Supporting Information for

_In situ_ Characterization of Ceria Oxidation States in High-temperature Electrochemical Cells with Ambient Pressure XPS

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Cell Fabrication Details – Yttria Stabilized Zirconia (YSZ) electrolyte supports (purchased from Coating and Crystal Technology and MTI Corporation) were 1.2 cm X 1.2 cm in area and 1 mm thick. Dense ceria films, 4.2 mm X 6.0 mm, were sputter-deposited on this support using a Kurt J. Lesker PVD75 system, with an RF power of 150 W applied for 30 minutes, under 5% O₂/Ar gas mixture of 5 mTorr, and with a throw distance of 65 mm. The Au patterned current collector included eight 4.8 mm long parallel bars, each 100 μm wide with 400 μm spacing between them. Two cross bars also 100 μm wide connected all 8 Au bars at each end and a pad approximately 1 mm X 1 mm was placed at the middle of one of the cross bars on the outside of the pattern for a solid lead connection to the Au pattern. These patterns are illustrated in Figure 1 and the insets of Figures 3b and 4. The Au pattern leaves approximately ~200 μm wide border of ceria around 3 sides of the Au pattern. Pt-slurry (Engelhard Corp.) was used to form a porous Pt counter electrode (CE) 2 mm wide X ~8 mm long. Pt gauze (52 mesh from Alfa Aesar) was pressed into the slurry paste before baking for 3 hours at 800 °C to remove solvents and pore formers from the paste and to anneal the electrodes. The exposed YSZ between the adjacent edges of the ceria and the Pt electrode was ~600 μm wide.

The sputter-deposited ceria electrodes and Au current collectors were characterized by SEM images. SEM images of cross-section as exemplified by Figure S1 were used to assess film

Figure S1. SEM cross-section of thin-film, sputter-deposited ceria anode on YSZ electrolyte and with Au current collector pattern deposited on top surface of ceria.
thickness and structure. Cross-section images show continuous contact between the ceria and YSZ thereby allowing for facile $O^2-$ transport across the phase boundary. Dense Au current collectors (250-300 nm thick) were then sputter-deposited over the ceria films and patterned via optical lithography. The cross-section images also indicate the thickness of the Au current collector on top of the ceria electrode.

2-D Simulation of Electric Potential Distribution – With the single-chamber geometry having electrodes on the same side, the electrochemical activity was expected to be non-uniform over the area of the ceria electrode. In order to estimate the regions of high electrochemical activity to provide guidance for the ambient pressure XPS measurements, a 2-D simulation of the electric potential field and the $O^2-$ conduction through the YSZ electrolyte and ceria electrode was performed with simple electrode models used to estimate $\eta_{WE}$ and $\eta_{CE}$.

For this analysis, steady-state electric potential in the ion-conducting phases (YSZ electrolyte and ceria WE) is governed by Laplace’s equation:

$$\nabla^2 \phi = 0$$

(S1)

The modeled geometry matches that of the electrochemical cells with the rectangular Pt CE used in the majority of the experiments. There are four separate boundary conditions required for this model: (i) at the external YSZ surface in contact with the Pt CE, (ii) at the Ceria/YSZ interface, (iii) at the external Ceria surface in contact with the Au current collector bars, and (iv) at all other external boundaries. As such, the lateral distribution of Faradaic currents at the Pt/YSZ interface and over the ceria WE surface will affect the distribution of current and thus Ohmic losses in the YSZ electrolyte. Boundary condition (i) is written as a Neumann boundary condition, where the ion current in the YSZ must match the local Faradaic current in the Pt CE, which is approximated by a Tafel expression in equation S2:

$$\sigma_{O^2-,YSZ} \nabla \phi_{YSZ} = i^0 \exp\left(\frac{2\alpha n_{CE}}{RT}\right)$$

(S2)
where $\sigma_{O_2,\text{YSZ}}$ is the ionic conductivity of the YSZ (taken from literature values\(^1\)), $i_o$ the exchange
current density, $n_{\text{elec}}$ the number of electrons transferred, $\alpha$ the charge-transfer coefficient, $\eta_{\text{CE}}$ the
overpotential associated with charge transfer at the Pt/YSZ interface, $R$ the universal gas constant, and
$T$ the temperature. For this analysis, standard values were assumed for the Tafel parameters, $n_{\text{elec}} = 2$
and $\alpha = 0.5$, while simulations explored a range of exchange current densities ($5 \times 10^{-5} \text{ A cm}^{-2} \leq i^0 \leq$
$2.5 \times 10^{-4} \text{ A cm}^{-2}$). Simulations assume that the charge-transfer overpotential at the ceria/YSZ
interface is not significant. Boundary condition (ii) is thus set such that the ion currents on either
side of the YSZ/Ceria interface are equal:

$$\sigma_{O_2,\text{YSZ}} \nabla \phi_{\text{YSZ}} = \sigma_{O_2,\text{CeO}_x} \nabla \phi_{\text{CeO}_x} \tag{S3}$$

