# MECHANICAL, THERMAL, AND ELECTROCHEMICAL PROPERTIES OF MIXED IONIC ELECTRONIC CONDUCTORS FROM WAFER CURVATURE MEASUREMENTS

By

Yuxi Ma

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#### ABSTRACT

#### MECHANICAL, THERMAL, AND ELECTROCHEMICAL PROPERTIES OF MIXED IONIC ELECTRONIC CONDUCTORS FROM WAFER CURVATURE MEASUREMENTS

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Mixed ionic electronic conductors (MIECs) are a group of materials that have been widely used in various applications including Solid Oxide Fuel Cells, gas separation membranes, memristors, electrostrictive actuators, chemical sensors and catalytic converters. The functionality of these materials are based on their large, quickly-changeable point defect concentrations, which also produces a mechanical response in the material. Unfortunately, considerable disagreement over the ionic point defect concentrations, surface exchange coefficients, and mechanical properties of even the most widely-used MIECs exists in the literature.

This dissertation demonstrates that the Young's modulus, thermo-chemical expansion coefficient, oxygen nonstoichiometry, oxygen surface exchange coefficient, oxygen surface exchange resistance and stress state of MIEC thin films can all be obtained as a function of temperature and/or oxygen partial pressure using an *in-situ*, non-contact, current-collector-free wafer curvature measurement platform. The validity of this wafer curvature technique was evaluated by experiments on identically-prepared  $SrTi_{0.65}Fe_{0.35}O_{3-x}$  films which showed that nearly identical oxygen surface exchange coefficients could be obtained from optical relaxation (another current-collector-free technique), and experiments on a single  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  film which showed that nearly identical Young's Moduli could be obtained from more traditional X-ray diffraction based techniques. Wafer curvature experiments performed on  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  films with Si surface impurities showed that Si can reduce the oxygen surface exchange coefficient of  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  films with Si surface impurities showed that Si can reduce the oxygen surface exchange coefficient of  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  films with Si surface impurities showed that Si can reduce the oxygen surface exchange coefficient of  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  films with Si surface impurities showed that Si can reduce the oxygen surface exchange coefficient of  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  films with Si surface impurities showed that Si can reduce the oxygen surface exchange coefficient of  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  films with be suitable for real-word

Solid Oxide Fuel Cell operation in dusty conditions. Additionally, experiments performed on  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  films with intentionally-added Pt surface impurities showed that the precious metal current collectors used to measure oxygen surface exchange coefficient via traditional techniques (such as electrical conductivity relaxation, electrical impedance spectroscopy, etc.) artificially enhance the  $Pr_{0.1}Ce_{0.9}O_{1.95-x}$  oxygen surface exchange coefficient, and hence likely contribute to the large oxygen surface exchange coefficient discrepancies observed in the literature.

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# **KEY TO SYMBOLS AND ABBREVIATIONS**

Α	Area
а	Lattice parameter
AFC	Alkaline fuel cell
AFM	Atomic force microscopy
lphathermochemical	Thermo-chemical expansion coefficient
$\alpha_c$	Chemical expansion coefficient
$\alpha_{tc}$	Thermo-chemical expansion coefficient
$\alpha_1$ and $\alpha_2$	Thermal expansion coefficients of substrate 1 and 2
Δα	Change in optical absorption coefficient
b	Width
β	Dimensionless constant regarding the geometry of the indenter
CHP	Combined heat and power
Cv	Concentration of oxygen vacancy
C <sub>0</sub>	Oxygen concentration
D	Diffusion coefficient
<i>D*</i>	Tracer diffusion coefficient
Dchem	Chemical diffusion coefficient
δ	Oxygen nonstoichiometry
E	Young's modulus
ECR	Electrical conductivity relaxation
EIS	Electrical impedance spectroscopy
$E_f$	Young's modulus of the film

$E_S$	Young's modulus of the substrate
E <sub>eff</sub>	Effective Young's modulus
8	Strain
ε	Chemical strain
F	Faraday's constant
$f_f$	Flexural frequency
γ	Thermodynamic factor
h <sub>f</sub>	Film thickness
$h_s$	Substrate thickness
HTXRD	High temperature X-Ray diffraction
Ι	Transmitted light intensity
IET	Impulse excitation technique
j <sub>ex</sub>	Exchange current density
<i>k</i> <sub>chem</sub>	Chemical oxygen surface exchange coefficient
k	Oxygen surface exchange coefficient
$k^*$	Tracer oxygen surface exchange coefficient
k <sup>q</sup>	Electrically measured oxygen surface exchange coefficient
κ	Curvature of the sample
κR	Curvature relaxation
1	Film thickness
l <sub>c</sub>	Characteristic thickness
L	Sample length
L <sub>0</sub>	Initial gauge length

$\Delta L$	Change in gauge length
LSM	Lanthanum strontium manganese
$\Lambda_o^*$	Surface permeability
M <sub>f</sub>	Biaxial modulus of the thin film
M <sub>S</sub>	Biaxial modulus of the substrate
MCFC	Molten carbonate fuel cell
MgO	Magnesium oxide
MIEC	Mixed ionic electronic conductor
MOSS	Multi-beam optical stress sensor
μ	Poisson's ratio
$\Delta \mu_0$	Surface oxygen chemical potential
N <sub>A</sub>	Avogadro's constant
OTR	Optical relaxation
Ox	Oxidation
PAFC	Phosphoric acid fuel cell
PEMFC	Proton exchange membrane fuel cell
pO <sub>2</sub>	Oxygen partial pressure
РСО	Praseodymium doped ceria
PLD	Pulsed laser deposition
Rs	Surface polarization resistance
R	Ideal gas constant
Red	Reduction
ρ	Density

S	Unloading stiffness
SAFC	Solid acid fuel cell
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
σ	Stress
σ <sub>c</sub>	Chemical stress
$\sigma_t$	Thermal stress
$\sigma_{Total}$	Total stress
ToF-SIMS	Time-of-flight secondary ion mass spectroscopy
V	Poisson's ratio
$v_s$	Poisson's ratio of the substrate
$v_f$	Poisson's ratio of the film
V <sub>l</sub>	Wave velocity at longitude direction
V <sub>m</sub>	Molar volume
Wo	Thermodynamic factor
XRD	X-Ray Diffraction
XPS	X-Ray photoelectron spectroscopy
YSZ	Yttria-doped zirconia

#### 1. Introduction

#### 1.1 Energy and Environment Challenges

With the growth of population and the development of industry, the energy demand is steadily increasing over the past decade and will continue to grow in the future<sup>1</sup>. Also, the emission of carbon dioxide increased accordingly<sup>1</sup>. Utilizing the existing non-renewable fossil fuel efficiently has become a must to meet the energy demand as well as reducing the emission of carbon dioxide. Conventional energy conversion techniques like internal combustion not only have low efficiencies, but combustion exhaust also contains pollutants such as carbon monoxide, nitric oxide, and sulfur dioxide.<sup>2</sup> Therefore, new energy conversion techniques that are both efficient and environmentally friendly is needed to tackle these energy and environment challenges.

#### 1.2 Fuel Cells and Applications

A fuel cell is an energy conversion technology that converts chemical energy into electrical energy. There are different types of fuel cells, including the proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), solid acid fuel cell (SAFC), alkaline fuel cell (AFC), solid oxide fuel cell (SOFC), and molten carbonate fuel cell (MCFC). Based on the operating temperature and the power output, fuel cells can be utilized for a variety of applications, ranging from portable devices (100 W) to a centralized power generator (100 MW).<sup>3</sup> Because of its versatility, 62, 000 fuel cell systems have been shipped worldwide in 2016, and the total megawatts of fuel cells shipped worldwide increased from 300 MW at 2015 to over 500 MW at 2016.<sup>4</sup>

#### 1.3 Advantages and Progress of Solid Oxide Fuel Cells (SOFCs)

Figure 1.1 shows the schematic of a SOFC. At high temperature (600~1000°C), one oxygen ion gets incorporated into the cathode materials, transported through electrolyte, and then reacts with the fuel (H<sub>2</sub>, hydrocarbons, CO) at the anode side. Meanwhile, to maintain the electroneutrality, two electrons are transported through the interconnect between anode and cathode, which generates electricity. Compared to other types of fuel cells, as shown in Table 1.1



Figure 1.1 Schematics of an operating solid oxide fuel cell

SOFC has the highest combined head and power (CHP) efficiency and the most flexible fuel choices.<sup>5-8</sup>

When compared to other energy conversion techniques, as shown in Figure 1.2<sup>9, 10</sup>, SOFC has the highest gravimetric and volumetric power density. However, SOFC requires high operating temperature for the transport of oxygen ions. Degradations processes such as particle coarsening,



*Figure 1.2 Gravimetric and volumetric power density comparison of different energy* 

### conversion techniques<sup>9,10</sup>

interdiffusion between different components, and dopant segregation can shorten the lifetime of SOFC and therefore hindering the further development of SOFC.

To mitigate the degradation issue, one solution is to decrease the operating temperature of SOFC. Over the past decade, a variety of studies have been conducted to develop new cathode materials or different cathode microstructures to reduce the operating temperature.<sup>11-18</sup> As a result, with the help of the high-performance cathodes that have the fast oxygen surface exchange kinetics, the operating temperature of SOFCs have been brought down to ~500°C,<sup>17</sup> a significant advance from the previous prototype using a lanthanum strontium manganese (LSM) cathode, which operates at 1000°C.

#### 1.4 Challenges and Objectives

In order to incorporate a cathode material into a SOFC, multiple physical/chemical properties must be known in order to meet the performance and stability requirements. For example, Young's modulus and the thermo-chemical expansion coefficient are needed to evaluate the mechanical stability at the interface between cathode and electrolyte. The oxygen surface exchange coefficient is needed to quantify the performance of cathode materials. These properties have to be measured *in-operando* to be meaningful for SOFC applications. However, due to the difficulty of *in-situ* measurements, there is a lack of studies about Young's modulus at high



Figure 1.3 Reported oxygen surface exchange coefficient of lanthanum strontium ferrite

temperature. Additionally, as shown in Figure 1.3,<sup>19-22</sup> for a conventional SOFC cathode material, there is  $\sim$ 5 orders of magnitudes discrepancy in the oxygen surface exchange coefficient. This discrepancy makes it even harder to compare the performance across different cathode materials.

Therefore, the objective of this work, as shown in Figure 1.4,<sup>23</sup> is to develop an *in-situ* technique that can measure stress ( $\sigma$ ), strain ( $\varepsilon$ ), Young's modulus (E), biaxial modulus (M), thermo-chemical expansion coefficient ( $\alpha_{thermochemical}$ ), thermal expansion coefficient ( $\alpha_{thermal}$ ) oxygen surface exchange coefficient ( $k_{chem}$ ), oxygen nonstoichiometry ( $\delta$ ), and surface polarization resistance ( $R_s$ ); Then use this technique to detect the effect of surface



Figure 1.4 Graphic summary of objectives of this work

#### contaminants on the oxygen surface exchange process.

Of the following chapters, Chapter 2 will review basic knowledge of mixed ionic electronic conductors (MIECs), chemical expansion, oxygen surface exchange process, and the conventional

characterization techniques to measure Young's modulus. Chapter 3 will introduce the curvature measurement platform, multibeam optical stress sensor (MOSS), and its application using the dual substrate method to obtain Young's modulus, the thermo-expansion coefficient and oxygen nonstoichiometry from thin film materials. Chapter 4 will examine the curvature relaxation technique and its applications in measuring the oxygen surface exchange coefficient and surface polarization resistance. Chapters 5 and 6 will illustrate the results of Young's modulus, thermo-chemical expansion coefficient, and oxygen surface exchange coefficient from other measurement techniques for cross-checking the reliability of the MOSS platform. Chapters 7 and 8 will report the effect of surface contaminants on the oxygen surface exchange process. Chapter 9 will sum up the conclusions from this dissertation and present recommendations for future work.

Fuel Cell	Electrolyte	Operating Temperature	Fuel	Charge Carriers	Electrode Reactions	Electrical Efficiency	CHP Efficiency	Problems
PMEFC	Nafion	70-110°C	H <sub>2</sub>	$H^+, e^-$	$\frac{1}{2}O_{2(g)} + H^+ + 2e^- \to H_2O$ $H_{2(g)} \to 2H^+ + 2e^-$	40-50%	NA	H <sub>2</sub> O Management, CO intolerant
AFC	Aqueous KOH	100-250°C	H <sub>2</sub>	OH <sup>°</sup> , e <sup>°</sup>	$\frac{1}{2}O_{2(g)} + H_2O_{(g)} + 2e^- \to 2OH^-$ $H_{2(g)} + 2OH^- \to 2H_2O_{(g)} + 2e^-$	50%	NA	CO <sub>2</sub> intolerant
PAFC	H <sub>3</sub> PO <sub>4</sub>	150-250°C	H <sub>2</sub>	$H^+, e^-$	$\frac{1}{2}O_{2(g)} + H^{+} + 2e^{-} \to H_{2}O$ $H_{2(g)} \to 2H^{+} + 2e^{-}$	40%	NA	Electrolyte Leaks
MCFC	(Na,K) <sub>2</sub> CO <sub>3</sub>	500-700°C	HCs, CO	CO <sub>3</sub> <sup>2-</sup> , e <sup>-</sup>	$\frac{1}{2}O_{2(g)} + CO_{2(g)} + 2e^{-} \rightarrow CO_{3}^{2-}$ $H_{2(g)} + CO_{3}^{2-} \rightarrow H_{2}O_{(g)} + CO_{2(g)} + 2e^{-}$	50%	80%	Long Start-up, corrosive electrolyte
SOFC	$Y_2O_3-ZrO_2,$ Gd <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub>	600-1000°C	H <sub>2</sub> , CO, HCs	0 <sup>2-</sup> , e <sup>-</sup>	$\frac{1}{2}O_{2(g)} + 2e^{-} \rightarrow 0^{2-}$ $H_{2(g)} + 0^{2-} \rightarrow H_2O_{(g)} + 2e^{-}$	45-65%	90%	Long start-up, high temperature degradation

Table 1.1 Fundamentals of Different Types of Fuel Cells<sup>5-8</sup>

#### 2. Literature Review

#### 2.1 Conventional Young's Modulus Measurement Techniques

#### 2.1.1 Existing Young's Modulus Measurement Techniques

Tensile test and nano-indentation are two of the most commonly used measurement techniques to measure Young's modulus. For tensile test, the sample is placed in the testing instrument and then extended. The elongation of the sample and the force are recorded during the test. To calculate the Young's modulus, one needs to know the stress and strain of the tested sample, which are defined as:

$$\sigma = \frac{F}{A} \tag{2.1}$$

and

$$\varepsilon = \frac{\Delta L}{L_0} \tag{2.2}$$

where  $\sigma$  is the stress, *F* is the tensile force, A is the cross-section area,  $\varepsilon$  is the strain,  $\Delta L$  is the change in gauge length, and  $L_0$  is the initial gauge length. Based on the equation:

$$E = \frac{\sigma}{\varepsilon}$$
(2.3)

Young's modulus can be calculated.

Nano-indentation, on the other hand, uses the slope of the load-displacement curve during unloading to calculate the Young's modulus of the sample. Specifically, based on the slope of loading-displacement curve, namely the unloading stiffness, the effective Young's modulus can be calculated:<sup>24</sup>

$$S = \beta \frac{2}{\sqrt{\pi}} E_{eff} \sqrt{A}$$
(2.4)

where S is the unloading stiffness,  $\beta$  is a dimensionless constant regarding the geometry of the indenter, A is the contact area, and  $E_{eff}$  is the effective Young's modulus, which is defined as:<sup>24</sup>

$$\frac{1}{E_{eff}} = \frac{1 - v^2}{E} + \frac{1 - v_i^2}{E_i}$$
(2.5)

where *E* and *v* are the Young's modulus and Poisson's ratio of the sample,  $E_i$  and  $v_i$  are the Young's modulus and Poisson's ratio of the indenter.

The impulse excitation technique (IET) and ultrasonic wave technique are two of the methods to measure Young's modulus based on the propagation of the wave. The IET measures the resonant frequency in order to extract Young's modulus of the measured sample. The excitation is induced by using a small projectile to tap the sample. Then the resulting vibration signal is recorded with a microphone/piezoelectric sensor/laser vibrometer/accelerometer. The acquired data in the time domain is processed with fast Fourier transformation. Then the resonant frequency is determined to calculate Young's modulus. The equations for calculating the Young's modulus depends on the geometry of the sample. For example, for a rectangular bar, the Young's modulus can be calculated by:<sup>25</sup>

$$\mathbf{E} = 0.9465 \left(\frac{mf_f^2}{b}\right) \left(\frac{L^3}{t^3}\right) T \tag{2.6}$$

where E is the Young's modulus, m is the mass,  $f_f$  is the flexural frequency, b is the width, L is the length, t is the thickness, and T is the correction factor, which is defined as:

$$T = 1 + 6.585 \left(\frac{t}{L}\right)^2$$
(2.7)

Note that the correction factor will be necessary only if  $L/t \ge 20$ .

The ultrasonic wave technique determines the elastic properties of the material by detecting the propagation speed of ultrasonic waves. Specifically, the elastic modulus and density determines the velocity of the ultrasonic wave:<sup>26</sup>

$$V = \left(\frac{M}{\rho}\right)^{\frac{1}{2}} \tag{2.8}$$

where V is the velocity of the wave propagation, M is the elastic moduli, and  $\rho$  is the density of the sample. For isotropic materials, the Young's modulus can be determined by:<sup>26</sup>

$$E = V_l^2 \rho (1+\mu) (1-2\mu) / (1-\mu)$$
(2.9)

where  $V_l$  is the wave velocity at longitude direction, *E* is the Young's modulus, and  $\mu$  is the Poisson's ratio.

