Oxygen Electrocatalysis on Epitaxial La\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3-} Perovskite Thin Films for Solid Oxide Fuel Cells

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Hetero-structured interfaces of oxides, which can exhibit reactivity characteristics remarkably different from bulk oxides, are interesting systems to explore in search of highly active fuel cell catalysts for oxygen electrocatalysis. (001)-oriented $La_{0.6}Sr_{0.4}CoO_3\cdot\delta$ (LSC60-40113) films having thicknesses from tens to hundreds of nanometers were grown epitaxially on (001)-oriented yttria-stabilized zirconia (YSZ). Atomic force microscopy showed that all the film surfaces were of high quality with average surface roughness approximately one nanometer. The surface oxygen exchange kinetics of these films were determined by electrochemical impedance spectroscopy. While (001)-oriented LSC60-40113 thin films were found to have similar surface oxygen exchange coefficients to LSC60-40113 bulk, surface coverage of (001)-oriented $La_{0.55}Sr_{0.45}CoO_3\cdot\delta$ (LSC214) on the LSC60-40113 thin films led to significant enhancement in the surface oxygen kinetics up to ~3 orders of magnitude. Interestingly, LSC214-decorated LSC60-40113 films have comparable surface exchange kinetics (~1·10^3 cm·s⁻¹ at 550 °C) to similarly prepared LSC214-decorated $La_{0.3}Sr_{0.7}CoO_3\cdot\delta$ films. Such high surface oxygen kinetics are among the most active SOFC cathode materials reported to date.

The efficiency of solid oxide fuel cells (SOFCs) is limited primarily by the oxygen reduction reaction (ORR) at the cathode, particularly for SOFCs operated at intermediate temperatures. Therefore, there is a need to search for electrode materials with enhanced ORR activity. Mixed electronic and ionic conductors such as ABO₃ perovskites and A₂B₂O₆ Ruddlesden-Popper materials, are promising cathode materials due to their high oxygen ion diffusivity and surface exchange properties. Hetero-structured oxide interfaces have shown surprisingly high oxygen surface exchange properties. Recently, Sase et al. have reported enhanced ORR kinetics of ~3 orders of magnitude at the interfaces between bulk $La_{0.6}Sr_{0.4}CoO_3\cdot\delta$ (LSC60-40113) grains and secondary (La,Sr)₂CoO₄ (LSC214) particles epitaxially grown on the (001)-oriented $La_{0.55}Sr_{0.45}CoO_3\cdot\delta$ thin films, which are epitaxially grown on ytttria-stabilized zirconia (YSZ), can lead to marked enhancement in the surface oxygen exchange kinetics up to three orders of magnitude relative to bulk, approaching that of the LSC60-40113/LSC214 interfaces of composite ceramics.

In this study, we investigate the surface oxygen exchange kinetics of (001)-oriented LSC60-40113 and LSC214-decorated LSC60-40113 thin films epitaxially grown on YSZ. First, (001)-oriented $La_{0.6}Sr_{0.4}CoO_3\cdot\delta$ (LSC80-20113) thin films have shown enhanced ORR kinetics by one order of magnitude relative to bulk; we are interested in understanding if (001)-oriented LSC60-40113 thin films would also exhibit enhanced surface oxygen kinetics relative to bulk. Polycrystalline LSC60-40113 thin films supported on a sintered Gd₂Ce₀.₈O₂ (GDC) substrate show comparable surface oxygen exchange coefficients to that of bulk LSC60-40113 pellet. Considering previous studies have shown that X-ray-diffraction-amorphous LSC60-40113 films have enhanced ORR activity than crystalline films supported on YSZ(001), single-crystalline, (001)-oriented LSC60-40113 films might have different surface oxygen kinetics from polycrystalline LSC60-40113 thin films reported previously. Second, although previous work qualitatively confirm the enhancement at the interfaces between polycrystalline LSC60-40113 and (La,Sr)₂CoO₄ thin films, we aim to quantify the degree of enhancement in the surface oxygen exchange kinetics associated with LSC214 decoration on (001)-oriented LSC60-40113 films. In this study, we report ORR activities for epitaxial (001)-oriented LSC60-40113 thin films comparable to bulk LSC60-40113. In addition, surface LSC214 decoration grown epitaxially on the (001)-oriented LSC60-40113 thin films can provide activity enhancement up to 3 orders of magnitude relative to bulk, and have surface oxygen exchange coefficients comparable to those found for LSC214-decorated LSC80-20113 reported previously.
covered LSC60-40113 was 85 nm. A reference film of LSC60-40113 decorated with 25 pulses of LSC60-40113 was also fabricated for comparison.

