Pt current collectors artificially boosting praseodymium doped ceria oxygen surface exchange coefficients†

Yuxi Ma,†a Theodore E. Burye†abc and Jason D. Nicholas†d,*a

The chemical oxygen surface exchange coefficient ($k_{chem}$) values used to quantify and rank oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) catalyst performance for high-temperature, oxygen-exchange-enabled devices (such as Solid Oxide Fuel Cells, Solid Oxide Electrolysis Cells, oxygen sensors, etc.) are often determined electrically, with the aid of precious metal current collectors. However, the curvature relaxation ($\kappa R$) and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) analyses performed here on Pulsed Laser Deposited thin films of the oxygen exchange catalyst Pr$_{0.1}$Ce$_{0.9}$O$_{2-x}$ (PCO) show that unpolarized platinum current collectors dramatically improve the $k_{chem}$ of Si-contaminated PCO by reducing the Si concentration at the PCO surface and/or diffusing into the PCO; even for PCO thin films only exposed to mild temperatures of 500 °C. This suggests that precious metal current collectors are likely responsible for some of the large $k_{chem}$ variation reported in the literature for “identical” materials tested under “identical” conditions.

\[ J = k_{chem} (C_o - C_s) \]  

(1)

where $J$ is the oxygen flux across a surface, $C_o$ is the oxygen concentration just inside the material, and $C_s$ is the oxygen concentration on the surface required to maintain equilibrium with the surrounding atmosphere. As such, $k_{chem}$ can be regarded as a “materials property” that can be used to rank a surface’s ability to facilitate oxygen transport between a material’s interior and the surrounding environment. For today’s most common Mixed Ionic Electronic Conducting (MIEC) oxygen exchange catalysts, all of which have electronic transference numbers close to 1, this ranking can be done through a direct $k_{chem}$ comparison (assuming that the materials have similar lattice oxygen concentrations that vary similarly with oxygen partial pressure ($P_{O_2}$), as is often the case as shown in Fig. S1 of the ESI†), or through its official conversion into a near-open-circuit oxygen surface exchange resistance, $R_s$, via the equation:

\[ R_s = \frac{k_B T}{4e^2 C_o k_o} \]  

(2)

where $k_B$ is Boltzman’s constant, $T$ is the temperature in Kelvin, $e$ is the elementary charge of an electron, $C_o$ is the oxygen ion concentration just inside the material, and $k_o$ is the oxide ion surface exchange rate constant (which is often approximated as the electrically-determined oxygen surface exchange coefficient, $k_e$ (ref. 10)) defined as:

\[ k_o = k_{chem} \gamma_o \]  

(3)

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are solid state chemical to electrical energy conversion devices that exhibit high power density, high energy density, high energy conversion efficiency, and fuel flexibility. In addition, SOFCs can be used in reverse as Solid Oxide Electrolysis Cells (SOECs) to store energy, produce chemicals, and/or generate fuels. Unfortunately, high system costs, high operating temperatures, and high degradation rates have complicated the commercial deployment of these Solid Oxide Cells (SOCs). With time however, it seems likely that improved materials will help lower these commercialization barriers. Since today’s “State-of-the-Art” SOCs are typically limited by poor oxygen ion transport (1) through the bulk of the solid electrolyte, (2) across the solid electrolyte-solid electrode interface, and/or (3) across the solid electrode-gas phase interface, it seems likely that future material sets will feature increased bulk oxygen ion conductivities, reduced interfacial resistivities, and/or increased chemical oxygen surface exchange coefficients.

The chemical oxygen surface exchange coefficient, $k_{chem}$, is commonly defined as:

*[Michigan State University, Chemical Engineering and Materials Science Dept., East Lansing, MI 48824, USA. E-mail: jdn@msu.edu  
†Contemporary Amperex Technology USA Inc, Rochester Hills, MI 48309, USA  
‡U.S. Army Combat Capabilities Development Command Ground Vehicle Systems Center, Warren, MI 48392, USA  
† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ta06237a]
Fig. 1  Literature-reported oxygen surface exchange properties of La$_{0.6}$Sr$_{0.4}$FeO$_3$ (LSF, squares), La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$ (LSFC, diamonds), La$_{0.6}$Sr$_{0.4}$CoO$_3$ (LSC, up-pointing triangles), Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC, left-pointing triangles), Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (BSCF, right-pointing triangles) and Pr$_{0.1}$Ce$_{0.9}$O$_{1.95}$ (PCO, pentagons) in air. Color denotes directly-measured values. Dark gray denotes values converted via eqn (2)–(4) with data from the same study as the directly-measured value. Light gray denotes values converted via eqn (2)–(4) with $C_0$ and $g_0$ values obtained from other studies (i.e. those shown in Fig. S1 of the ESI†). Here, $k_0$ was assumed to be $k_0 = k_q$, as commonly done in the literature. The ESI† contains a description of the minor equations and the actual spreadsheets used to perform the oxygen surface exchange conversions.

