Electrochemical studies of capacitance in cerium oxide thin films and its relationship to anionic and electronic defect densities

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Small polaron carrier density in epitaxial, doped CeO$_2$ thin films under low oxygen partial pressure was determined from electrochemically-measured capacitance after accounting for interfacial effects and shown to agree well with bulk values.

The electronic properties of thin film oxides are relevant in a broad range of phenomena and devices. In many instances, these properties are strongly influenced by point defect formation and the extent of deviation of the material stoichiometry away from that of the perfect crystal. This strong connection between material chemistry and physical properties has motivated the development of advanced techniques, such as electron energy-loss spectroscopy and positron annihilation spectroscopy, for accurately measuring nonstoichiometry in thin films. Nevertheless, the small sample mass and the constraints of a substrate continue to hinder such measurements. Even a relatively straightforward Hall effect measurement is precluded in the case of low mobility materials. Thus, a reliable and precise method for determining nonstoichiometry and carrier concentration in thin film oxides may be useful for a number of fields.

In this work, we show that it is possible to determine oxygen nonstoichiometry ($\delta$) in situ, which, in turn, can yield electronic carrier concentration, from an analysis of the capacitance of thin film oxides measured by electrochemical impedance spectroscopy in a cross-plane configuration. The conventional dielectric capacitance is given by

$$C_{\text{dil}} = \frac{\partial q}{\partial \phi}$$

where $q$ is the accumulated charge and $\phi$ is the applied electric potential. In the case of a metal oxide that undergoes a change in oxygen content in response to a change in oxygen chemical potential, the electrical equivalent of the chemical driving force, $\mu'_i = \frac{z_i q}{T}$ (where $z_i$ is the charge on species $i$ and $\mu'_i$ is the chemical potential of species $i$), similarly induces a change in stored charge. For a slab sample that is spatially homogenous, the accumulated charge per species is

$$q_i = e z_i c_i A L$$

where $c_i$ is the concentration, and $A$ and $L$ are the sample cross-section area and thickness, respectively. In the limits of ideal solution behavior and local electroneutrality ($\sum_i e z_i c_i(x) = 0$), these definitions imply a chemical capacitance given by

$$C_{\text{chem}} = \frac{e^2}{k_B T A L} \left( \sum_i \frac{1}{z_i^2 c_i} \right)^{-1}$$

where $k_B$, $T$ and $e$ have their usual meanings. Thus, a measurement of $C_{\text{chem}}$ can yield the concentration of charged species.

In a sufficiently thick film or bulk sample the area-specific chemical capacitance is several orders of magnitude larger than the interfacial capacitances at gas|solid and solid|solid boundaries. For a typical 0.1 cm thick nonstoichiometric oxide, the former falls in the range of 1 to $10^2$ F cm$^{-2}$, whereas the latter is typically $10^{-3}$ to $10^{-5}$ F cm$^{-2}$. As a result, the chemical capacitance can be treated as the prevailing capacitance and the interfacial capacitance ignored. In thin films, however, although the relative magnitudes of the capacitance terms are not $a$ priori known, the interfacial capacitance, which is independent of film thickness, can become significant relative to the chemical capacitance, which is proportional to thickness. Difficulties in extracting the individual contributions to the observed capacitance as well as other experimental challenges have precluded establishment of a rigorous link between thin film chemical capacitance and carrier concentration.

We show here that by varying the film thickness, or, alternatively, the oxygen partial pressure (more specifically, the oxygen activity), we can deconvolute chemical and interfacial capacitance terms. The study is carried out using epitaxial, nonstoichiometric samarium doped cerium oxide (Sm$_x$Ce$_{1-x}$O$_2$|x$+$0.5, SDC), a wide band gap material for which the thermodynamics of electron carrier formation are well characterized and the defect chemistry is well known. Under low oxygen partial pressures, both localized electronic defects (small polarons) and oxygen vacancies are relevant for the transport properties of acceptor doped cerium oxide, and the material becomes a mixed ion and electron conductor (MIEC). The reaction for the formation of ionic and electronic charge carriers can be written as:

$$2\text{Ce}^{2+} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{Ce}^3^+ + \text{O}_2^- + 2\text{Ce}^{3+}$$

where the Kröger-Vink notation is used. Under equilibrium conditions and in the dilute limit, the electron concentration,
and the oxygen vacancy concentration, \( c_{\text{ion}} \), are related to the oxygen partial pressure, \( p_{O_2} \), according to:

\[
\exp \left( -\frac{\Delta G_r}{k_B T} \right) \approx \frac{1}{2} c_{\text{con}}^2 c_{\text{dop}} p_{O_2}^{1/2} (c_{\text{con}} - c_{\text{dop}})^2 (c_{\text{con}}^0 - 1/2 c_{\text{dop}})(p_{O_2}^0)^{1/2} \]