#### 2.1.2 Limitation of Existing Techniques

For tensile tests and nano-indentation, the first limitation is the destructive testing procedure. The second limitation is that it is hard to incorporate the testing instrument into a high temperature environment. For nano-indentation, specifically, as described in Eqn 2.5, the change of Young's modulus at high temperature could also happens to the indenter, which may lead to the inaccurate results.

For IET, although it is non-destructive, the constant used in determining Young's modulus, as shown in Eqn 2.6 varies among different materials and sample geometries.<sup>25</sup> Additionally, it takes special design of the test rig for the IET to measure Young's modulus at high temperature.<sup>25</sup>

For the ultrasonic wave technique, Young's modulus is calculated under the assumption of stress-free sample, which doesn't hold for the case of a thin film on a rigid substrate. Again, it is hard to incorporate the whole system into a high temperature environment.

# 2.2 Mechano-Chemical Coupling and Oxygen Surface Exchange of Mixed Ionic Electronic Conductors (MIECs)

#### 2.2.1 Chemical Expansion in MIECs

Mixed ionic electronic conductors are a group of materials that can conduct both ion and electrons. For the MIEC used as cathode material under SOFC operation conditions, it goes through the following defect reaction, expressed in Kröger-Vink notation:<sup>27</sup>

$$0_0^x \to \frac{1}{2} O_2 + V_0^{"} + 2e^-$$
 (2.10)

This reaction can be triggered by increasing the sample temperature and/or decreasing the oxygen partial pressure. After the formation of an oxygen vacancy, the lattice tends to expand due to the expulsion resulting in a positively charged cation and the oxygen vacancy. This behavior is described as mechano-chemical coupling. The resulting strain from a changing chemical environment can be expressed by the following equation<sup>28</sup>:

$$\varepsilon_c = \alpha_c \Delta \delta \tag{2.11}$$

where  $\varepsilon_c$  is the chemical strain,  $\alpha_c$  is the chemical expansion coefficient,  $\delta$  is the oxygen nonstoichiometry of the material, and  $\Delta\delta$  is the change in the oxygen nonstoichiometry of the material.  $\delta$  is related to the concentration of oxygen vacancies:

$$\delta = \frac{c_v V_m}{N_A} \tag{2.12}$$

where  $c_v$  is the concentration of oxygen vacancy,  $V_m$  is the molar volume of the material, and  $N_A$  is the Avogadro's number. For conventional MIEC used in SOFC applications, the chemical expansion coefficient ranges from 0.01 to 0.1,<sup>29</sup> even with a typical change of 0.02 in oxygen nonstoichiometry, the resulting chemical expansion could be quite substantial compared to the thermal expansion, leading to internal strain energy that can drive microstructural changes and

damage. Therefore, being able to measure chemical expansion of a MIEC material can be of great importance for the mechanical stability of SOFC applications.

#### 2.2.2 Oxygen Surface Exchange

For oxygen transport in MIECs, it is typically a mixed combination of oxygen diffusion and oxygen surface exchange processes. The oxygen exchange process, specifically, consists of oxygen adsorption and dissociation. The competition between those two processes can be described with the characteristic thickness (detailed derivation can be found in Appendix A):<sup>30</sup>

$$l_c = \frac{D}{k} \tag{2.13}$$

where  $l_c$  is the characteristic thickness, D is the diffusion coefficient, and k is the oxygen surface exchange coefficient. If the sample thickness l is less than  $1/100^{\text{th}}$  of the characteristic thickness, the oxygen transport is predominately controlled by oxygen surface exchange kinetics.<sup>19</sup> Table 2.1 shows the characteristic thickness of commonly used MIEC materials for SOFC applications.<sup>18, 31-</sup> *Table 2.1 Characteristic thickness of common MIEC materials* 

	Temperature (°C)	pO <sub>2</sub> (kPa)	Characteristic Thickness (cm)
La <sub>0.5</sub> Sr <sub>0.5</sub> MnO <sub>3-δ</sub>	700	70.0	2*10 <sup>-7</sup>
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	700	70.0	3*10 <sup>-3</sup>
$La_{0.9}Sr_{0.1}CoO_{3-\delta}$	900	4.5	2*10 <sup>-3</sup>
La <sub>0.9</sub> Sr <sub>0.1</sub> FeO <sub>3-δ</sub>	900	6.5	6*10 <sup>-3</sup>
La <sub>0.6</sub> Sr <sub>0.4</sub> FeO <sub>3-ð</sub>	1000	6.5	5*10 <sup>-2</sup>
	800	101.3	2*10 <sup>-3</sup>
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	800	20.7	6*10 <sup>-3</sup>
	800	5.1	$2*10^{-2}$
	800	1.3	5*10 <sup>-2</sup>
$Pr_{0.1}Ce_{0.9}O_{2-\delta}$	670	20.7	0.4

<sup>33</sup> With the current geometries of SOFC cathodes, the electrode size is much smaller than the characteristic thickness. Therefore, oxygen surface exchange process is the rate limiting step of oxygen transport in the MIECs used for SOFC applications.

Depending on the measurement techniques, there are three types of oxygen exchange coefficients in the literature, which include chemical (ambipolar) exchange coefficient ( $k_{chem}$ ), tracer exchange coefficient ( $k^*$ ), and electrically determined exchange coefficient ( $k^q$ ).

The chemical exchange coefficient is defined as:<sup>34</sup>

$$k_{chem} = \frac{4j_{ex}^{o}w_{o}}{c_{o}} = \left(\frac{j_{0}}{\Delta\mu_{0}}\right)\frac{RTw_{o}}{c_{0}} = \Lambda_{o}^{*}\frac{RTw_{o}}{c_{0}}$$
(2.14)

where  $j_{ex}^{o}$  is the exchange current density,  $c_{o}$  is the oxygen concentration,  $\Delta \mu_{0}$  is the surface oxygen chemical potential, R is the ideal gas constant, T is the temperature,  $\Lambda_{o}^{*}$  is the surface permeability, and  $w_{o}$  is the thermodynamic factor, which is defined as (detailed derivation of thermodynamic factor can be found in Ref 34):<sup>35</sup>

$$w_o = \frac{1}{RT} \frac{\partial \mu_o}{\partial lnc_o} \tag{2.15}$$

The chemical exchange coefficient represents the exchange process involving oxygen vacancies and electrons without the applied current or voltage.

The tracer exchange coefficient is defined as:<sup>34</sup>

$$k^* = \Lambda_o^* \frac{RT}{c_0} \tag{2.16}$$

which only represents the exchange process of oxygen vacancies without the involvement of electrons.

The electrically determined exchange coefficient is defined as:<sup>34</sup>

$$k^q = \Lambda_o^* \frac{RT}{c_0} \tag{2.17}$$

which also represents the exchange process containing oxygen vacancies and electrons. However, in this case, there is an external circuit, therefore the oxygen flux is not related with the electron flux.

#### 2.3 Oxygen Surface Exchange Coefficient Measurements from Literature Studies

#### 2.3.1 Oxygen Permeation

The oxygen permeation technique requires a membrane material to be sealed inside a chamber with feed gas on one side and sweep gas on the other side, and the flux of oxygen is calculated via the composition results analyzed by gas chromatography. The measured chemical oxygen exchange coefficient ( $k_{chem}$ ) is related to the permeability as described in Eqn 2.14.

#### 2.3.2 Electrical Impedance Spectroscopy (EIS)

The EIS requires a symmetrical cell in order to measure the oxygen surface exchange coefficient. The symmetrical cell is composed of one electrolyte and two identical electrodes at each side of the electrolyte. After applying an AC voltage across the cell and measuring the impedance spectroscopy of the sample, the resistance of the electrode is equal to the diameter of the semi-circle impedance signal divided by two (considering two identical electrodes in the measurement). Since the oxygen surface exchange process is the rate limiting step of the oxygen transport process in the electrode, therefore, the areal specific resistance of the electrode is related to the electrically determined oxygen exchange coefficient ( $k^q$ ):<sup>36</sup>

$$k^q = \frac{RT}{4F^2 R_s c_o} \tag{2.18}$$

where F is the Faraday's constant,  $R_s$  is the area specific resistance.

#### 2.3.3 Isotope Depth Profiling

Isotope depth profiling uses the <sup>18</sup>O isotope to determine both isotope oxygen surface exchange (k\*) and diffusion (D\*) coefficient of a material. Specifically, the sample pre-annealed

in normal gas atmosphere (normal  ${}^{18}\text{O}/{}^{16}\text{O}$  abundance) is exposed to  ${}^{18}\text{O}_2$  at designated temperature. Then after quenching the sample to room temperature, the composition profile of  ${}^{18}\text{O}$  is determined by secondary ion mass spectroscopy (SIMS). According to Fick's second law, the  ${}^{18}\text{O}$  profile is fitted with the following equation: ${}^{37}$ 

$$g(x,t) = \frac{c(x,t) - c_{bg}}{c_g - c_{bg}} = erfc \left\{ \frac{x}{2\sqrt{D^*t}} \right\} - \exp(hx + h^2 D^*t) \, erfc \left( \frac{x}{2\sqrt{D^*t}} + h\sqrt{D^*t} \right) \quad (2.19)$$

where g(x, t) is the normalized concentration of oxygen isotope, c(x, t) is the instantaneous concentration of oxygen isotope,  $c_{bg}$  is the oxygen isotope concentration at the background,  $c_g$  is the oxygen isotope concentration in the gas, t is the exposure time, and  $h = \frac{k^*}{D^*}$ .

#### 2.3.4 Electrical Conductivity Relaxation (ECR)

The ECR technique relies on the relaxation of the conductivity after an abrupt change in oxygen partial pressure in the surrounding gas atmosphere of the sample. Under the assumption of a linear relationship between oxygen concentration and conductivity (assuming constant mobility of oxygen ion), with the sample thickness l significantly smaller than the characterization thickness ( $L_c$ ), the k<sub>chem</sub> value can be determined by fitting the conductivity relaxation curve to a simplified version of Fick's second law:<sup>38-41</sup>

$$g(t) = \frac{\sigma(t) - \sigma_0}{\sigma_{\infty} - \sigma_0} = \frac{c(t) - c_0}{c_{\infty} - c_0} = 1 - \exp\left(\frac{-tk_{chem}}{l}\right)$$
(2.20)

where  $\sigma(t)$  is the instantaneous conductivity,  $\sigma_0$  is the initial conductivity and  $\sigma_{\infty}$  is the final conductivity. c(t),  $c_0$ ,  $c_{\infty}$  represents the instantaneous, initial and final oxygen concentration, respectively. The detailed derivation of Eqn 2.20 can be found in Appendix A.

#### 2.3.5 Isothermal Isotope Exchange

Isothermal isotope exchange is an *in-situ* technique to measure the isotope oxygen surface exchange coefficient of powder materials. It monitors the change in  $^{18}$ O concentration at the gas

outlet after an abrupt change in oxygen partial pressure. The concentration relaxation of <sup>18</sup>O can be fitted with one of the solutions to Fick's second law:<sup>42</sup>

$$g(t) = \frac{c(t) - c_0}{c_\infty - c_0} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 \exp\left(-\frac{\beta_n^2 D^* t}{a^2}\right)}{\beta_n^2 [\beta_n^2 + L(L-1)]}$$
(2.21)

where

$$\beta_n \cot\beta_n + L - 1 = 0 \tag{2.22}$$

andd

$$L = \frac{k^* a}{D^*} = \frac{a}{l_c} \tag{2.23}$$

*a* is the radius of particles which are assumed to be spherical, and  $l_c$  is the characteristic thickness. 2.3.6 Electrical Titration

Electrical titration uses the current relaxation of an electrochemical cell after a small step change of potential to determines the chemical oxygen surface exchange coefficient. Specifically, the electrochemical cell is surrounded by the gas atmosphere of interest, and sealed in a testing chamber. After a step change in potential, the oxygen vacancies were generated, therefore creating the driving force for oxygen exchange. The exchange process is accompanied with current relaxation, by fitting the current relaxation to a solution of Fick's second law in order to obtain the chemical oxygen surface exchange coefficient can be acquired:<sup>43</sup>

$$I(t) = Q \sum_{n=1}^{\infty} \frac{2\Lambda^2 D_{chem} \exp\left(-\frac{\lambda_n^2 D_{chem} t}{l^2}\right)}{l^2 (\lambda_n^2 + \Lambda^2 + \Lambda)}$$
(2.24)

where Q is the amount of passing charge within the time of t,  $\lambda_n$  is defined as:

$$\lambda_n tan\lambda_n = \Lambda \tag{2.25}$$

and

$$\Lambda = \frac{k_{chem}l}{D_{chem}} \tag{2.26}$$

#### 2.3.7 Thermogravimetric Relaxation

Thermogravimetric relaxation measures the weight change of the sample after an abrupt change in oxygen partial pressure in order to obtain chemical oxygen surface exchange coefficient. The relaxation of weight can be fitted with:<sup>44</sup>

$$g(t) = \frac{c(t) - c_0}{c_\infty - c_0} = \frac{m(t) - m_0}{m_\infty - m_0} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp\left(-\frac{\beta_n^2 D_{chem} t}{l^2}\right)}{\beta_n^2 [\beta_n^2 + L^2 + L]}$$
(2.27)

where m is the mass of the sample, and  $\beta_n$  is defined as:

$$\beta_n tan \beta_n = \frac{k_{chem}l}{D_{chem}} = \frac{l}{l_c} = L$$
(2.28)

#### 2.3.8 Optical Relaxation

Optical relaxation measures the relaxation of transmitted light intensity to determine the chemical oxygen surface exchange coefficient. Specifically, some MIEC materials (*e.g.* praseodymium doped ceria) will absorb light with certain wavelengths due to the effect of the dopant. The oxidation state of the dopant is related to the level of absorption and is also related to the concentration of oxygen vacancies. Therefore, after an abrupt change of oxygen partial pressure, by monitoring the relaxation of transmitted light intensity, the chemical oxygen surface exchange coefficient can be determined by fitting the relaxation curve with the following equation:<sup>45</sup>

$$g(t) = \frac{\ln I(t) - \ln I_0}{\ln I_\infty - \ln I_0} = \frac{c(t) - c_0}{c_\infty - c_0} = 1 - \exp\left(\frac{-tk_{chem}}{l}\right)$$
(2.29)

where *I* is the transmitted light intensity.

#### 2.3.9 Strain Relaxation

Strain Relaxation measures the lattice parameter relaxation to obtain chemical oxygen surface exchange coefficient. Specifically, a time-resolved X-Ray diffractometer is needed to measure the simultaneous lattice parameter change (chemical strain change) after an abrupt change in oxygen partial pressure.<sup>46</sup> Assuming a linear relationship between chemical strain and oxygen nonstoichiometry (constant chemical expansion coefficient), the k<sub>chem</sub> value can be acquired by fitting the relaxation curve with Eqn 2.27 and 2.28.

2.3.10 Limitations of k<sub>chem</sub> Measurement Techniques Reported in the Literatures

As shown in Table 2.1, these techniques have their own limitations.<sup>37,44,47-61</sup> An affordable, current collector-free, contact-free, versatile, *in-situ* technique that can measure oxygen surface exchange coefficient at different temperature and gas atmosphere is needed to be able to evaluate the performance of various MIEC materials

	Conductivity Relaxation	Permeation	Electrical Titration	Impedance Spectroscopy	Gravimetric	Optical Relaxation	Strain Relaxation	Isotope Depth Profiling	Isothermal Isotope Exchange
k <sub>chem</sub> /k <sup>q</sup> /k*	k <sub>chem</sub>	k <sub>chem</sub>	k <sub>chem</sub>	k <sup>q</sup>	k <sub>chem</sub>	k <sub>chem</sub>	k <sub>chem</sub>	k*	k*
Current Collector Needed?	Yes	No	Yes	Yes	No	No	No	No	No
in-situ	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Contact- Free?	No	No	No	No	Yes	Yes	Yes	Yes	Yes
Thin Film Capable?	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
Versitality	Good	Good	Good	Good	Good	Bad	Good	Good	Good
Cost	\$	\$	\$	\$	\$	\$\$	\$\$\$	\$\$\$\$	\$\$\$\$

Table 2.2 Pros and Cons for Oxygen Surface Exchange Coefficient Measurement Techniques<sup>37, 44, 47-61</sup>
#### 3. Dual Substrate Measurements

(This chapter has been adapted from a published paper)

#### 3.1 Introduction

A variety of advanced functional materials, including those used in batteries,<sup>62, 63</sup> fuel cells,<sup>64-68</sup> electrolysis cells,<sup>69-72</sup> memristors,<sup>73, 74</sup> electrostrictive actuators,<sup>75, 76</sup> gas separation units,<sup>77</sup> chemical sensors,<sup>78</sup> electrochromic windows,<sup>79</sup> catalytic converters,<sup>80</sup> etc., obtain their functionality from a high concentration of ionic point defects. Since point defect concentration changes typically result in lattice parameter changes,<sup>67, 81, 82</sup> a coupling exists between the mechanical and electrochemical states of most high performance mixed ionic electronic conducting (MIEC) materials.<sup>83</sup> In traditional batteries, solid oxide fuel cells (SOFCs) and other electrochemical devices made from bulk particles (i.e. grain sizes >> ~100 nm), this mechanochemical coupling is problematic because it produces stress gradients that crack and mechanically pulverize the material if, and when, a material experiences compositional changes during device operation.<sup>84-86</sup> However, the higher fracture toughnesses and higher Griffiths critical cracking stresses exhibited by thin film materials<sup>87</sup> have spured interest in using externally applied stress to intentionally increase the point defect concentrations and electrochemical performance of thin film MIEC devices.<sup>88-94</sup>

For either situation, knowledge of a material's *in situ/ in operando* mechanical, thermal and electrochemical performance is critical for engineering the stress profiles that help determine device performance and/or durability. Unfortunately, such data is scarce in the existing literature, especially at the elevated temperatures often encountered during device operation.

