research will provide greater scientific understanding of the chemomechanics of materials essential to energy conversion and storage devices, which can in turn facilitate engineering development and widespread deployment of devices for conversion and storage of renewable energy.
Bibliography


Appendix A

Statistical Methods and Error Assessments

This appendix concerns useful background derivations, statistical methods, and error assessments that provide further supporting information for the studies presented in the earlier parts of the thesis. Sections A.1 and A.2 concern Chapter 2, while Section A.3 discusses analysis of variance for *operando* nanoindentation (Chapter 3), Section A.4 describes error assessment for DFT computations of biaxial elastic constants (Chapter 4), and Section A.5 concerns statistical information related to the indentation measurements of composition-dependent mechanical properties in Li$_x$CoO$_2$ (Chapter 6).

A.1 Derivations for nanoscale electrochemomechanical spectroscopy (NECS)

Chapter 2 presented analysis of chemical expansion in Pr$_x$Ce$_{1-x}$O$_2$-$\delta$ (PCO) films based on nanoscale dynamic measurements of amplitude $A$ and phase lag $\phi$ of sample displacement during electrochemical stimulation. These parameters were presented both as measured (Fig. 2-5(a)-(b)) and in the complex plane (Fig. 2-5(c)), and were related to a complex function $Y$ known as the *electrochemomechanical admittance*, which has units of nm/V and is defined according to equation A.2 in the time domain, and equation A.1 in the frequency domain.

$$Y[\omega] = \frac{A[\omega]}{E_0}(\cos(\varphi[\omega]) + i\sin(\varphi[\omega]))$$  \hspace{1cm} \text{(A.1)}

$$Y[t] = \frac{D}{E} = \frac{A[\omega]\sin(\omega t + \varphi[\omega])}{E_0\sin(\omega t)}$$  \hspace{1cm} \text{(A.2)}

In the above equations, $D$ is displacement, $E$ is electrical bias (which has amplitude $E_0$), and $\omega$ is frequency. Although $|Y|$ is generally normalized by $E_0$ (constant for all frequencies in a given condition), this bias normalization factor can be omitted when comparing datasets under constant bias amplitude to indicate the measured mechanical response in units of nm, as was done in the Bode plots Figs. 2-5(a)-(b).
The following is a discussion of how such a model describes the measured $\phi$ and $A$ of the mechanical response of the films according to fundamental processes within the material. This derivation was developed in collaboration with Dr. Sean Bishop. This discussion can also be found in the Supplementary Material to Ref. [1]. A more detailed presentation of predictive defect modeling related to these measurements is the subject of an additional manuscript in preparation.[2]

The components of $Y$ may be modeled using an equivalent circuit with a real component, conductance $G$, and an imaginary component, susceptance $B$, in series. The admittance of these two components is denoted $G$ and $1/i\omega B$, respectively, giving rise to a total admittance described by Eq. A.3:

$$\bar{Y} = (\frac{1}{G} + \frac{1}{B})^{-1} = \frac{G'}{1 + (\omega G'B')^2} - \frac{G' i \omega G'B'}{1 + (\omega G'B')^2}$$  \hspace{1cm} (A.3)$$

In this representation, $Y = G$ when $\omega = 0$ (equilibrium), and $GB$ represents a characteristic time constant $\tau$ for the response. Therefore, $G = D_0/E_0$ and $GB = \tau$, where $D_0$ is the equilibrium expansion amplitude for $E_0$ (a constant across all frequencies), and values for $\tau$ are determined as described in Chapter 2. With these substitutions, we have Eq. A.4:

$$\bar{Y} = \frac{D_0/E_0}{1 + (\omega \tau)^2} - \frac{(D_0/E_0 i \omega \tau)}{1 + (\omega \tau)^2}$$ \hspace{1cm} (A.4)$$

As shown in Figs. 2-5(a)-(b), it is common to provide the modulus of admittance and phase angle on a Bode plot. The modulus is given by the root of the sum of the squared real and imaginary parts of $Y$, and the phase angle is equal to the inverse tangent of the ratio of the imaginary and real components as described in the following equations:

$$|Y| = ((\frac{D_0/E_0}{1 + (\omega \tau)^2})^2 + (\frac{(D_0/E_0 i \omega \tau)}{1 + (\omega \tau)^2})^2)^{1/2} = \frac{D_0/E_0}{\sqrt{1 + (\omega \tau)^2}}$$ \hspace{1cm} (A.5)$$

$$\varphi(\omega) = \tan^{-1}[-\frac{D_0/E_0 i \omega \tau}{D_0/E_0}] = \tan^{-1}[-\omega \tau]$$ \hspace{1cm} (A.6)$$

Multiplying Eq. A.5 by the constant applied voltage amplitude $E_0$ results in equation 2.10 reproduced here, and rearranging Eq. A.6 results in Eq. A.8, which can be equivalently written as Eq. 2.11.

$$A(\omega) = \frac{D_0}{\sqrt{\omega \tau)^2 + 1}}$$ \hspace{1cm} (A.7)$$

$$\varphi(\omega) = -\phi = \tan^{-1}(-\omega \tau)$$ \hspace{1cm} (A.8)$$

$A(\omega)/E_0$ and $\phi(\omega)$ are the modulus and phase angle, respectively, of Eq. A.1, confirming that Eq. A.3 is an equivalent representation of $Y$. These are shown schematically in Fig. 2-4.

With the above equations, $D_0$ and $\tau$ can be derived based on the mechanical measurement of $A$ and $\phi$ and related to the fundamental processes contributing to the measured electromechanical admittance.

Note that as equilibrium is approached ($\omega \rightarrow 0$), the admittance will be entirely real,
and equivalent to \( G = D_0/E_0 \). This value gives us information about the total possible mechanical response, and is proportional to the charge storage capacity of the PCO film, given by the chemical capacitance \( (C_{\text{chem}}) \), as shown by the following proportionality relation:

\[
\frac{D_0}{E_0} \propto \frac{\alpha_c \Delta \delta}{E_0} \propto \frac{\Delta q_\delta}{E_0} \propto C_{\text{chem}}
\]  

(A.9)

where \( D_0 \) is proportional to \( \alpha_c \Delta \delta \), the chemical expansion given by Eq. 1.4, which, in turn, is proportional to the change in number of charges stored as oxygen vacancies, \( \Delta q_\delta \), with \( C_{\text{chem}} \) being the ratio of stored charge for the given applied voltage.[3]

We also validated this correlation by the fact that charge accumulation in the film determined from I-V data during experiments tracked displacement data with the same phase lag relative to the applied voltage sinusoids. In Fig. 2-5(c), this quantity was also equivalent to the diameter of the semicircle. Since \( E_0 \) is a constant (128 mV), an Arrhenius fit such as that shown in Fig. 2-6(a) to the equilibrium expansion amplitude \( D_0 \) gives an activation energy corresponding to that of chemical capacitance in this PCO film. The value measured is 0.53 ± 0.14 eV (standard deviation of 6 measured activation energies), which agrees well with previously reported values for chemical capacitance in PCO and the values reported in this study measured by impedance spectroscopy on these same samples.[4]

Turning to \( B \), when the response of the system is completely out of phase \( (\phi = -\pi/2) \) to the applied signal, the complex admittance will be entirely imaginary and equivalent to \( B = 1/i\omega B \), where \( B = \tau/G = \tau E_0/D_0 \). As described earlier, \( \tau \) is a time constant describing the rate of a process and, following an equivalent circuit representation, can be recast as a resistance multiplied by a capacitance (i.e., RC time constant). As \( E_0/D_0 \) is the inverse of \( C_{\text{chem}} \), \( B \), from this approach, is equal to a resistance, \( R \) (i.e. the resistance to charge passage into the PCO thin film). As described next, this resistance is equivalent to the resistance for ionic transport through the YSZ electrolyte.

As shown schematically in Fig. 2-1(b), during these experiments electrical bias \( V_{WE} \) was applied between the PCO/Pt working electrode and the reference electrode on the yttria stabilized zirconia (YSZ) substrate. Since resistance to oxygen gas exchange at the PCO/Pt electrode is much higher than that of oxygen transport through the YSZ (> 100 Ωcm² vs. 10 Ωcm², respectively at 650°C), as the PCO film adjusted its vacancy content to match the \( p_{O_2, \text{eff}} \) caused by \( V_{WE} \), oxygen was pumped primarily through the YSZ electrolyte. [3, 5] The rate of adjusting oxygen content in the PCO film was then limited by diffusion through the YSZ, which in turn determined the expansion rate. This interpretation is further validated by comparing the activation energy for \( \tau/D_0 \) (1.05 ± 0.13 eV, see Fig. 2-6(a)) with the activation energy for ionic conduction in YSZ (~1 eV).[6]

### A.2 Sensitivity analysis for direct measurement of chemical expansion

This section concerns an analysis of detection sensitivity and parameter estimation error for the type of measurement ("direct measurement of chemical expansion" or NECS) described in Chapter 2. This sensitivity analysis was also published in the Supplementary Information to Ref. [1]. A full description of the experimental procedures for that study is available in
Section 2.5, and a step-by-step Standard Operating Procedure for conducting measurements using the tools available in the Van Vliet lab can be found in Appendix B. Here, we assess the measurement error for individual data points collected for phase lag and amplitude, as well as estimation error for parameters $D_0$ and $\tau$ determined based on fits to measurements across the frequency spectrum of interest. Finally, we assess the error in activation energies obtained from measurements conducted at multiple temperatures for the same sample.

At each experimental condition, oscillatory loading (with real-time analysis) was performed until the phase lag $\phi$ converged to within 0.1 radians and the amplitude $A$ to within 0.5 nm, typically $>30$ cycles. The values of $A$ and $\phi$ vs. frequency $\omega$ reported in Fig. 2-5 and used for all data sets to fit to Eqs. 2.10 and 2.11 are the averages of the fitted amplitude and phase lag of the last ten cycles of each measurement, which generally had standard deviations of less than 0.3 nm and 0.1 radians, respectively. In Fig. 2-5, these standard deviations are smaller than the data points. For the slowest frequency measurements (corresponding to the largest measured amplitudes, phase lags nearest to 0, and the most opportunity for mechanical noise and signal drift to affect signal-to-noise ratio), these standard deviations were occasionally larger ($<1$ nm or 0.2 rad). For replicate measurements performed in the same conditions (temperature, film thickness, applied bias range, etc.) near the centers of the samples, the range of fitted values for $D_0$ was generally $\pm 3 - 8\%$, and for $\tau$ was $\pm 2 - 6\%$, except in the case of the sample tested for curvature (described in Section 2.2.2), for which the range of $\tau$ across a wider lateral spacing range (which could conceivably introduce additional variation) was $\pm 11\%$.

![Figure A-1: Amplitude (a) and phase lag (b) measured for three replicate experiments near the center of the sample with film thickness 883 nm. Data points overlapped up to the highest frequency, when deviation in measured amplitude and phase lag was still less than 1 nm or 0.1 radians.](image)

We show in Fig. A-1 the result of one of these experiments ($650^\circ$C, 883 nm film thickness) where we tested the same condition at 3 locations near the sample center. Data points overlapped significantly until the highest frequency when some small deviation occurred in the amplitude data. At this point, the amplitude was $\sim 1$ nm, which is our stated lower limit.
of displacement detection. This set of measurements reflected a worst-case scenario in terms of sampling repeatability, and the actual deviations in the resultant calculated magnitudes of \( \tau \) and \( D_0 \) from this set of measurements was only 6% and 8%, respectively. Calculated \( D_0 \) and \( \tau \) values are therefore robust to experimental variability, and the error of any reported values can be estimated to be within the ranges reported above.

