Mechanical, Electrical, and Optical Properties of (Pr,Ce)O$_2$ Solid Solutions: Kinetic Studies

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Mechanical, Electrical, and Optical Properties of (Pr,Ce)O₂ Solid Solutions:
Kinetic Studies

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Praseodymium doped cerium oxide (PCO) shows mixed ionic and electronic conducting (MIEC) characteristics at relatively high pO₂ (e.g. air) and enhanced oxygen storage capacity (OSC), of interest for solid oxide fuel cell (SOFC) cathodes and three way catalysts, resulting from the ready reduction of Pr to its trivalent state. This reduction also results in a change of lattice parameter, known as chemical expansion, and changes in optical absorption related to the formation of a Pr impurity band. These properties can be measured as a function of time, yielding oxide ion diffusion and surface exchange coefficients. In this manuscript, the diffusivity and/or surface exchange of PCO is explored using TGA and dilatometry of bulk specimens and HTXRD and optical absorption of thin films. The HTXRD and optical absorption measurements promise the ability to monitor both thermodynamic and kinetic properties of thin film materials exhibiting wide swings in oxygen stoichiometry.

Introduction

Many oxygen ion and mixed conducting oxides absorb or release significant levels of oxygen upon changes in temperature and oxygen partial pressure (pO₂), sometimes resulting in deleterious changes in their electrical or mechanical properties. For example, solid oxide fuel cell (SOFC) electrolytes, such as acceptor doped CeO₂, when exposed to a large pO₂ gradient (air to fuel), become mixed ionic and electronic conductors (MIEC), resulting in a reduction in open circuit voltage. Loss of oxygen serves to expand the lattice, resulting in stresses that can lead to mechanical failure. It is therefore important to characterize these properties and develop models capable of predicting optimum materials compositions and operating conditions. (Pr,Ce)O₂ (PCO) solid solutions are particularly interesting given that both Pr and Ce exhibit valence changes, but under different pO₂ regions, resulting in different transport regimes (ionic vs MIEC) while undergoing chemical expansion (1-4). Stoichiometry changes and chemical expansion induced by step changes in oxygen pressure and/or temperature are time dependent with the equilibration rate depending on the oxygen chemical diffusivity and oxygen surface exchange steps. In the area of solid state ionics, there is a growing interest in applying thin films in, for example, micro-SOFCs and micro-sensors (5, 6). Due to thin film-substrate interactions, film properties often differ from their bulk counterparts. In this
study, these transients were monitored using dilatometry and thermo-gravimetric analysis (TGA) on bulk samples and high temperature x-ray diffraction (HTXRD) and optical absorption on thin films to examine the differences that may exist in the PCO system. To the best of the authors’ knowledge, this if the first time in-situ HTXRD and optical absorption measurements have been performed to monitor transient stoichiometry changes in thin films in an effort to extract meaningful kinetic parameters.

Experimental Methods

The following is a summary of the experimental details presented more fully in their respective references. Metal nitrate gel/precipitation/calcination methods were applied to prepare Pr$_x$Ce$_{1-x}$O$_{2-\delta}$ powders where the notation 100xPCO is used to denote Pr concentration (1, 3, 7). The PCO powders, examined by X-ray diffraction (Rigaku H3R Cu-source Powder Diffractometer), were found to form a single phase fluorite structure. Targets for the pulsed laser deposition of a 10PCO thin film on a sapphire substrate were prepared by pressing the PCO powders into pellets and sintering at >1400°C. Bulk samples for dilatometry and thermogravimetric analysis (TGA) were similarly prepared. Dilatometry and TGA were performed with an Orton dilatometer and TGA with a Cahn 2000 microbalance respectively, both with in-situ pO$_2$ measurements. Oxygen partial pressure was controlled using a yttria-stabilized zirconia pump, N$_2$/O$_2$ and CO/CO$_2$ mixtures. HTXRD was carried out using a PANalytical Expert Pro MPD diffractometer equipped with programmable incident-beam divergence slits and a high-speed high-resolution X’Celerator position-sensitive detector using Cu K$_\alpha$ radiation (7). Light transmission spectra were acquired using a 532 nm solid state, chopped laser source transmitted through the sample and recorded using a photodetector and lock-in amplifier.

Results and Discussion

Previously, our group has shown that PCO exhibits a transition from MIEC to ionic conductor and then back to MIEC with increasing pO$_2$ which is consistent with the corresponding valence changes of Ce and Pr (1, 2, 4). At low pO$_2$ (<10$^{-15}$ atm at 700°C) PCO undergoes the well known reduction of Ce$^{4+}$ to Ce$^{3+}$. This can be described by the following defect reaction, written in Kröger-Vink notation (8)(9)(10).

\[
O^\circ \leftrightarrow V_{O}^{**} + 2e^' + 1/2O_2(g) \tag{1}
\]

At intermediate pO$_2$, Pr is fully reduced and trivalent and thus acts like a standard acceptor dopant (e.g. fixed valent Gd or Sm), thereby fixing the oxygen vacancy concentration, described by:

\[
[Pr_{Pr}^+ ] = 2[V_{O}^{**}] \tag{2}
\]

thereby leading to predominantly pO$_2$ independent ionic conductivity.