This Chapter demonstrates that the biaxial modulus (M), Young's Modulus (E), thermal expansion coefficient ( $\alpha_t$ ), thermo-chemical expansion coefficient ( $\alpha_{tc}$ ), oxygen

nonstoichiometry ( $\delta$ ), of Pr<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> (10PCO) can all be obtained as a function of simultaneously measured 10PCO chemical stress ( $\sigma_c$ ), chemical strain ( $\varepsilon_c$ ), thermal stress ( $\sigma_t$ ), thermal strain ( $\varepsilon_t$ ), total stress ( $\sigma_{Total}$ ), total strain ( $\varepsilon_{Total}$ ), temperature (T), and oxygen partial pressure ( $p_{O_2}$ ) conditions using *in situ*, non-contact, current-collector-free wafer curvature measurements. Doped ceria was chosen for study based on its importance as a catalytic converter oxidation catalyst,<sup>80, 95</sup> oxygen sensor material,<sup>96</sup> water-splitting/alternative fuel production catalyst,<sup>72,97</sup> and SOFC material.<sup>18, 98, 99</sup> 10PCO, in particular, was chosen because of its conveniently large chemical expansion coefficient,<sup>100</sup> easily accessible mixed ionic electronic conducting state (i.e. mechano-chemically active regime),<sup>101</sup> well-established point defect model<sup>102</sup> and status as a model material.<sup>102</sup>

## 3.2 Theory

## 3.2.1 Wafer Curvature to Measure In-Situ Film Stress

Mechanics theory indicates that the average biaxial stress ( $\sigma_{Total}$ ) within a dense thin film on top of a dense thick substrate (such that the film thickness ( $h_f$ ) to substrate thickness ( $h_s$ ) ratio is less than 0.001) can be extracted from the wafer curvature ( $\kappa$ ) (without knowledge of the film elastic properties) using Stoney's Equation:

$$\sigma_{Total} = \kappa \frac{M_S h_S^2}{6h_f} \tag{3.1}$$

where  $M_S$  is the substrate biaxial modulus defined as  $E_S/(1 - v_S)$ ,  $E_S$  is the substrate Young's modulus, and  $v_S$  is the substrate Poisson's Ratio.<sup>103-105</sup> Hence Eqn. [1] was used to extract the *in situ* film stress from the wafer curvature using the procedures described in the Experimental Methods of Section 3.3. Detailed equipment set-up and curvature measurement guide can be found in our previous work.<sup>106</sup>

3.2.2 Dual Substrate Stress-Temperature Measurements to Determine Film Elastic and Expansion Coefficients

Previous studies have shown that the stress-temperature behavior of electrochemically inactive thin films on multiple substrates can be used to determine thin film elastic constants and thermal expansion coefficients.<sup>107-109</sup> Here, this approach was extended to also measure the thin film thermo-chemical expansion coefficients of mechano-chemically active materials. Specifically, the stress-temperature derivatives  $\left(\frac{\partial \sigma}{\partial T}\right)$  of 10PCO thin films atop two mechano-chemically inactive substrates with different thermal expansion coefficients (i.e.  $(Y_2O_3)_{0.095}(ZrO_2)_{0.905}$  (YSZ) and MgO with 280-700°C averaged  $\alpha$  values of 9.5 and 14.3 ppm/°C, respectively) were measured and related to the film biaxial modulus  $(M_f)$ , the substrate thermal expansion coefficients ( $\alpha_1$  and  $\alpha_2$ ), and the film thermo-chemical expansion coefficient ( $\alpha_{tc}$ ) using the relationships:

$$\frac{\partial \sigma_1}{\partial T} = M_f(\alpha_1 - \alpha_{tc}) \tag{3.2}$$

and

$$\frac{\partial \sigma_2}{\partial T} = M_f (\alpha_2 - \alpha_{tc}) \tag{3.3}$$

Application of temperature-dependent substrate thermal expansion data calculated from the literature<sup>110, 111</sup> to Equations 3.2 and 3.3, allowed  $M_f$  and  $\alpha_{tc}$  to be determined by solving these two equations (both with two unknowns) simultaneously. For those temperatures where mechanochemical coupling was inactive as indicated by previous 10PCO oxygen nonstoichiometry measurements (i.e. below ~400°C), <sup>101, 102, 112-115</sup> the thermochemical expansion coefficient was treated as simply representing the thermal (not thermo-chemical) expansion coefficient.

The film Young's modulus  $(E_f)$  was then determined from the measured  $M_f$  data using the definition of the biaxial modulus:

$$E_f = \frac{M_f}{\left(1 - v_f\right)} \tag{3.4}$$

by assuming a 10PCO film Poisson's ratio  $(v_f)$  of 0.33, as has been done previously in the literature.<sup>116, 117</sup> (Note,  $v_f$  could also have been measured directly by performing experiments on anisotropic substrates, as has been done in the literature,<sup>118</sup> but this was not attempted here due to the minor temperature variation in Poisson's Ratio observed for most materials, even as they encounter oxygen nonstoichiometries similar to those encountered here<sup>119, 120</sup>).

3.2.3 Extraction of the Film Strains, Oxygen Nonstoichiometry, and Film Stresses from Dual Substrate Stress-Temperature Measurements

The total film strain ( $\varepsilon_{Total}$ ) was extracted from the measured film stress ( $\sigma_{Total}$ ) by assuming the film and substrate behaved as elastic solids and applying the thin film version of Hooke's Law:<sup>104</sup>

$$\varepsilon_{Total} = \frac{\sigma_{Total}}{M} \tag{3.5}$$

The ceria, YSZ, and MgO in this study were elastic over the entire 280-700°C temperature range evaluated here as demonstrated by the reproducible stress-curvature trajectories in in Figure S2 of the Supplemental Materials. This is consistent with the disappearance of ceria's oxygen-vacancy-induced elastic dipole anelasticity<sup>76</sup> above 250°C.<sup>121</sup>

Since literature studies have shown that 10PCO exhibits insignificant oxygen nonstoichiometry below 400°C, <sup>101, 102, 112-115</sup> and<sup>114</sup>

$$\varepsilon_{Total} = \varepsilon_t + \varepsilon_c \tag{3.6}$$

the 280-400°C chemical strain ( $\varepsilon_c$ ) was assumed to be zero such that the 280-400°C  $\varepsilon_{Total}$  represented only the thermal strain ( $\varepsilon_t$ ). A similar argument was made for the 280-400°C chemical, thermal, and total stress. As a rough approximation, the 280-400°C  $\varepsilon_t$  was assumed to vary linearly

with temperature, in keeping with previous reports of the near-linear thermal expansion of 10PCO,<sup>112, 122</sup> doped ceria,<sup>123, 124</sup> 8YSZ<sup>123</sup> and MgO<sup>125</sup> over the 280-700°C temperature range.  $\varepsilon_t$  was then extrapolated to temperatures > 400°C using this fit so that  $\varepsilon_c$  could be extracted from  $\varepsilon_{Total}$  via Eqn. 6. A similar treatment was given to the 400-700°C thermal and chemical stress data. With knowledge of  $\varepsilon_c$ , the thin film 10PCO oxygen nonstoichiometry ( $\delta$ ) was determined using the relationship:<sup>81, 114, 126</sup>

$$\varepsilon_C = \frac{\Delta l}{l} \Big|_T = \alpha_C \Delta \delta \tag{3.7}$$

using a (100) oriented 10PCO chemical expansion coefficient ( $\alpha_c$ ) of 0.067<sup>76</sup> and a  $\delta = 0$  below 400°C (as has been assumed in other studies<sup>114, 115</sup>). Use of a constant  $\alpha_c$  was warranted over the 280-700°C range because of the dilute nature of the oxygen vacancies encountered here ( $\delta < 0.015$ ) and the fact that past ceria experimental<sup>114, 127-131</sup> and modeling<sup>76, 81, 132</sup> studies have shown that the lattice strain per oxygen vacancy (i.e.  $\alpha_c$ ) is constant for  $\delta < 0.03$  and temperatures up to 1000°C (Note, studies on 10PCO have shown that  $\alpha_c$  remains constant to at least  $\delta = 0.055$ ).<sup>112, 114</sup> A  $\alpha_c$  value of 0.067 was chosen because that is the DFT-predicted value for (100) oriented ceria<sup>76</sup> and is consistent with the 650-800°C thin film 10PCO  $\alpha_c = 0.064 \pm 0.005$  measured previously<sup>131</sup> (Note, although convenient, a constant  $\alpha_c$  is not required to reliably extract materials properties from wafer curvature measurements).

### 3.3 Experimental Methods

#### 3.3.1 Sample Preparation

One-side polished, (100) oriented, circular, 200  $\mu m$  thick, 25 mm diameter  $(Y_2O_3)_{0.095}(ZrO_2)_{0.905}$  (YSZ) and magnesium oxide (MgO) single crystal (Crystec GmbH, Berlin, Germany) were used as PLD substrates. Prior to deposition, all the substrates were annealed at 1450°C for 20 hours with a 5°C/min nominal heating and cooling rate to relieve any residual

internal stress. Afterwards, the 25-700°C curvature changes of only the substrates were measured to ensure that any substrate residual stresses capable of producing unwanted curvature changes during later film stress-temperature measurements were adequately removed. Only substrates exhibiting 25-700°C curvature changes less than 0.005 m<sup>-1</sup> were used for subsequent Pulsed Laser PLD deposition.

Targets for PLD deposition were produced by pellet pressing and sintering  $Pr_{0.1}Ce_{0.9}O_{2.6}$ powders. These powders were produced using the glycine nitrate combustion method<sup>133</sup> using 18.2 M $\Omega$  water (Millipore, Burlington, MA) , Pyrex glassware (Sigma Aldrich, St. Louis, MO), Teflon coated stir bars (Fischer Scientific, Pittsburgh, PA), a stainless steel reaction vessel (Polar Ware, Kiel, WI), 99.9% pure praseodymium nitrate (Strem Chemicals, Newburyport, MA), 99.9% pure cerium nitrate (Strem Chemicals, Newburyport, MA), and 99% pure glycine (Sigma Aldrich, St. Louis, MA) with a 1:1 glycine to nitrate ratio. After synthesis, the powder was calcined in an 99.8% pure alumina crucible (CoorsTek, Golden, CO) at 1000°C in air using a 5°C/min nominal heating and cooling rate. Then, the powder was transferred to a 38 mm diameter stainless steel die (MTI, Richmond, CA) and uniaxially compacted to ~63 MPa of pressure. The pressed target pellet was then sintered at 1450°C for 20 hrs with 3°C/min nominal heating and a 10°C/min nominal cooling rate to produce a 25 mm diameter PLD target.

PLD was conducted with a XeF laser emitting at 353 nm. The chamber was first pumped down to  $10^{-6}$  torr and then heated to a substrate temperature of ~580°C. After the substrate temperature was stable, the chamber was backfilled with oxygen until the pressure reached 9\*10<sup>-3</sup> torr. 10PCO was then simultaneously deposited onto the previously described YSZ and MgO substrates for 20 minutes using a 350 mJ laser power, a 10 Hz pulse frequency, a ~50 rpm sample rotation, and a substrate to target distance of ~6 cm.

After removal from the PLD, the samples were re-equilibrated in air under protective 99.9% alumina crucibles at 1000°C for 1 hour with 3°C/min nominal heating and cooling rates.

Given the known effect of surface impurities on the oxygen exchange properties of 10PCO,<sup>134</sup> the 10PCO|YSZ samples used for later oxygen surface exchange measurements were surface etched using the procedures described in Zhao et al.<sup>134</sup> Specifically, the samples were placed in 65°C 50% NaOH-50% H<sub>2</sub>O solution for 24 hours with 100 rpm stirring speed. As shown



Figure 3.1 AFM images (a) before and (b) after the etching proces

in Figure 3.1, this procedure was capable of removing Si surface impurities without significantly altering the surface roughness.

3.3.2 Film Microstructure and Crystallographic Orientation Characterization

X-Ray diffraction (XRD) was conducted using a Rigaku SmartLab diffractometer with a 44 kV voltage and a 40 mA current. Scans were carried out between 20 and 80° with a 0.01°/min scan rate and a 1 second dwell time.

Scanning electron microscopy (SEM) imaging was conducted on fractured sample crosssections coated with ~5 nm of Pt using a TESCAN MIRA3 Field Emission SEM (TESCAN Inc.) using a 20 kV beam voltage.

3.3.3 Dual Substrate Measurements

For Dual Substrate measurements, the curvature of both 10PCO|YSZ and 10PCO|MgO samples were measured from 280 to 700°C with 5°C/min heating and 0.2°C/min cooling rates in



Figure 3.2 Reproducibility of the 0.2°C/min stress-temperature data on cooling for two representative a) PCO/MgO and b) PCO/YSZ samples.

25 sccm synthetic air. Analysis temperatures  $\geq$  280°C and synthetic air were chosen to avoid stress changes caused by water adsorption<sup>135</sup> and to avoid complications introduced by potentially orientable elastic dipoles present in ceria present below 250°C.<sup>121</sup> As shown in Figure 3.2, two thermal cycles were conducted in synthetic air to ensure reproducibility, and the stress-temperature results were averaged together to produce the values in Figure 3.6. The 10PCO|MgO samples went directly from the PLD chamber to the 1000°C re-oxidation furnace to the XRD and then directly to the synthetic-air-flushed Multibeam Optical Stress Sensor (MOSS) test rig in an attempt to minimize hydration of the MgO substrate. The simultaneously produced 10PCO|YSZ samples were stored in a CaCl<sub>2</sub> containing desiccator for ~2 weeks while the 10PCO|MgO samples were being MOSS tested, before being analyzed.

#### 3.3.4 Chemical Strain Determination

The  $p_{0_2} = 0.21$  chemical strain data was determined by first fitting the 10PCO|YSZ stress-temperature curve with a 3<sup>rd</sup> order polynomial equation over its entire 280-700°C range. The 3<sup>rd</sup> order polynomial fits used here don not have any physical meaning, it was chosen because it can represent the stress vs. temperature relationship on 10PCO|YSZ without picking up the little disturbances in the signal. The low temperature (280-400°C) 10PCO|YSZ stress vs. temperature curve was then fitted with a linear equation, assuming a near constant thermal expansion coefficient for 10PCO and the YSZ. The difference between the linear extrapolation and 3<sup>rd</sup> order polynomial at high temperature was used to measure the amount of temperature-induced chemical stress. The chemical strain was then calculated using the fitted chemical stress and the temperature dependent biaxial moduli obtained from the Dual Substrate method of Section 3.2.2. 10PCO|YSZ was chosen instead of 10PCO|MgO for this purpose because of the lower sample noise shown in Figure 3.6.

Since Dual Substrate measurements were not taken in  $p_{0_2} = 0.021$ , the  $p_{0_2} = 0.021$ chemical strain values of Figure 5a were determined by combining the measured chemical stresses generated by switching from a  $p_{0_2}$  of 0.21 to 0.021 with the temperature dependent biaxial moduli obtained from the Dual Substrate method of Section 3.2.2, and adding the result to the  $p_{0_2} = 0.21$ chemical strain values shown in Figure 3.6.

## 3.4 Results and Discussion

3.4.1 Crystallography and Morphology of the Film



Figure 3.3 Representative X-Ray Diffraction (XRD) results for a) 10PCO|MgO and b) 10PCO|YSZ indexed using CeO<sub>2</sub>, MgO, and YSZ JCPDS card numbers 81-0792, 87-0653, and 70-4436, respectively. The asterisks denote impurity peaks not caused by the 10PCO, as

proven in Figure 3.4b

Figure 3.3 shows representative X-ray Diffraction (XRD) scans of the oxygen reequilibrated 10PCO films. These results indicate that the 10PCO films were phase pure and highly crystallized on both (100) oriented MgO and (100) oriented YSZ substrates. Further, the 10PCO



Figure 3.4 Representative a) survey and b) detailed X-Ray Diffraction (XRD) scans of a bare (100) oriented MgO wafer showing that the 34.2° and 35.2° peaks shown in Figure 3.3

# (denoted by asterisks) were not from the 10PCO film.

films on both substrates had a similar, predominantly (100) preferred orientation. Specifically, the 10PCO on YSZ films displayed only the (100) orientation, while ~97% of the 10PCO on MgO grains were (100) oriented and ~3% of the 10PCO on MgO grains were (111) oriented (based on the ~100:9 intensity ratio of the 10PCO (200):(111) in Figure 3.3a and the 28.5:100 CeO<sub>2</sub> JCPDS PDF #34-394 (200):(111) intensity ratio<sup>136</sup> for a randomly oriented polycrystal). This grain orientation behavior was identical to that reported in the literature for CeO<sub>2-x</sub> on (100) MgO,<sup>137</sup> CeO<sub>2-x</sub> on (100) YSZ,<sup>137-140</sup> and 10PCO on (100) YSZ.<sup>18, 141</sup> A Scherrer Equation<sup>142</sup> analysis indicated that the average 10PCO grain size on the MgO and YSZ substrates was ~28 nm and ~21 nm, respectively. (Note, the limited number of XRD peaks resulting from the 10PCO preferred orientation prevented a more accurate Williamson-Hall<sup>143</sup> grain size determination).