In fact, the parameters used to fit activation energies were \( D_0 \) and \( \tau / D_0 \). The sample with film thickness 1028 nm was the only one for which multiple positions near the sample center were tested at multiple temperatures, but for those three tests the activation energies of \( D_0 \) and \( \tau / D_0 \) were found to vary by less than 8% and 6%, respectively, displaying minimal sensitivity to experimental variation. Figure A-2 shows the variation in \( \tau / D_0 \) that was observed when assessment was possible; the variability of \( D_0 \) alone is reported in Fig. 2-6(b).

![Figure A-2: The error in measured inverse deflection rate (\( \tau / D_0 \)) vs. film thickness was small whenever replicate measurements were conducted. Error bars denote the range (maximum and minimum) values for each condition.](image)

To consider sample-to-sample variability, we can turn to variation in the quantities that were derived based on data from all samples: activation energies and amplification factor. We report in Chapter 2 the average and standard deviation for a total of at least 6 measured activation energies across three samples as: \(-1.05 \pm 0.13 \) eV (for \( \tau / D_0 \)), and \( 0.53 \pm 0.14 \) eV (for \( D_0 \)). Thus the sensitivity of the activation energy to experimental and sample-to-sample deviations was on the order of 0.1 eV. For amplification factor (the slope shown in Fig. 2-6(d) that compares measured displacement \( D_0 \) to predicted film thickness change), we applied a bootstrapping algorithm (resampling with replacement) to assess the variation in the linear fit for 1000 bootstrapped samples.[7] Based on this assessment, we determined 95% confidence intervals for the amplification factor and goodness-of-fit parameter \( R^2 \) as (4.4, 5.5 nm/nm), and (0.83, 0.98), respectively. Therefore, the sensitivity of the detected amplification factor to sources of variation including but not limited to film thickness measurement error, probe centering error, and sample clamping differences, was on the order of 10%. We also note that the amplification factor is related to the specific substrate thickness (1 mm) and film area (0.64 cm\(^2\)) used throughout this work- differing sample geometry
A.3 Analysis of variance (ANOVA) for *operando* nanoindentation

Chapter 3 described an environmental instrumented indentation study conducted to measure the Young’s elastic modulus of PCO films under *operando* conditions of elevated temperature and controlled oxygen environment. As discussed in Section 3.3.1, there are many sources of error in high temperature nanoindentation. To manage these concerns and make conclusions about the significance of measured differences, we applied analysis of variance, which we discuss in this section. This discussion was also previously published in *ECS Transactions*.\[8\]

Analysis of variance (ANOVA) is a statistical technique generally used to identify to what degree variance in multiple measurement sets is due to differences in testing conditions as opposed to the intrinsic variability of the thing being measured.\[9, 10\] It is largely based on computing the $F$-statistic, which compares variance within a group to variance between groups.\[10\] Often, ANOVA is applied in the context of biology when trying to identify which treatments in multiple "treatment groups" have a statistically significant effect.\[9\] In the work reported in Chapter 3, we used ANOVA to determine the best way to account for variance among nominally equivalent measurement sets (where the only differences in test conditions were the time and location on the sample). We designed the experiments presented in Chapter 3 to support using one-way ANOVA to manage the variability of high temperature indentation experiments.

![Figure A-3](image)

Figure A-3: Schematic of multiple indentation arrays on a PCO sample surface, indicating inter-indentation spacing of 30 $\mu$m within an array and inter-array spacing of 150 $\mu$m. From Ref. [8].

For each sample and condition tested, we executed four arrays of indentations at different sites on the sample surface (Fig. A-3). Within each array of $\sim$25 positions, we spaced
indentations of maximum depths <100 nm (<10% of film thickness) 30 μm apart to minimize interactions among indentation locations at that site. The minimum distance between each array was 60 μm, but more typically above 150 μm, as shown in Fig. A-3, to account for any variation in film thickness or morphology changes across the sample surface. We computed the Young's modulus $E$ and, at room temperature, hardness $H$ for each measurement as described in Chapter 3. Additionally, we note here that at room temperature certain arrays had 30-60 individual indentation positions, so for the discussion below (which focuses on the room temperature case for illustration), the total number of indentations may occasionally exceed the number analyzed for high temperature tests described in Chapter 3.

To evaluate the uncertainty in these measurements and properly report the mechanical properties of a given sample condition defined by material composition and physical environment, we used one-way analysis of variance (ANOVA) based on the method presented by Sokal and Rohlf to compare variance within an array to variance among arrays on a given sample surface.[9] This technique can be used to determine whether there is added variance among arrays that precludes pooling of data into one large population with $n =$ number of indentations for a given sample condition. If data acquired at multiple locations on a given sample cannot be pooled, this would prompt one to consider the data from the standpoint of a smaller number $N =$ number of indentation arrays for each sample condition. Here, indentation arrays varied not only spatially by probing different regions of the sample surface, but also chronologically because arrays were acquired at different times of day or on different days. The signal-to-noise (SNR) ratio for a given array is a function of many factors, and while generally machine noise was kept to a minimal level, the SNR can still affect measured results.

In general, when multiple comparisons are made for a set of $N > 2$ indentation arrays, a simple $t$-test will not be sufficient to identify significance at the stated level $\alpha$ if corrections are not applied for repeated testing. Analysis of variance accounts for the increased chance of false-positives or false-negatives when analyzing multiple pairwise comparisons by considering the data set as a whole. Specifically, ANOVA compares variance within groups to variance among groups to make determinations about which groups may be considered "significantly different" from each other.

We used three metrics to assess whether the variance among arrays was too great as compared to the variance within an array to consider the data to come from the same population; these metrics were: $p$-value $< 0.05$, the Tukey-Kramer minimum significant difference (TKMSD), and the Gabriel comparison interval.[9] The $p$-value considered here takes into account the number of pairwise comparisons and includes an inherent Bonferroni-type correction for repeated $t$-tests.[10] The TKMSD is a metric based on the studentized range, the number of arrays, and the average sample size that identifies the minimum difference that must exist between the means of any pair of arrays within a set to consider them as statistically different at a chosen significance level. The Gabriel comparison interval method is an approximate method that is based on the studentized maximum modulus distribution; in this test, lower and upper comparison intervals are computed for each array based on the variance within that array relative to the variance between two given arrays. If the comparison intervals of two arrays do not overlap, they are considered statistically different from each other at the chosen significance level. Here, all metrics used a significance level $\alpha$ of 0.05.
We determined these three metrics for the 4 indentation arrays acquired on each sample and condition. If two of the three metrics indicated that at least two of the four groups were statistically significantly different, then we inferred that the four arrays were not statistically indistinguishable and did not pool all the indentation results acquired for that sample condition. In this case, the reported $E$ and $H$ values were the grand mean of the four arrays with the standard error of the mean applied, and $N = \text{number of arrays}$. Otherwise, if ANOVA identified no statistical difference in the calculated mechanical property among arrays, the mean of all indentations (pooled results from all arrays in that sample condition) was reported with standard error of that mean calculated according to $n = \text{number of indentations}$.

After we applied the ANOVA procedure to all samples, we calculated the TKMSD for the samples of different compositions to determine which pairwise comparisons of the compositions could be considered statistically different at the significance level $\alpha = 0.05$. Finally, a two-tailed Bonferroni-corrected Welch's $t$-test was used to compare the resultant measured $E$ and/or $H$ of doped or undoped $\text{CeO}_2$ thin films to the previously reported results for the same properties determined on bulk samples.

### A.3.1 Room temperature example case

According to the ANOVA metrics described above, the elastic modulus results for the four arrays of indentations on the undoped $\text{CeO}_2$ sample tested in air and at room temperature were not statistically different. Therefore, we reported the mean and standard error of $n = 126$ indentations for $E$ of that sample condition. The remaining two sample conditions, $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ samples with $x = 0.1$ or $x = 0.2$ tested in air and at room temperature, were found by ANOVA to have at least one array that was statistically different from the others in terms of calculated $E$. Therefore, for those $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ sample conditions we reported the results as the grand mean of the four arrays $\pm$ the standard error of that mean.

An intuitive way to visualize these distinctions with ANOVA results is provided by Gabriel comparison intervals. Figure A-4(a) shows the Gabriel comparison intervals, depicted by vertical black lines, for the four batches of the undoped $\text{CeO}_2$ sample. Note that these lines extending from each datapoint are not "error bars," but that the vertical length of these lines defines the comparison interval for that indentation array. It is apparent visually that the intervals of each array overlap with the other three arrays, indicating that these arrays are statistically indistinguishable within the stated significance level. The other two metrics ($p$-value and TKMSD) agreed with this assessment, and so these data were pooled together as described above.

In contrast, Fig. A-4(b) shows the Gabriel comparison intervals for $E$ at the four arrays acquired for PCO with $x = 0.2$. Here, the interval for the leftmost array in the Fig. does not overlap with those of two of the others, indicating that the leftmost array is statistically different from these other two. Again, the calculated TKMSD and $p$-value agreed with this assessment. Therefore, we reported the grand mean of the four arrays, which is the mean computed from the mean value determined at each of these four arrays.

For measured hardness $H$, the four arrays were statistically indistinguishable for sample $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ tested in air at room temperature. Therefore, we reported the mean and standard error of $H$ for $n = 139$ indentations. The remaining two sample conditions included...
Figure A-4: Gabriel comparison intervals for Young's elastic modulus measured for arrays of indentations on (a) undoped CeO$_2$ and (b) Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ thin films at room temperature. Vertical lines extending from red data points indicate comparison intervals. Such intervals for (a) CeO$_2$ show no statistical differences, while those for (b) Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ show that one array is statistically distinguishable with non-overlapping intervals. From Ref. [8].

at least one array that was statistically distinguishable from the others, so we reported the grand mean of the four arrays and standard error of that mean for $H$ of samples with $x = 0$ and $x = 0.2$.

These statistical analyses allowed us to calculate $E$ for a given sample condition, with objective choices about the number of replicate experiments (pooled indentation mean or array grand mean) considered for each sample condition. With this information, we calculated TKMSDs for the three sample conditions, and found that $E$ did not vary with Pr composition, while $H$ did increase for doped samples as compared to undoped CeO$_2$. Chapter 3 contains analysis and interpretation of indentation data for room temperature and *operando* measurements of PCO thin films. Table A.1 reports the total number of indentations and indentation arrays as well as whether or not the data were pooled, for each condition explored for environmental nanoindentation (and reported in Fig. 3-3).

### A.3.2 Sources of variance

In general we expected that individual indentations within an array would give similar results because they were made on the same sample under the "same" conditions. Indentations within a grid should not interact with each other because of their distant spacing (30 $\mu$m) as compared to the plastic region surrounding any one indent ($\sim$1 $\mu$m radius). In general, for conditions where the option of pooling existed, the mean of $E$ for all indentations for a given condition was within a GPa ($<$1%) of the grand mean of the arrays for that condition. This variation is less than half of the standard error reported for any condition. The standard error of the mean for all indentations may be slightly higher or lower than that for the arrays...
Table A.1: Statistical parameters for Pr<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-δ</sub> environmental nanoindentation

<table>
<thead>
<tr>
<th>Pr content (x)</th>
<th>T(°C)</th>
<th>pO&lt;sub&gt;2&lt;/sub&gt; (atm)</th>
<th>n</th>
<th>N</th>
<th>Pooled? (Y/N)</th>
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</thead>
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<tr>
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</tr>
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<td>Y</td>
</tr>
<tr>
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<td>8</td>
<td>N</td>
</tr>
<tr>
<td>0</td>
<td>600</td>
<td>7.5 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>34</td>
<td>3</td>
<td>Y</td>
</tr>
<tr>
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of indentations. Thus, no significant or systematic bias in either the reported mean or the reported standard error of data was introduced by the choice to pool certain data sets.

Some variation was expected within arrays due to compositional or structural variation in the sample, such as differences in surface roughness or local variation in defect density (e.g., grain boundaries, vacancies). Ideally, ANOVA would find no variation among arrays, and all data could be pooled. In practice, this was not the case, as ANOVA identified that only four of 10 data sets could be pooled (see Table A.1). The remaining six data sets showed significant enough variation among arrays as compared to the variation within arrays that they could not be pooled.