where \( \Delta G_r \) is the standard Gibbs free energy of the reduction of Ce from the 4+ to the 3+ valence state, \( c_{\text{dop}} \) is the trivalent dopant (Sm) concentration, symbols with superscript “0” designate the standard states (\( p_{O_2}^0 = 1 \) atm, and \( c_{\text{con}}^0 \) and \( c_{\text{ion}}^0 \) are given by the concentration of Ce and O crystallographic sites, respectively), and \( K' \) is a constant. The simplification given in (4) applies under conditions at which the oxygen vacancy concentration (\( c_{\text{con}} = 1/2(c_{\text{dop}} + c_{\text{con}}) \)) is much greater than the small polaron concentration (\( c_{\text{con}} = 2d c_{\text{con}}^0 \)), at which, furthermore, the chemical capacitance becomes:

\[
C_{\text{chem}} = \frac{e^2}{k_B T} \left( \frac{1}{c_{\text{con}}^0} + \frac{1}{2c_{\text{dop}}} \right) \]

Measurement of \( C_{\text{chem}} \) in nonstoichiometric MIEC oxide films by impedance spectroscopy is facilitated here by deposition onto both sides of a pure oxygen ion conductor (IC). It has been shown elsewhere,\(^{15,17}\) from a solution of the fundamental transport equations, that the analytical impedance response of a MIEC can be rigorously mapped to an equivalent circuit in which \( C_{\text{chem}} \) explicitly appears. Modification of that result for the present configuration, in which the bulk electronic and ionic resistances of the MIEC thin film are much smaller than the surface reaction resistance,\(^{16,24,34}\) the MIEC|IC interface is taken to be reversible to oxygen ions and blocking to electrons, and the porous metal|MIEC interface is taken to be reversible to electrons, yields an equivalent circuit model that is remarkably simple (Fig. 1, inset), particularly given the complexity of the network in the absence of the pure ionic conductor substrate.\(^{15,17}\) Specifically, the circuit here consists of a resistor, \( R_{\text{ion}} \), representing the oxygen ion transport property of the substrate, in series with a parallel capacitor–resistor subcircuit, in which the capacitor represents the sum of chemical, dielectric and interfacial capacitances and the resistor, \( R_{\text{ion}}^{\text{ext}} \), represents the inverse of the linearized surface reaction rate for the electrochemical reaction at the porous metal|MIEC interface.

Thin films of SDC, with thickness ranging from 195 to 2241 nm (much greater than the Debye length \( L_D = 0.18 \) nm to justify use of a 1-D impedance model), were deposited onto both sides of \( Y_{0.16}Zr_{0.84}O_1.92 \) (YSZ) (100), (110) and (111) oriented single crystal substrates via pulsed-laser deposition (KrF, \(~2 J \) cm\(^{-2}, 20 \) Hz) at a substrate temperature of \(~650 \) °C and under 20 m Torr oxygen pressure. Electron probe microanalysis confirmed that the film Sm/Ce ratio was identical, within error, to that of the \( \text{Sm}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925} \) polycrystalline target. Out-of-plane X-ray diffraction (XRD) (20 scan) showed only peaks corresponding to the substrate orientation and a lattice constant (5.441 Å) that was independent of film thickness, whereas rocking curve measurements revealed a FWHM of 0.4° (for the (100) peak). The number and position of diffraction peaks observed by in-plane XRD (2θ scan) was consistent, for each film orientation, with the rotational symmetry of the crystallographic plane normal to the incident beam, indicating alignment registry between the film and the substrate. The epitaxial nature of the SDC thin film was further confirmed by selective area diffraction and dark-field imaging using transmission electron microscopy (TEM); film thickness uniformity was found to be ±4% by scanning electron microscopy (SEM). The independence of the lattice constant on film thickness suggests that residual stress in these films, despite their epitaxial nature, is small. In the case of molecular beam epitaxy (MBE) grown films, the ceria-YSZ interface has been found to be semi-coherent with the lattice mismatch accommodated mainly by misfit dislocations,\(^{35}\) and such a stress–release mechanism may also be operative here; alternatively, stresses in these relatively thick films might not propagate far beyond the interface.

To simulate the electrical measurement conditions, films were annealed at 900 °C for 24 hr. Electron microscopy observations, combined with chemical analysis by energy dispersive spectroscopy, showed insignificant morphological evolution and the absence of detectable cation or dopant interdiffusion between the substrate and the thin film. X-ray
photoelectron spectroscopy and atomic force microscopy (post heat-treatment) revealed negligible differences in the surface composition and microstructure of the films grown to various thicknesses.