The Au current collector, with its high electronic conductivity, is assumed equipotential, and thus
boundary condition (iii) is written as a Dirichlet boundary condition, with $\phi_{\text{Au}} = 0.0 \text{ V}$ directly
beneath the current collector. Finally, it is assumed that no current crosses the remaining external
surfaces, and thus boundary condition (iv) is a Neumann condition that enforces zero electric
potential gradient in the direction of the outward unit normal vector at these boundaries.

The model assumes uniform conductivity throughout the ceria electrode and does not attempt to
model changes in cerium valence states or chemical species concentrations. The model requires that
$\text{O}^{2-}$ flux lines terminate near the Au/ceria three-phase boundary and as such, does not capture the
spreading of the ceria surface reactions and subsequent lateral polaron transport in the ceria.
Nonetheless, the model results provide critical insight into how bulk Ohmic processes, particularly
in the YSZ, affect the distribution of $i$ over the area of the ceria electrode and as such provide
guidance for the XPS measurements.

Figure S2a shows the simulated electric potential distribution in the YSZ for a temperature of
700 °C. For the plotted distribution, the exchange current density at the Pt electrode $i^0 = 2 \times 10^{-4}$
A·cm$^{-2}$. In addition, the Pt CE width is set at 1500 µm. The ceria WE is not discernible in Fig. S2a
due to its 300 nm thickness. All the same, the simulation results demonstrate that the current (which
runs perpendicular to the equipotential lines in Figure S2a) is distributed throughout the full 1 mm
thickness of the YSZ electrolyte. The distribution of the potential across the YSZ surface is shown in Figure S2b, and the results show the distribution in overpotential across the width of the Pt CE and also across the width of the ceria WE. The locations of the Au current collectors are indicated by the location of near zero potential at the YSZ surface. The non-zero potentials along the YSZ surface on the right-hand side of the ceria WE indicate the regions of the cell that are electrochemically active and thereby have an overpotential through the ceria WE.

The model results in Figure S2a and S2b provide critical insight into how bulk Ohmic processes affect the distribution of $i$ over the area of the WE. The simulation indicates that the voltage distribution in the YSZ underneath the ceria WE (i.e., $\phi_{YZS@WE}$) varies strongly up to the first current collector bar and thereafter approaches $\phi_{Au} (= 0 \text{ V})$ as the local current density in the ceria film falls...
to zero. The model thus predicts that electron transfer between the Au and the ceria WE occurs primarily at the current collector bar closest to the CE, with a small fraction occurring at the second current collector bar. Thus, the impact of electrochemical activity on near-surface oxidation states in the ceria will be most readily observed by in situ XPS measurements of the ceria around the first Au bar. For in situ XPS measurements on the ceria further from the Pt CE, it is expected that the cerium near-surface oxidation state should more closely match the equilibrium surface configuration seen at zero current. The modeling results thus inform experimental measurements by providing an estimate of the physical extent of electrochemical activity on the ceria WE surface. Because of the localized nature of the electrochemical activity, the XPS spectra on the ceria WE were almost exclusively taken in the region between the Au bar and the edge of the ceria film closest to the active Pt electrode. The primary measurement locations are indicated in the inserts in Figures 3b and 4.

*Interpretation of Ce3d XPS Spectra* – By treating each spectrum as a linear combination of pure Ce\(^{4+}\) and Ce\(^{3+}\) reference spectra, the in situ XPS spectra taken during the simultaneous electrochemical testing were fitted as shown in Figure S3. The reference spectrum for the Ce3d transition for Ce\(^{4+}\)

\[ \text{Figure S3: Representative Ce3d spectrum (black dots) taken with photon energy of 1180 eV with cells operating at 635 °C at two currents: a) } I_{\text{tot}} = -474 \mu\text{A with 89% Ce}^{3+} \text{ and 11% Ce}^{4+}, \text{ and b) } I_{\text{tot}} = +144 \mu\text{A with 52% Ce}^{3+} \text{ and 48% Ce}^{4+}. \text{ The fits (red lines) were obtained using a linear regression of reference Ce}^{3+} \text{ (blue hashes) and Ce}^{4+} \text{ (solid cyan) spectra.} \]
Fitting of Ceria Bulk-phase Oxidation Data – While ceria oxidation/reduction most likely occurs via the pathway in R1, the change in free energy due to ceria reduction is more clearly discussed by considering equilibrium with an effective partial pressure of oxygen ($P_{O2}$) in the gas-phase:

$$2\text{Ce}_x^+(\text{CeO}_x) + O_x^+(\text{CeO}_x) \leftrightarrow 2\text{Ce}_x^+(\text{CeO}_x) + V_o^{2+}(\text{CeO}_x) + \frac{1}{2}O_2(g)$$  \hspace{1cm} (R4).