A = Mosleh et al., B = Søgaard et al., C = Søgaard et al., D = Yang et al., E = ten Elshof et al., F = Armstrong et al., G = Ishigaki et al., H = Baumann et al., I = Tripkovic et al., J = Plonczak et al., K = Bouwmeester et al., L = Cox-Galhota and McIntosh, M = Dalslet et al., N = Huang et al., O = Lane et al., P = Li et al., Q = Ried et al., R = Wang et al., S = Chater et al., T = Steele and Bae, U = Simrick et al., V = Moreno et al., W = Berenov et al., X = Egger et al., Y = Søgaard et al., Z = Januschewsky et al., AA = Siebenhofer et al., AB = Adler, AC = Hayd et al., AD = Preis et al., AE = Yeh et al., AF = Fullarton et al., AG = Fu et al., AH = Burriel et al., AI = Wang et al., AJ = Bucher et al., AK = Bucher et al., AL = Chen and Shao, AM = Girdauskaite et al., AN = Baumann et al., AO = Wang et al., AP = Falkenstein et al., AQ = Lohne et al., AR = Nicollet et al., AS = Nicollet et al., AT = Chen et al., AU = Ma and Nicholas, AV = Chen et al., AW = Simons et al., AX = Zhao et al.,AY = Chen et al. Bold studies were performed on thin films, italic studies were performed on loose or partially sintered powders, and unformatted studies were performed on bulk pellets with relative densities >92%.
where \( \gamma_o \) is the thermodynamic factor for oxygen defined as: \(^{11-15} \)

\[
\gamma_o = \frac{1}{2} \ln(p_{O_2}) \quad (4)
\]

A material’s oxygen surface exchange properties \((i.e.\ a \ material’s \ k_{chem}, k_o, k_q, R_e \ etc.)\) can also be combined with SOC structure–property-performance models\(^{16-18} \) to predict SOC electrode polarization resistances\(^{19-21} \) and/or identify optimal SOC electrode microstructures.\(^{22} \) Other devices (such as solar thermochemical cells,\(^{23} \) oxide memristors,\(^{24} \) oxygen separation membranes,\(^{25} \) catalytic converters,\(^{26} \) oxygen sensors,\(^{27} \) etc.) can also have their performance and/or efficiency impacted by the oxygen surface exchange properties of the materials within them.

However, before the scientific community can effectively engineer oxygen surface exchange coefficients for improved device performance, it must first figure out how to reliably measure them. Specifically, Fig. 1 shows that, even for the most common MIEC materials, huge \( k_{chem} \), \( k_o \), and \( R_e \) variations exist in literature for “identical” materials under “identical” conditions. For instance, in Fig. 1 there is a >10,000 times variation in the extrapolated 700 °C \( \text{Pr}_{0.5}\text{Ce}_{0.5}\text{O}_{2-x} \) (PCO) \( k_{chem} \) values, a >10,000 times variation in the measured 650 °C \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) (LSF) \( k_{chem} \) values, and a >100,000 times variation in the measured 500 °C \( \text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x} \) (BSCF) \( k_{chem} \) values.

The reasons for these oxygen surface exchange property variations are manifold. For instance, previous studies have shown that systematic differences in film crystallinity,\(^{28,29} \) grain size,\(^{29} \) surface orientation,\(^{31-34} \) surface chemistry,\(^{35-39} \) and/or surface gas phase adsorbates\(^{34,40,41} \) can all impact a material’s measured oxygen surface exchange properties. Experimental complications such as poor gas phase mixing,\(^{42} \) non-instantaneous atmospheric switching times,\(^{43} \) and/or large amounts of sample oxygen release that can undesirably alter the atmospheric \( p_{O_2} \) (ref. 44) can also produce \( k_{chem} \) variations.

However, despite the fact that precious metal surface additions are well known to improve the performance of the MIEC materials used as SOC electrodes, oxygen sensors, vehicular catalytic converters \( etc. \),\(^{45-48} \) an examination of how current collectors (especially the precious metal current collectors commonly used in the existing oxygen surface exchange literature\(^{30,40,49-62} \)) affect oxygen surface exchange properties is less clear. This uncertainty is perpetuated by the fact that (1) today’s most-common \( k_{chem} \), \( k_o \), and \( R_e \) measurement techniques \((i.e. \) Electrical Conductivity Relaxation (ECR) and Electrochemical Impedance Spectroscopy (EIS)\)) require the electrical polarization of a current collector, and (2) many ECR and EIS studies do not include descriptions of the current collector microstructure, materials, thickness, pattern geometry, and/or electrical-polarization used to perform the oxygen surface exchange measurements. This is problematic because electrically-polarized current collectors could alter oxygen exchange through (1) the enhanced oxygen exchange properties of some precious metals have been shown to catalyze at metal-MIEC–air interfaces,\(^{47,63-65} \) (2) the chemical gettering of surface-segregated MIEC ions/impurities that some current collecting materials are known to possess,\(^ {66} \) (3) current collector coefficient of thermal expansion (CTE) mismatch stress induced alterations in the point defect and/or surface chemistry that some mechano-chemically-active MIECs are known to exhibit,\(^ {67,68} \) (4) electric-field induced alterations in the point defect, surface chemistry, and/or metal-MIEC–air triple-phase-boundary widths that are known to occur in some MIECs,\(^ {69-72} \) etc.