Current collectors were attached by applying Pt paste onto both sides of the SDC/YSZ/SDC structure and curing for 2 h at 900 °C. For measurements, the sample was placed in a gas-tight quartz tube positioned inside an electric furnace (500 to 650 °C). A mixture of H2–H2O–Ar or O2–Ar (100 mL min−1 total flow rate, 0.6 cm s−1 linear gas velocity at standard conditions) was delivered to the chamber, and the oxygen partial pressure calculated by assuming equilibrium between H2, O2, and H2O. The A.C. impedance response was measured at frequencies between 1 or 10 mHz to 10 MHz with a Solartron 1260 A frequency response analyzer at 20 mV amplitude perturbations. Because the cross-plane, rather than the in-plane, electrochemical response is measured in our cell, the current is typically large and not limited by the bulk electrical conductivity of the material (SDC bulk conductivity: 7 × 10−3 to 2 × 10−2 S cm−1 at 500 °C for pO2 between 0.21 and 2 × 10−31 atm).17

Under all experimental conditions, the impedance response, presented in a Nyquist plot (Fig. 1, top), appeared as a large, nearly perfect, half circle displaced from the origin along the real axis by an amount that corresponds precisely to that expected for the area-normalized resistance of the YSZ single crystal substrate. The impedance response is readily modeled using the physically derived equivalent circuit described above. The constant phase element (CPE) used to represent Cint showed a relatively large exponent parameter, exceeding 0.93 for all conditions examined, indicating a relatively small dispersion in the relaxation frequency of the system. Physically, the total capacitance, Ctot, is the sum of the chemical capacitance (Cchem), the interfacial (ionic) capacitance at the external SDC|gas electrode interface (Cchem), and the interfacial (electronic) capacitance at the internal SDC|YSZ interface (Cint), where a factor of 1 accounts for the presence of the two thin films on both sides of the substrate. The dielectric capacitance (Cdielectric) is more than 4 orders of magnitude smaller than the lowest observed capacitance, and, though in principle a component of Ctot, is safely neglected. To satisfy the dilute limit assumption as well as to minimize chemical expansion of SDC upon reduction, δ was kept below 0.014 during the experiment (corresponding to a chemical expansion −0.1% to 36). Furthermore, the observed capacitance at a given condition remained unchanged during the course of the experiment after cycling T and pO2.

By fitting the parameters of the equivalent circuit to the impedance data, the volume-specific capacitance (Cint/AL) was obtained as a function of pO2 at temperatures between 500 and 650 °C for all of the films (Fig. 2). For the thickest film examined (2241 nm, average thickness of films on both sides), the isothermal capacitance is proportional to pO2−1/4, which is expected if the capacitance is indeed dominated by the chemical capacitance (as implied by eqn (4) & (5)). However, as the film thickness decreases, the isothermal capacitance curves deviate strongly from the pO2−1/4 dependence, approaching a constant at higher pO2 and lower temperatures. The dependency of the volume-specific capacitance on film thickness implies that contributions other than chemical capacitance are indeed present in our system. Given that the volume-specific chemical capacitance depends only on the electron carrier concentration (or equivalently, oxygen nonstoichiometry), the total capacitance can be expressed as:

\[
C_{\text{tot}} = \frac{e^2 A}{k_B T} \left( \frac{1}{C_{\text{chem}}(pO_2, T)} + \frac{1}{2x_{\text{dop}}} \right)^{1/2} L + C_{\text{int}}(pO_2, T) \quad (6)
\]

where Cint = Cion + Cchem is the sum of interfacial capacitances and it is implicitly assumed that the Gibbs free energy of carrier formation is independent of film thickness, consistent with the low residual stress of these relatively thick films. Fig. 3 shows the capacitance plotted as a function of film thickness and fit to eqn (6). Varying the film thickness while...
holding the cell area constant permits the extraction of the thickness-dependent chemical capacitance and the thickness-independent interfacial capacitances. The electron carrier concentration and the oxygen nonstoichiometry computed from the chemical capacitance values exhibit excellent agreement with the expected $pO_2^{1/4}$ dependence (Fig. 4). Furthermore, the interfacial capacitances obtained from this analysis (not shown) display a very weak $pO_2$ dependence and nearly no temperature dependence.