Assuming equilibrium and ideal gas behavior, the change in ceria free energy upon reduction $\Delta G_{\text{red}}$ can be characterized by equation S4:
\[ \Delta G_{\text{red}}(T, x) = \mu_{\text{CeO}_3}(T, x) - \mu_{\text{CeO}_4}(T, x) = \frac{1}{2} \left( \mu_{o_2} + RT \ln \left( \frac{P_{o_2}}{P_{o_2}^0} \right) \right), \]  

(S5)

where \( x \) is the degree of reduction, \( \mu_{o_2} \) is the chemical potential of \( O_2 \) at \( T \) and \( P_{o_2} \), and \( \mu_{o_2}^0 \) is the chemical potential at \( T \) and standard pressure \( P_{o_2}^0 (= 1.0 \text{ atm}) \). Equation S4 makes for facile comparison with published data for bulk samples, which typically correlate the degree of reduction with \( P_{o_2} \). \(^{11-13}\) Mogensen et. al. compile a number of these measurements, \(^{11}\) which show a high degree of agreement. Arrhenius-type fits of this data give estimates of \( \Delta H_{\text{red,bulk}} \) and \( \Delta S_{\text{red,bulk}} \), estimated as a function of \( X_{\text{Ce}^{3+}} \) and \( T \). As seen in Table 1, these fits are used to predict \( X_{\text{Ce}^{3+}} \) as a function of \( T \) and \( P_{o_2,eq} \) – the predicted bulk composition for the conditions in this study – with \( P_{o_2,eq} \) for the experimental conditions found by equilibrium gas calculations using Cantera software and JANAF polynomials for the gas-phase thermodynamics of the relevant species for \( H_2/O_2 \) equilibria. \(^{14}\) To estimate \( \Delta G_{\text{red,surf}} \), the fits are used to predict \( P_{o_2(b)} \) as a function of \( T \) and \( X_{\text{Ce}^{3+}(s)} \) – the \( P_{o_2} \) at which \( X_{\text{Ce}^{3+}(b)} \) equals the observed \( X_{\text{Ce}^{3+}(s)} \). The two effective \( P_{o_2} \) values – \( P_{o_2(b)} \) and the \( P_{o_2,eq} \) listed in Table 1 – allows for comparison of \( \Delta G_{\text{red,bulk}} \) and \( \Delta G_{\text{red,surf}} \) for a given \( X_{\text{Ce}^{3+}} \), via eq. S5.

**Electrochemical Impedance Spectra:** Along with the complementary LSV data shown in Figure 7, potentiostatic EIS measurements were taken at higher pressures with Ar dilution for a range of cell biases. The linear response of the cell to a small AC voltage excitation (10 mV amplitude) was measured over a range of excitation frequencies (200 kHz down to 20 mHz). The measurements

**Table S1** – Total currents of single-chamber cells with ceria WE as a function of \( V_{\text{cell}} \) for a range of \( P_{\text{H}_2} \) and \( P_{\text{H}_2O} \) at \( T = 700-705 \text{ °C} \).

<table>
<thead>
<tr>
<th>( P_{\text{H}_2} ) (Torr)</th>
<th>( P_{\text{H}_2O} ) (Torr)</th>
<th>Total current at ( T \sim 700 \text{ °C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>@ 1.0 V</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4</td>
<td>-575</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>-614</td>
</tr>
<tr>
<td>10.0</td>
<td>2.0</td>
<td>-1251</td>
</tr>
<tr>
<td>10.0</td>
<td>10.0</td>
<td>-1386</td>
</tr>
</tbody>
</table>
provided a basis for approximating the magnitude and characteristic time constants of impedances associated with the electrochemical processes in the entire cell. The EIS measurements in this study were done in the two-electrode configuration without a reference electrode because of difficulties in using a reference with solid oxide electrolytes\textsuperscript{15}. Thus, the EIS measurements did not fully separate ceria WE processes from those of the Pt CE. Nonetheless, the impedance measurements do provide a valuable semi-quantitative assessment of how changes in cell bias and operating gas pressures influence dominant impedance contributions in the single-chamber ceria cells.