Although a few studies to the contrary exist,\(^ {72} \) many more studies have found that precious metal surface decoration can significantly alter a material’s measured oxygen surface exchange properties. For instance, ECR measurements by Eger and Sitte\(^ {72} \) showed that a thin layer of silver increased the 600 °C \( k_{chem} \) of \( \text{La}_2\text{NiO}_3 \) by an order of magnitude, and Zhang \( et \ al. \)\(^ {72} \) observed similar ECR \( k_{chem} \) improvements for lanthanum strontium manganate decorated with platinum or palladium nanoparticles. EIS and oxygen isotope depth profiling experiments by Sahibzada \( et \ al. \)\(^ {71} \) showed that palladium surface decoration decreased the 700 °C \( k_o \) of \( \text{La}_0.6\text{Sr}_{0.4}\text{FeO}_3 \) (LSF) by an order of magnitude but improved the electrochemical performance of LSF at lower temperatures. Similarly, microelectrode EIS measurements performed by Riedl \( et \ al. \)\(^ {74} \) showed that platinum surface decoration either increased or decreased the \( R_e \) of \( \text{La}_0.6\text{Sr}_{0.4}\text{FeO}_3 \) (LSF) by up to ~100 times depending on the \( p_{O_2} \). Further, Ma and Nicholas\(^ {75} \) found that the 600 °C \( k_{chem} \) values obtained from current-collector-free curvature relaxation \((\kappa R)) \) and current-collector-free optical transmission relaxation \((\kappa R)) \) experiments were identical, but more than ~10–100 times lower than those obtained from \( k_{chem} \) techniques utilizing precious metals. Similarly, simultaneous ~300–600 °C measurements by Perry and coworkers\(^ {29,76} \) on strontium titanate thin films showed that roughly identical \( k_{chem} \) values were obtained from OTR and in-plane ECR measurements utilizing current collectors that only covered a small portion of the MIEC surface, but that ~10 times higher \( k_{chem} \) values were obtained via through-sample EIS measurements utilizing current collectors covering a large portion of the MIEC surface.

Despite these reports, precious metal current collectors are still being actively used to measure the oxygen surface exchange properties of MIEC materials.\(^ {36,49-60} \) Hence, the first objective of this work was to dramatically demonstrate the role that even minute amounts of unpolarized precious metals can have on
the $k_{\text{chem}}$ of MIEC materials. The second objective of this work was to go beyond the aforementioned past studies and identify any local chemistry changes likely responsible for the observed $k_{\text{chem}}$ alteration. These objectives were achieved by pairing (1) the remarkable ability of the curvature relaxation technique to obtain direct $k_{\text{chem}}$ measurements on PCO thin films that were either uncovered, partially Pt-covered, or completely Pt-covered, with (2) Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analyses of the sample chemistry before and after curvature relaxation.

2. Experimental methods

Here, PCO thin films were produced by Pulsed Laser Deposition (PLD), optionally coated with one of the platinum current collector geometries shown in Fig. 2, and tested via curvature relaxation ($kR$).

2.1 Sample fabrication

Prior to thin film deposition, 25.4 mm diameter, one-side-polished, 200-micron-thick, (100)-oriented $\text{Y}_2\text{O}_3$/$\text{ZrO}_2$ (YSZ) single crystal substrates (Crystec GmbH, Berlin, Germany) were air-annealed at 1450 °C for 20 h utilizing 5 °C min$^{-1}$ nominal heating and cooling rates to remove any residual stress within them. This wafer annealing schedule was chosen because it had previously been shown capable of reducing the curvature changes observed upon heating these YSZ wafers from 25 to 700 °C to less than 0.005 m$^{-1}$ (so that residual stress changes would not obscure the $\sim$0.002 m$^{-1}$ curvature changes caused by film reduction or oxidation at a single, constant temperature). In addition, $\sim$94% dense $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_2$ (PLD) targets were produced from PCO powder fabricated via the glycine nitrate combustion (GNC) method. This GNC process was conducted by first dissolving 99.9% pure cerium nitrate (Strem Chemicals, Newburyport MA), 99.9% pure praseodymium nitrate (Strem Chemicals, Newburyport MA), and 99% pure glycine (Millipore Sigma, Burlington, MA) in 18.2 MΩ water (Millipore Sigma, Burlington, MA) at a 1:1 glycine:nitrate molar ratio using a Teflon coated stir bar (Fischer Scientific, Pittsburgh, PA) in a Pyrex beaker (Fischer Scientific, Pittsburgh, PA). The resulting solutions were then ignited over a hotplate in a stainless-steel reaction vessel (Polar Ware, Kiel, WI). To remove unreacted glycine, the resulting powder was calcined in a 99.8% pure alumina crucible (CooresTek, Golden, CO) at 1000 °C in air for 1 hour using 5 °C min$^{-1}$ nominal heating and cooling rates. The calcined powder was then uniaxially compacted to $\sim$63 MPa in a 38 mm stainless-steel die (MTI, Richmond, CA) and sintered at 1450 °C for 20 h in air using nominal 3 °C min$^{-1}$ heating and 10 °C min$^{-1}$ cooling rates. The resulting sintered target was then ground down to 25 mm diameter and 2.5 mm thick using 240 grit SiC sandpaper and bonded with silicone to a $\sim$2.5 mm thick, 25 mm diameter copper backing.