As indicated by the cross-section scanning electron microscopy (SEM) images of Figure 3.5, the 10PCO films on MgO and YSZ were dense and  $235 \pm 2$  nm and  $230 \pm 5$  nm in thickness, respectively. Post analysis SEM and XRD scans (not shown) did not reveal any changes in the crystallographic or microstructural character of the 10PCO films caused by the 25-700°C thermal cycling and elevated temperature holds encountered during wafer curvature testing.



Figure 3.5 SEM Images of (a) 10PCO|MgO and (b) 10PCO|YSZ

3.4.2 Stress vs. Temperature Data

Figure 3.6 shows representative stress-temperature curves for the 10PCO|MgO and 10PCO|YSZ samples taken with a 0.2°C/min cooling rate. The red lines are 3<sup>rd</sup> order polynomial fits to the measured data. For 10PCO|MgO,  $\sigma_{total} = (486.0 \pm 1.638) + (-2.389 \pm 0.001059) \times T + 0.007670 \pm 2.201 \times 10^{-5}) \times T^2 + (-7.020 \times 10^{-6} \pm 1.479 \times 10^{-8}) \times T^3$ and for 10PCO|YSZ,  $\sigma_{total} = (1241.7 \pm 4.065) + (-3.788 \pm 0.02622) \times T + (0.008090 \pm 5.446 \times 10^{-5}) \times T^2 + (-7.562 \times 10^{-6} \pm 3.654 \times 10^{-8}) \times T^3$ . The 3<sup>rd</sup> order polynomial fits used here don not have any physical meaning, they were chosen because they can represent the stress vs. temperature relationship on both samples without picking up the little disturbances in the signal. As demonstrated in Figure 3.7, heating rates faster than 0.2°C/min (0.5°C/min, 1°C/min) gave different stress vs. temperature responses due to the thermal equilibrium issue. However, the stress vs. temperature curve collected with 0.1°C/min is near identical as the data collected with 0.2°C/min. This indicates that 0.2°C/min was slow enough to ensure that the samples remained in thermal equilibrium as the stress-temperature data was collected. The initial increase in film stress with increasing temperature displayed by the Figure 3.6a 10PCO|MgO sample is consistent with the fact that from 280-500°C the 10PCO  $\alpha_{tc}$  value (which ranges from 8 to 14 ppm/K)<sup>114</sup> is less than the 280-500°C MgO  $\alpha_t$  (which ranges from 13 to 14 ppm/K).<sup>110</sup> Similarly, the subsequent decrease in film stress with increasing temperature above ~500°C is consistent with the fact that the 500-700°C 10PCO  $\alpha_{tc}$  (which ranges from ~14 to 24 ppm/K)<sup>114</sup> is greater than the 500-700°C MgO  $\alpha_t$  (which ranges from 14 to 15),<sup>110</sup> due to the onset of chemical expansion in 10PCO. The constant decrease in film stress with temperature for the 10PCO|YSZ sample of Figure 3.6b is consistent with the fact that the 280-700°C 10PCO  $\alpha_{tc}$  (which ranges from 9 to 10 ppm/K).<sup>111</sup>



Figure 3.6 Representative averaged stress vs. temperature plots for a) 10PCO|MgO and b) 10PCO|YSZ. The red lines are fits to the measured data.

It is interesting to note that these thermal-expansion-mismatch induced stresses were in addition to tensile  $\sim$ 580°C 10PCO growth stresses of  $\sim$ 300 and  $\sim$ 250 MPa on MgO and YSZ, respectively (even larger 10PCO growth stresses have been observed in the literature<sup>131</sup>).



Figure 3.7 The effect of cooling rate on the stress vs. temperature measurements of representative 10PCO|YSZ samples. Note, samples tested with either 0.1 or 0.1°C/min cooling rates were considered to be in thermal equilibrium from 280-700°C since the additional tim time at each temperature with a slower 0.1°C/min cooling rate had no effect on the stress-temperature trajectory.

3.4.3 Young's Modulus Measurements from Dual Substrate Measurements

Figure 3.8 shows the temperature-dependent Young's Modulus values measured here in comparison to all the 10PCO *E* measurements presently available in the literature. The essentially 170-180 GPa constancy of 280-700°C GPa Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95- $\delta$ </sub> (CGO) *E* values is likely related to the



Figure 3.8 PCO Young's moduli values measured by the Dual Substrate method compared to the literature measurements. (DS stands for Dual Substrate, NI stands for Nano-Indentation, MOSS stands for Multi-beam Optical Stress Sensor, and XRD stands for X-Ray Diffraction) small magnitude of the 10PCO  $\delta$  encountered here (and discussed later). The slight dip in the

Figure 3.8 E values is likely an artifact of the 10PCO|MgO ~400-500°C fitting error shown in

Figure 3.6. The  $\pm \sim 10\%$  error bars shown in Figure 3.8, calculated using the procedures described in Appendix B, are similar to those reported in other Dual Substrate literature studies.<sup>109</sup>

The *E* values obtained here agree well with the 750°C MOSS stress/XRD stain determined (100) 10PCO *E* value from Sheth *et al.*<sup>117</sup> However, they do not agree as well with the 600°C nanoindentation determined *E* value from Swallow *et al.*<sup>116</sup> This may result from the inherent difficulty in performing reliable high temperature nano-indentation experiments or the fact that unlike all the other studies in Figure 3 which were performed on 10PCO, Swallow *et al.*<sup>116</sup> examined 20PCO. Room temperature extrapolations of the *E* values obtained here agree with the fast (but not the slow) 25°C 10PCO nano-indentation measurements in the literature.<sup>116, 144</sup> This is consistent with the idea that nano-indentation-determined *E* values taken too quickly to be impacted by reorientation of the anelasticity-inducing oxygen-vacancy-generated elastic dipoles<sup>76</sup> present in ceria below 250°C<sup>121</sup> should be similar to the *E* values extrapolated from high temperature ceria samples not containing orientable, oxygen-vacancy-generated elastic dipoles.

3.4.4 Thermo-Chemical Expansion Coefficient from Dual Substrate Measurements

Figure 3.9 shows the temperature-dependent  $\alpha_{tc}$  values measured here in comparison to all the 10PCO  $\alpha_{tc}$  measurements presently available in the literature. Similar to the Figure 3.8 results which do not display a systematic difference between the *E* values obtained from bulk/micro-grained samples compared to those from thin film and/or nano-grained samples, the thin film  $\alpha_{tc}$  values obtained here agreed very well with previous *in situ* XRD literature measurements on bulk, micro-sized grain samples.<sup>114</sup> The  $\pm \sim 4\% \alpha_{tc}$  error bars shown in Figure 3.9, calculated using the procedures described in Appendix B, are similar to those reported for  $\alpha_t$ in other Dual Substrate literature studies.<sup>109</sup>



Figure 3.9 10PCO thermo-chemical expansion coefficients from the Dual Substrate method compared to the literature measurements of Bishop et al. (DS stands for Dual Substrate, XRD stands for X-Ray Diffraction, and Dil stands for Dilatometry).
 3.4.5 Chemical Strain & Oxygen Nonstoichiometry

Figure 3.10a and 3.10b show the measured 10PCO chemical strain, and the oxygen nonstoichiometry extracted from it, respectively, compared to literature values. Interestingly, the measured thin films of Figure 3.10a experience less in-plane chemical strain than bulk 10PCO, but experience a  $\delta$  similar to bulk PCO. This is caused by the lower  $\alpha_c$  values of ~0.07 for (100) oriented, thin film 10PCO<sup>122, 131</sup> compared to ~0.09 for bulk 10PCO.<sup>114</sup> The good agreement



Figure 3.10 10PCO (a) chemical strain and (b) oxygen nonstoichiometry values from the 10PCO YSZ sample compared to the literature measurements

between the Figure 3.10b  $p_{O_2} = 0.21$  thin film  $\delta$  values obtained here and the bulk 10PCO data of Bishop *et al.*<sup>114</sup> may be caused in part, by the relatively low (i.e 300 to -50 MPa) 600-700°C 10PCO film stress stresses encountered here. The  $\delta$  values obtained under a  $p_{O_2}$  of 0.21 and 0.021 are also both in good agreement with other thin film 10PCO studies that did,<sup>115</sup> and did not,<sup>131</sup> utilize precious metal current collectors to determine  $\delta$ . The unphysical (i.e. slightly negative) ~375-500°C chemical strain and oxygen nonstoichiometry values in Figure 3.10 result from spurious differences between the linear and third-order polynomial fits to the data caused by signal drift (i.e. waviness) in the Figure 3.6b data below ~500°C.

# 3.5 Summary

This chapter demonstrates for the first time that wafer curvature measurements can be used to <u>directly</u> measure a variety of disparate and technologically-relevant thin film physicochemical properties (i.e. the oxygen nonstoichiometry, biaxial modulus, thermo-chemical expansion coefficient, and thermal expansion coefficient) under well-characterized film stress states, strain states, temperatures and atmospheric conditions. With application of an externally-derived Poisson's ratio, the Young's modulus was also determined (Note, studies have shown that wafer curvature experiments can also be used to directly measure the Poisson's ratio<sup>118</sup>).

### 4. Curvature Relaxation Measurements

### 4.1 Introduction

Mixed ionic electronic conductors (MIECs) have been used in various applications including solid oxide fuel cells,<sup>3, 145-148</sup> gas separation membranes,<sup>149</sup> oxide memristors,<sup>150, 151</sup> electrostrictive actuators,<sup>152, 153</sup> chemical sensors,<sup>154</sup> catalytic converters,<sup>155</sup> and electrochromic windows.<sup>156</sup> The functionality and performance of MIECs are based on the oxygen transport through/within the material. The oxygen surface exchange coefficient ( $k_{chem}$ ) is one of the kinetic constants that determines the speed of oxygen transport process. Being able to accurately measure the  $k_{chem}$  enables performance evaluation and material selection when designing a device involving a MIEC. However, even for a conventional MIEC like lanthanum strontium ferrite, there is still an ~5 orders of magnitude difference in  $k_{chem}$ .<sup>19</sup> The usage of current collectors during in-situ k<sub>chem</sub> measurements may be one of the reasons for this variation.<sup>23, 157</sup> Therefore, an *in-situ*, contact-free and current collector-free technique is needed to measure  $k_{chem}$  without the influence of a surface-altering noble metal.

This chapter demonstrates that with known oxygen nonstoichiometry ( $\delta$ ), the chemical oxygen surface exchange coefficient ( $k_{\text{chem}}$ ) and oxygen surface exchange resistance ( $R_S$ ) of Pr<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> (10PCO) can all be obtained as a function temperature (T), and oxygen partial pressure ( $p_{O_2}$ ) using *in situ*, non-contact, current-collector-free wafer curvature measurements.

## 4.2 Theory

### 4.2.1 Curvature Relaxation Measurements

According to Eqn 3.5 (Stoney's equation), the biaxial stress of a dense thin film on a dense thick substrate/wafer can be calculated from the curvature of the sample without knowing the biaxial modulus of the film. For a mechano-chemical active material, after an abrupt change in

oxygen partial pressure, the oxygen nonstoichiometry in the thin film changes accordingly, which can be described by the solution of Fick's Second Law <sup>158</sup>:

$$\frac{\delta - \delta_0}{\delta_\infty - \delta_0} = 1 - \exp\left(-\frac{k_{chem}t}{h_f}\right) \tag{4.1}$$

where  $\delta$  is the instantaneous oxygen nonstoichiometry,  $\delta_0$  is the initial oxygen nonstoichiometry,  $\delta_{\infty}$  is the new-pO<sub>2</sub>-equilibrated oxygen nonstoichiometry, k is the chemical oxygen surface exchange coefficient, and t is time.

The change in oxygen nonstoichiometry induces chemical strain, which can be described by equation <sup>159</sup>:

$$\varepsilon_C = \frac{\Delta l}{l} \Big|_T = \alpha_C \Delta \delta \tag{4.2}$$

where  $\varepsilon_c$  is the chemical strain, *l* is the sample length,  $\alpha_c$  is the chemical expansion coefficient. The change in chemical strain induces a change in chemical stress according to Hooke's Law:

$$\Delta\lambda_c = M_f \varepsilon_c \tag{4.3}$$

Combining Eqn 4.2 and 4.3, the film stress changes can be expressed as:

$$\Delta\lambda_c = M_f \alpha_C \Delta\delta \tag{4.4}$$

Then combining Equation 3.5 and 4.4, it yields the following relationship:

$$\Delta \kappa \frac{M_S h_S^2}{6h_f} = M_f \alpha_C \Delta \delta \tag{4.5}$$

where  $\kappa$  is the curvature of the sample.

Since  $M_S$ ,  $M_f$ ,  $h_s$  and  $h_f$  are all constant, the change in curvature is proportional to the change in oxygen nonstoichiometry. Therefore, Equation 4.2 can also be expressed as <sup>19, 106, 160</sup>:

$$\frac{\delta - \delta_0}{\delta_\infty - \delta_0} = \frac{\kappa - \kappa_0}{\kappa_\infty - \kappa_0} = 1 - \exp\left(-\frac{kt}{h_f}\right)$$
(4.6)

The oxygen surface exchange coefficient of thin film with thickness 1000 times smaller than the characteristic thickness  $L_C$  ( $L_C = D/k$ ) can then be obtained by monitoring the curvature change of a bilayer sample.

### 4.2.2 Surface Polarization Resistance

The surface polarization resistance  $(R_S)$  of 10PCO can be expressed as:

$$R_S = \frac{RT}{4F^2 c_o k_q} \tag{4.7}$$

where R is the ideal gas constant, T is the absolute temperature, F is Faraday's constant,  $c_o$  is the lattice oxygen concentration, and  $k_q$  is the electrical oxygen surface exchange coefficient.  $c_o$  was calculated from  $\delta$  reported in the literature<sup>161</sup> with the following relationship:

$$c_o = \frac{4(2-\delta)}{a^3 * N_A}$$
(4.8)

where  $N_A$  is Avogadro's Number and *a* is the 10PCO lattice constant reported in the literature at different temperatures.<sup>112</sup>  $k_q$  is calculated from the chemical oxygen surface exchange coefficient (k<sub>chem</sub>) using a simplified version of Equation 6.102 from ref<sup>162</sup>:

$$k_q = \frac{k_{chem}}{\gamma * t_e} \tag{4.9}$$

where  $t_e$  is the transference number of the electrons,  $\gamma$  is the thermodynamic factor with the definition (detailed derivation of thermodynamic factor can be found in Ref 163): <sup>163</sup>

$$\gamma = \frac{1}{2} * \left[ \frac{\partial \ln(pO_2)}{\partial \ln(2 - \delta)} \right]$$
(4.10)

The oxygen nonstoichiometry data used for the Rs calculation are from chapter 3.161

## 4.3 Experimental Methods

## 4.3.1 Sample Preparation

Details about sample preparation can be found in Section 3.3.1. In this work, only 10PCO|YSZ was measured by the curvature relaxation technique.

## 4.3.2 Crystallography and Morphology Characterization

The crystallography and morphology characterization of 10PCO thin film was conducted with XRD and SEM. Details about the parameters of those measurements can be found in Section 3.3.2.

#### 4.3.3 Curvature Relaxation Measurements

Prior to high temperature curvature relaxation measurements, the 10PCO|YSZ samples were heated up to 500°C in synthetic air with a 5°C/min heating rate. Curvature relaxation measurements were then conducted on 10PCO|YSZ samples from 500 to 600°C with 25°C increments, following the procedures described in detailed previously.<sup>19, 160, 164, 165</sup> Wafer curvature relaxations were triggered by switching between 100 sccm of synthetic air (20% O<sub>2</sub>-80% Ar) and 100 sccm of 10% synthetic air-90% Ar (i.e. 10 times diluted air). To minimize possible Si contamination from the fused quartz curvature relaxation test rig (which is a time-dependent process), only 1 reduction and 1 oxidation cycle were measured at each temperature between 500-575°C. Multiple oxidation/reduction cycles were then tested at 600°C, as shown in Figure 4.1, to determine if the curvature measurements were reproducible with redox cycling.

# 4.4 Results and Discussion

4.4.1 Crystallography and Morphology of the Film

Details about the film orientation and film thickness can be found in Section 3.4.1. The 10PCO thin film has a (100) preferred orientation on YSZ substrate and has a uniformed thickness of ~230 nm.

4.4.2 Relaxation Data and Curve Fitting

Figure 4.1 shows representative stress redox cycle data for a 10PCO film  $k_{chem}$  tested at 600°C. While a steady-state equilibrium was obtained after each  $p_{O_2}$  cycle (allowing a reliable k



Figure 4.1 Representative raw curvature relaxation data for a 10PCO|YSZ sample at 600°C



determination), the equilibrium film stress after each oxidation and reduction cycle was slightly altered (shown in the red dotted guideline). This behavior is similar to an alteration in the

Figure 4.2 a) Normalized curvature fits to the 10PCO|YSZ data, and b) ln(1-Normalized Curvature) plots for the 10PCO|YSZ samples. Note that the generally good single time constant (red line) fits to the data of part a) and a single slope in the ln(1-Normalized Curvature) plots in part b) at times before the equilibrium state is reached suggest only one mechano-chemically active process is active with redox cycling between synthetic air and 10% diluted synthetic air.

10PCO|YSZ equilibrium film stress with redox cycling reported in previous 10PCO measurements<sup>131, 134</sup> and attributed to stress-relaxing alterations of the grain boundary structure.<sup>131</sup>

Figure 4.2 shows representative curve fitting and the alternatively plotted relaxation data. The fact that only one physical process is observed in Figure 4.2b suggests that whatever the mechanism, it is purely the result of, and occurs on the same timescale, as oxygen exchange



Figure 4.3 Raw wafer curvature relaxation data for the 10PCO|YSZ samples from all tested temperatures (500, 525, 550, 575, and 600°C)

into/out of the film.