Figure S4 shows impedance spectra for positive (S4a), zero (S4b), and negative (S4c) cell biases at 700 °C and at some of the $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ conditions presented in the voltammetry plots of Figure 7. In Figure S4, impedance spectra are plotted as Nyquist curves of real and imaginary impedance where the high-frequency $Z_{\text{real}}$-axis intercept to the left approximates the $R_{\text{bulk}}$ of the YSZ electrolyte and the estimated low-

**Figure S4.** Electrochemical impedance spectra of single chambers cells with 250 nm thin-film ceria cell with Pt counter showing the impact of $P_{\text{H}_2}$ and $P_{\text{H}_2\text{O}}$ partial pressure for a range of cell biases, $V_{\text{cell}}$: a) at + 1.0 and + 0.3 V, b) at 0.0 V, and c) at - 0.3 V and - 1.0 V.
frequency $Z_{\text{real}}$-axis intercept provides the sum of $R_{\text{bulk}}$ and the total polarization resistance $R_{\text{pol}}$ of the ceria WE and Pt CE. The current densities at the different biases in the EIS plots are given in Table S1 for the different $P_{\text{H}_2}/P_{\text{H}_2O}$ conditions as well as for a common condition used in the ambient pressure XPS experiments ($P_{\text{H}_2} = P_{\text{H}_2O} = 0.40$ Torr). Table S1 reiterates the positive impact of increased $P_{\text{H}_2}$ not only on the H$_2$ oxidation on the ceria but also on the H$_2$O electrolysis on the ceria. This is further highlighted by comparing the $R_{\text{pol}}$ for the different $P_{\text{H}_2}/P_{\text{H}_2O}$ combination in Figure S4a. Under the positive cell biases, increasing $P_{\text{H}_2}$ from 2 Torr to 10 Torr suppresses a low-frequency process likely associated with electrolysis activity and electron transport on the ceria surface. The resulting reduction in $R_{\text{pol}}$ with increasing $P_{\text{H}_2}$ and increases in electrochemical activity as indicated by total current magnitude for the positive biases listed in Table S1 are also accompanied by an increase in characteristic frequency associated with the cell impedance. The characteristic frequency for the different biases and $P_{\text{H}_2}/P_{\text{H}_2O}$ conditions are given in Table S2 and are determined as the frequency with the largest value of $-Z_{\text{imag}}$. As shown in Table S2, the suppression of the low-frequency process results in increases of characteristic frequencies by a factor of 4 or more. Further work must be done both in modeling and experiments to fully explore the impact of $P_{\text{H}_2}$ on ceria electrode impedances.

Under zero and negative biases, the impedances are much larger and characteristic frequencies much smaller than for the positive biases over the range of $P_{\text{H}_2}$ and $P_{\text{H}_2O}$ presented in Table S2. The higher impedances are a result of a low-frequency process which contributes the bulk of $R_{\text{pol}}$, particularly for the $V_{\text{cell}} = 0.0$ and −0.3 V as shown in Figures S4b and S4c. A larger negative bias

**Table S2** – Characteristic frequencies (associated with the highest imaginary impedance) of single-chamber cells with ceria WE as a function of $V_{\text{cell}}$ for a range of $P_{\text{H}_2}$ and $P_{\text{H}_2O}$ at $T = 700$-705 °C. The biases are used for the impedance measurements in Figure S4.

<table>
<thead>
<tr>
<th>$P_{\text{H}_2}$ (Torr)</th>
<th>$P_{\text{H}_2O}$ (Torr)</th>
<th>Characteristic Frequency of Largest $R_{\text{pol}}$ Contribution in Hz @ 1.0 V</th>
<th>@ 0.3 V</th>
<th>@ 0.0 V</th>
<th>@ -0.3 V</th>
<th>@ -1.0 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.4</td>
<td>25</td>
<td>--</td>
<td>16</td>
<td>--</td>
<td>20.0</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>252</td>
<td>16</td>
<td>10.0</td>
<td>40</td>
<td>40.0</td>
</tr>
<tr>
<td>10.0</td>
<td>2.0</td>
<td>1000</td>
<td>502</td>
<td>159</td>
<td>25</td>
<td>252</td>
</tr>
<tr>
<td>10.0</td>
<td>10.0</td>
<td>1588</td>
<td>63.2</td>
<td>3.2</td>
<td>4.0</td>
<td>126</td>
</tr>
</tbody>
</table>
\( V_{\text{cell}} = -1.0 \text{ V} \) greatly suppresses this low-frequency impedance, as shown in Figure S4c, and increases the characteristic frequency.

References