PCO PLD thin films were produced from the aforementioned target by depositing $\sim$265 nm of PCO onto 700 °C-preheated YSZ wafers within 30 mTorr of oxygen using the PLD/MBE 2300 system (PVD Products, Inc) at the Northwestern University PLD User Facility. PLD was conducted using a 100 mm target-to-substrate distance and 15 000, 10 Hz, 200 mJ, 248 nm KrF excimer laser pulses. All the PCO/YSZ samples reported here were (1) cooled to room temperature at 10 °C min$^{-1}$ upon the completion of PCO deposition, (2) produced consecutively during a single PLD session, and (3) stored within individual polypropylene wafer containers when not undergoing subsequent processing or characterization. After thin film deposition, each PCO/YSZ sample had its oxygen vacancy defect concentration re-equilibrated with air via an hour-long 1100 °C hold utilizing nominal 3 °C min$^{-1}$ heating and cooling rates.

To produce patterned platinum current collectors covering $\sim$2.7% of the PCO geometric surface area (such as those for the partially Pt-covered PCO/YSZ samples shown on the right-hand side of Fig. 2) some of the 1100 °C re-equilibrated PCO/YSZ samples were subjected to an acetone rinse, a methanol rinse, a deionized water rinse, and then baking it in air at 115 °C for 20 h utilizing nominal 3 °C min$^{-1}$ heating and cooling rates.

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To produce “completely” Pt-covered PCO/YSZ samples such as those shown in the left side of Fig. 2 (i.e. those where 100% of the geometric PCO surface area was covered with 89% dense Pt films), some PCO/YSZ samples were placed in the aforementioned Axis PVD system and subjected to the same platinum sputtering conditions used for the partially Pt-covered PCO/YSZ samples. However, these completely Pt-covered samples were not subject to the solvent cleaning, photoresist application, UV curing, or photoresist removal processes needed for the partially Pt-covered samples.

To make sure the $kR$ signal of the completely Pt-covered PCO/YSZ samples came from oxygen exchange into/out of the PCO (instead of the Pt), a bare YSZ wafer was completely covered...
with platinum using the same procedures as those used for the completely Pt-covered PCO/YSZ samples.

2.2 Oxygen surface exchange measurements

Here, thin film PCO oxygen surface exchange coefficient measurements were performed using the \( kR \) method described, and derived, previously in the literature.\textsuperscript{75-79,82} In brief, the curvature relaxation techniques determines \( k_{\text{chem}} \) from the PCO volume changes accompanying small, isothermal, \( p_{O_2} \)-induced changes in the oxygen nonstoichiometry (\( \Delta \delta \)) that occur in PCO above \( \sim 400 \) °C in air via the reaction:\textsuperscript{75,83-85}

\[
2\text{Pr}^{+}\text{Ce}^3 + \frac{1}{2} \text{O}_2 \rightarrow 2\text{Pr}^{3+}\text{Ce}^3 + \text{O}_2^\cdot
\]

Assuming that as this mecha-chemically-active defect reaction proceeds (1) the oxygen-exchange-active thin film remains well bonded to an oxygen-exchange-inactive substrate, (2) the film and substrate only deform in a linear elastic manner, (3) the film is more than \( \sim 500 \) times thinner than the substrate but is thick enough to ensure that its volume changes bend the wafer in a detectable manner, (4) the film thickness is at least \( \sim 500 \) times lower than the film materials characteristic thickness \( L_c = D_{\text{chem}}/k_{\text{chem}} \), where \( D_{\text{chem}} \) is the chemical diffusion coefficient, to ensure that the sample response is only controlled by surface exchange and not partially or fully controlled by oxygen diffusion in the bulk of the film, and (5) the \( p_{O_2} \) step size is small enough to ensure that (a) the oxygen surface exchange process remains linear, and (b) the resulting change in oxygen nonstoichiometry (\( \Delta \delta \)) is small enough to ensure that the film strain \((\varepsilon_c)\) can be described by:

\[
\varepsilon_c = \frac{\Delta f}{f_0} = a_c \Delta \delta
\]

where \( a_c \) is the chemical expansion coefficient, the PCO oxygen surface exchange coefficient can be mathematically extracted from how quickly the PCO/YSZ sample curvature equilibrates to a new \( p_{O_2} \) by fitting the observed curvature relaxation to the following solution to Fick’s second law:\textsuperscript{86}

\[
\frac{k - k_0}{k_{sw} - k_0} = 1 - \exp\left(-\frac{K_{\text{chem}} t}{h_t}\right)
\]

where \( k \) is the instantaneous sample curvature, \( k_0 \) is the sample curvature before the relaxation, \( k_{sw} \) is the sample curvature after the relaxation, \( t \) is time, and \( h_t \) is the film thickness. In addition to being a non-contact, \textit{in situ} thin film \( k_{\text{chem}} \) measurement technique that works with, or without, overlying current collecting layers, the \( kR \) technique has the benefit that no specific film or substrate materials property values are required to obtain accurate thin film \( k_{\text{chem}} \) values \textit{via} eqn (7) (so long as the film and substrate have isotropic in-plane mechanical properties, as was the case here).

To determine if multiple processes with different time constants (or different rates of the same process in different parts of the sample) were active, all curvature data was replotted to search for slope changes in \( \ln \left[ \frac{1 - KK}{K_{sw} - K_0} \right] \) vs. time plots during each relaxation, as has been done previously.\textsuperscript{31,79,86-88}

Fig. 3 shows a schematic of the controlled atmosphere multi-beam optical stress sensor setup used to perform the \( kR \) measurements reported here (see Nicholas\textsuperscript{84} for the exact dimensions). In preparation for \( kR \) experiments, each PCO/YSZ sample was placed atop the central quartz support tube shown in Fig. 3, covered with the controlled-atmosphere gas-heating manifold shown in Fig. 3, heated to 500 °C at 5 °C min\(^{-1}\), and held at 500 °C for 1 hour in air to equilibrate and homogenize the PCO oxygen vacancy concentration. Then, the uncovered, partially Pt-covered, and completely Pt-covered PCO/YSZ samples were measured in 25 °C increments from 675 to 725 °C, 500 to 725 °C, and 500 to 425 °C, respectively, after holding for at least 30 minutes at each temperature to promote thermal equilibrium. Curvature relaxations were triggered by switching the \( p_{O_2} \) around each sample from 100 sccm of 0.21 (21% \( O_2 \)-79% \( Ar \), \textit{i.e.} synthetic air) to 100 sccm 0.021 (2.1% \( O_2 \)-97.9% \( Ar \), \textit{i.e.} 10 times diluted synthetic air) using a four-way valve. Since the same synthetic gas mixtures were used to test all the samples, atmospheric impurity content differences should not have contributed to the observed differences in sample behavior. As shown in Fig. S2–S4 of the ESI,\textsuperscript{†} each sample was allowed to re-equilibrate at each \( p_{O_2} \) for at least 5 times the characteristic relaxation time (to allow for reliable \( kR \) fitting, as explained in den Otter et al.).\textsuperscript{89} Only \( k_{\text{chem}} \) values that were not reactor flush time limited (\textit{i.e.} those where switching between two 100 sccm gas flows or between two 300 sccm gas flows yielded the same \( k_{\text{chem}} \) values) were reported here.

2.3 Additional sample characterization

To evaluate PCO thin film phase purity, X-Ray Diffraction (XRD) was performed in room temperature air from 20 to 80° with a 0.01° step size and a 1 s per step dwell time using unfiltered Cu
k_x radiation from a SmartLab diffractometer (Rigaku, The Woodlands, TX) operated at 44 kV and 40 mA with 10 mm-wide detector and source slits.

To evaluate PCO thin film surface composition, X-Ray Photoelectron Spectroscopy (XPS) was performed at room temperature and 10^{-9} torr on uncovered PCO/YSZ samples after (1) post-deposition re-equilibration in air and (2) after curvature relaxation. XPS was performed using the Al Kz X-ray radiation inside a Phi 5600 XPS (PerkinElmer, Waltham, MA). XPS survey scans were collected with a step size of 0.4 eV and a pass energy of 187.5 eV. XPS peak positions were calibrated with the carbon 1s peak at 284.8 eV. Due to concerns that the vacuum encountered during XPS analysis might alter the PCO oxygen vacancy concentration, the samples used for XPS analyses were not used for kR experiments.

To evaluate film thickness, Scanning Electron Microscopy (SEM) was performed on fractured PCO/YSZ samples coated with ~5 nm of Ti and imaged using a TESCAN MIRA3 Field Emission SEM (Tescan, Brno, Czechia).