Additionally, Figure 4.3 shows the relaxation data from all tested temperature, which shows that the 10PCO thin film is mechano-chemical active and the curvature relaxations have good signal to noise ratio from 500 to 600°C.

## 4.4.3 Oxygen Surface Exchange Coefficient of 10PCO Thin Film

Figure 4.4 shows the oxygen surface exchange coefficient values, in comparison with other literature measurements. As seen in many other studies on various oxygen exchange materials,<sup>160,</sup> <sup>166, 167</sup> the oxidation kinetics were faster than the reduction kinetics. As postulated in other studies, <sup>166, 167</sup> this is likely due to the larger  $\delta$  at the beginning of the oxidation process than at the



Figure 4.4 10PCO chemical oxygen surface exchange coefficients from the curvature relaxation method compared to the literature measurements (κR stands for Curvature Relaxation. MB stands for Micro-Balance, EIS stands for Electric Impedance Spectroscopy and OR stands for Optical Relaxation). The curvature-determined k error is less than the size

of the symbol

beginning of the reduction process, which speeds up the initial oxygen exchange. The measured k values displayed Arrhenius behavior over the entire 500-600°C range, which is consistent with only one oxygen exchange process being active. Tests on select samples performed with smaller  $p_{0_2}$  step sizes using air and 5 times (instead of 10 times) diluted air gave k values with the same  $0.9 \pm 0.1$  eV activation energy as those in Figure 4.4, but with absolute values between the reduction and oxidation data of Figure 4.4, suggesting that the oxygen surface exchange kinetics remained linear at a 10 times dilution, as observed previously in the literature for other materials.<sup>167</sup>

The 600°C k values measured here agreed exactly with those obtained from the optical relaxation studies of Zhao *et al.*<sup>134</sup> even though the samples were subjected to different thermal histories before testing (Zhao *et al.*<sup>134</sup> do not report re-equilibrating their samples in 1000°C air before testing, as was done here) and the specimens were grown in different Pulsed Laser Deposition (PLD) chambers that likely contain different impurities. The likely source of this agreement is that, as shown in Table 4.1, the samples used for both studies were produced in the same manner, had similar final microstructures, had similar final stress states, did not use precious metal current collectors, and were both surface etched before testing.

Samples	Deposition Technique	Orientation	Current Collectors	Deposition Temperature (°C)
PCO YSZ from This Work	Pulsed Laser Deposition	(200)	No	680
PCO YSZ from Zhao et al.	Pulsed Laser Deposition	(200)	No	725

Table 4.1 Comparison of PCO|YSZ samples between this work and Zhao et al.

In contrast, the measured k values were much lower than those determined from microbalance and EIS studies. Although Simons *et al.*<sup>166</sup> attributed their observed k enhancement to grain boundary effects in their randomly-oriented polycrystalline films,<sup>166</sup> this seems unlikely

to be able to explain the ~1000 times difference with the present results because other literature studies have only observed *k* differences within an order of magnitude for ceria<sup>168</sup> or lanthanum strontium cobalt iron oxide<sup>169</sup> when examining thin films with intentionally-varied crystallographic orientations. Instead, based on the documented ability of precious metals such as Pt,<sup>170-172</sup> Ag,<sup>170,173</sup> Au,<sup>171</sup> to catalyze the oxygen exchange reaction on a variety of MIEC materials (including PCO), it is more likely that catalytically active Pt migrated onto the surface of Simons *et al.*'s 10PCO films from the underlying Pt current collector during subsequent 10PCO deposition and/or testing. Catalytic enhancement provided by the porous Au current collectors covering Chen *et al.*'s 10PCO films may also explain why their EIS-measured *k*'s were higher than those measured here. Interestingly, the similar activation energies obtained for Chen *et al.*'s study and the present work suggests that surface decorating Au particles do not change the 10PCO oxygen incorporation pathway, but instead simply increased the surface area available for incorporation via a spill-over mechanism.

Although precious metal electrode *k*-enhancement may be an exciting pathway to realize improved device performance, the 10PCO *k* results in Figure 7 contribute to the growing body of evidence<sup>170, 171, 173</sup> indicating that *k* measurements obtained from past studies performed with significant amounts of intentional or inadvertent precious metal surface coverage may be artificially enhanced. These include 1) electrochemical impedance spectroscopy,<sup>18</sup> mechanical impedance<sup>174</sup> or other experiments performed with porous, surface-coating precious metal current collectors, 2) electrical conductivity relaxation experiments performed with interdigitated precious metal electrodes,<sup>175-178</sup> 3) resonant microbalance experiments using supporting Pt layers,<sup>166</sup> etc. As such, the *k* values obtained from such studies would not be expected to accurately describe the performance of conventional MIEC micro-porous, MIEC micro-composite, or MIEC infiltrated

electrodes (since the MIEC surfaces in those electrodes are unlikely to be decorated with significant amounts of precious-metal catalyst).

## 4.4.4 Oxygen Surface Exchange Resistance

Figure 4.5 shows the oxygen surface exchange resistance values measured here, compared with the literature. Consistent with the behavior observed in Figure 4.4, the wafer curvature measured 10PCO  $R_S$  values were significantly higher than those obtained from the precious-metal-contaminated EIS experiments of Chen *et al.*<sup>18</sup> The slightly higher wafer-curvature-determined  $R_S$ 



Figure 4.5 10PCO oxygen surface polarization resistance (R<sub>s</sub>) values obtained here compared to the literature values for 10PCO, LSCF, LSF, LSC, and SSC

activation energy, compared to that from Chen *et al.*,<sup>18</sup> comes from the slightly different oxygen nonstoichiometries shown in Figure 3.10. That being said, the 1.5  $\pm$  0.1 eV 10PCO wafercurvature-determined  $R_S$  activation energy measured here is similar to the activation energy of other many MIEC oxygen exchange materials.<sup>179, 180</sup>

Figure 4.5 also shows that the wafer-curvature measured 10PCO  $R_S$  values were two orders of magnitude higher than the  $R_S$  values of the SOFC material La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (LSCF). Unlike EIS measurements performed on large surface area samples requiring current collectors to distribute the charge, the small lateral dimensions of the microelectrode samples used to measure the La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3-δ</sub> (LSF),<sup>179</sup> La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> (LSC),<sup>179</sup> LSCF,<sup>179, 180</sup> Sr<sub>0.5</sub>Sm<sub>0.5</sub>CoO<sub>3-δ</sub> (SSC),<sup>179</sup> and Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF)<sup>179</sup>  $R_S$  values reported in Figure 8 ensured that these EIS microelectrode  $R_S$  values could be measured without the presence of precious metal current collectors. The trustworthiness of these EIS microelectrode  $R_S$  values is also indicated by the fact that the open-circuit performance of LSF, LSFC, LSCF, LSC, and SSC infiltrated SOFC cathodes can be successfully modeled using them.<sup>181-184</sup> Taken together, the data in Figure 8 suggests that low-stress, precious-metal-free, (100)-oriented 10PCO is a poor choice as a SOFC cathode material. However, with future strain engineering, grain boundary engineering, precious metal surface decoration, etc. PCO may become SOFC cathode material.

#### 4.5 Summary

This chapter demonstrates that an *in-situ*, contact-free, current-collector-free technique can be used to evaluate the oxygen surface exchange kinetics of 10PCO thin film. With the knowledge of oxygen nonstoichiometry from chapter 3, the oxygen surface exchange resistance can also be calculated. The difference between EIS and curvature relaxation measurements suggests that previous measurements using precious-metal current collectors, support layers, etc. may report spuriously large oxygen surface exchange coefficient values and spuriously low oxygen surface exchange resistances. The comparison of oxygen surface exchange resistance between 10PCO and other commonly used MIECs suggests that 10PCO may not be an effective material for solid oxide fuel cell applications.

#### 5. HTXRD (High Temperature X-Ray Diffraction) - MOSS Combined Test

### 5.1 Introduction

Ceria and doped ceria have been widely used in various applications including solid oxide fuel cells (SOFCs),<sup>146, 185, 186</sup> solid oxide electrolysis cells (SOECs),<sup>69</sup> catalytic converters,<sup>155</sup> chemical sensors,<sup>187, 188</sup> and electrochromic devices.<sup>189</sup> There are extensive studies exploring the thermal,<sup>114, 190-194</sup> mechanical,<sup>144, 193-196</sup> electrical<sup>197-200</sup> and chemical properties<sup>18, 114, 201-204</sup> of these materials in order to characterize, and improve the performance and mechanical stability of such devices. However, at high temperature, due to the limitation of measurement platforms and the geometry of thin film samples, there is a lack of data for Young's modulus of thin film ceria and doped ceria at high temperature.<sup>205, 206</sup>

Chapter 3 showed that the Young's modulus and the thermo-chemical expansion coefficient can be obtained by combining two sets of stress vs. temperature data of two identical thin films on top of two different substrates.<sup>194</sup> The results showed that the Young's modulus stays constants at high temperature. However, this method requires two near-identical film to have a similar orientation on different substrates, which is not always applicable for every material. Additionally, the error generated from both sets of data significantly boost the error bar of the Young's modulus, which is ~15% of the actual value. Therefore, using another approach to measure high-temperature Young's modulus and the thermo-chemical expansion coefficient with one thin film sample can be beneficial for general measurements on other thin film materials in the future. The Young's modulus and the thermo-chemical expansion coefficient from an alternative measurement method can also provide a validation to the dual substrate work.

In this chapter, a  $Pr_{0.1}Ce_{0.9}O_{2-\delta}$  (10PCO) | 9.5% yttria stabilized zirconia (YSZ) bilayer sample was measured using high temperature X-Ray diffraction (HTXRD) and multi-beam optical stress sensor (MOSS). It shows that by combing the strain measurement from HTXRD and the stress measurement from MOSS, the thermo-chemical expansion coefficient and Young's modulus of the (100)-oriented 10PCO thin film can be extracted at different temperatures between 500~700°C.

### 5.2 Theory

By monitoring the position change of the 10PCO (200) peak, according to Bragg's law, the lattice constant of 10PCO thin film at different temperatures can be extracted. Then, the out-of-plane strain can then be obtained through the following equation:

$$\varepsilon_z = \frac{\Delta a}{a_0} \tag{5.1}$$

where a is the instantaneous lattice constant of 10PCO, and  $a_0$  is the lattice constant at room temperature.

The out-of-plane strain can also be expressed as the sum of thermal strain and the strain from Poisson's expansion/contraction (i.e. the contribution of strain along the in-plane directions), which can be expressed as:

$$\varepsilon_z = \alpha_{tc} \Delta T - \frac{2\nu}{1-\nu} (\alpha_s - \alpha_{tc}) \Delta T$$
(5.2)

where  $\alpha_s$  is the thermal expansion coefficient of the substrate and v is the Poisson's ratio of 10PCO. Differentiating Eqn 6 with respect to temperature leads to:

$$\frac{\partial \varepsilon_z}{\partial T} = \alpha_{tc} - \frac{2\nu}{1 - \nu} (\alpha_s - \alpha_{tc})$$
(5.3)

The  $\varepsilon_z$  vs. temperature data was fitted with the following equation:

$$\varepsilon_z = A e^{BT} \tag{5.4}$$

where A and B are all fitting constants. The exponential part  $(Ae^{BT})$  represents the chemical expansion of the 10PCO thin film at high temperature, which corresponds to the following relationship:

$$\Delta \varepsilon_C \propto \Delta \delta \propto \exp\left(\frac{\Delta G_{formation}}{kT}\right)$$
(5.5)

where  $\Delta \varepsilon_c$  is the change in chemical strain,  $\Delta \delta$  is the change in oxygen nonstoichiometry, and  $\Delta G_{formation}$  is the formation energy of oxygen vacancy in 10PCO. By differentiating the fitting equation with respect to temperature,  $\frac{\partial \varepsilon_z}{\partial T}$  can be obtained. The thermal expansion coefficient of YSZ substrate ( $\alpha_s$ ) was also measured via HTXRD. With known v (v=0.33 for 10PCO),<sup>205</sup> the thermo-chemical expansion coefficient of 10PCO can be extracted. Detailed error analysis for this methodology is described in Appendix C of the supplementary material.

#### 5.3 Experimental Details

### 5.3.1 Sample Preparation

Detailed sample preparation for 10PCO|YSZ can be found in Section 3.3.1.

## 5.3.2 Microstructural and Crystallographic Characterization

The cross-sectional images were taken via a TESCAN MIRA3 Field Emission Scanning Electron Microscope (SEM) (TESCAN Inc.) with a 20 kV beam voltage on the sample with ~5 nm Pt coating.

XRD measurements were conducted on a Rigaku SmartLab Diffractometer with a 44 kV voltage and a 40 mA current. A survey scan was conducted between 20 and 80° with a 0.01° step size and a 1 second dwell time.

5.3.3 High Temperature X-Ray Diffraction Measurements

10PCO|YSZ was first heated up to 700°C, then cooled down with a 1°C/min cooling rate, during which the positions of the (200) 10PCO peak were measured with 25°C increments in air.
The range of the scans was 31~34°, the increment was 0.01° and the dwelling time was 1 second. The sample dwell time was set for 10, 20, 30, 40, 40, 50, 60, 60 min before each measurement at 675, 650, 625, 600, 575, 550, 525, 500°C, respectively. For each temperature, 3 measurements were taken to check for thermal/chemical equilibrium (25 and 700°C excluded).

#### 5.3.4 Stress Measurements

Detailed information of stress measurements via multi-beam optical stress sensor (MOSS) can be found in Section 3.3.3 for 10PCO|YSZ sample.

#### 5.4 Results and Discussion

### 5.4.1 Microstructural and Crystallographic Characterzation

The XRD survey scan of the 10PCO|YSZ sample in Figure 5.1 shows that the 10PCO film has a preferred (100) orientation on the (100)-oriented YSZ substrate. The orientation of the 10PCO thin film is consistent with other studies of 10PCO thin films on (100)-oriented YSZ substrates.<sup>18, 23, 57, 204-207</sup> The full width half max (FWHM) of the (200) 10PCO peak is 0.682° and the FWHM of the (200) YSZ is 0.079°. Since the single crystal YSZ substrate is strain free and has a grain size of 2.54 cm, the FWHM of the (200) YSZ is considered as instrumental broadening. According to the equation:

$$B_M^2 = B_I^2 + B_S^2 \tag{5.6}$$

where  $B_M$  is the measured peak broadening,  $B_I$  is the broadening from the instrument, and  $B_S$  is the peak broadening from the sample.<sup>208</sup> Applying the  $B_M$  and  $B_I$  values mentioned above to Eqn 5.6, a  $B_S$  value of 0.677° was obtained. Based on Sherrer's equation<sup>209</sup>:an estimated crystallite size of ~21 nm was obtained on the 10PCO|YSZ sample. Although a more accurate Williamson-Hall method would be more suitable for the grain size estimation,<sup>210</sup> the limited number of peaks resulted from the preferred orientation, which hinders the implementation of this approach. Therefore, the grain size reported here is the lower limit without considering the strain broadening. Additionally, the film thickness of the 10PCO|YSZ sample is  $\sim$ 230 nm according to the SEM image shown in Figure 3.5. Comparable grain size was obtained for 10PCO (400) peak with a  $\sim$ 39 nm grain size.



Figure 5.1 X-Ray diffraction survey scan of 10PCO|YSZ at 25°C, the asterisk denotes the (400) YSZ diffraction peak from tungsten radiation

As shown in Figure 5.2, the pole figure of 10PCO|YSZ sample indicates the presence of low-angle grain boundaries within the 10PCO thin film. Therefore, the brick-layer-model, as reported by Sheth et al,<sup>117</sup> was not used here for the analysis of thermo-chemical expansion coefficient and Young's modulus because the grain interior and the low-angle grain boundary of doped ceria have similar structure and near-identical oxygen vacancy formation energy.<sup>211</sup> Therefore, the brick-layer-model, which typically requires significantly different grain boundary and grain interior properties (2.5~5 times difference in expansion coefficient),<sup>212</sup> are not used in this situation.



Figure 5.2 Pole figure and zoomed-in image of (111) peak of preferred-oriented 10PCO thin

film at room temperature

# 5.4.2 HTXRD Characterization

Figure 5.3 shows the representative XRD scans of the (200) 10PCO peak at different temperatures during cooling of the sample. As the temperature increases, the (200) peak shifts to a lower 2-theta value, which indicates an expansion of the lattice in PCO thin film.



Figure 5.3 Raw data summary of HTXRD measurements from 25 to 700°C

Furthermore, as shown in Figure 5.4, the full width half max of the peak at each temperature didn't change, suggesting no grain growth or grain growth related strain during the measurements. Therefore, the peak shift in Figure 5.3 is mainly caused by the thermo-chemical expansion of the lattice.



Figure 5.4 Full width half max of (200) 10PCO peak at different temperatures during

HTXRD measurements

Figure 5.5 shows the XRD scans of (400) YSZ peak at different temperatures. As the temperature increases, the (400) peak shifts to a lower 2-theta value, which indicates an expansion of the YSZ lattice.



Figure 5.5 XRD scans of (400) YSZ peak at different temperatures during HTXRD

measurements



Figure 5.6 Peak fitting of HTXRD data using Pearson VII function

Figure 5.6 shows the peak fitting for 10PCO thin films. All the HTXRD peaks were fitted with the Pearson VII function to obtain the peak position for strain calculation. As shown in the plot, the Pearson VII function yields a good fit of HTXRD peaks at each temperature.