When ANOVA finds that data sets cannot be pooled, it is an indication that some added bias affected results from array to array. Such sources of variance should not be intrinsic to the sample, but instead should be related to external factors or "measurement error." There are several examples of what could cause this kind of variation. For example, the samples were mounted on a heated sample stage using porous cement that provided a varying degree of thermal contact between the heating block and the sample. In the extreme, regions of the sample could be separated from the heated stage by ∼0.3 mm of air. The schematic of the stage shown in Fig. A-5 illustrates how differences in the contact between the heated stage and the sample could lead to temperature variations across the sample surface. Such variations could affect not only the actual properties of films in those regions (due to differing degrees of thermal expansion), but also the relative temperature matching between the probe and sample surface. More extreme temperature differences between probe and surface lead to decreased signal-to-noise ratio during indentation.

This variation due to temperature mismatch is exacerbated by the fact that there is a limit to the precision of control over the temperature matching between the probe and the sample surface. Figure A-5 shows that the thermocouples used to measure the probe and surface temperatures are located at some distance (mm-scale for the probe, cm-scale for the sample surface) from the actual probe tip and sites of indentation. Therefore, there is some finite difference between the actual temperatures at the contact and the temperatures estimated by these thermocouples. From day to day and location to location, the degree of this mismatch varies.
Figure A-5: Schematic of stage set-up for high-temperature nanoindentation, highlighting sources of array-to-array variation in measured $E$. Air pockets in the thermal cement used to mount samples could lead to variation in the temperature of sample surfaces. Distance between the thermocouples used to estimate surface and probe temperature and the actual contact point limit the achievable control of temperature matching between probe and sample.

Another important source of error between arrays is the probe geometry. Especially at elevated temperature, the probe was found to exhibit variations in geometry. There are two main sources that are believed to cause these variations. First is wear of the cBN due to repeated contact with the hard surfaces of the PCO. The second cause is related to the occasional fracture or plastic deformation of the cement that connects the cBN to the metal shaft of the indenter. Fracture or plastic deformation of this cement could cause changes in the orientation of the cBN with respect to the sample, which could in turn affect the projected contact area of the probe at depths less than 100 nm. These variations in probe geometry could be either abrupt or gradual. We repeatedly measured and calibrated the probe geometry to account for these effects. However, some variability in the accuracy of the calibrated function describing probe geometry could be expected between arrays of indentations, further contributing to the observed array-to-array variation.

A final source of variance is the ambient noise, both mechanical and electrical, affecting measurement signal-to-noise on different days or at different times of day.

The array-to-array variation that precluded pooling of data for six of 10 conditions is therefore attributed to problems with temperature control, probe geometry control, and ambient noise.

A.4 Error assessment for DFT computation of biaxial constants

In Section 4.3 we applied a method for computing the biaxial elastic constant $C_{biax}$ of several compositions of PCO that was based on fitting a quadratic function to a set of points
computed at several discrete strains. Some testing was necessary in order to determine the appropriate strain range for these calculations, and the expected error for this type of fitting procedure. To determine these pieces of information, we used the undoped CeO$_2$ bulk cell as a test case. For this composition, we computed the energy at 15 strains (relative to the fully relaxed volume) and then computed the elastic constants with several subsets of these data. Four types of subsets were used: removing individual points from the original 15 (leaving 14 points behind), removing two randomly selected points, removing points from the outer boundaries of the strain range, and removing points at intervals (so, every other point or every third point).

Figure A-6: Computed biaxial elastic constants $C_{biax}$ determined from subsets of an original 15 points computed for energy as a function of strain for bulk CeO$_2$. When the density of points is 1 per $\sim$0.2% strain, with a strain range of at least $\pm$0.4%, the error in computed $C_{biax}$ is $\pm$5%.

Figure A-6 shows that there was a $\pm$5% spread in the computed value of $C_{biax}$ due to error caused by discrete point selection. This result provides an estimate of error to assess the relative significance of differences observed in all calculations. Applying this to Fig. 4-7, for example, the differences in computed bulk $C_{biax}$ for constant $x$ but varying $\delta$ are somewhat larger than this expected error, while the differences observed between compositions for $\delta = 0$ are not. Since increased $\delta$ also correlates with increased lattice parameter of this system, this result agrees with our hypothesis that chemical expansion due to reducing PCO (increasing $\delta$) leads to decreased stiffness.

This procedure also helped determine that a strain range of $\pm$0.4 -- 0.5%, with a point density of about one point per 0.2% strain ($\sim$6-7 data points), would keep us within this range of $\pm$5% error. Figure A-6 reflects a worst-case scenario; when the same procedure was applied to structures containing two Pr dopants or an oxygen vacancy, the spread of the data points was smaller, and a smaller subset of data points was necessary to remain within this error bound. In order to make the most efficient use of computational resources, calculations were conducted for 7-8 data points within this strain range.
A.5 Statistical analysis for nanoindentation measurements of Li$_x$CoO$_2$

A.5.1 Fracture toughness distributions

The values of fracture toughness $K_{Ic}$ measured for individual grains in a given sample were not well described by a normal or Gaussian distribution. Figure A-7(a) shows the histogram of $K_{Ic}$ values determined for individual grains of Li$_x$CoO$_2$ (LCO) charged for 500 hours at a rate of C/1000 (LCO-500), as an example of the typically right-skewed data set obtained for all samples. Figure A-7(b) shows $K_{Ic}$ for all samples reported in Fig. 6-6(c), represented in this case by median ± upper and lower quartile. In general, the median values of $K_{Ic}$ were slightly less than the mean values reported in Fig. 6-6(c). For electrochemically charged samples, the upper and lower quartiles encompassed less than 0.3 MPa-m$^{1/2}$. For all charged samples, two-thirds of the grains were measured to have $K_{Ic}$ below 0.3 MPa-m$^{1/2}$; for uncharged LCO-0 and thermally shocked LCO-TS, the minimum measured $K_{Ic}$ for any grain was 0.32 and 0.36 MPa-m$^{1/2}$, respectively. Importantly, data reported in the form of medians and quartiles does not change any of the trends reported in the manuscript, which reported means and standard errors of the mean. Furthermore, reported values represent grand means of many indentations on many grains, permitting application of the Central Limit Theorem.[10]

![Figure A-7](image-url)

Figure A-7: (a) Distribution of fracture toughness $K_{Ic}$ values measured for thirty individual grains for LCO-500 (Li$_x$CoO$_2$ charged at a rate of C/1000 for 500 hours) is representative of the typical skew-right distribution seen for other samples. (b) Median fracture toughness $K_{Ic}$ for several nominal first-cycle charge durations, as well as for the compact subjected to thermal shocking (LCO-TS), as determined by the pop-in method. After charging for as little as 50 h, the $K_{Ic}$ decreased by about 70%. Error bars are upper and lower quartiles. Figure from Supporting Information to Ref. [11].
A.5.2 Statistical analysis

The $p$-values for statistical significance testing of Young’s elastic modulus $E$ and hardness $H$ were calculated according to Student’s $t$-test using a two-tailed distribution and an $N$ of 30 (28 degrees of freedom) in the case of surface measurements with 30 grains and 20 (18 degrees of freedom) for interior measurements with 20 grains. As multiple $t$-tests were conducted, resultant $p$-values were multiplied by the square root of the number of $t$-tests performed (7) to account for error due to repeated $t$-testing (Bonferroni correction). These $t$-tests used the mean and standard deviation of the $E$ and $H$ measured for $N$ grains.
Bibliography


Appendix B

Standard Operating Procedures

B.1 Nanoscale Electrochemomechanical Spectroscopy (NECS)

B.1.1 Sample Preparation and Attachment

For this method, samples consist of a film of the non-stoichiometric oxide of interest (e.g., PCO, STF) grown on an ionically conducting substrate, such as yttria stabilized zirconia (YSZ), with Pt electrodes added with the geometry shown in Figure B-1. Film thickness and substrate thickness can depend on the targeted signal to noise, but for a $10 \times 10 \times 1$ mm thick YSZ substrate, PCO film thickness $>300$ nm will be sufficient. For a $10 \times 10 \times 0.5$ mm thick YSZ substrate, STF film thickness of $>300$ nm was sufficient for the studies conducted in Chapter 2. Porous Pt electrodes should be deposited as described in Section 2.5, with Pt paste applied afterwards on the counter electrode and the working electrode in order to improve overall connectivity. Note that the working electrode geometry and the film geometry may be adjusted depending on the experimental goals, as shown for example in Figure 2-3.

Once the sample is in hand, it is necessary to attach Pt wire current collectors to the three electrodes, and cement the sample to the stage. Figure B-1 shows a diagram of the final sample setup. Follow these steps:

1. Lay your sample face down on a flat, clean surface, such as a piece of weigh paper attached to a flat plastic box or petri dish, or the back of a weighing boat (the working surface).

2. Using thin strips of Scotch tape, carefully secure the sample to the working surface by taping two corners. Be careful to avoid putting tape directly on the sample edges, as this can cause the reference electrode to delaminate.

3. Cut a piece of Pt wire (Long enough to cross the high temperature stage and exit behind the shroud, $\sim8-10$ cm) using a razor blade, and attach with a thin strip of tape to the working surface.

4. Using tweezers and wearing gloves, bend the wire so that it contacts the Pt counter electrode with mechanical pressure.
5. Check the contact between the wire and the counterelectrode using a multimeter. To avoid removing parts of the counterelectrode with the multimeter probes, you may wish to wrap old Pt wires around the ends of the probes and contact with those, which will be somewhat more gentle.

6. Using a toothpick, dab Ag paste onto the Pt wire where it rests on the Pt counter-electrode. Try not to jostle the Pt-Pt contact.

7. Check contact again with the multimeter.

8. Wait 20 minutes for the Ag paste to dry. In the meantime, mix high temperature cement (Omegabond 600).

9. Cement recipe: 195 \(\mu\text{L}\) DI water per 1500 mg cement powder. Mix with a toothpick and apply a small bead to the wire near the sample edge, to allow a more robust mechanical attachment (Ag paste peels away quite easily).

10. Wait at least one hour for this cement to set.

11. Once the cement has set, you are ready to attach the sample to the stage. Mix a new batch of cement using the same recipe as described above.

12. Using a toothpick, put four, roughly equally-sized beads of cement onto the sample stage, spaced so that the four corners of the sample will land on top of them. The beads should be small enough to avoid linking together when the sample sits on top of them.

13. Place the sample on top of the beads with the Pt wire oriented either up, down, or to the right. If the wire exits the stage on the left, it will be much harder to grasp with the electrical contacts once it is loaded onto the indenter stage.

14. Using tweezers, apply gentle pressure to flatten the sample. Avoid pushing the sample all the way into contact with the stage, as this will likely cause the cement beads to connect and block air flow to the back of the sample.

15. Visually check that the sample is flat.

16. Give the cement 2-4 hours to set.

17. Now it is time to attach Pt wires to the reference and working electrodes. If there are old wires still attached to the stage that can be reused, do so. Otherwise, attach new wires, again, 8-10 cm in length and lined up to exit from the stage on the top, right, or bottom, but not the left. Usually I make the three electrodes exit in three different directions to make sure I can easily keep track of them later.

18. Tape the new wires to the stage with thin strips of tape and mark the tape with a black marker so that they are easy to see. Usually I tape in one place on the stage surface and one place on the stage side for each wire.
19. Bend wires to mechanically contact the electrodes of interest. Try to avoid having them stick out very far in front of the stage, as this may interfere with indenter contact later. Do not obstruct the open area where the indenter will contact the sample.