To evaluate PCO thin film bulk composition, PCO/YSZ samples were analyzed via ToF-SIMS depth profiling conducted by EAG Labs (East Windsor, NJ, USA). The absolute concentrations of Zr, Y, and O in the films were calculated from the relative concentrations produced by SIMS by setting the SIMS-detected concentrations in the bulk of the YSZ substrate equal to those found in (Y_2O_3)(0.095)(ZrO_2)(0.905). Likewise, the absolute concentrations of Pr and Ce were calculated from the measured SIMS profiles by offsetting each Pr and Ce SIMS profile until the Pr and Ce concentrations in the interior of the film equaled those found in Pr_0.1Ce_0.9O_2. Likewise again, the Pt concentration profiles were offset until those in the Pt current collector equaled those found in dense Pt metal. In contrast, a single Ta_2O_5 standard with a known amount of Si was used to estimate the Si concentrations in all the PCO films, assuming that the SIMS matrix effects in Ta_2O_5 and PCO were similar. Even if this assumption was incorrect and as a result introduced errors in the absolute Si concentration values, the fact that the same Si calibration, SIMS collection settings, and SIMS equipment were used for all the samples suggests that any relative Si concentration differences between the samples, and within each sample, should be valid.

3. Results and discussion

Fig. 4 shows representative XRD scans indicating that only crystalline, fluorite-structured PCO and crystalline, fluorite-structured YSZ peaks were present in the PCO/YSZ samples. Consistent with previous literature reports, all the PCO films here exhibited (100) preferred orientation, consistent with the (100) oriented YSZ substrates they were grown upon.

Fig. 5 shows representative XPS scans indicating that the sample fabrication procedures used here produced “clean” PCO surfaces containing only Ce, Pr and O. No Si, Zr, Y or any other element was found in any of the XPS scans, even for uncovered PCO/YSZ samples kR tested to 725 °C in a Si-containing kR test rig known to vapor deposit Si on samples held for extended times at and above 600 °C. This suggests that any surface impurities in the PCO/YSZ samples here were present in amounts below the ~1 atomic percent XPS detection limit. Fig. S2–S4 of the ESI† show representative curvature relaxation data for the uncovered, partially Pt-covered, and completely Pt-covered PCO/YSZ samples. These plots show that all the PCO/YSZ samples here exhibited reproducible equilibrium stress levels and oxygen surface exchange constants with P_02 cycling. Further, as indicated by the linear nature of the In [1 - \frac{K - K_0}{K = K_0}] data during the portion of time each sample was equilibrating to a new P_02, only a single oxygen exchange process was active for all the measured samples. The small deformations involved, the mechano-chemical inactivity of YSZ under the conditions used here, the chemical compatibility of...
YSZ and ceria under the conditions used here, a $h_f/h_s < 0.002$, a $h_r < 0.0001 \times L_c$ (based on the reported 450–725 °C PCO $L_c$ values, $D_{\text{chem}}$ activation energies$^{100,101}$ and $k_{\text{chem}}$ activation energies$^{31,75,90,102}$), and the reproducible curvature behavior with $p_O$, switching for all the PCO/YSZ samples tested here and shown in Fig. S5 of the ESI, ensured that all the assumptions needed to ensure the validity of eqn (7) were met.

Fig. 6 shows that covering either ~2.7% or 100% of the PCO surface with unpolarized Pt current collectors significantly boosted the PCO oxygen surface exchange coefficient. Further, uncovered PCO/YSZ samples measured at the beginning (green circles) and end (red triangles) of the $k_{\text{chem}}$ measurement series yielded identical $k_{\text{chem}}$ values, attesting to the high reproducibility of the sample fabrication and measurement procedures used here. Interestingly, compared to uncovered PCO/YSZ samples from Ma and Nicholas$^{75}$ that were prepared in a different PLD chamber, grown at a lower temperature, and (unlike the present samples) alkaline etched to remove surface-segregated impurities, the uncovered PCO/YSZ samples here had lower $k_{\text{chem}}$ values. However, the ~0.6 eV activation energies observed for the present study’s uncovered PCO/YSZ samples were similar to those measured above 500 °C in the curvature relaxation measurements on uncovered PCO PLD thin films from Ma and Nicholas,$^{75}$ the optical transmission relaxation measurements on uncovered PCO PLD thin films from Chen et al.,$^{102}$ the electrochemical impedance spectroscopy measurements on Ag-paste-covered PCO PLD thin films from Chen et al.,$^{76}$ and the optical transmission relaxation measurements on uncovered PCO PLD thin films from Nicollet et al.$^{31}$ This suggests that the same rate-determining step for oxygen incorporation into PCO was active above ~500 °C for all the PCO samples here and in the literature, even its rate was faster in some samples versus others.