5.4.3 Out-of-Plane Strain of the 10PCO Thin Film

Figure 5.7 shows the out-of-plane strain values calculated from HTXRD data. The strain values increase as the temperature rises from 500 to 700°C, which agrees with the trend observed in other studies,<sup>114, 213</sup> indicating thermal and/or chemical expansion of the 10PCO film. The dashed line is the fitting line using Eqn 5.4. The data are well-represented with a 0.999 R<sup>2</sup> value.



Figure 5.7 Out-of-plane thermo-chemical strain and its fitting of 10PCO|YSZ sample

Note that the out-of-plane strain value reported in Figure 5.7 is a combination of the grain interior expansion and Poisson's expansion/contraction (in-plane strain contribution). Therefore, a direct comparison with strain values from dilatometry is not appropriate in this situation.

5.4.4 Thermal Expansion Coefficient of YSZ

Figure 5.8 shows the thermal expansion coefficient of YSZ based on the (400) peak position change of the YSZ substrate. The thermal expansion coefficient stays almost constant at  $\sim 10.3 \text{ ppm}^{\circ}\text{C}$  from 25 to 700°C.



Figure 5.8 Thermal expansion coefficient of YSZ substrate

## 5.4.5 Thermo-Chemical Expansion Coefficient via HTXRD

Figure 6.9 shows the thermo-chemical expansion coefficient of 10PCO measured in this work, compared with other literature studies.<sup>23, 114</sup> The thin film value measured in this work is comparable with both microcrystalline and thin film data in the literature studies.<sup>23, 114</sup> The



Figure 5.9 Thermo-chemical expansion coefficient of 10PCO measured from this work,

### compared with other literature studies

similarity between bulk and thin film sample is consistent with what Sheth et al. reported at  $pO_2=0.21$ .<sup>206</sup> Additionally, for film with preferred-orientation, it is reported that there is no difference for oxygen vacancy formation energy for between bulk and thin film samples due to the structural similarity between grain interior and low angle grain boundary.<sup>211</sup> Therefore, because of the high oxygen partial pressure and the low angle grain boundaries, the difference between the

thermo-chemical expansion coefficient of bulk and thin film samples is either negligible or nonexisting. The thermo-chemical values from the HTXRD measurements is slightly lower than the values from dual substrate measurements, this variation is expected since:

(i) Unlike the dual substrate method, which requires two samples (namely 10PCO|YSZ and 10PCO|MgO), the HTXRD measurements were conducted on one sample (10PCO|YSZ). Besides, the calculations to obtain thermo-chemical expansion coefficient are different for these two methods. Therefore, a small variation is expected between these two data sets.

(ii) The increment of the HTXRD measurements is 25°C while the increment of dual substrate method is 0.1°C. Therefore, the fitting for the stress vs. temperature data used in the dual substrate method is more accurate than the out-of-plane strain fitting used in HTXRD measurements. As a result, the difference in curve fitting propagates and then generates the difference in thermo-chemical expansion coefficient.

## 5.4.6 Young's Modulus via HTXRD-MOSS

Figure 5.10 shows that by combining the stress data from MOSS with the strain data from HTXRD, the Young's modulus of 10PCO thin film can be determined. The slope of the linear fit between stress change and strain change is the Biaxial modulus of the 10PCO thin film. Assuming a Poisson's ratio of 0.33, the Young's modulus can be calculated.



Figure 5.10 Stress change vs. strain change plot of 10PCO thin film

Figure 5.11 shows Young's modulus of 10PCO measured in this work in comparison with other literature data.<sup>23, 144, 205</sup> Young's modulus is nearly constant with temperature at a value of ~165 GPa and it agrees well with the data reported by Sheth et al. at 750°C.<sup>206</sup> However, it does not agree with the nano-indentation data at either 600°C or 25°C. The difference at 600°C might



*Figure 5.11 Young's modulus measured in this work, compared with other literature studies.* be caused by the difficulty in performing the nano-indentation at high temperature or a different dopant level (20PCO was used by Swallow et al.).<sup>205</sup> The difference between slow-loading room temperature nano-indentation and this work might result from the reorientation of the elastic dipole caused by oxygen vacancy formation, where the dipoles resulted from the formation of oxygen

vacancies were re-oriented towards a preferred direction due to the effect of an external electric field or force.<sup>144</sup> The difference between fast-loading room-temperature nano-indentation and this work might be that the loading speed of a fast-loading nanoindentation is still not able to get rid of the dipole reorientation effect.

## 5.5 Summary

This Chapter demonstrates that the thermo-chemical expansion coefficient and Young's modulus of a thin film can be extracted by combining the HTXRD strain measurements and MOSS stress measurements. It also shows that with the HTXRD-MOSS method, the magnitude of the error bar for thermo-chemical expansion coefficient and Young's modulus were significantly reduced. The data from HTXRD-MOSS is comparable with other literature studies, especially with the work in Chapter 3, which validates the reliability of dual substrate method.

### 6. kchem Measurements Compared with Other Electrode-Free Techniques

### 6.1 Introduction

As discussed in previous sections, MIECs have been widely used in various applications. The functionality and performance of MIECs are based on the oxygen transport through/within the material. The oxygen surface exchange coefficient ( $k_{chem}$ ) is one of the kinetic constants that determines the speed of the oxygen transport process. Being able to accurately measure the  $k_{chem}$  enables performance evaluation and material selection when designing a device involving MIEC. However, even for a conventional MIEC like lanthanum strontium ferrite, there is still an ~5 orders of magnitudes difference in  $k_{chem}$ . The use of a current collector during in-situ  $k_{chem}$  measurements may be one of the reasons for this variation.<sup>23, 157</sup> Therefore, an *in-situ*, contact-free and current-collector-free technique is needed to measure  $k_{chem}$  without the influence of surface-altering noble metal.

In this work, the  $k_{chem}$  of two near identical SrTi<sub>0.65</sub>Fe<sub>0.35</sub>O<sub>3- $\delta$ </sub> (STF35) thin films were deposited on yttria doped zirconia (YSZ) single crystals and measured *in-situ* by curvature relaxation ( $\kappa$ R) and optical relaxation (OTR) to validate the consistency of various contact-free, current collector-free, *in-situ* k<sub>chem</sub> characterization techniques.

## 6.2 Theory

For STF35, when there is no interaction between the oxygen vacancies (the dilute case), there is a linear relationship between the change of  $Fe^{4+}$  and the change of the optical absorption coefficient.<sup>214,215</sup> The transmitted light intensity is related with the change of the optical absorption coefficient:

$$\Delta I = I_0 \exp(-\Delta \alpha L) \tag{7.1}$$

where  $\Delta I$  is the change in transmitted light intensity,  $I_0$  is the incident light intensity,  $\Delta \alpha$  is the change in optical absorption coefficient, and L is the thickness of the sample.

Similar to curvature relaxation, the relaxation curve of transmitted light intensity can be fitted by a solution of Fick's second law:

$$\frac{\delta - \delta_0}{\delta_\infty - \delta_0} = \frac{\ln I - \ln I_0}{\ln I_\infty - \ln I_0} = 1 - \exp\left(-\frac{k_{chem}t}{h_f}\right)$$
(7.2)

where the subscripts have similar meanings as mentioned above.

### 6.3 Experimental Details

## 6.3.1 Sample Preparation

The STF35 target was manufactured by a solid state diffusion process. Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SrCO<sub>3</sub> were grounded together, pressed uniaxially and then isostatically at 300 MPa at room temperature. The pressed pellet was sintered at 1425°C for 6 hours with 5°C/min heating and cooling rates. The substrates for curvature relaxation measurements were annealed at 1450°C for 20 hours to release the residual stress in the substrate.

A ~200 nm thick STF35 thin film was deposited on a 200-micron thick, one side polished, (100)–oriented, 1 inch diameter, 13% YSZ substrate (MTI Corporation, CA) via PLD for curvature relaxation measurements.

A ~70 nm thick STF35 thin film was deposited on a two-sides polished, (100)-oriented, 10\*10\*0.5 mm, 13% YSZ substrate (Dalian Keri Optoelectronic Technology Co. Ltd., Dalian, China) via PLD for optical relaxation measurements.

The films were deposited at 700°C with 5 Pa  $O_2$  with 75~80 mJ laser power and 5 Hz pulse frequency. The target rotation speed was 25°/s and the substrate rotation speed was 10°/s. The target to substrate distance was 55 mm. After the deposition, the samples were cooled in 20 Pa  $O_2$ 

with  $10^{\circ}$ C/min cooling rate. The samples for both curvature relaxation and optical relaxation were aged at 850°C at pO<sub>2</sub>=0.21 to re-equilibrate their oxygen content.

6.3.2 Crystallographic Characterization

The XRD measurements were made with a Rigaku SmartLab 9kW AMK instrument. The XRD signal was measured from 10 to 90° with a scan rate of 1°/min with 45 kV voltage and 40 mA current.

6.3.3 Curvature Relaxation Measurements

The relaxation of curvature was triggered by an abrupt change in oxygen partial pressure, between compressed air ( $pO_2=0.21$ ) and 10% air diluted in N<sub>2</sub> ( $pO_2=0.021$ ). The k<sub>chem</sub> values were measured from 850°C to 700°C with 25°C increments.

## 6.3.4 Optical Relaxation Measurements

The optical relaxation was performed by switching between synthetic air (20%  $O_2$  - 80%  $N_2$ ) and 5 times diluted synthetic air (4%  $O_2$  – 96%  $N_2$ ). The k<sub>chem</sub> values were measured from 750 to 580°C.

## 6.4 Results and Discussion

# 6.4.1 XRD Characterization

Figure 6.1 shows the representative X-ray diffraction scan of one of two STF35|YSZ samples, indicating a well-crystallized STF35 thin film. The peaks at ~32 and 68° show that the film is (110) preferred-oriented.



*Figure 6.1 Representative XRD scan for STF35*|*YSZ sample* 

## 6.4.2 Curvature and Optical Relaxation of STF35 Thin Films

Figure 6.2 shows the raw data for the curvature relaxation (200 nm STF35 thin film) and optical relaxation measurements (70 nm STF35 thin film) at 700°C. After an abrupt oxygen partial pressure change, the curvature and the transmitted light intensity changed accordingly, indicating an oxygen transport process in the STF35 thin film. The difference of the equilibration times between the optical and curvature relaxations is the result of different STF35 film thicknesses. The

oscillation in the curvature relaxation was caused by the vibration of the testing environment, and the oscillation in the optical relaxation was caused by the thermal vibration at high temperature.



Figure 6.2 Raw data of (a) curvature relaxation and (b) optical relaxation at 700°C



Figure 6.3 Representative curve fitting of (a) curvature relaxation and (b) optical relaxation of reduction relaxation at 700°C

Figure 6.3 shows the representative curve fit of the  $\kappa R$  and the OTR using Eqn 4.6 and Eqn 7.2, respectively. Additionally, the two relaxation curves can both be fitted with one relaxation time constant, indicating there is only one relaxation process happening during the relaxation period.

### 6.4.3 Oxygen Surface Exchange Coefficient Comparison

Figure 6.4 shows  $k_{chem}$  measured by  $\kappa R$  and OTR. Both techniques obtained similar  $k_{chem}$ and activation energy values. The data range of kR and OTR are different because the flush time limitation (when the rate limiting step is the process of gas refilling the testing chamber) appeared above 725°C for OTR measurements and due to the slow curvature relaxation response at temperatures below 700°C. As a result, only one temperature point was measured by both kR and OTR. Although the film thicknesses were different for the samples used in  $\kappa R$  (200 nm) and OTR (70 nm), the oxygen transport process was dominated by the oxygen surface exchange because the film thicknesses for both samples are well below the characteristic thickness of the STF35 (no actual characteristic thickness data for STF35, 10<sup>-1</sup>~10<sup>-3</sup> cm for conventional MIEC materials).<sup>18,</sup> <sup>31</sup> Therefore, similar  $k_{chem}$  values should be expected for the  $\kappa R$  and OTR samples. Additionally, the values at 700°C are comparable for both techniques, but it is still not solid proof to validate the current-collector-free techniques. The variation between the  $\kappa R$  and OTR could be a result of different gas compositions used for testing. For  $\kappa R$ , the usage of compressed air may introduce carbon dioxide, which could potentially form a Sr(CO<sub>3</sub>)<sub>2</sub> layer at the surface, thus deteriorating the oxygen surface exchange kinetics. In conclusion, the similarity between the data reported by  $\kappa R$ and OTR showed a promising start in validating different current collector-free techniques.



Figure 6.4 Comparison of kchem values measured from curvature relaxation (kR) and optical

relaxation (OTR)

# 6.5 Summary

In this work,  $k_{chem}$  measurements were conducted on two near identical STF35 thin film with two current collector-free techniques, namely curvature relaxation and optical relaxation. The  $k_{chem}$  values from the two data sets are comparable, which indicates a promising start for validating the  $k_{chem}$  measurements of different current-collector-free techniques. However, the reasons for the difference between two data sets are still unclear. Further investigation is needed to identify the cause of this variation.

## 7. 7. Effect of Silicon Contaminants

## 7.1 Introduction

The oxygen surface exchange coefficient ( $k_{chem}$ ) is crucial to a variety of applications. It determines the current density, efficiency, and response time for applications like solid oxide fuel cells, <sup>64-66, 68</sup> electrolysis cells, <sup>69-72</sup> gas separation devices,<sup>77</sup> catalytic converters,<sup>80</sup> gas sensors,<sup>78</sup> and memristors.<sup>216</sup> Typically, a group of materials called mixed electronic conductors (MIECs) are used for these applications for their fast oxygen surface exchange process. Praseodymium doped ceria (PCO), for example, is one of the most studied of MIEC materials because (a) it can exchange oxygen with the surrounding gas atmosphere in air at elevated temperatures <sup>18</sup> (b) it has the well-studied defect chemistries,<sup>57, 204, 207</sup> mechanical properties, <sup>144, 161, 205</sup> and electrochemical properties.<sup>18</sup> Those advantages make it an ideal model material for studying oxygen surface exchange behavior. During the oxygen exchange process, PCO goes through the following defect reaction:<sup>29, 217</sup>

$$2Pr'_{ce} + V_{\ddot{o}} + \frac{1}{2}O_2 \to 2Pr^X_{ce} + O^X_0$$
(5.1)

However, surface exchange reactions of MIEC materials can be affected by impurities,<sup>218-232</sup> Siliceous contaminants, for example, are common impurities that can be introduced during fabrication and operation. <sup>226, 227, 233-235</sup> It can hinder the surface exchange reactions of commonly used MIEC materials like lanthanum strontium cobalt iron oxide <sup>228-230</sup> and lanthanum strontium cobalt oxide <sup>231</sup>. It was also reported that the bulk conductivity of ceria-based materials can be easily affected by Si.<sup>236</sup> Furthermore, there is no systematic, quantitative study about the effect of Si contaminants in the literature.<sup>232</sup> Especially for the surface exchange process, knowledge of the chemical environment at the surface is crucial for  $k_{chem}$  measurements.

Therefore, the objectives of this work were to determine the surface content of the PCO thin films after the aging process in the Si-rich environment, and to measure the  $k_{chem}$  values for the aged PCO thin films. These objectives were achieved by doing the *in-situ*, contact-free, current-collector-free and non-destructive curvature measurements, accompanied by the surface characterization methods like X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS).

#### 7.2 Experimental Method

#### 7.2.1 Sample Fabrication

Detailed thin film deposition information can be found in Section 3.3.1. After deposition, all three samples were re-oxidized at 1000°C for 1 hour with a 3°C/min heating and cooling rate to alleviate the extremely high oxygen nonstoichiometry in 10PCO thin film resulting from the deposition process. Then two 10PCO|YSZ samples were etched with 50% NaOH solution at 65°C for 24 hours with 100 rpm stirring speed in order to remove any possible Si contaminants that is on the surface of the sample before the aging process.<sup>161</sup> To ensure there was no Si contamination on the etched samples during curvature relaxation measurements, one of the etched 10PCO|YSZ samples was sectioned into 4 pieces. Later, they were aged at 525°C, 525 / 550°C, 525/550/575°C, and 525/550/575/600°C with 5°C/min heating rate. The dwell time was 1.5 hour at 525°C, 1 hour at 550°C, 50 min at 575°C, and 30 min at 600°C. Then these aged samples were characterized *exsitu* with XPS to determine if Si contaminants were on the surface. To further quantify the amount of Si contamination, the near-surface Si concentration of Si was measured by the ToF-SIMS.

7.2.2 Microstructural and Crystallographic Characterization

Scanning electron microscopy (SEM) images were taken via a TESCAN MIRA3 Field Emission SEM (Tescan Inc) of the cross section of a fractured sample. Prior to the imaging process, the fractured samples were coated with ~5 nm of Ti.

X-Ray Diffraction (XRD) was conducted using a Rigaku SmartLab diffractometer with 40 mA current and 44kV voltage. The measurements were conducted from  $2\theta = 20^{\circ}$  to  $2\theta = 80^{\circ}$  with 0.01° step size and 1s dwell time.

### 7.2.3 XPS Measurements

XPS measurements were conducted using a Physical Electronics (PHI) 5400 X-Ray photoelectron spectroscopy system. An aluminum X-Ray was operated at 300 W and 23.50 eV pass energy. The peak positions were calibrated with the C 1s peak at 284.8 eV. Survey scans of binding energy were conducted from 70 eV to 180 eV.