At higher pO$_2$, the Pr begins to oxidize to the 4+ state, which is isovalent with the Ce host ion, leading, according to equation 2, to a corresponding decrease in the oxygen
vacancy concentration. With increasing pO₂, δ (oxygen vacancy concentration in Pr_{0.1}Ce_{0.9}O_{2-δ}) decreases consistent with the following reaction.

\[
2 \text{Pr}^{\text{Ce}}_{\text{c}} + V_o^{**} + 1/2 \text{O}_2 (g) \leftrightarrow 2 \text{Pr}^{\text{x}}_{\text{c}} + O_o^{**}
\]  

[3]

The rates at which reactions 1 and 3 proceed are central to the performance of SOFC electrodes, permeation membranes and oxygen storage materials. In the following, the redox kinetics of PCO is investigated by a number of experimental means and the results compared. Several of these methods lend themselves towards the study of thin films and thereby allow for the comparison in response of bulk vs. thin film specimens. The five transient measurement approaches include TGA and dilatometry of bulk samples and HTXRD, optical absorption, and impedance of thin films. In each case (except for impedance), either pO₂ or temperature was rapidly changed to induce a corresponding, slower change in defect concentration, resulting in a change of mass, lattice parameter, sample length, or optical absorption. The resulting transients were then modeled using the following diffusion equation (11).

\[
\frac{M(t)}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp\left(-\beta_n^2Dt/L^2\right)}{\beta_n^2 \left(\beta_n^2 + L^2 + L\right)}
\]  

[4]

where \(M(t)\) and \(M_\infty\) are the parameters being measured (e.g. length, mass) at any time \(t\) and at equilibrium, respectively. \(L\) is the bulk sample half-width or film full width and \(L\) is given by

\[
L = \frac{k}{D}l
\]  

[5]

where \(k\) and \(D\) in this paper are the chemical surface exchange coefficient and diffusivity, respectively. \(\beta_n\) are the roots of the following equation (12).

\[
\beta_n \tan \beta_n = L
\]  

[6]

The previous set of equations apply to diffusion in one dimension; applicable to the high aspect ratio TGA and thin film samples. For dilatometry samples, which have a rectangular geometry, a modified equation was used, though based on the same principle as equation 4 (13).

The normalized mass change as a function of time is shown in figure 1 at 700°C for a change in pO₂ also shown in the figure. The pO₂ step results in a change in δ and thus a change in \([\text{Pr}_{\text{c}}^{\text{O}}]\) by equation 2. The values for \(D\) and \(k\) shown in the figure were input into equations 4-6 resulting in the model line in figure 1. These values can be compared with our previously determined defect chemical and electrical conductivity models (1, 2). Using the following equation, which relates measured (or in this case predicted) ionic (\(\sigma_{\text{VO}}\)) and electronic (\(\sigma_{\text{Pr}_{\text{Ce}}^{\text{Pr}}}-\text{electronic charge carries hop within the Pr impurity band}\)) conductivity and defect concentration of the dominant charge carriers, the chemical diffusivity is determined (14).
The chemical surface exchange coefficient can be calculated using $k_{\text{elec}}$, determined from our group’s previously determined surface oxygen exchange resistance ($R_{\text{surf}}$) measurements (via impedance spectroscopy) on thin films (15, 16) using the following equations (14).

$$k_{\text{elec}} = \frac{kT}{4e^2 R_{\text{surf}}} \left[ \frac{1}{O_2} \right]$$  \hspace{1cm} \text{(8)}$$

$$k = \frac{1}{2} \frac{d \ln P_{O_2}}{d \ln [O_6^{\text{surf}}]} k_{\text{elec}} = 2 \times 10^{-5}\text{ cm}^2\text{s}^{-1} \hspace{1cm} \text{(9)}$$

The predicted values for $D$ and $k$ are in reasonably agreement to those determined by fitting figure 1, particularly since the exchange coefficient is sensitive to the surface treatment of the specimen.

Figure 1. Change in normalized stoichiometry (mass) of 10PCO at 700°C for the step change in $pO_2$ shown on the right axis. Spikes in the data (green line) are electrical noise in the measurement (raw data from the TGA output) and the dashed line is the model.