In contrast, Fig. 6 shows that at temperatures less than ~500 °C, the completely Pt-covered PCO/YSZ samples (blue diamonds) had activation energies essentially double those of the uncoated PCO/YSZ samples measured above ~500 °C. Similarly, although not mentioned by the authors, high sub-500 °C PCO activation energies of ~1.3 eV can also be seen in the optical transmission spectroscopy data of Chen et al.$^{102}$ on uncovered (i.e. Pt-free) PCO PLD thin films that transitioned to $k_{\text{chem}}$ activation energies of ~0.5 eV above ~500 °C. (Unfortunately, the exceeding-fast, low-temperature oxygen exchange kinetics of the completely Pt-covered PCO/YSZ samples meant that reactor flush time limitations prevented them from being measured above 500 °C, when their $k_{\text{chem}} > 1 \times 10^{-6} \text{ cm s}^{-1}$.) The fact that this previously unrecognized $k_{\text{chem}}$ activation energy transition was seen in Chen et al.’s$^{102}$ samples without platinum current collectors indicated that it is a general characteristic of PCO, and is not related to the absence or presence of precious metal current collectors. The observation of a higher activation energy at lower temperatures is the opposite of (1) what is commonly observed in other doped ceria compositions,$^{103}$ and (2) what might be expected based on the idea that lower temperatures would de-activate higher activation energy barrier pathways for oxygen exchange into/out of a static
identical near-surface reductions in the Ce and Pr concentrations). This position also corresponded to the midpoint in oxygen substrate majority cation concentrations (i.e. the Ce and the Zr concentrations). This position also corresponded to the midpoint in oxygen substrate majority cation concentrations (i.e. the Ce and the Zr concentrations).

Regardless of the exact reason for this newly-recognized 500 °C activation energy change, Fig. 6 makes it clear that completely covering the PCO surface with sputtered Pt dramatically boosts the measured $k_{\text{chem}}$. The fact that sputtered Pt did not reduce the measured $k_{\text{chem}}$ is consistent with the thin nature of the sputtered Pt current collectors, the low grain boundary and/or surface-path resistivities observed previously for oxygen transport in sputtered Pt films,\textsuperscript{94,104} and the likely-percolated ~11% porosity of the sputtered Pt films\textsuperscript{78} facilitating gaseous oxygen transport to the PCO surface.

Fig. 6 also shows that the partially Pt-covered PCO/YSZ samples exhibited $k_{\text{chem}}$ Values between those of the uncovered and completely Pt-covered PCO/YSZ samples. With only ~2.7% of the PCO surface covered by Pt, the observed $k_{\text{chem}}$ enhancements were modest and hence the partially Pt-covered PCO/YSZ samples could only be measured above 500 °C, where they displayed activation energies similar to those measured previously.

Fig. 7 provides a graphical summary of just how much faster oxygen exchange was in the completely Pt-covered PCO/YSZ samples than in either the uncovered or partially Pt-covered PCO/YSZ samples. Specifically, even though the temperature for the completely Pt-covered PCO/YSZ curvature relaxation is 250 °C lower than the uncovered or partially Pt-covered PCO/YSZ samples in Fig. 6, the time required to complete the oxygen exchange process is ~2 times less.

Fig. 8 suggests that the platinum current collectors used here improved the PCO $k_{\text{chem}}$ by removing Si from the PCO surface and/or diffusing into the PCO. Specifically Fig. 8a and b show that the uncovered PCO films had approximately 1 Si atom for every 100 Pr atoms in their bulk and had enriched amounts of Si at their air-PCO and PCO-YSZ interfaces. This Si contamination probably resulted from the silica-based glassware used to produce the PCO powder utilized in PLD target fabrication (this contamination could likely have been avoided through the use of polyethylene beakers but was retained here to illustrate the interaction common processing and environmental contaminants can have with PCO platinum current collectors). Si enrichment at the air-PCO interface may help explain the low $k_{\text{chem}}$ values observed in the uncovered PCO/YSZ samples, since surface-segregated Si impurities are well-known for inhibiting oxygen surface exchange and bulk oxygen transport in PCO and a variety of other ceria-based compositions.\textsuperscript{96,105-109} Fig. 8a and b also show a slight enhancement of Zr and Ce at the PCO surface, but since those elements occurred at concentrations 10 to 100 times less than the Si concentration, Si was assumed to be responsible for the low $k_{\text{chem}}$ values observed in the uncovered PCO/YSZ samples. Fig. 8a and b also show interdiffusion of Pr, Ce, Zr, and Y between the film and substrate, and diffusion of Si from the film into the substrate,
the majority of which presumably happened during the 1 hour, 1100 °C re-equilibration in air. Interestingly, a comparison of Fig. 8a and b shows that although the bulk Si level in the film and near the exposed surface roughly doubled (presumably due to silica vaporization from the silica kR test rig known to occur at and above ~600 °C)\(^{96,105}\) and some of the bulk Si migrated to the PCO/YSZ interface, no other significant changes in the sample chemistry, or chemical distribution, occurred during kR testing up to 725 °C.