## 7.2.4 ToF-SIMS Measurements

The ToF-SIMS depth profiling was performed by EAG Labs (East Windsor, NJ, USA). Only the sample aged at 600°C was measured using ToF-SIMS due to the cost of performing depth profiling measurements.

#### 7.2.5 Curvature Relaxation Measurements

For the Si-free sample, the curvature relaxation signals were measured from 500°C to 600°C in synthetic air in 25°C increments. For Si-contaminated sample, the curvature relaxation signals were measured from 675°C to 725°C in synthetic air in 25°C increments. The relaxations were triggered by switching between synthetic air (20% O<sub>2</sub>-80% Ar) and diluted synthetic air (10% synthetic air - 90% Ar). Noted that the temperature ranges of the measurements are different. It is

because for the Si-contaminated sample, the relaxation process was too slow to measure between 500~600°C.

To prove that an oxygen partial pressure from 0.21 to 0.021 did not change the oxygen surface exchange coefficient, the relaxations between synthetic air and 5 times diluted synthetic air (20% synthetic air - 80% Ar) were also measured.

### 7.3 Results and Discussion

## 7.3.1 Crystallography and Morphology of the Film

Figure 7.1 shows representative XRD scans of the Si-free and Si-contaminated samples. It indicates that both 10PCO films are phase pure and well-crystallized. Both 10PCO thin films have the (100) preferred-orientation on (100) oriented YSZ substrates. This preferred orientation is identical to what was reported in the literature studies using (100) YSZ substrate.<sup>18, 141, 161, 237,240</sup> The averaged grain size is 24 nm for the Si-free sample and 21 nm for the Si-contaminated sample, which were calculated using Scherrer's Equation.<sup>209</sup> Due to the limited peaks for a preferred oriented 10PCO thin film, the more accurate Williamson-Hall method <sup>210</sup> was not used for grain size determination. Therefore, the peak broadening generated because of the strain effect was not accounted for. The reported grain sizes here are only the lower limits. Note that the peak intensities of the Si-free and Si-contaminated sample are similar, the peak height difference is caused by different intensity ratios between 10PCO (200) and YSZ (200) peaks (no amorphous peak). This ratio variation can be caused by different batches with different sample height calibrations. Therefore, the crystallinities of the Si-free and the Si-contaminated samples are similar, which is not a variable in the discussion below.



Figure 7.1 Representative XRD scans of (a) etched and (b) non-etched 10PCO|YSZ samples using using CeO<sub>2</sub>, and YSZ JCPDS card numbers 81-0792 and 70-4436, respectively.

Figure 7.2 shows the representative SEM image of 10PCO thin film after the deposition, which indicates that the 10PCO thin films were dense and uniform with a thickness of  $230 \pm 5$  nm. The film thickness is significantly smaller than the characteristic thickness of 10PCO <sup>18</sup>, ensuring that oxygen transport was dominated by the surface exchange process. After testing, the SEM scan did not show any microstructural change in the 10PCO thin films.



Figure 7.2 Cross-sectional back-scattered electron image of 10PCO|YSZ

Figure 7.3 shows the representative AFM images of 10PCO|YSZ samples before and after the etching process, showing that the surface roughness of the film did not have a significant change after the etching process. This was expected because ceria is not reactive to a KOH solution <sup>241</sup>. Therefore, the difference in oxygen surface exchange coefficients between the etched and nonetched samples would not be a result of surface roughness.



Figure 7.3 AFM scans of 10PCO|YSZ sample (a) before and (b) after etching

## 7.3.2 Near-Surface Si Content Characterization

Figure 7.4. shows the XPS spectrum of the etched, aged, and non-etched samples. The XPS spectrum of the non-etched sample at 25°C shows that the as-deposited sample have surface Si contaminants, which could be introduced during the deposition process since the deposition chamber was used to deposit silicate materials prior to the 10PCO deposition. Therefore, the etching process is needed to guarantee a 10PCO thin film with Si-free surface. Comparing the XPS Spectra of etched and non-etched sample at 25°C, the etching process completely removed surface



Figure 7.4 XPS spectra of (a) non-etched and (b) etched sample aged at different temperatures, noting that below 600°C, there is no Si contamination detected for etched

samples

Si-contaminants. The XPS results are in good agreement with the etching rate of Si and SiO2 reported by Seidel *et al.*<sup>242</sup> The XPS peak patterns of etched and non-etched 10PCO also match well with the XPS data reported previously for Si-free and Si-contaminated 10PCO thin films.<sup>232</sup> Comparing the XPS spectrum of aged and etched samples, for curvature relaxation measurements, there are no Si contaminants detected at 525, 550 and 575°C. The Si contaminants were detected after the curvature relaxation measurements at 600°C. Those results were expected since the optical relaxation work of Zhao *et al.* reported noticeable Si-contamination after aging the sample in a Si-based test-rig for 60 hrs at 600°C <sup>232</sup>. Since the deposition speed of Si became lower with lower temperatures, and with the exposure of a short amount of time, the surface of the sample is therefore free from detectable Si-contamination below 600°C.

Figure 7.5 shows the ToF-SIMS depth profile near the etched and 600°C-aged 10PCO|YSZ sample surface. The concentration of Pr, Ce, and O rises significantly as the depth increases while the concentration of Si drops from 3\*10<sup>21</sup> to 4\*10<sup>20</sup> atoms/cm<sup>3</sup> at a depth of ~10 nm, indicating a surface covered with Si contaminants. The slight increase in Si concentration between 10~20 nm could be that there is a Si-rich region in the bulk of the film, which could form during the deposition in a Si-contaminated deposition chamber. However, the Si in the bulk of the film do not dominate the oxygen transport in the 10PCO thin films since the oxygen surface exchange process is the rate limiting step. Therefore, the effect of Si in the bulk is not considered in later discussion. On the other hand, Zr and Y are also detected at the surface and stays relatively constant as the depth increases. However, compared to the concentration of Si contaminants, the oxygen to cerium ratio is significantly larger than the stoichiometry of ceria, indicating a lack of oxygen vacancies, which may hinder the oxygen surface exchange process of the 10PCO thin film. Additionally, the

thickness of the contaminants is ~10 nm. Therefore, an overnight etching at 65°C in 50% NaOH is sufficient to remove the surface silicate contaminants, according to previous Si and SiO<sub>2</sub> etching studies  $^{242}$ .



Figure 7.5 Near-surface Si concentration of etched and 600°C-aged 10PCO|YSZ measured by ToF-SIMS

## 7.3.3 Curvature Relaxation Measurements

Figure 7.6 shows the representative curvature relaxation data for Si-free and Sicontaminated samples. The data from the Si-free sample was measured at 600°C while the data for the Si-contaminated sample was measured at 750°C. Measurements on both samples have



Figure 7.6 Representative curvature relaxation data of Si-free and Si-contaminated samples. The relaxation time for the Si-contaminated sample is significantly longer than Si-free sample (note difference in horizontal time scale)

reproducible time constants after reduction and re-oxidation. Both samples reached a steady-state equilibrium after being exposed to a different oxygen partial pressure. Curvature relaxation data measured at other temperatures is shown in Figure 5.7.



Figure 7.7 Curvature relaxation raw data at different temperatures for (a) Si-free sample and (b) Si-contaminated sample, note that the relaxation time of the Si-contaminated sample is significantly longer than etched sample

Comparing Figure 7.6(a) and Figure 7.6(b), it is obvious that even if the Si-contaminated sample was measured at a higher temperature, its relaxation process is significantly slower than the Si-free sample. The larger relaxation time constant of the non-etched sample indicates that oxygen surface exchange process of 10PCO was blocked by surface Si contaminants. The increase of relaxation time was also observed by Zhao *et al.*<sup>232</sup>



Figure 7.8 Multiple 750°C Curvature relaxations performed on the same 10PCO thin film by switching between (a) synthetic air ( $pO_2=0.21$ ) and a 10 times diluted air (10% synthetic air - 90% Ar,  $pO_2=0.021$ ) mixture, and (b) synthetic air ( $pO_2=0.21$ ) and a 5 times diluted air (20% synthetic air – 80% Ar,  $pO_2=0.042$ ) mixture
As shown in Figure 7.8, curvature relaxation measurements were also conducted between 0.21 and 0.042. They were conducted to prove that the step size of oxygen partial pressure (0.21 to 0.021) is small enough to ensure a linear relationship between curvature and oxygen nonstoichiometry.

Detailed fittings for all the relaxation curves can be found in Figure 7.9, 7.10 and 4.2, indicating that there is only one mechano-chemically active process during the redox cycling.



Figure 7.9 Fittings of curvature relaxation measurements at different temperatures for non-

etched samples



Figure 7.10 ln(1-Normalized Curvature) plots for the non-etched sample. Note that the generally good single time constant (red line) fits to the data of Figure 7.9 and a single slope in the ln(1-Normalized Curvature) plots of Figure 7.10 at times before the equilibrium state is reached suggest only one mechano-chemically active process is active with redox cycling between synthetic air and 10% diluted synthetic air.

# 7.3.4 Oxygen Surface Exchange Kinetics

Figure 7.11 (a) shows the oxygen surface exchange coefficient measured in this work compared to those measured from other literature studies. As reported in other studies, the oxidation process measured here is kinetically faster than the reduction process. A larger oxygen vacancy concentration at the beginning of the oxidation process might be responsible for a faster oxygen transport process.<sup>160, 243, 244</sup> The k<sub>chem</sub> values for both Si-free and Si-contaminated samples showed Arrhenius behavior over the temperature range of their



Figure 7.11 (a)10PCO oxygen surface exchange coefficient from curvature relaxation comparing with other literature studies (b) 10PCO surface polarization resistance ( $R_S$ ) values compared to literature reporting 10PCO  $R_S$  values and other  $R_S$  values of conventional solid oxide fuel cell cathode materials

measurements, indicating that there was only one mechano-chemically active process on both samples. Most importantly, the k<sub>chem</sub> value of Si-free samples is ~3 orders of magnitudes higher than Si-contaminated samples. The discrepancy between those two data sets agrees with the variation reported by Zhao *et al.* between Si-free and Si-contaminated samples,<sup>232</sup> which is likely to be a result of Si contaminants covering the surface reaction sites, which comes from the fused silica test-rig during high temperature measurements. Additionally, the activation energy of the oxygen surface exchange process was almost doubled for the Si-contaminated sample, indicating that not only do the Si contaminants cover the surface reaction sites, it hinders the migration of oxygen ions. When comparing the *k<sub>chem</sub>* from this work with the values measured by electrical impedance spectroscopy (EIS),<sup>18</sup> the values measured by curvature relaxation ( $\kappa$ R) are ~5 times smaller. As indicated by other literature studies,<sup>157, 161, 245</sup> this discrepancy can be a result of applying surface-altering Au/Pt current collector.

It is worth noting that the 600°C  $k_{chem}$  data measured in this study is very likely to be affected by surface Si contaminants according to XPS data. However, the value of  $k_{chem}$  agrees well with what Zhao *et al.* <sup>232</sup> reported in the Si-free film. This result is expected because Zhao *et al.* aged their samples for 60 hrs at 600°C to get a significant change (~3 orders of magnitudes) in the oxygen surface exchange coefficient. With only 2 hours of aging at 600°C. It is possible that the film is not fully covered by Si contaminants judging by the Arrhenius behavior between 500~600°C, resulting in a similar  $k_{chem}$  value as Zhao *et al.* On the other hand, even for the Si-free sample from Zhao *et al.*, it is still possible that there were already Si-contaminants on the surface during their optical relaxation measurements (No XPS results were provided after the measurements for the Si-free samples).<sup>232</sup> Therefore, with the reasons mentioned above, the  $k_{chem}$  value at 600°C still represents the response of the PCO thin film.

Figure 7.11 (b). shows the surface polarization resistance, compared to those measured in other literature studies. It shows that the Si-contaminated sample has a higher resistance than the Si-free sample. There are  $\sim$ 3 orders of magnitudes of difference between these two data sets. This variation is mainly caused by a difference in  $k_{chem}$  as it was shown in Figure 5.11 (a)., which also have  $\sim$ 3 orders of magnitudes difference between Si-free and Si-contaminated samples. Consistent with  $k_{chem}$ , there are also differences between EIS and curvature relaxation measured data for the Si-free samples. As mentioned above, this discrepancy can be explained by the catalytic effect of the Au current collector used in EIS measurements.

#### 7.4 Summary

In this work, a systematic aging and characterization processes was conducted to investigate the influence of Si contaminants on the oxygen surface exchange process of the 10PCO thin films. The XPS results show that Si contaminants were introduced after the aging process at 600°C due to the usage of fused silica for the current curvature relaxation test-rig. The oxygen surface exchange coefficient, surface polarization resistance, and activation energy of 10PCO thin films are all affected by Si contamination. With the measurement via curvature relaxation technique, ~3 orders of magnitudes degradation of these properties have been observed. Also, ~3 orders of magnitudes higher Rs and ~2 times larger activation energy has been measured from Si-contaminants block the surface reaction sites for the oxygen surface exchange process, which hinders the oxygen migration process in 10PCO thin films.

# 8. Effect of Surface Platinum Coverage

#### 8.1 Introduction

The oxygen surface exchange coefficient ( $k_{chem}$ ) is a material property determining the speed of oxygen exchange in the mixed ionic electronic conductors (MIEC) used in oxygen sensors, Solid Oxide Fuel Cells, Solid Oxide Electrolysis Cells, mechano-chemical actuators, and other electrochemical devices. Historically, *in-situ* techniques like electrical impedance spectroscopy (EIS) and electrical conductivity relaxation (ECR) have been used to measure  $k_{chem}$ .<sup>18, 21</sup> Unfortunately, these techniques require noble-metal electronic current collectors that may alter the underlying MIEC stress state (potentially altering MIEC  $k_{chem}$  performance through mechano-chemically-induced point defect concentration changes) or interfering with an accurate MIEC  $k_{chem}$  measurement through catalysis of the oxygen exchange reaction.<sup>23, 157</sup> Recently there are studies which implementing current-collector-free, contact-free, in-situ techniques to study the oxygen surface exchange coefficient with the purpose of excluding the effect of Pt enhancement.<sup>23, 157, 246</sup> However, the effect of platinum enhancement was only shown with the comparison between different studies, there is a lack of systematic studies for the effect of platinum surface coverage on the oxygen surface exchange process of a MIEC.

In this work, two identical PCO|YSZ samples were manufactured using PLD. One of the samples went through a photolithography process and has a Pt patterns deposited on the surface of the sample (which is shown in Figure 8.1). The  $k_{chem}$  of two samples were then measured via curvature relaxation technique and then compared with each other in order to show the influence of Pt surface coverage.

#### 8.2 Experimental Details

#### 8.2.1 Pulsed Laser Deposition

~200 nm thick  $Pr_{0.1}Ce_{0.9}O_{2-\delta}$  (PCO) thin films were deposited onto (100) oriented, 200 micron thick, 1-inch diameter, one-side-polished, 9.5% YSZ substrate (Crystec GmbH, Berlin, Germany). Thin films were deposited at 700°C (setpoint of the substrate thermostat) with 30 mTorr oxygen for 15000 pulses. The target to substrate distance was 100 mm. The pulse frequency was 10 Hz. The samples were cooled with a 10°C/min cooling rate in 30 mTorr oxygen. After the deposition, the samples were annealed in air at 1000°C for 1 hour in order to re-equilibrate its oxygen content.

# 8.2.2 Crystallographic Characterization

The detailed XRD parameters can be found in Chapter 3.3.2.

#### 8.2.3 Photolithography

The surface of PCO|YSZ were cleaned with acetone wash followed by a methanol wash, dipped in water, and N<sub>2</sub> gas drying. The sample was pre-heated to 115°C for 5~10 min to get rid of the residual water on the surface. Then the sample was placed in a spin coater. The spinning program was set to rotate at 700 rpm for 10 seconds and them 3000 rpm for 30 seconds. The Photoresists S1813 (Microchem Corp, Westborough, MA) was dripped onto the sample with a pipette when the sample was rotating at 700 rpm. After the spin coating process, the coated sample was then baked at 116°C for 1 min. Then the sample was transferred into a Karl Suss (MJB3) mask aligner (SUSS MicroTec SE, Garching, Germany) with a mask from Photoscience (Photoscience Inc, Lexington, KY). The coated photoresist was exposed to 274 watts of ultra-violet light for 90 seconds and then developed with photoresist remover MF 319 (Microchem Corp, Westborough,

MA) for 45 seconds. The developed sample was then rinsed with water and then baked at 116°C again for 5 min.

8.2.4 Pt Deposition and Photoresist Removal

The Pt was deposited by a sputtering process. The PCO|YSZ sample masked with photoresist was placed into the deposition chamber, pumped down to  $10^{-7}$  torr before deposition. Then the chamber was filled with Ar to 10 mTorr. The Pt was deposited with 200W power for 2 min with a sample rotation speed of 30 rpm.

The remaining photoresist was cleaned after the Pt deposition. The sample was dipped into acetone to remove the photoresist and then cleaned with isopropanol to remove the remaining acetone on the surface of the sample. Figure 8.1 shows the image of bare wafer, PCO|YSZ and Pt|PCO|YSZ.



Figure 8.1 Image of bare YSZ wafer, PCO|YSZ and Pt|PCO|YSZ

# 8.2.5 Curvature relaxation measurements

The curvature relaxations were triggered by switching oxygen partial pressure from 0.21 (21%  $O_2$ -79% Ar) to 0.021 (2.1%  $O_2$ -97.9% Ar). The platinum coated PCO|YSZ (Pt|PCO|YSZ)

was measured from 500 to 725°C with 25°C increments. The PCO|YSZ sample was measured from 675 to 725°C with 25°C increments. To ensure a linear response between oxygen nonstoichiometry change and curvature change, curvature relaxations between 0.21 and 0.042 oxygen partial pressure were also measured for Pt|PCO|YSZ at 725°C

#### 8.3 Results and discussion

# 8.3.1 X-Ray Diffraction Analysis

Figure 8.1 shows the XRD results from the PCO|YSZ sample. The PCO thin film has a (100) preferred orientation on YSZ substrate, which agrees with the results in Chapter 3, 4, 5, and 6 despite a difference in deposition conditions.