20. Attach each electrode with a dab of silver paste and check contact with multimeter.


22. Attach wires to the stage surface with small beads of cement. Usually I put one on the stage surface, outside of the place where I taped the wire down. I put a second dab on the stage side and make sure to flatten it as much as possible to make it so that the hot stage shroud has space to fit around the stage.

23. Take a photo of the stage and make note of which electrodes exit in which directions.

24. Let stage sit (cement drying and setting) for a few hours before setting up curing steps.

25. Set up the curing steps for the Omega-bond. This process must start at least 18 hours after the electrodes were attached to the stage, and at most 24 hours after the sample was attached to the stage.

26. Curing steps: 82.2°C for 4 hours, then 104.4°C for 4 hours. You can use the time-delay on the hot stage control to manage this.

27. When the cement is done curing, remove tape.

**B.1.2 Experiment Setup**

To set up the experiment, you will need to map the sample using the NanoTest microscope to identify the sample center (or other contact points of interest), attach the electrode grippers to the sample, and hook up the impedance analyzer and data acquisition card.

1. Calibrate the NanoTest microscope using standard protocols and the probe you intend to use for the NECS experiment.

2. Load a high temperature sample stage onto the NanoTest, with the shroud. Make sure you removed the tape from the electrode attachment.

3. Using the NanoTest microscope, find the four corners of the film on the sample surface and calculate the center of the film based on these positions. Visually check with the microscope that your calculated center position is within the open area for probe contact (and preferably also in the middle of this).

4. An error of ±500μm is acceptable for this center mapping.

5. Having moved back to the indenter contact plane and ensured that the pendulum is balanced and the damping plates are correctly spaced, line up your sample so that the probe will contact your targeted position.

6. Make contact and retract 500 μm.
Figure B-1: Sample setup for direct measurement of chemical expansion. The films of interest, in this case Pr\textsubscript{x}Ce\textsubscript{1−x}O\textsubscript{2−δ} (PCO) were grown by pulsed laser deposition on a yttria stabilized zirconia (YSZ) substrate. A thin layer of porous Pt was then sputtered onto the front and back of the sample to make working and counterelectrodes, and Pt paste was painted over these to improve electrode connectivity except in the sample center where the probe would contact the sample. Pt paste was also painted around the sample side to make the reference electrode. Silver paste was used to attach Pt wires to the three Pt electrodes. The samples were attached to the stage with high temperature cement, leaving space for sample deflection and gas flow.

7. Make sure all high temperature control wires (heating wires, thermocouples, cooling coils) are appropriately connected.

8. Move the shroud forward to help with temperature management - but do not allow the shroud to contact the indenter’s heat shield.

9. You may want to remove the damping plates at this point to make it easier to do the next step. If you do, be sure to replace them later.

10. Grab each electrode with a wire gripper that feeds out of the indenter chamber. Usually it helps to figure out how you plan to line up the gripper, attach some lab tape to the wire gripper, grip the wire of interest, and then use the tape already on there to attach it to flat surfaces on the stage motor-control or sample holder that will not shift during the experiment.

11. The grippers should firmly contact the electrodes, but avoid pulling them very taut or having the plastic of the gripper in contact with the hot stage.
12. Trace the electrode gripper feeds out of the indenter chamber toward their BNC connectors to make sure you know which electrode is which.

13. Replace the damping plates and check that the pendulum is balanced and unobstructed before closing the door.

14. Attach the BNC connectors to the reference, counter, and working outputs of the impedance analyzer. Make sure that the T-connectors also connect the working and reference electrodes to the data acquisition card.

15. Make sure that the indenter output is connected by t-connector to both the Nanotest control box and the data acquisition card.

16. The data acquisition card should be set up as shown in Fig. B-2.

17. Plug the data acquisition card into the computer.

18. Open the LabView program *Lock-in amplifier emulator (v1.4 6-6-14).vi*.

19. Set the stage to heat overnight to your starting temperature such that it will have an hour to equilibrate prior to you coming into the lab in the morning.

![Figure B-2: Data acquisition card setup. Analog channels 1 and 2 should come from the working electrode (WE). Analog channels 3 and 16 come from the reference electrode (RE). Analog channels 5 and 6 come from the indenter. Channels 1, 6, and 16 come from the external cladding of each BNC cable.](image)

**B.1.3 Running Experiments**

There are a lot of types of experiments you may want to run with a single sample, most importantly impedance tests, single frequency NECS tests, and DC-biased NECS tests. Before running a multi-day experiment, you should have a plan of which tests you will do and how long they should take. To run an experiment, this is a general protocol you can follow, and adjust as needed depending on your specific goals.
1. At the beginning of the day, make sure you have updated the LabView program with your chosen folder name, starting experiment number, sampling density (max. 512, usually I use 1), and frequency and made a note of the voltage to displacement conversion on the indenter software (nm/V). Usually this is about 2000 nm/V. The conversion can be found in Calibration → Review all calibrations → Measured Depth Calibration (nm/V).

2. Once the sample is at the temperature of interest (with sufficient time to reach equilibrium), check the pendulum, make contact and then retract about 20 μm. Run a standard impedance test to make sure that all components are working correctly. Impedance tests with an amplitude of ± 10 or 20 mV between 10 mHz and 1 MHz are standard for PCO experiments.

3. Make a note of the stage, surface, and indenter temperatures. Make sure you also record the date and sample identity on your worksheet and any other pertinent information, like contact point.

4. If the impedance test has no glitches, bring the sample into contact with the pendulum. Put signs on the door to the lab and the indenter room saying that indentations are in progress.

5. Reduce the stage speed to 0.5 μm/s and gradually step the stage toward the 0 V measurement plane of the pendulum. It is extremely important to be moving at a slow speed while you do this and to pay close attention - over stepping the stage can damage the pendulum! Aim to have the pendulum rest between -0.2 and 0.2 V.

6. You will notice that during the course of the experiment the pendulum voltage will drift - I recommend re-establishing contact after each frequency sweep (roughly every 1.5-2 hours).

7. Run a frequency sweep. Usually I work with the following frequencies and durations (min:s) per frequency: 2 Hz (0:40), 1 Hz (1:20), 0.5 Hz (2:00), 0.25 Hz (4:00), 0.1 Hz (8:20), 0.05 Hz (16:40), 0.025 Hz (26:40), 0.01 Hz (58:20). The slowest frequencies are optional depending on your sample and your goals for the experiment. Ideally you want your frequency sweep to reach 0 radians phase lag for your slowest frequency, but in practice achieving 0.3 radians is acceptable. You will also likely want to use external ground (which is in practice the indenter ground) during the tests to prevent ground loops.

8. To run a frequency:

   (a) Check that the pendulum is still on scale (between -0.2 and 0.2 V) - if not, then step the stage slightly to correct this. Do not do this step more than twice for frequency sweep - if that is necessary you may do better to re-establish contact or use a different probe.

   (b) Update the frequency on the LabView program, and the filename and frequency information in the impedance analyzer.
(c) Press reset on the LabView program

(d) Press start on the impedance analyzer. It will begin recording open circuit voltage.

(e) Press ‘Record’ on the LabView program to start recording data.

(f) Press the play button on the impedance analyzer to move to the frequency timeline.

(g) Immediately press ‘Reset’ on the LabView program to collect signal data.

(h) After at least 50% of the allotted time has passed (long enough for signals to lock in), make a note of key information in your lab notebook or worksheet, such as LabView experiment number, frequency, DC bias, applied bias amplitude, displacement amplitude, phase lag, signal to noise ratio, amplitude ratio, etc.

(i) When you reach the time target for that frequency, press ‘Record’ again to stop recording on the LabView program. This will also cause the experiment number (Exp’t #) to auto-update.

(j) Stop the impedance analyzer

(k) If you accidentally were too late stopping the LabView recording, make a note of this for manual correction in the later data analysis phase.

9. At the end of your frequency sweep, re-establish contact (exit contact and then re-step to the 0 V measurement plane) before running additional tests.

10. If you wish to apply a DC bias, make this change in the impedance analyzer software and note this in your lab notebook.

B.1.4 NECS Data Analysis

The LabView program will output three files per recorded experiment (indexed by experiment number): a ‘data’ file, a ‘flat, norm’ file, and an ‘analysis’ file. The data file contains the raw data (time, reference voltage, and indenter voltage which corresponds to displacement) of the experiment from the point of initial recording in the experiment. The flat, norm file contains the flattened, normalized voltage signal and flattened, normalized displacement signal determined continuously during the last ten minutes of the experiment, or from the point of last ‘reset’ if the experiment was less than 10 minutes long. The analysis file contains the continuously determined signal (displacement amplitude in volts), phase lag (rad), amplitude ratio, and signal to noise (columns are labeled in the file). You can convert the signal into nm using the volts to nm conversion factor and use the amplitude ratio to convert the flat-norm data to the correct units if desired.

To analyze the data, you must first extract the mean amplitude and phase lag at each frequency (using the analyzeDCX.m Matlab file, see Appendix D) Here are the steps for using analyzeDCX.m:

1. Break your data files into subfolders by frequency, using your recorded information about which experiment numbers correspond to which frequencies. The key files are the analysis files. You may also want to shorten the file names to just the part starting with the experiment number.
2. Update the folder name you are analyzing (dirname), window (duration in seconds of last ten cycles at this frequency), and volts-to-displacement conversion factor (Vtonm).

3. Run the program. This will output the means of all columns except time in each file in the file ‘means.txt’. You can easily modify the code to output standard deviations instead.

4. After doing this for each set of frequencies, you can upload your means.txt data into a spreadsheet and re-organize the data back into their respective frequency sweeps for function fitting.

5. Some data may need to be analyzed manually (e.g., if there was a ‘late stop’ during recording or if the phase lag is very close to zero.)

6. To analyze ‘late stop’ data manually, load the files into Microsoft Excel or your preferred program, keeping track of all metadata. Determine the point toward the end of the experiment where the signal-to-noise ratio suddenly started rapidly decreasing, and average the ten cycles of data preceding this point.

7. If the phase lag is very close to 0, the LabView program may have started to record phase lags closer to 2\(\pi\). If this is the case, you can manually analyze the phase lag, setting a threshold value above which phase lag is set to 0 (e.g., 5.8 radians).

8. Individual frequency sweeps should be fit to your target functions (Eqs. 2.10 and 2.11, for example). I did this with Matlab, fitting Eq. 2.11 first and then using the resulting value of \(\tau\) to fit Eq. 2.10.

The resulting amplitude and phase lag vs. frequency information can be fit to the functions described in Chapter 2 to determine the equilibrium displacement amplitude \(D_0\) and time constant(s) \(\tau\) for each condition of interest.

A final note on analysis: the displacement data output from the indenter with the usual sample set up will have a positive change in displacement voltage for a contraction of the film - this is somewhat counterintuitive to those not familiar with our setup, so in all publications associated with this work we reverse the sign convention for clarity. Therefore, when a paper shows ‘positive’ displacement, this is actually a ‘negative’ change in the indenter’s voltage value.

B.2 High temperature nanoindentation with gas control

High temperature indentation experiments can be done with or without gas control. If gas control is involved, all preparatory steps (sample mapping, probe attachment, pendulum balancing, thermocouple and heater coil connection, etc.) must be done before beginning to flow gas. Gas flow should be done overnight to ensure that a steady-state composition has been achieved, so making adjustments after starting the gas flow is a major inconvenience.

Prior to starting high temperature experiments, it is useful to know the calibration information for temperature and gas flow for your particular stage and thermocouple arrangement. High temperature stages should always include a thermocouple mounted on the
stage surface (in addition to the internal control thermocouple) that enable tracking of the surface temperature (where the sample is) relative to the internal control temperature. You can collect this calibration for a new thermocouple by heating the stage up (with the shroud loaded and while the stage is within 500 μm of the indenter heat shield) and keeping track of the surface thermocouple readings as compared to the set point readings. This should give a linear calibration that you can use to predict surface temperature for a given set point temperature and vice versa. This calibration is especially important at high temperatures, where the set point temperature and the surface temperature can differ by over 50°C. You will always set the stage to heat to a set point that is ≥ the target sample temperature in order to account for this offset. You should not use the surface thermocouple to control the stage temperature, as this thermocouple is the most likely one to sustain damage or become disconnected during experiment setup or operation, potentially endangering your sample and the hot stage.