The film thicknesses of LSC60-40113 films are considerably smaller than the critical thickness, \( t_{\text{crit}} \), of \( \approx 20 \) \( \mu \)m found for bulk LSC60-40113 at 518 \( ^\circ \)C and \( p(O_2) = 0.23 \) bar. \( k_{\text{ex}} \) is defined as \( D^{*} / k^{*} \), where \( D^{*} \) is the tracer oxygen diffusivity and \( k^{*} \) the tracer surface exchange coefficient, below which surface oxygen exchange limits the ORR kinetics. Therefore, the ORR kinetics of these films were governed primarily by surface oxygen exchange kinetics. With this understanding, the EIS data (Figure 1c) were analyzed using a simplified equivalent circuit shown in Figure 1d, from which the ORR resistance \( R_{\text{ORR}} \) and oxygen surface exchange coefficients were obtained as follows. The extracted low-frequency resistance values \( (R_{\text{LF}} = R_{\text{ORR}}) \) were used to calculate the surface exchange.
coefficient \( k^4 \) by\(^{5,12,18} \),

\[
k^4 = \frac{RT}{4F^2 R_bK_Ae_{\text{c}} c_0}
\]

where \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature (793 K), \( F \) is the Faraday’s constant (96,500 C mol\(^{-1}\)), \( A_{\text{electrode}} \) is the area of the microelectrode, and \( c_0 \) is the lattice oxygen concentration in LSC.

### Results and Discussion

Normal X-ray diffraction (XRD) data (Figure 2a) clearly show the presence of the (001)pc of LSC60-40113 and the (001)\(_{\text{cubic}} \) \((l = 1)\) peaks of GDC, and YSZ, which indicates the pseudo-cubic notation, where the rhombohedral structure of LSC60-40113 bulk is approximated with an average for all film thicknesses of \( a_{\text{pc}} \approx 3.847 \) Å (Table I).\(^{5,12} \) With LSC214 coverage equal to or greater than \( \sim 5 \) nm in thickness, the (001)tetragonal peaks \((l = 1)\) of LSC214 become visible (Figure 2b), which indicates the in-plane crystallographic relationships between GDC and YSZ (a in-plane 45° rotation), having [100]pc-LSC60-40113/[110]cubic-GDC/[110]cubic-YSZ (Figure S1b).\(^{21} \) These results are in agreement with our previously published findings for LSC60-40113 thin films.\(^{5,12} \) The in-plane crystallographic relationship between LSC60-40113 and LSC214 was not independently measured but is likely to have [100]pc-LSC60-40113/[100]tetragonal-LSC214 as shown previously for LSC214 decoration on (001)-oriented LSC80-20113.\(^{5} \)

LSC60-40113 films were found dilated in-plane and compressed in the direction normal to the film surface at room temperature with good crystallinity (Table I and Figure S2\(^{21} \)). It is interesting to note that the in-plane and normal strains decrease with increasing film thickness from 25 to 157 nm. The origin of these strains might be a consequence of different thermal expansion coefficients between YSZ (~11×10\(^{-6}\) C\(^{-1}\))\(^{22,23} \) and LSC60-40113 films (~15.8×10\(^{-6}\) C\(^{-1}\))\(^{24} \) for bulk.\(^{25} \) Experiments are ongoing to examine how these strains change upon heating to high temperatures. Of significance to note is that the LSC60-40113 films have slightly smaller relaxed lattice parameters than bulk (3.855 Å\(^{3} \)) at room temperature. The relaxed lattice parameter, \( \hat{a}_{\text{pc}} \), can be estimated by assuming a Poisson ratio of 0.25\(^{25} \) for LSC60-40113, which gives rise to \( \hat{a}_{\text{pc}} = 3.847 \) Å, 3.849 Å and 3.845 Å for the films of 25, 77 and 157 nm, respectively. Having different relaxed unit cell volume from bulk,\(^{23} \) unlike (001)-oriented epitaxial LSC80-20113 films that have larger relaxed lattice parameter than bulk,\(^{5,12} \) (001)-oriented epitaxial LSC60-40113