Figure 8.2 XRD scan of PCO|YSZ sample

# 8.3.2 Curve Fitting of Pt|PCO|YSZ

Figure 8.2 shows the representative fitting of the relaxation curve of Pt|PCO|YSZ at 725°C. The fitting showed that although there is Pt surface coverage, Eqn 4.6 is still sufficient to fit the relaxation signal, meaning there is only one oxygen surface exchange process during the relaxation period.



Figure 8.3 Representative curve fitting of Pt|PCO|YSZ at 725oC

## 8.3.3 Effect of Pt surface Coverage

Figure 8.4 shows the comparison of  $k_{chem}$  values between PCO|YSZ and Pt|PCO|YSZ. Both data sets show Arrhenius behavior, indicating only one dominant oxygen transport process dominating the relaxation. When comparing the  $k_{chem}$  between PCO|YSZ and Pt|PCO|YSZ, the  $k_{chem}$  value of Pt|PCO|YSZ is 2~3 times higher than the  $k_{chem}$  value for PCO|YSZ. Additionally, the activation energy reduced from 0.8 eV to 0.4 eV. This behavior indicates that the Pt improves the oxygen migration process at the surface of the PCO thin film. The boost of oxygen surface exchange is expected due to the similar mechanism as the spillover effect, where the gas molecule can be adsorbed and dissociated on a transition metal surface, and then diffused into a non-metal substrate.<sup>247</sup> The current oxygen surface exchange coefficient measurement technique can only determines the overall time constant for oxygen surface exchange process at the gas/solid interface, therefore, a reduction of energy barrier for oxygen adsorption and dissociation does not get detected in the relaxation curve fit but it still gives an overall boost of oxygen surface exchange coefficient.

Additionally, the  $k_{chem}$  values measured between 0.21~0.021 pO<sub>2</sub> is similar to the value measured between 0.21~0.042 pO<sub>2</sub>, indicating that there is still a linear response between the curvature and the oxygen nonstoichiometry changes of 10PCO with the pO<sub>2</sub> step size from 0.21 to 0.021, making sure that Eqn 4.6 is applicable to fit the relaxation curves.



Figure 8.4 k<sub>chem</sub> comparison between PCO|YSZ and Pt|PCO|YSZ

8.3.4 XPS Analysis

Figure 8.5 shows the XPS scan of the as-deposited PCO|YSZ sample. The XPS signal shows that there are Mo, and Cs on the surface of the PCO thin film. This may be the reason for the ~1 order of magnitude lower  $k_{chem}$  value measured in this chapter in contrast to the data from Chapter 4. The Mo may come from the heating element of the PLD system. The Cs may come



Figure 8.5 XPS scan for as-deposited PCO|YSZ

from the previous depositions that deposited Cs-containing materials.

# 8.4 Conclusions

This chapter investigated the effect of Pt surface coverage on the oxygen surface exchange process of PCO thin film. Two identical PCO|YSZ samples were used with one of them deposited with Pt pattern on the surface. The  $k_{chem}$  results from curvature relaxation shows that the Pt Surface coverage not only boost the  $k_{chem}$  values 2~3 times, it also decreases the activation energy required for oxygen migration. Therefore, techniques that require a current collector (ECR, EIS, etc.) at the surface can overestimate the oxygen surface exchange coefficient of MIEC, which could be one

of the sources of  $k_{chem}$  variation in the literature studies among different research groups. However, the relationship between  $k_{chem}$  enhancement and area coverage of Pt is still unclear, which will be investigated in the future work.

# 9. Dissertation Summary

The objective of this work, as shown in Figure 9.1,<sup>23</sup> is to develop an *in-situ* technique that can measure Young's modulus (E), thermo-chemical expansion coefficient ( $\alpha_{thermochemical}$ ), oxygen surface exchange coefficient ( $k_{chem}$ ), oxygen nonstoichiometry ( $\ddot{o}$ ), and surface polarization resistance ( $R_s$ ). Then using this technique to detect the effect of surface contaminants on the oxygen surface exchange process.



Figure 9.1 Graphic summary of objectives of this work

The conclusions from this dissertation are shown below:

(1) wafer curvature measurements can be used to <u>directly</u> measure a variety of disparate and technologically relevant thin film physicochemical properties (i.e. the oxygen nonstoichiometry, biaxial modulus, thermo-chemical expansion coefficient, and thermal expansion coefficient) under well-characterized film stress states, strain states, temperatures and atmospheric conditions. Using an externally-derived Poisson's ratio, Young's modulus was also determined (Note, studies have shown that wafer curvature experiments can also be used to directly measure the Poisson's ratio<sup>118</sup>).

(2) An *in-situ*, contact-free, current-collector-free technique can be used to evaluate the oxygen surface exchange kinetics of 10PCO thin film. With the knowledge of oxygen nonstoichiometry from dual substrate measurements, the oxygen surface exchange resistance can also be calculated.

(3) The comparison of the oxygen surface exchange resistance between 10PCO and other commonly used MIECs suggests that 10PCO may not be an ideal material for solid oxide fuel cell applications.

(4) The thermo-chemical expansion coefficient and Young's modulus of a thin film can be extracted by combining the HTXRD strain measurements and MOSS stress measurements. Similar results from HTXRD-MOSS and the dual substrate method validate the reliability of dual substrate method.

(5) With HTXRD-MOSS method, the magnitude of the error for thermo-chemical expansion coefficient and Young's modulus were significantly reduced compared to the data from dual substrate measurements.

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(6) A cross-check with other electrode-free  $k_{chem}$  measurement techniques shows that the data from curvature relaxation technique is comparable with the data from optical relaxation technique.

(7) Si contaminants on the surface not only degrade the value of  $k_{chem}$ , but also increase the migration energy of surface oxygen transport.

(8) Pt surface coverage boosts the value of  $k_{chem}$  2~3 times while decreasing the migration energy for surface oxygen transport.

### **10. Future Work**

High temperature X-Ray diffraction was used to verify the reliability of Young's modulus and the thermo-chemical expansion coefficient measured by the dual-substrate method. It also provides an alternative option for measuring Young's and the thermo-chemical expansion coefficient of the thin film samples. However, in the case of PCO, the films have a (100) preferred orientation. Due to the structural similarity between low-angle grain boundary and grain interior and the near-atmospheric oxygen partial pressure ( $pO_2=0.21$ ), there is no significant difference between the expansion coefficient of the grain interior and grain boundary. But in real SOFC applications, a polycrystalline microstructure is often seen in a MIEC electrode. As reported by Sheth et al,<sup>206</sup> an ~200 MPa compositional stress difference was observed between two PCO|YSZ samples with different grain sizes (27 nm vs. 72 nm) in PCO thin films. The change in compositional stress could be crucial for the mechanical stability of the devices. Therefore, measuring the grain boundary, grain interior, and overall thermo-chemical expansion coefficient of the PCO thin films with different grain sizes can be a useful guide to improve the manufacturing process and the design of SOFC related applications.

The results from curvature relaxation measurements showed that the Pt surface coverage provides 2~3 times enhancement for the oxygen surface exchange coefficient of the PCO thin films. However, the relationship between the area of surface coverage and the magnitude of enhancement is still unclear. Additional curvature relaxation experiments with different surface coverage areas are therefore needed to systematically quantify the influence of Pt surface coverage.

Given that the oxygen surface exchange coefficient of PCO can be boosted by Pt, the effect of other noble metal (Au, Ag, etc.) surface coverages can also be important since the silver and gold paste are commonly used in the electrochemical measurements. On the other hand, since Pt, Au, and Ag are all transition metals, the effect of non-precious transition metals (Fe, Ni, Co, Cu, etc.) could also be explored and potentially provide an alternative way to boost the performance of the MIECs.

APPENDICES

The oxygen surface exchange coefficient measurement of a thin film MIEC can be modeled as a case of surface evaporation. The rate of losing evaporating substance on a planar sheet can be described as:

$$-D_{chem}\frac{\partial C}{\partial x} = k_{chem}(C_0 - C_S)$$
(A.1)

where  $C_0$  is the concentration of oxygen in the gas atmosphere,  $C_S$  is the oxygen concentration in the bulk of the thin film.

The concentration of oxygen at the beginning of the relaxation was defined as:

$$C_0 = \mathcal{C}(\mathbf{x}, \mathbf{t}) \tag{A.2}$$

Since the oxygen concentration of surrounding gas atmosphere didn't change:

$$\frac{\partial C(0,t)}{\partial t} = 0 \tag{A.3}$$

Additionally, the oxygen transport through the thin film can be describe via Fick's Second Law:

$$\frac{\partial C(x,t)}{\partial t} = D_{chem} \frac{\partial^2 C(x,t)}{\partial x^2}$$
(A.4)

with A.1, A.2, A.3, and A.4, the solution to Fick's Second Law can be expressed as:

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp\left(-\frac{\beta_n^2 D_{chem} t}{l^2}\right)}{\beta_n^2 (\beta_n^2 + L^2 + L)}$$
(A.5)

where  $M_t$  is the amount of oxygen transported into the film at a certain time,  $M_{\infty}$  is the amount of oxygen transported into the film after infinite amount of time, and:

$$\beta_n \tan \beta_n = L \tag{A.6}$$

and

$$L = \frac{k_{chem}}{D_{chem}} * l = \frac{l}{L_c}$$
(A.7)

where l is the film thickness.

In the case of  $k_{chem}$  measurements, for most of the MIEC thin films,  $l \ll L_c$ . Therefore, L is a very small number, in which case:

$$\beta_n \tan \beta_n = \beta_n^2 = \mathcal{L} \tag{A.8}$$

Applying A.7 and A.8 to A.5, A.5 can then be simplified into:

$$\frac{M_t}{M_{\infty}} = \frac{C(t) - C_0}{C_{\infty} - C_0} = \frac{\delta - \delta_0}{\delta_{\infty} - \delta_0} = 1 - \exp\left(\frac{-k_{chem}t}{l}\right)$$
(A.9)

#### APPENDIX B: Error Analysis for Dual Substrates Techniques

The following equations were used for fitting the stress (y) – temperature (x) data:

$$y = ax^3 + bx^2 + cx + d$$
 (B.1)

$$y' = 3ax^2 + 2bx + c$$
 (B.2)

Separating out the temperature from the fitting parameters a, b, and c, the slope of the stress-temperature curve (denoted S) was expressed as:

$$y' = f(a, b, c) = 3x^2 * a + 2x * b + c$$
 (B.3)

where the error bars of *a*, *b* and *c* is automatically calculated when fitting the raw data in the origin computer program. Mathematical error analysis<sup>248</sup> indicates that the error in  $\frac{d\sigma}{dT}$  (i.e. *S*) can then be expressed as:

$$\delta y' = \sqrt{\left(\frac{\partial y'}{\partial a} * \delta a\right)^2 + \left(\frac{\partial y'}{\partial b} * \delta b\right)^2 + \left(\frac{\partial y'}{\partial c} * \delta c\right)^2} = \sqrt{(3x^2 * \delta a)^2 + (2x * \delta b)^2 + \delta c^2}$$
(B.4)

Based on Equations 2 and 3 in the literature, the equation for the calculation of thermochemical expansion coefficient is:

$$\frac{S_{YSZ} * \alpha_{MgO} - S_{MgO} * \alpha_{YSZ}}{S_{YSZ} - S_{MgO}} = \alpha_{PCO}$$
(B.5)

where  $S_{YSZ}$  is the slope of the stress vs. temperature curve for 10PCO|YSZ,  $S_{MgO}$  is the slope of stress vs. temperature curve for 10PCO|MgO,  $\alpha_{MgO}$  is the thermal expansion coefficient of MgO substrate from the literature,<sup>125</sup>  $\alpha_{YSZ}$  is the thermal expansion coefficient of YSZ substrate from the literature,<sup>111</sup> and  $\alpha_{PCO}$  is the thermo-chemical expansion coefficient of PCO. For an equation like S5 of the form of  $\frac{A}{B}$  (in Equation S5  $A = S_{YSZ} * \alpha_{MgO} - S_{MgO} * \alpha_{YSZ}$  and  $B = S_{YSZ} - S_{MgO}$ ) mathematical error analysis<sup>248</sup> indicates that the error for A can be calculated by:

$$\delta A = \sqrt{\left(\alpha_{Mg0} * \delta S_{YSZ}\right)^2 + \left(\alpha_{YSZ} + \delta S_{Mg0}\right)^2} \tag{B.6}$$

and the error for B can be calculated by:

$$\delta B = \sqrt{\delta S_{YSZ}^2 + \delta S_{MgO}^2} \tag{B.7}$$

assuming that there is no error in  $\alpha_{Mg0}$  and  $\alpha_{YSZ}$  (an assumption based on the fact that no errors were reported for these literature studies<sup>111, 125</sup>).

Plugging in Equation S4 to S6-7, the error for  $\frac{A}{B}$  the error equals:

$$\delta \alpha_{PCO} = \alpha_{PCO} * \sqrt{\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta B}{B}\right)^2}$$
(B.8)

The equation for calculation of Young's Modulus is:

$$E_{PCO} = \frac{S_{YSZ}}{\alpha_{YSZ} - \alpha_{PCO}} * 1000 * 0.67$$
(B.9)

Using the same approach as that described previously for the thermo-chemical expansion coefficients, the error for Young's modulus is:

$$\delta E_{PCO} = E_{PCO} * 1000 * 0.67 * \sqrt{\left(\frac{\delta S_{YSZ}}{S_{YSZ}}\right)^2 + \left(\frac{\delta \alpha_{PCO}}{\alpha_{YSZ} - \alpha_{PCO}}\right)^2}$$
(B.10)

Mathematical error analysis<sup>248</sup> indicates that the error caused by fitting the total stress with an equation for the form:

$$y_{tot} = ax^3 + bx^2 + cx + d$$
 (B.11)

is:

$$\delta y_{tot} = \sqrt{\left(\frac{\partial y_{tot}}{\partial a} * \delta a\right)^2 + \left(\frac{\partial y_{tot}}{\partial b} * \delta b\right)^2 + \left(\frac{\partial y_{tot}}{\partial c} * \delta c\right)^2 + \left(\frac{\partial y_{tot}}{\partial d} * \delta d\right)^2} = \sqrt{(x^3 * \delta a)^2 + (x^2 * \delta b)^2 + (x * \partial c)^2 + \partial d^2}$$
(B.12)

Mathematical error analysis<sup>248</sup> indicates that the error caused by fitting the thermal stress with an equation for the form:

$$y_{thermal} = ax + b \tag{B.13}$$

is:

$$\delta y_{thermal} = \sqrt{\left(\frac{\partial y_{thermal}}{\partial a} * \partial a\right)^2 + \left(\frac{\partial y_{thermal}}{\partial b} * \partial b\right)^2} = \sqrt{(x * \delta a)^2 + \delta b^2}$$
(B.14)

The chemical film strain  $(\varepsilon_c)$  is calculated by the equation:

$$\varepsilon_c = \frac{\sigma_{tot} - \sigma_{thermal}}{M_f} \tag{B.15}$$

where  $\sigma_{tot}$  is the total stress on the film,  $\sigma_{thermal}$  is the thermal stress on the film, and  $M_f$  is the biaxial modulus of the film. Considering that Equation S18 has the form of  $\frac{A}{B}$  (where  $A = \sigma_{tot} - \sigma_{thermal}$  and  $B = M_f$ ), the error of A can be calculated as:

$$\delta A = \sqrt{\delta \sigma_{tot}^2 + \delta \sigma_{thermal}^2} \tag{B.16}$$

and

$$\delta B = \delta M_f \tag{B.17}$$

Hence, then the error on the chemical strain can be calculated as:

$$\delta \varepsilon_c = \varepsilon_c * \sqrt{\left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta B}{B}\right)^2} \tag{B.18}$$

The Oxygen nonstoichiometry is determined from the chemical strain via the equation:

$$\varepsilon_C = \frac{\Delta l}{l}\Big|_T = \alpha_C \Delta \delta$$
 [S22]

Assuming chemical expansion coefficient is 0.067, remains constant,<sup>114</sup> and has no error associated with it (based on the fact that none was provided in its measurement<sup>114</sup>) the error on the oxygen nonstoichiometry can be calculated with the equation:

$$\Delta \delta = \frac{\delta \varepsilon_c}{0.067}$$
[S23]

# APPENDIX C: Error Analysis for HTXRD-XRD Measurements

The strain vs. temperature data was fitted by:

$$\varepsilon_z = A e^{BT} \tag{C.1}$$

The first-order derivatives of the strain values with respect to temperature can be expressed as:

$$y = \frac{\partial \varepsilon_z}{\partial T} = ABe^{BT} \tag{C.2}$$

The error of the fitting can be expressed as:

$$\delta y = \sqrt{(Be^{BT} * \delta A)^2 + ((Ae^{BT} + AB^2 e^{BT}))^2}$$
(C.3)

According to Eqn 3, the error of thermo-expansion coefficient is:

$$\delta \alpha_{tc} = \frac{1-\nu}{1+\nu} \sqrt{(\delta y)^2 + \left(\frac{2\nu}{1-\nu}\delta\alpha_s\right)^2}$$
(C.4)

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