For gas control, it is useful to know the pO$_2$ calibration prior to setting up an experiment. Table B.1 gives a chart of the conversion between mV and atm for the Nernst-type YSZ-based pO$_2$ sensor in the Van Vliet lab - this is based on an internal temperature of 620°C which was measured for a furnace set point of 600°C. In my experience, flowing pure nitrogen (Channel 1, 1000 sccm maximum flow rate, from a tank at 240 psi) overnight produced a pO$_2$ for the indenter chamber of -108 to -112 mV = 8 × 10$^{-4}$ atm. Flowing oxygen at a set point of 64% for Channel 2 (200 sccm maximum flow rate, from a tank with 50 psi) along with 100% flow for nitrogen gave a pO$_2$ of -58 to -64 mV, or 8 × 10$^{-3}$ atm. Of course, these values will change depending on how successfully any leaks in the chamber are plugged. To run high temperature indentation experiments, follow these steps:

1. Calibrate the area function for your intended high temperature probe using the standard method immediately before and/or after any high temperature experiments.

2. Attach your sample to a high-temperature stage using Omega-bond 600 cement mixed as described above. This kind of water-based cement does not outgas solvent at elevated temperatures, protecting your sample surface from contamination. In this case (unlike for NECS), the sample should be mounted with an even, thin layer of Omega-bond cement applied to the entire back of the sample in order to minimize temperature variations.

3. Allow the cement to cure.

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</table>

Table B.1: Oxygen sensor conversions for environmental nanoindentation
4. If necessary, calibrate the microscope and map your sample (with the shroud already loaded around the hot stage).

5. It is a good idea to at least do a few test indents on your sample prior to high temperature testing in order to make sure you are familiar with the kind of load range you will want to use.

6. Set the stage and indenter to heat to your target temperature, leaving enough time for equilibration before indentation (at least an hour).

7. Check the pendulum. You will likely need to re-balance and adjust the depth signal offset prior to running the experiment when you change the temperature.

8. Check that you have adequate temperature matching between the probe and the sample surface by running a series of load ramp tests close to the location where you intend to indent your sample. To run a load ramp test:

   (a) Make a note of the output power for the indenter (using the temperature controllers on the hot stage control unit).

   (b) Make contact between the probe and sample

   (c) Go to *Maintenance* → *Load Ramp Test*

   (d) Specify a load, load rate, and dwell time, with 1 cycle. It is a good idea for these to be representative of the shallowest indents you intend to run during actual testing. Usually I use 1-5 mN, with a loading time of about 10 s and a dwell time of 30 s. The test should be shallow (about 10-50 nm).

   (e) Start the load ramp test and make a note of: the depth of the indent, the drift (positive or negative and magnitude) and the shape of the loading and unloading profiles.

   (f) The goal of this test is to ensure that your indentation conditions are stable - large oscillations anywhere in the load ramp tests suggest that the temperature matching is not good enough. You want smooth loading and unloading curves and a small but positive drift at the maximum load, without a nose during unloading.

   (g) If the load ramp test doesn’t look good enough, disconnect from contact, adjust the indenter power by 0.1 or 0.2, and try again in a slightly new location (e.g., 20 \( \mu \text{m} \) away). Pay attention to how the drift changes during these adjustments and how the probe temperature changes during contact at each output power, as these pieces of information will help you to narrow onto the optimal setting.

9. After you have settled on an adequate output power, run a single test indent using a normal schedule to see if the conditions you specified give acceptable results. If not, you may need to adjust the indenter output power further.

10. To set up your tests, here are some suggested parameters. These should be adjusted depending on your experience with your own samples and probes:
(a) Make sure that you are on **MANUAL** hot stage control (Automatic control will make your experiments take an extremely long time without necessarily improving your results).

(b) Dwell time: 10-30 s depending on temperature

(c) Thermal stabilization time: 60-120 s at a distance of 0 μm

(d) Retraction distance: 20-30 μm. Increase if you will be moving long distances across your sample surface.

(e) Load rates chosen so that load times are on the order of 10-30 s.

Keep these tips in mind when you are ready to set up full indentation schedules: at high temperature you get about 5 indents per hour. If you want to run tests at multiple locations (hundreds of μm away from each other) on a sample, you should check your output power calibrations (load ramp tests) at each of these locations. You should also probably divide your experiment files into sets of 25 indentations or less - this will minimize the possibility of a malfunction during an experiment causing you to lose an entire day’s worth of data. If you are having trouble with temperature matching, you can try increasing your loading and unloading rates to try to overcome drift or increasing your thermal stabilization time. It is also a good idea to check on high temperature experiments regularly, although you can run them overnight. Finally, if you notice that your probe area function has changed drastically before and after indentation testing, you can clean the probe off by indenting into a soft metal like gold at room temperature. If the area function changes back after that, then there is a good chance that your probe was dirty by the end of your previous test.

After you collect high temperature indentations, you need to decide on consistent criteria by which you will judge which individual indentations should be eliminated from your data set due to poor data quality prior to analysis. For example, indentations that show a significant nose on unloading should be eliminated, as this is a sign that creep or thermal drift is overwhelming the crucial unloading portion of the load-depth hysteresis. Similarly, indentations that exhibit a negative drift during the hold at maximum load should also be eliminated. It is fairly straightforward to correct for contact errors if that is a common problem, by simply recalculating the stiffness based on the contact-corrected plastic depth. Fracture during loading is generally cause for elimination, but the judgement as to what quantity of "pop-in" constitutes a fracture vs. a normal noise error is left to the user.

For gas control, there are some additional steps that you should follow to set up. Before running gas lines, you should make sure that everything else about your experiment is correctly set up, including connections between heating wires and thermocouples, pendulum balancing, damping plate adjustment, sample loading and mounting, or anything else that might require you to open the chamber door. You should also ensure that you have sealed any leaks in the indenter chamber, have gas cylinders available, and have hooked up to the gas lines through proper regulators prior to starting your experiment. To run gas control, follow these steps:

1. Turn on the multichannel reader (underneath the indenter vibration table) by flipping the switch on the far left to the ON position.

2. On the gas control panel above the hot stage controller, make sure that the switch is in the ON position. Usually we just leave this on.
3. Open the appropriate valves on the gas tanks and gas lines to allow gas to flow toward the mass flow controllers (MFCs) in the indenter room.

4. Flip the switches for the channels that you want to flow gas through to the ON positions. (Usually Channels 1 (N₂) and/or 2 (O₂))

5. Using a small flathead screwdriver like the one you use for loading probes onto the pendulum, set the flow rates for the channels that you will be using for the experiments. You can choose the channel (1, 2, 3, or 4) that the multichannel reader displays by turning the knob on the right of the multichannel reader. Then, while holding the appropriate lever in the SET position, turn the neighboring screw carefully and watch the numbers on the display. They should be between 0 and 100, which represents the percentage of flow through the associated MFCs.

6. When gas initially starts flowing, the bead on the right side of the gas control panel should jump. If you aren’t sure, have a lab mate close and open the gas flow valves and watch to see if this happens when the valves re-open.

7. Set up a bubbler for the exit tubing by filling an Erlenmeyer flask with water and allowing the tubes to exit just below the water line. When gas is flowing, you should see bubbles forming in the bubbler. There are two tubes: the blue one is exiting from the pO₂ sensor and the clear one is exiting from the indenter chamber. Bubbles may be very lethargic depending on how leaky the system is.

8. Turn on the oxygen sensor and set it to heat to 600°C.

9. When the oxygen sensor is on, open the valve to allow gas to flow into the sensor (you can use the bubbler to check if this is working as well). Wait a while for equilibrium. You can check the oxygen partial pressure by measuring the voltage between the two wires attached to the sensor and following Table B.1

### B.3 Strain-conductivity tests

This section describes protocols for setting up an experiment for testing the relationship between mechanical strain and conductivity in thin oxide films. The premise of this experiment is to grow a film of the oxide of interest on a flexible, insulating cantilever, with interdigitated electrodes patterned on the film surface. Using an apparatus developed for the purpose, we bend the cantilever while simultaneously measuring the impedance spectrum for the material. The entire setup can be placed inside of a tube furnace to facilitate gas and oxygen partial pressure control. These protocols include the interdigitated electrode and cantilever fabrication steps, as well as the experiment setup steps.

#### B.3.1 Preparation of interdigitated electrodes

This protocol is intended for the EML (Exploratory Materials Laboratory) at MIT (a part of MTL, the Microsystems Technology Lab). See the document "MTL Procedures and Mask Fabrication" on the Van Vliet Group Wiki for information on how to get access to MTL and
how to order masks. Note that this protocol uses transparency masks, which are ordered in
the same way as chrome-on-glass masks except that you must specify "Mylar", "Emulsion",
and "0.007 inches" for the mask order form. Transparency masks are capable of resolution
of $\sim 20 \mu m$.

You will need to be trained on the following tools in EML: coater, MA-4 mask aligner,
and diesaw-3240.

1. Get films of your desired oxide (I use $\sim 200-300$ nm of PCO, but this should be adjusted
dependent on your substrate thickness, required signal to noise, and any growth chal-
lenges) grown on thin sapphire substrates. I use 0.25 mm or 0.1 mm thickness (10×10 mm area) R-plane sapphire wafers purchased from Valley Design.

2. Reserve time on the coater and the MA-4 exposure tools in EML. These are under
"photolithography". I usually take a 2 hour slot for $\sim 4$ substrates. If you are new to
this protocol, you will need more time.

3. Go to EML, bringing your transparency mask, substrates, and your favorite clean
tweezers. Currently we have two mask designs, each with four sizes of electrode (20,
40, 50, or 100 $\mu m$ IDEs).

4. The first step is photoresist deposition, which is done by spincoating. Clean your wafer
on the spincoater by spinning at $\sim 2500-3000$ rpm for $\sim 30$ s and squirting with acetone
and isopropyl alcohol. Use the chuck for the spincoater that is designed for very small
substrates.

5. In the meantime, set hotplates to 155$^\circ$C and 105$^\circ$C. When you have finished cleaning
your wafers, set them on the hotplate for $\sim 10$ minutes to allow solvent to evaporate.

6. While that is happening, you can set up the other parts of this protocol (e.g., checking
that the MA-4 is set up in the way you need, getting out the photoresist, setting up
your timers, etc.).

7. You will need to use the gray tape available in EML to cover excess holes in the mask
aligner to ensure that your 10×10 mm substrate produces a vacuum seal.

8. To use the transparency mask, you will need to tape the mask to the square glass
blank using gray tape.

9. You will need to line up your mask appropriately on a test wafer to ensure that the
IDE size that you want will be aligned with your wafer when it is on the chuck.

10. For this protocol we use NR71-3000 photoresist, which is a negative photoresist. Hope-
fully your mask has been designed with this in mind.

11. Spin-coat photoresist onto your sample: use $\sim 5$ drops of photoresist to cover the entire
substrate at 2500 rpm for 30 seconds. Be sure to add the drops to the sample so as to
avoid bubble formation in the photoresist.
12. Bake 2 minutes at 155°C on the hotplate. Use a metal tray weighed down with tweezers to support your substrate and ensure good thermal contact. This is generally a good practice when using hot plates during photolithography.

13. Expose for 40 seconds on the MA-4 mask aligner.

14. Post-exposure bake for 2 minutes at 105°C.

15. Remove from hot plate promptly. The next step is developing.

16. Using the RD6 developer (available in the chemical cabinet), prepare a developer bath and a water bath in the developer hood. Have a basket ready for holding your very thin, small substrate. Have tweezers ready to assist with this step as well.