Next, the redox kinetics was examined by measuring the sample length change by dilatometry following a step change in $\delta$. Similar dilatometric kinetic studies on perovskite structured oxides were recently reported (13). Ceria is known to exhibit dilation (chemical expansion) upon loss of oxygen, which should follow the change in oxygen vacancy concentration induced by a corresponding change in the Pr$^{3+}$/Pr$^{4+}$ ratio. The experimental procedure followed included a) reduction of sample (to increase $\delta$) by annealing in a ~1% CO/CO$_2$ atmosphere above 700°C, b) cooling to room temperature, c)
atmosphere changed to air, d) heating in air to 100°C (small degree of re-oxidation occurs as confirmed by isothermal length change), e) rapid heating to 200°C, and f) holding at this temperature while sample contracts (as $\delta$ decreased due to reoxidation). The low temperature reoxidation kinetics is shown in figure 2 (for step f) along with the fit to the data. The measured $D$ and $k$ values are surprisingly large for such a low temperature and do not agree with the modeled values predicted using the previous technique and extrapolated to reduced temperatures. The disparity may arise from starting from a non-equilibrium state in which a significant diffusion profile may already have developed prior to the beginning of the measurement.

Next dilation was examined again, but this time by monitoring changes in lattice parameter with HTXRD. A thin film specimen was first reduced at low pO$_2$ (using ~1% CO/CO$_2$ gas) at elevated temperature, similarly to the dilatometry experiment, and quenched to room temperature, to retain a large value of $\delta$. The non-stoichiometry was confirmed by the change in color of the sample due to the presence of a Pr impurity band as explained in our other work (2, 17). The sample was then placed in the HTXRD setup in air and rapidly heated to 600°C, and then held isothermally. The isothermal data is shown in figure 3, along with a fit to the data. Only $k$ is reported for this measurement since the characteristic length, $D/k = 375$ μm (determined using the TGA values), is much larger than the film thickness ~ 440 nm and thus the film will be dominated by oxygen surface exchange. The value determined for $k$ is considerably lower than values obtained by TGA. In this measurement, equilibrium was not achieved during the course of the measurement, so $M_\infty$ was estimated by calculating the amount of chemical expansion that should occur for a change in $\delta \sim 0.05$ (oxidation of all Pr$^{3+}$ to Pr$^{4+}$). Some re-oxidation may have occurred during the initial temperature change as well as during the time for equilibration with temperature, all resulting in errors in the assumption of a step change in sample conditions. At this point it is unclear why the derived $k_{chem}$ is so low.
Figure 3. Normalized expansion of initially reduced 10PCO 440 nm thin film on sapphire measured by HTXRD as it oxidizes after heating from room temperature to 600°C. The chemical surface exchange coefficient from fitting the model is shown.

The final study in this paper demonstrates the ability to observe changes in $\delta$ using optical absorption. As mentioned for the previous HTXRD measurement, PCO absorbs light in the visible spectrum upon oxidation due to electron excitation from the valence band into the Pr impurity band. When all Pr is trivalent, the impurity band is full and the sample is clear, and upon oxidation (equation 3), the band empties and absorption occurs, probed here by measuring the transmission of a 532 nm laser through the sample. Figure 4 shows the oxidation of a 10PCO film at ~650°C (the same film used in figure 3). Prior to the reported measurement, the film was isothermally reduced in ~2% CO/CO$_2$ at ~650°C.

Figure 4. Change in 10PCO thin film absorption (same film as in figure 3) calculated from transmission measurements at a wavelength of 532 nm upon oxidation, assuming no change in reflection during the measurement.
and then when the reported measurement started, the gas was changed briefly to N₂ for purging and then to 100% O₂. The k used to achieve the model fit is also shown in the figure. There is good agreement between the optically and HTXRD derived k values, though the origin of the relatively low values remains unclear. Difficulties in controlling boundary conditions and extremely large chemical driving forces are suspected to have caused difficulties in obtaining reliable data for the thin film specimens. Nevertheless, these techniques promise the ability to monitor both the thermodynamic and kinetic properties of thin film materials exhibiting wide swings in oxygen stoichiometry. As the interest in thin films continues to grow in the field of Solid State Ionics, such techniques will be of growing importance.

Summary

The kinetics of defect formation were studied in dense, microcrystalline bulk samples of Pr₀.₁Ce₀.₉O₂₋δ (10PCO) by following transients in δ and chemical expansion via TGA and dilatometry, respectively. The oxygen chemical diffusivity and surface exchange rate derived from the TGA data agreed well with predictions based on defect chemistry and reported conductivity measurements. Also the changes in lattice parameter and optical absorption driven by transients in δ were studied using HTXRD and optical absorption, respectively. While there were difficulties in achieving consistent results, both the HTXRD and optical absorption techniques promise the ability to monitor the thermodynamic and kinetic properties of thin film materials exhibiting wide swings in oxygen stoichiometry. As the interest in thin films continues to grow in the field of Solid State Ionics, such techniques will be of growing importance.

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