Having demonstrated the $pO_2^{1/4}$ dependence of $C_{\text{chem}}$ and the relatively $pO_2$-independent $C_{\text{int}}$, each isothermal capacitance data set in Fig. 1 can be described according to the following approximation:

$$C_{\text{tot}} = \frac{e^2AL}{k_B T} \left( \frac{1}{c_{\text{con}}(T)pO_2^{1/4}} + \frac{1}{2c_{\text{dop}}} \right)^{-1} + C_{\text{int}}(T)$$

where $c_{\text{con}}$ is the $pO_2$-independent component in the polaron concentration ($c_{\text{con}} = c_{\text{con}}(pO_2^{1/4})$). In contrast to the analysis associated with eqn (6) for which multiple films of differing thicknesses are used to deconvolute capacitance terms, application of eqn (7) requires only the capacitance of one sample measured under several oxygen partial pressures. Utilizing eqn (4) and $c_{\text{con}}$ obtained from eqn (7) at multiple temperatures, we compute the $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ standard reduction enthalpy and entropy of SDC reduction according to eqn (3) for each of the films. The thermodynamic quantities (Table 1) are not only essentially independent of film thickness and orientation, but also identical, within experimental error, to the values measured for bulk materials. The agreement demonstrates that the chemical capacitance has been correctly extracted from the total capacitance, and that impedance spectroscopy, under ideal conditions, can be utilized to determine carrier concentrations and thermodynamic quantities even in thin films. The results further imply that our films are essentially bulk-like in nature, with low strain energy, consistent with the thickness independent lattice constant, and minimal influence of low-angle tilt boundaries present in the growth direction, consistent with the narrow FWHM measured in the rocking curve diffraction experiment. In contrast, in very thin films, 10 nm or less, and in nanostructured bulk materials, large decreases in reduction enthalpy have been reported, indicating that size and strain effects can, under different circumstances, induce substantial deviations in chemical bonding state.

In summary, we have determined electron carrier concentration and $\delta$ as low as $10^{-3}$ in epitaxial, doped ceria thin films using electrochemical impedance spectroscopy. Interfacial capacitance exceeded 65% of the observed capacitance for a moderate $\delta$ of $10^{-3}$ in 195 nm thick SDC, underscoring the importance of extracting bulk and interfacial contributions to capacitance to permit quantification of carrier concentrations. The reduction thermodynamics of our SDC films are in excellent agreement with the behavior of bulk samples. Barring an unlikely situation in which multiple errors conveniently cancel one another, this agreement validates the approach and ultimately points to a systematic methodology for probing the thermodynamics of thin film materials.

**Acknowledgements**

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**Table 1** Comparison of standard enthalpies ($\Delta H_r$) and entropies ($\Delta S_r$) for the reduction reaction expressed in eqn (3), on a per atom basis, obtained in thin film and bulk materials. Electron carrier formation enthalpy is given by $\Delta H_r/2$. Number after “SDC” indicates Sm doping level (%). Note: ref. 17 employs a slightly different definition of the equilibrium constant of reduction and the thermodynamic quantities have been recalculated in a manner that is consistent with the present work and with ref. 31.

<table>
<thead>
<tr>
<th>SDC&lt;br&gt;thickness (nm)</th>
<th>$\Delta H_r$ (eV)</th>
<th>$\Delta S_r$ ($10^{-3}$ eV K$^{-1}$)</th>
<th>Measurement method</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>SDC15(100) 195 nm</td>
<td>4.16 ± 0.02</td>
<td>1.10 ± 0.03</td>
<td>Thin film impedance</td>
<td>This work</td>
</tr>
<tr>
<td>SDC15(100) 380 nm</td>
<td>4.17 ± 0.03</td>
<td>1.12 ± 0.03</td>
<td>Thin film impedance</td>
<td>This work</td>
</tr>
<tr>
<td>SDC15(100) 591 nm</td>
<td>4.18 ± 0.04</td>
<td>1.15 ± 0.04</td>
<td>Thin film impedance</td>
<td>This work</td>
</tr>
<tr>
<td>SDC15(100) 770 nm</td>
<td>4.18 ± 0.04</td>
<td>1.14 ± 0.04</td>
<td>Thin film impedance</td>
<td>This work</td>
</tr>
<tr>
<td>SDC15(100) 2241 nm</td>
<td>4.18 ± 0.02</td>
<td>1.17 ± 0.03</td>
<td>Thin film impedance</td>
<td>This work</td>
</tr>
<tr>
<td>SDC15(110) 2124 nm</td>
<td>4.19 ± 0.06</td>
<td>1.17 ± 0.07</td>
<td>Thin film impedance</td>
<td>This work</td>
</tr>
<tr>
<td>SDC15 (polycrystalline)</td>
<td>4.18 ± 0.05</td>
<td>1.15 ± 0.05</td>
<td>Bulk impedance</td>
<td>17</td>
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<tr>
<td>SDC10 (polycrystalline)</td>
<td>4.15</td>
<td>1.10</td>
<td>Thermogravimetry</td>
<td>31</td>
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<tr>
<td>SDC20 (polycrystalline)</td>
<td>3.99</td>
<td>1.13</td>
<td>Thermogravimetry</td>
<td>31</td>
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References