17. Develop in RD6 for 1 minute, 20 seconds. Lightly agitate the bath or sample during development to ensure photoresist comes loose.

18. Rinse in the water bath and lightly with the water nozzle and then dry with compressed air - be very careful here to hold your substrate firmly with the tweezers to ensure it will not blow away. It is extremely difficult to pick up one of these thin substrates if it gets a water-surface tension seal to the benchtop.

19. Inspect your resulting photoresist mask using the microscope in the room - look for scratches in the photoresist or other flaws. If it is an unusable batch, you can lift-off the photoresist and try again from step 2.

20. If your mask is in good shape, then you can hand off to a collaborator for sputter deposition of dense Pt. ~50 nm should be enough.

21. Once Pt has been deposited, you will need to lift off the part that is on top of the photoresist. This is done in the developer hood in MTL by immersing the sample for 9-10 minutes with occasional gentle agitation in Fujifilm Microstrip 2001 heated using a hot plate to just under 100°C. I find that doing this with a metal boat works well, as long as something (like a piece of foil) is in the boat to prevent the sample from forming a seal and being difficult to pick up. Fujifilm Microstrip 2001 is hazardous waste that must be disposed of in the waste hood.

22. Inspect your resulting Pt IDEs using the microscope, and take photos in our lab.

23. The next step is to cut the sample with a die-saw. You will need to glue them to a carrier wafer (silicon should be fine) using Loctite-4013 glue. When you go to the die-saw, use the black blade (for cutting not Si). This blade has a 0.25 mm street. Use a cut speed of 0.5 mm/s and follow directions for the die-saw when cutting sapphire. You will need to decide beforehand what dimensions you want for your cantilevers, accounting for the street width. (e.g., 2 mm width or 3 mm width, etc) Once you have cut the wafer, you can soak the samples in acetone for half an hour to lift them off. You can clean them with acetone/IPA/DI water after that.
B.3.2 Sample set-up for measuring ionic conductivity as a function of strain in a tube furnace

Once you have an acceptable cantilever, you will need to load it into the cantilever bending apparatus (hereafter called "the apparatus"), attach Pt wires to the IDEs, wait for the sample to dry, set your desired strain, slide the apparatus into the the furnace tube, attach gas control fittings to the tube, and set up the furnace and gas lines. The apparatus for these measurements was designed with the help of Andrew Ryan of the MIT Central Machine Shop and is shown in Fig. B-3. Experiment setup was developed with the help of Thomas Defferriere of the MIT Crystal Physics and Electroceramics Lab (Tuller group).

Figure B-3: Diagram of the cantilever bending apparatus. This apparatus, made from Macor, was produced in the MIT Central Machine Shop. Measurements are in inches, with mm in parentheses. Drawing by Andrew Ryan.

Figure B-3 shows a Solidworks diagram of the apparatus, which was made in the MIT Central Machine Shop out of Macor. This apparatus consists of a ledge where the sample is attached, and a screw that can be turned to bend the cantilever to a known displacement. The distance between the ledge and the screw is 7.5 mm. The ledge height is 1 mm. The screw is an M2 alumina screw with a 0.4 mm pitch.

You will need: the apparatus, Pt wire, silver paste, high temperature cement, a 3/4 inch diameter quartz furnace tube, an input rod (The input rod is an alumina rod, about a quarter inch in diameter, see Fig. B-4(e) that has four 1 mm-diameter holes bored through its length and is attached to a gas-control inlet fitting. The input rod should have two thicker Pt wires pre-threaded through two of the holes, and the thermocouple should be threaded through the other two.), and appropriate fittings for gas lines. When you run the experiment, you will need to modify gas flow rates, monitor temperature and pO\textsubscript{2}, and collect impedance spectra using an impedance analyzer.
Figure B-4: Photos of the strain-conductivity measurement setup. (a) A cantilever cemented to the ledge in the apparatus, with Pt wires attached. (b) Screw lowered to contact with the cantilever. (c) Cantilever under strain inside the apparatus. This image represents 1.5 full turns of the screw (0.6 mm displacement). (d) The apparatus inside of a quartz furnace tube with the inlet tube attached. (e) View of the experiment from outside the furnace, showing the input tube and attached thermocouple, gas line, and electrical clamps.

1. Prepare a clean workspace, and tape down kimwipes or other padding to protect the ceramic apparatus and quartz tube during setup.

2. Un-screw the screw in the apparatus so that you have space to work with. However, do not remove the screw - just open a gap so that only maybe a mm of screw is sticking out on the downward side of the screw hole.

3. Using a C-clamp, clamp the apparatus so that the ledge will rest securely and horizontally on the benchtop. The clamp should be snug, but tighten gently as Macor is brittle and will fracture under too much stress.

4. Stack two fragments of silicon wafer (each will be 0.5 mm thick) underneath the screw in the apparatus. This will help you place the cantilever flat while the cement sets.

5. Using a small quantity of high temperature cement, attach the cantilever to the ledge so that one end of the cantilever is directly underneath the screw. You will need to use tweezers to assist with this alignment process. This is harder than it seems, as the surface tension of the cement will try to pull your cantilever in certain directions. The cement should lip over the back corners of the cantilever, but should not cover the electrode pad where you will need to attach the Pt wires. Once you are confident in your alignment, you can lower the screw to see if it really lines up well. Do not actually make contact with the cantilever, just use the screw as a guide to your eyes...
in both alignment planes. Ideally the screw will contact within about 0.5 mm of the end of the cantilever.

6. Allow the cement to set (at least 2 hours, preferably longer).

7. Attach Pt wires to the two electrode pads using silver paste. As usual, try to ensure a mechanical pressure-based contact between the Pt wire and the Pt patterned electrode prior to adding silver paste. Use the multimeter with thin Pt wires twisted around the probes (for lightweight contact) to check for good Pt-Pt contact. As for the counterelectrode wire attachment in Section B.1.1, you may want to use scotch tape to secure your wires during this process to a consistent external point. **Take your time and do a good job on this step, as poor electrode attachment can make the entire data set from the cantilever useless.**

8. Allow the silver paste to dry thirty minutes.

9. Secure the Pt wires to the apparatus ledge with dabs of cement in a place where they can be easily scraped off later. Also attach the Pt wires to the input rod that also contains the thermocouple. Using tweezers and possibly a helping pair of hands, you will twist the thick Pt wires from the input rod with your wires that are already attached to your sample and use a dab of cement to secure that connection, after checking it with the multimeter. Wait for the cement to dry. Figure B-4(a) shows a fully attached cantilever.

10. Allow a full 18 hours for the cement to dry.

11. Release the clamp on the apparatus.

12. Make sure that the thermocouple and the Pt wires are not shorted. Set your desired strain by turning the screw a controlled number of turns after contact, and calculating displacement based on the pitch of the screw and number of turns. You can compute the strain applied to the film based on the geometry of your cantilever and this known displacement. Usually the first experiment should be done for zero strain. After you test a set of temperatures and pO$_2$’s, you can cool down the setup, remove the input tube and apparatus, reset the strain, and run a new set of temperatures and pO$_2$’s. Figure B-4(c-d) show different strain settings in the apparatus.

13. Slide the quartz tube (with the second half of the input rod gas fitting around it) over the apparatus, being careful not to overly kink the wires. This may be easier with two people, and using a long, thin object, such as an unused ziptie, to steady the apparatus as it slides into the tube. Ideally the Pt wires will remain extended during this process. Eventually, the quartz tube should reach the metal fitting on the input rod - when this happens, join the metal fittings together snugly, creating a gas-tight seal. Figure B-4(d) shows the apparatus inside the quartz tube.

14. You may want to check the alumina tube on the input rod where it exits the fitting and secure the thermocouple to prevent kinking and/or seal any leaks with HT cement.
15. Surround the quartz tube with steel wire mesh that will be used to create a Faraday cage.

16. Put the entire setup into the tube furnace, clamping the end with the gas fitting so that it doesn’t become unbalanced and fall out of the furnace. Ideally there should be at least an inch of space between the furnace and the teflon parts inside the gas fitting.

17. Attach the wire mesh to ground.

18. Attach a gas line input to the inlet for the gas fitting. The input gas line should have control for mixing oxygen and nitrogen. During my pilot experiments, we used three settings: pure oxygen flow (giving a $pO_2$ of 1 atm), mixed flow (about 5 sccm $O_2$ and 300 sccm $N_2$, $pO_2 \sim 0.019$ atm), and pure $N_2$ flow ($\sim 10^{-4}$ atm). The $pO_2$ for pure $N_2$ will depend on consistent leak control for the system.

19. Attach an outlet gas fitting to the free end of the quartz tube. The outlet tube should flow into an oxygen sensor, followed by a bubbler to prevent back pressure from building up in the line and to show continuous flow.

20. Hook up the thermocouple to the relevant computer and clip the Pt wires exiting the input tube to the working and reference/counter electrodes for the impedance analyzer. Figure B-4(e) shows the input tube side of the setup while in the furnace.

21. Set the sample to heat overnight to your target temperature (during pilot testing, we conducted measurements between 575 and 650°C), flowing nitrogen to purge the tube and achieve the lowest possible $pO_2$.

22. In one day, you can test up to four temperatures for each of three $pO_2$’s. At each condition, run an impedance test. Good settings are between 10 mHz and 1 MHz, with amplitude of 10 or 20 mV. For each condition, I allow 10 minutes to change temperature, 30 minutes to equilibrate, and 20 minutes for the impedance test to run and complete. If a $pO_2$ transition is also involved, this requires an extra 10-15 minutes of equilibration time, especially for mixed $pO_2$.

23. Keep track of the following information for each test: experiment file ID, temperature setting, temperature reading (from the thermocouple), $pO_2$, strain state, experiment time, and any other pertinent details. Ideally impedance spectra will appear as single semi-circles which can be analyzed as a function of $T$ and $pO_2$ to determine the ionic and electronic contributions of conductivity for each strain state. There may be additional electrode arcs; ideally these will be small if the Pt wires have been well-attached to the sample.

24. When you are done for the day, set the furnace to cool down and then turn off. The next day you can carefully disassemble the setup, pulling the apparatus (still attached to the input tube) out of the quartz tube, adjusting the strain, and then resetting the experiment to be run the following day.
25. When you are totally done testing a cantilever, remove it and all other cement attach-
ments from the apparatus ledge with a razor blade.

One key limitation of this setup is the need to remove the apparatus from the furnace in
order to reset the strain. A key improvement would allow remote control of the strain, for
example by adding a stepper motor to an adjusted version of this apparatus, possibly with
a larger diameter tube furnace and quartz tube.
Appendix C

INCAR files for density functional theory

This Appendix contains example INCAR files for running density functional theory (DFT) calculation on VASP.