Fig. 8c suggests that the completely Pt-covered PCO/YSZ current collectors applied here cleaned the air-PCO interface by serving as a chemical getter for the surface-segregated Si, Zr and Ce present on uncoated films. The ability of Pt current collectors to act as Si getters to improve the PCO \(k_{\text{chem}}\) is not completely surprising since (1) Ma and Nicholas\(^{96}\) recently quantified the relationship between the PCO Si surface content and \(k_{\text{chem}}\) and (2) Zhao et al.\(^{105}\) found that La or Sm PCO surface additions improved \(k_{\text{chem}}\) by gettering surface Si. However, it is also possible that the near-surface dips in the Si, Zr, and Ce profiles could be artifacts caused by the SIMS front transitioning from the metal to the oxide.

In addition to suggesting that Pt cleared Si from the PCO surface, Fig. 8c shows that significant quantities of Pt diffused into the PCO film (with the Pt concentration exceeding the Pt doping level for more than 50 nm into the PCO film). This is somewhat surprising because the completely Pt-covered PCO-YSZ samples only saw temperatures up to 500 °C during kR testing. However, this behavior is consistent with prior reports that platinum can diffuse into ceria at room temperature,\(^ {110}\) especially when ceria experiences reducing conditions,\(^ {111}\) as likely occurred during the Pt current collector sputtering process.

Whether from the removal of Si from the PCO surface, Pt diffusion into the ceria, or some of the other mechanisms proposed in the literature,\(^ {63,110,111}\) the results here make it clear that completely covering a significant portion of a material’s surface with Pt current-collectors can lead to \(k_{\text{chem}}\) values significantly different from those the material would display on its own. As such, the small \(k_{\text{chem}}\) enhancements observed here for the partially Pt-covered samples in Fig. 6 were assumed to be due to the portion of the PCO close to the Pt current collectors behaving like the completely Pt-covered PCO/YSZ samples, while those portions of the PCO further away from the Pt current collectors behaved more like the uncoated PCO/YSZ samples.

Fig. 9 compares the curvature response of a completely Pt-covered PCO/YSZ sample to a completely Pt-covered YSZ wafer. The fact that essentially no curvature response was observed in the completely Pt-covered YSZ wafer with \(p_{O_2}\) switching confirms that the observed \(k_{\text{chem}}\) enhancements were not the result of oxygen exchange into/out of the bulk of the Pt, but instead were related to Pt current collectors influencing oxygen exchange into/out of the PCO.

4. Conclusions

Despite many studies suggesting that precious metal current collectors and/or impurities can impact the performance of oxygen-exchange-enabled devices,\(^ {45-48}\) precious metal current collectors are still routinely used to transport electronic species into/out of oxygen exchange materials in Electrical Conductivity Relaxation,\(^ {56,49-58}\) and Electrical Impedance Spectroscopy\(^ {59,60}\) oxygen exchange experiments. The results here demonstrate that precious metal current collectors are not necessarily inert (i.e. they can diffuse into and/or chemically clean the surface of the oxygen exchange material of interest), can unexpectedly alter the measured \(k_{\text{chem}}\) values, and, hence, should be treated with caution when used for oxygen surface exchange measurements. This is especially true when performing oxygen exchange measurements on either bulk or thin film samples where a significant fraction of the oxygen-exchange-active surface is in close proximity to a precious metal current collector (such as ECR \(k_{\text{chem}}\) measurements on materials with low electronic resistivities that require the close placement of interdigitated electrodes to get measurable electronic conductivities, experiments performed with fine-grained colloidal precious metal pastes and/or precious metal thin films applied over most of the oxygen-exchanging surface, etc.). Further, if precious metal current collectors dramatically improve the oxygen exchange kinetics of the neighboring/underlying MIEC, artificially high \(k_{\text{chem}}\) values could also be recorded for electrical (ECR, EIS, etc.) \(k_{\text{chem}}\) measurements performed using small precious metal current collectors placed a significant distance apart (since the precious-metal-activated portions of the MIEC surface would act as “major leaks” for oxygen incorporation into the bulk of the material and hence would “drown-out” the

Fig. 9 Curvature changes upon 500 °C \(p_{O_2}\) switching for (a) completely Pt-covered PCO/YSZ sample and (b) a completely Pt-covered YSZ wafer.
response from slower oxygen incorporation along the bare MIEC surfaces). For all these reasons, it is likely that precious metal current collectors are responsible for a significant portion of the $k_{\text{chem}}$ variation reported in the literature for “identical” materials tested under “identical” conditions.

**Author contributions**

Y. Ma performed the thin film deposition and characterization, T. E. Burye performed the $k_{\text{chem}}$ literature review, and J. D. Nicholas conceptualized and led the write-up of this work.

**Conflicts of interest**

There are no conflicts to declare.

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