C.1 INCAR file for bulk DFT jobs from Acta paper, Section 4.2

```plaintext
SYSTEM = CeO2
 ISTART = 0
 INIWAV = 1
 ICHARG = 2

# Relaxation
 EDIFF = 1.e-6 ! Energy Convergence
 EDIFFG = -0.01 ! Force Convergence

# Magnetic calculation?
 ISPIN = 2
 VOSKOWN = 1

# On-site Coulomb interaction - U
 LDAU = .TRUE.
 LDAUTYPE = 2
 LDAUL = -1 3
 LDAUU = 0.0 5.0
 LDAUJ = 0.0 0.0
 LDAUPRINT = 2
 LASPH = .TRUE.
 IBRION = 1 ! Optimization algo
 POTIM = 0.5 ! Rescale forces
```

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NSW = 100 ! Number of ionic steps

# Change cell volume, thus lattice parameter?
ISIF = 3

# DOS related
# PREC = high
ENCUT = 500.0
ISMEAR = 0 ! Gaussian = 0
SIGMA = 0.10 ! Broadening
LORBIT = 11
IALGO = 48
LDIAG = .TRUE.
NELM = 40
NELMIN = 4

# Out-Put
# ISYM = 1 ! Want to keep the symmetry of the lattice?
LCHARG = .FALSE. ! No charge density is written
LWAVE = .FALSE. ! No wavefunction is written
LREAL = .TRUE.
LPLANE = .TRUE.
NPAR = 8

When this was run for relaxing elastic constants, the following tags were changed:
IBRION = 6 (To make cause elastic constant calculation)
POTIM = 0.005 (Small strains near the already relaxed minimum)
Commented out NPAR

When this was run for jobs containing Pr, the following tags were changed:
LDAUL = -1 3 -1
LDAUU = 0.0 5.0 0.0
LDAUJ = 0.0 0.0 0.0

C.2 INCAR file for bulk and membrane Pr\textsubscript{\textit{x}}Ce\textsubscript{\textit{1-x}}O\textsubscript{2-\textit{\delta}} simulations, Section 4.3

SYSTEM = CeO2

ISTART = 0 ! Change to 1 for restarts with CHGCAR and WAVECAR
# INIWAV = 1
# ICHARG = 2 ! Change to 1 for restarts with CHGCAR and WAVECAR

# Relaxation
EDIFF = 1.e-6 ! Energy Convergence
EDIFFG = -0.01 ! Force Convergence
SYMPREC = 1E-8

# Magnetic calculation?
  ISPIN = 2

# On-site Coulomb interaction - U
  LDAU = .TRUE.
  LDAUTYPE = 2
  LDAUL = -1 3
  LDAUU = 0.0 5.0
  LDAUJ = 0.0 0.0
  LDAUPRINT = 2
  LASPH = .TRUE.

IBRION = 2 ! Optimization algo
  POTIM = 0.1 ! Rescale forces
  NSW = 100 ! Number of ionic steps

# Change cell volume, thus lattice parameter?
  ISIF = 3

# DOS related
  PREC = ACCURATE
  ENCUT = 500.0
  ISMEAR = 0 ! Gaussian = 0
  SIGMA = 0.1 ! Broadening
  LORBIT = 11

# IALGO = 38
  # LDIAG = .TRUE.
  NELM = 40
  # NELMIN = 4

# Out-Put
  # ISYM = 1 ! Want to keep the symmetry of the lattice?
  LCHARG = .FALSE. ! charge density is NOT written
  LWAVE = .FALSE. ! No wavefunction is written

# LREAL = .TRUE.
  LPLANE = .TRUE.
  # NCORE = 8
  NPAR = 2

# Mixing tags LMAXMIX = 6
Jobs for this portion were done with the Ce\_h pseudopotential (rather than Ce as was used for jobs in *Acta* paper). Also, here a U was applied to Pr (not done in *Acta*). Jobs were relaxed to ensure only two cations hold charge opposing the vacancy. During restarts, POTIM was sometimes decreased to 0.05 to assist convergence. Also, for membrane relaxations on the NERSC computers, NSW was decreased to a value that would be sure to finish prior to the wall time in order to make sure that a usable WAVECAR and CHGCAR were written.

When this was run for jobs containing Pr, the following tags were changed:

- \texttt{LDAUL} = -1 3 3
- \texttt{LDAUU} = 0.0 5.0 5.0
- \texttt{LDAUJ} = 0.0 0.0 0.0

### C.3 INCAR file for Li\textsubscript{1+x}Mn\textsubscript{2-x}O\textsubscript{4-δ} simulations, Section 6.3

**SYSTEM** = LiMn2O4

**ISTART** = 0

# Relaxation

- **EDIFF** = 1.e-8 ! Energy Convergence
- **EDIFFG** = -0.01 ! Force Convergence
- **SYMPREC** = 1E-8

# Magnetic calculation?

- **ISPIN** = 2

# On-site Coulomb interaction - U

- **LDAU** = .TRUE.
- **LDAUTYPE** = 2
- **LDAUL** = 2 -1 -1
- **LDAUU** = 5.0 0.0 0.0
- **LDAUJ** = 0.0 0.0 0.0
- **LDAUPRINT** = 2
- **LASPH** = .TRUE.

**IBRION** = 2 ! Optimization algo

- **POTIM** = 0.1 ! Rescale forces
- **NSW** = 100 ! Number of ionic steps

# Change cell volume, thus lattice parameter?

- **ISIF** = 3

# DOS related

- **PREC** = ACCURATE
- **ENCUT** = 520.0
- **ISMUEAR** = 0 ! Gaussian = 0
SIGMA = 0.1 ! Broadning
LORBIT = 11

# IALGO = 38
# LDIAG = .TRUE.
NELM = 40
# NELMIN = 4

# Out-Put
# ISYM = 1 ! Want to keep the symmetry of the lattice?
# LCHARG = .FALSE. ! charge density IS written
# LWAVE = .FALSE. ! wavefunction IS written

# LREAL = .TRUE.
LPLANE = .TRUE.
# NCORE = 8
NPAR = 1

# Mixing tags
LMAXMIX = 6
Appendix D

Python codes for density functional theory analysis

The codes in this chapter comprise a module of functions (fslabs.py) and a script (slabscript.py) that were used to analyze CONTCAR files output from VASP calculations of Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ structures under biaxial strain.

The script slabscript.py is designed to apply to the membrane structures (that contain vacuum), but can be easily modified to handle bulk CONTCAR files.

```python
#This script will allow me to write a text file containing the slab heights and plane positions and plane spacings for each file in a directory dirname.

dirname = 'COFFEI/2nnsub_contcars/'
import os
import numpy as np
import fslabs as fs #This also includes importing the os and numpy as np modules
fnames = os.listdir(dirname) #Creates a list of filenames
nfiles = len(fnames) #How many files in the directory
zees = np.zeros((nfiles, 3)) #Initialize array to fill in with a,b, zheight values
i = 0 #initialize index

#Query to determine number of planes. Use file index ‘2’ to avoid hidden python files
    tester = fs.getcontdata(dirname + fnames[2])
    ptest = tester.planespace(0.01)
    nplanes = len(ptest[0])
    planes = np.zeros((nfiles, nplanes + 2)) #Number of planes + row for tracking a
    pspace = np.zeros((nfiles, nplanes + 2))

#Three arrays will be made: z height, plane position, and planespacing.
    #z height is in angstroms, but plane positions are still
    #in fractional coordinates.
    for f in fnames:
        if 'CONT' in f:
```

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dat = fs.getcontdata(dirname + f)
zes[i,0] = dat.dims[0]
zes[i,1] = dat.dims[1]
zes[i,2] = dat.zheight()
pstuff = dat.planespace(0.01)
planes[i,:] = [dat.dims[0]] + [dat.dims[2]] + pstuff[0]
pspace[i,] = [dat.dims[0]] + [dat.dims[2]] + pstuff[1]
i = i + 1

outz = dirname + ‘zheights_A.txt’
np.savetxt(outz, zees, header=‘a b zheight’)
outpl = dirname + ‘planes_rel.txt’
np.savetxt(outpl, planes, header=‘a list of planes in fractional coords’)
outspace = dirname + ‘pspace_A.txt’
np.savetxt(outspace, pspace, header=‘a z list of plane spacing in fractional coord’)

This is the module fslabs.py containing the class definition for the CONTCAR file data and associated functions. slabscript.py calls this module.

#!/usr/local/bin/ python3

#This is the numpy package that lets me deal with numbers
import numpy as np
import os

class contdata:
    """Data from CONTCAR file includes the list of atom types, atident, the number of atoms of each type, ats, the dimensions of the supercell, dims, and the coordinate data, xyz."""
    def __init__(self, atident, ats, dims, xyz):
        self.atident = atident
        self.ats = ats
        self.dims = dims
        self.xyz = xyz
        self.nat = sum(ats)

    def zheight(self): #Returns the height of the slab in Angstroms
        top = max(self.xyz[:,2])
bott = min(self.xyz[:,2])
zheight = (top - bott)*self.dims[2]
return zheight

    def planespace(self, splim): #Returns spacing relative coords between each plane in the slab, moving from bottom to top of slab. splim is the relative spacing minimum to separate planes. Splim will need to be specified differently for bulk vs. slab forms.
i = 0  #current index
npl = 0  #Tracks number of planes
ninp = 1  #Tracks atoms in plane
now = 0
planes = [0]  #Saves mean plane positions
zvals = sorted(self.xyz[:,2])  #sort in ascending order

#Average the values within each plane
    for zv in zvals:
        if abs(zvals[i+1] - zv) < splim:
            now = now + zv
            planes[npl] = now/ninp
            ninp = ninp + 1
        else:
            planes[npl] = (now + zv)/ninp
            planes.append(0)
            npl = npl + 1
            ninp = 1
            now = 0

i = i + 1
    if i == (len(zvals)-1):
        planes[npl] = (now + zv)/ninp
        break

#sort in ascending order
    planes = sorted(planes)

pspace = []  #initialize plane spacing array
    j = 0  #current index
    for pls in planes[0:-1]:
        #pspace.append((planes[j+1]-pls)*self.dims[2])
        pspace.append((planes[j+1]-pls))
        j = j+1
    pspace.append(0)  #So that planes and pspace have same length.

return (planes,pspace)
#return pspace

def getcontdata(filename):  #Return data pulled from CONTCAR file filename

    #First step is to open the file of interest and read in the relevant data
f = open(filename)
#Get past the first few headers and grab information on supercell size
header1 = f.readline()
header2 = f.readline()
alineline = f.readline()
bline = f.readline()
cline = f.readline()
Atident = f.readline()
Atnum = f.readline()

#Splitting strings into lists and then converting values to floats and ints
a = aline.split()
b = bline.split()
c = cline.split()
Atident = Atident.strip()
OCP = Atnum.split()
cellsize = [float(a[0]), float(b[1]), float(c[2])]
OCP = [int(i) for i in OCP]

#Imports data as floats.
#default delimiter is whitespace
coords = np.loadtxt(f, skiprows=1)
coords = coords[0:sum(OCP), :]

f.close()

#Return the important data as a contdata object.
output = contdata(Atident, OCP, cellsize, coords)

return output
E.1 Analyzing nanoscale electrochemomechanical spectroscopy (NECS) data

*analyzeDCX.m*

```matlab
% Right now the filename must include 'analysis'.

window = 400;
Vtonm = 2012.89;
dirname = 'COFFEI/20161121/0-025Hz/';

% Load all files in directory
Files = dir(dirname);

% Output filename and headers
outputfile = strcat(dirname, 'means.txt');
fileID = fopen(outputfile, 'w');
fprintf(fileID, '%1s\t %2s\t %3s\t %4s\t %5s\t %6s\n', 'SNR', 'Amp (V)', 'Amp ratio', 'Phase lag (rad)', 'Amp (nm)', 'expt');

% Go through the directory and grab all the filenames
for k = 1:length(Files)
    filename = Files(k).name;
    fname = strcat(dirname, filename);
    if not(isempty(strfind(filename, 'analysis')))
      means = meanextract(fname, window, Vtonm);
      fprintf(fileID, '%1f\t %2f\t %3f\t %4f\t %5f\t %6s\n', means, filename);
```

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meanextract.m

%A function definition
function [result] = meanextract(fname, window, Vtonm)

% This function takes a DCX analysis file, with 5 columns of data, as input, and outputs the mean values for the last window lines of data. Window length is based on the time required to make 10 cycles at the frequency of interest (e.g., 20 for 0.5 Hz). Vtonm should be determined based on the indenter calibration.

[labels,time,ref] = readColData(fname, 5);

%Make individual arrays for each data column.
SNR = ref(:, 1);
ampV = ref(:, 2);
rat = ref(:, 3);
phi = ref(:, 4);

%Extract the last window data points- supposedly converged part of the data
SNR_conv = wkeep(SNR, window, 'r');
ampV_conv = wkeep(ampV, window, 'r');
rat_conv = wkeep(rat, window, 'r');
phi_conv = wkeep(phi, window, 'r');

%Arithmetic mean of data in the analysis window
mSNR = (sum(SNR_conv))/window;
mampV = (sum(ampV_conv))/window;
mrat = (sum(rat_conv))/window;
mphi = (sum(phi_conv))/window;

%Convert amp from volts to nm
mampnm = mampV*Vtonm;

%print out the result- this should be added to a textfile in final usage and also should report filename.
result = [mSNR mampV mrat mphi mampnm];
end

analyzeMOSS.m

%This script is meant to analyze an input of voltage and stress*thickness data from MOSS measurements (Sheldon group) and determine the amplitudes and phase lags of these outputs.
You have to update ‘mtl’ and that should be all if the input file has the right format.

Starting values

\[
\begin{align*}
\text{mtl} &= \text{‘LMO’;} \\
\text{freq} &= \text{frequency}_\text{Hz}(1); \\
\text{missing} &= \text{isnan(stress}_\text{by}_\text{thickness}_\text{Gpa_nm}); \\
\text{y} &= \text{stress}_\text{by}_\text{thickness}_\text{Gpa_nm(not(missing))}; \\
\text{t} &= \text{time}_\text{hr3(not(missing))}; \\
\text{T} &= (1/\text{freq}); \\
\end{align*}
\]

You have to update ‘mtl’ and that should be all if the input file has the right format.

Number of data points per period-conversion is 36 s per 22 data points. Need to check this for other data sets as well.

\[
\begin{align*}
\text{dps} &= (22*\text{T}/36); \\
\text{wts} &= [(1/(2*\text{round(dps)}));\text{repmat}(1/\text{round(dps)},\text{int16(dps-1)}, 1); (1/(2*\text{round(dps)}))]; \\
\text{yS} &= \text{conv(y, wts, ‘valid’)}; \\
\end{align*}
\]

Need to exclude beginning and end points for plot.

\[
\begin{align*}
\text{first} &= \text{int32(dps/2)}; \\
\text{last} &= \text{length(y)-(int32(dps)-first)}; \\
\text{stressflat} &= \text{y(first + 1:last) - yS}; \\
\text{tflat} &= \text{t(first + 1:last)}; \\
\end{align*}
\]

figure

\[
\begin{align*}
\text{subplot}(2,1,1) \\
\text{plot(t, y, ‘b’, t(first + 1:last), yS, ‘r’) \\
\text{xlabel(‘Time (hr)’, yS, ‘r’) \\
\text{ylabel(‘Stress (GPa*nm)’, yS) \\
\text{subplot}(2,1,2) \\
\text{plot(tflat, stressflat); \\
\text{xlabel(‘Time (hr)’, yS) \\
\text{ylabel(‘Flattened stress (GPa*nm)’, yS) \\
\end{align*}
\]

Saves to file. For now this is just going to go by period length, since this is usually an integer.

\[
\begin{align*}
\text{filename} &= \text{strcat(mtl, sprintf(‘%d’, round(T)), ‘.mat’)}; \\
\text{save(filename, ‘tflat’, ‘stressflat’, ‘time_hr’, ‘voltage_V’, ‘freq’)}; \\
\end{align*}
\]
E.2 Making Lissajous plots

displacement_lissajous_PCO_singlefreq.m

% This script will output a Lissajous plot given an input file that is time vs. displacement data at a known frequency. This is modified from some code sent to me by Dr. Sean Bishop. Data is imported and labeled with ‘time06’, ‘bias06’, and ‘displacement06’

% Global variables

% This is the number of steps in one cycle at the frequency of interest.
steps = 200;
filename = 'DCX8_040815_628C_-05Hz.mat';

n = size(time06, 1);
cycles = floor(n/steps);
alldbias06 = zeros(1, steps);
alldisp06 = zeros(1, steps);

for step = 1:steps;
    for w = 1:cycles;
        allbias06(step) = allbias06(step) + bias06(step + (w-1)*steps);
        alldisp06(step) = alldisp06(step) + displacement06(step + (w-1)*steps);
    end
end

allbias06 = allbias06 ./ cycles;
alldisp06 = alldisp06 ./ cycles;

plot(allbias06, alldisp06, 'g-')
xlabel('Normalized bias')
ylabel('Normalized amplitude')
legend('0 mV')
save(filename, 'time06', 'allbias06', 'alldisp06')

Charge_Lissajous_STF.m

% This script will operate once a file of data from a DCX experiment is imported. The data file should include current, voltage, and time.
% The script will integrate the current - time data to produce a charge vs. time profile. It will then flatten the current data (this practically removes leakage and recenter the plot. Then, the script makes a Lissajous plot of the result. It will output the data inputs for the Lissajous plot.

% time is in hours, current in mA. Time applies to voltage as well as current data
mtl = 'PCO_628C_exp51'; % Seconds to datapoints conversion (for 72 seconds, how many data points?)
Need to update this for each imported data set - it is not always the same! 
dpper = 72;

t = time_s;
V = voltage_V;
I = current_A;
freq = 0.05;
dur = length(t);

%Initialize charge integration
qt = zeros(dur-1,1);

%Use trapz function to integrate I?
for i = 2:dur
    if i > 2
        qt(i-1) = qt(i-2) + dt*((I(i)+I(i-1)))/2;
    else
        qt(i-1) = dt*((I(i)+I(i-1)))/2;
    end
end

tmin = t/60;

figure
    subplot(2,1,1)
    %Plot charge vs. time
    plot(tmin(2:dur),qt)
    xlabel('Time (minutes)')
    ylabel('Charge (C)')

%Make lissajous plot
    subplot(2,1,2)
    plot(V(2:dur), qt)
    xlabel('Voltage (V)')
    ylabel('Charge (C)')

%Make averaged out lissajous plot
    %Calculates the period in seconds
    period = (1/freq);

%First need to identify number of data points per period.
\[
dps = \text{(dpper \times \text{period} / 72)};
\]

% Takes a moving average that includes an extra 22th of a period before or after.
\[
\text{wts} = [(1/(2 \times \text{round(dps)})); \text{repmat(1/\text{round(dps)}, \text{int16(dps-1)}, 1); (1/(2 \times \text{round(dps)})]};
\]
\[
\text{yS} = \text{conv(qt, wts, 'valid')};
\]

% Need to exclude beginning and end points for plot.
\[
\text{first} = \text{int32(dps/2)};
\]
\[
\text{last} = \text{length(qt)-(int32(dps)-first)};
\]

% Now, subtract the moving average from the main file in order to plot only the flattened signal, which will have an amplitude that is not normalized.
\[
\text{qflat} = \text{qt(first + 1:last) - yS};
\]
\[
\text{tflat} = \text{t(first + 2:last + 1)};
\]
\[
\text{Vflat} = \text{V(first + 2: last + 1)};
\]

% Now, need to find the non-zero values, as the end of the vector will often be 0's because of the difference in time between collection for the two runs.
\[
\text{V\_bool} = \text{not(isnan(tflat))};
\]
\[
\text{t\_adj} = \text{tflat(V\_bool)};
\]
\[
\text{V\_adj} = \text{Vflat(V\_bool)};
\]
\[
\text{q\_adj} = \text{qflat(V\_bool)};
\]

% Now, determine cycle length in seconds.
\[
\text{Npoints} = \text{length(t\_adj)};
\]
\[
\text{ttot} = \text{t\_adj(Npoints) - t\_adj(1)};
\]
\[
\text{Ncyc} = \text{ttot/period};
\]
\[
\text{ptbyT} = \text{round(Npoints/Ncyc)};
\]
\[
\text{allbias} = \text{zeros(ptbyT, 1)};
\]
\[
\text{allq} = \text{zeros(ptbyT,1)};
\]

% Nested for loop that runs through each step of each cycle and updates the sum of the data
\[
\text{for step} = 1:\text{ptbyT};
\]
\[
\text{for w=1:floor(Ncyc)};
\]
\[
\text{allbias(step)} = \text{allbias(step)} + \text{V\_adj(step)+(w-1)*ptbyT)};
\]
\[
\text{allq(step)} = \text{allq(step)} + \text{q\_adj(step)+(w-1)*ptbyT)};
\]
\[
\text{end}
\]
\[
\text{end}
\]

% Divide by total number of cycles (floored) to leave average Lissajous plot
\[
\text{allbias} = \text{allbias./floor(Ncyc)};
\]
\[
\text{allq} = \text{allq./floor(Ncyc)};
\]

\text{figure}
E.3 Statistical analysis Matlab code

permtest.m

% A function definition

function [b0, b1, r2, actual, pvalue] = permtest(X, Y, nruns)

% This function will output the b1 and b0 values calculated for variables X and Y after permuting the y variables, basically testing the null hypothesis that there is no relationship between the variables.

nvals = length(Y);
    newY = zeros(nvals, 1);
    coeffs = zeros(1, nruns);
    actualcorr = corrcoef(X, Y);
    actual = actualcorr(1, 2);
    % This index will track coefficients that are greater than the actual one.
    nmore = 0;

for i = 1:nruns

% Determines new order
    order = randperm(nvals);
    % Update vector with new order
    for j = 1:nvals
        newY(j) = Y(order(j));
    end
% Calculates the Pearson correlation coefficient between X and newY.
    new = corrcoef(X, newY);
% Record the X vs. newY correlation coefficient
    coeffs(i) = new(1, 2);

end
end
if coeffs(i) > actual
    nmore = nmore + 1;
end
end

hist(coeffs)
    xlabel('Correlation coefficient')
    ylabel('Counts')
end

pvalue = nmore/nruns;

Onevec = ones(length(X), 1);
    xvals = [Onevec, X];
    [b] = regress(Y, xvals);
    b0 = b(1);
    b1 = b(2);
    r2 = actual^2;
end

computereg.m
    %A function definition used in the bootstrap_linreg codes.
    function b = computereg(x,y)
    %Linear regression model that outputs slope
        X = [ones(size(x)), x];
        b = regress(y, X);
    end

bootstrap_linreg_slope.m
    %This function will run bootstrap resampling on two vectors. I will be resampling pairs
    with replacement and re-computing the slope and intercept in each case with 95% confidence
    intervals.
    
    %Global variables
        nruns = 1000;
        x = t90_film;
        y = y90_film;
        nsamples = length(x);
        low2_5 = round(nruns/40);
        up2_5 = nruns-low2_5;

    %Run bootstrap and calculate slope and intercept
        [bootstat, bootsam] = bootstrp(nruns, @(a,b)computereg(a,b), x, y);
% Find confidence interval of intercept
ordered = sort(bootstat(:,1));
mid = ordered(nruns/2);
low = ordered(low2_5);
high = ordered(up2_5);

% Find confidence interval of slope
ordered2 = sort(bootstat(:,2));
mid2 = ordered2(nruns/2);
low2 = ordered2(low2_5);
high2 = ordered2(up2_5);

% Make histogram
figure
subplot(1,2,1)
hist(ordered);
xlabel('Intercept')
ylabel('Counts')
subplot(1,2,2)
hist(ordered2);
xlabel('Slope')
ylabel('Counts')

bootstrap_linreg.m
% This function will run bootstrap resampling on two vectors. I will be resampling pairs with replacement and re-computing the correlation coefficient in each case.

% Global variables nruns = 1000;
x = t90_int;
y = y90_int;
nsamples = length(x);
low2_5 = round(nruns/40);
up2_5 = nruns-low2_5;

% Run bootstrap and calculate correlation. Choose Spearman or regular.
[bootstat, bootsam] = bootstrp(nruns, @(x,y)corr(x,y));

% Find confidence interval
ordered = sort(bootstat);
mid = ordered(nruns/2);
low = ordered(low2_5);
high = ordered(up2_5);

% Make histogram
figure
hist(bootstat);
xlabel('Correlation coefficient')
ylabel('Counts')