### Table I. Constrained and relaxed lattice parameters of LSC60-40113 films extracted from normal and off-normal XRD data from 100 mm\(^2 \) samples. Constrained normal and in-plane lattice parameters of LSC60-40113 films were calculated from combining the inter-planar distance of the (002)pc and (101)pc peaks. For reference lattice parameter and strain values for LSC80-20113 films is provided in Table S1.\(^{12,21} \)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Constrained in-plane ( a ) (Å)</th>
<th>Constrained normal ( c ) (Å)</th>
<th>Relaxed film lattice parameter(^ a ) (Å)</th>
<th>In-plane strain ( \varepsilon_{xx} = \frac{\hat{a} - a}{a} )</th>
<th>Normal strain ( \varepsilon_{zz} = \frac{\hat{c} - c}{c} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSC60-40113-25 nm (pc)</td>
<td>3.870</td>
<td>3.831</td>
<td>3.847</td>
<td>0.60%</td>
<td>−0.40%</td>
</tr>
<tr>
<td>LSC60-40113-77 nm (pc)</td>
<td>3.870</td>
<td>3.836</td>
<td>3.849</td>
<td>0.53%</td>
<td>−0.35%</td>
</tr>
<tr>
<td>LSC60-40113-157 nm (pc)</td>
<td>3.860</td>
<td>3.834</td>
<td>3.845</td>
<td>0.41%</td>
<td>−0.27%</td>
</tr>
</tbody>
</table>

\(^a\) \( \hat{a} \) was calculated from \( \frac{\Delta c}{\Delta a} = \frac{\Delta c}{\Delta x} \frac{\Delta x}{\Delta a} \), assuming \( \hat{a} = \hat{c} \) and \( \nu = 0.25 \) for LSC60-40113.

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\[ k^4 = \frac{RT}{4F^2 R_bK_Ae_{\text{c}} c_0} \]
films were found to have smaller relaxed lattice parameters than bulk, which is indicative of lower oxygen vacancies in the films.

AFM imaging revealed that the surface roughness of as-deposited LSC60-4013 films have low root-mean-squared (RMS) roughness less than ~1 nm (Figures 3 and S3). AFM images of LSC60-4013 of 25 nm, 77 nm, LSC214-decorated 0.1 nm and 5.0 nm are shown in Figure 3, and AFM images of remaining films are shown in Figure S3. With LSC214 coverage on LSC60-4013 films, there was no significant change in the surface roughness. The surface roughness of these LSC60-4013 and LSC214-decorated LSC60-4013 films are comparable to those of LSC80-2013 and LSC214-decorated LSC80-2013 films, respectively.

EIS data of all LSC60-4013 thin films were found to be very similar in shape, and typical features in the Nyquist plots are shown in the schematic in Figures 1c and S4. The predominant semicircle (assigned to the impedance of surface oxygen exchange kinetics) was found to increase with decreasing \( p(O_2) \). The electrical surface exchange coefficient, \( k^s \), was extracted from the real impedance while chemical surface exchange coefficient, \( k_{chem} \), which describes the rate of surface oxygen exchange with chemical driving force, was estimated from the semicircle peak frequency (Supplementary Information). The electrical surface exchange \( (k^s) \) and chemical surface exchange \( (k_{chem}) \) coefficients of LSC60-4013 films of different thicknesses at 520°C are plotted as a function of oxygen partial pressure, \( p(O_2) \) in Figures 4a and 4b, respectively. All LSC60-4013 films exhibited comparable \( k^s \) and \( k_{chem} \) which appeared to be thickness independent. It is interesting to note that the strains in LSC60-4013 thin films measured at room temperature do not appear to correlate with surface oxygen exchange coefficients (Figure S5). Assuming \( k^s \) can be approximated as \( k^s \sim k_0^s \cdot 10^{-q \cdot p(O_2)} \) these \( k^s \) and \( k_{chem} \) values of the LSC60-4013 thin films are comparable to those extrapolated for bulk LSC60-4013,9,14 as shown in Figure 4. It should be mentioned that the (001)-oriented epitaxial LSC60-4013 films in this study have comparable surface oxygen coefficients (∼3×10^-8 cm·s^-1) at 0.1 atm) than those from polycrystalline LSC60-4013 films extrapolated to 520°C at \( p(O_2) \) of 0.1 atm or lower.

LSC214 surface decoration on LSC60-4013 films led to markedly smaller real impedance and much greater surface oxygen exchange kinetics relative to LSC60-4013 and the LSC60-4013-covered reference film (Figure S6). At \( p(O_2) \) of 1·10^-1 atm and 1·10^-2 atm, LSC214-decoration increased \( k^s \) up to ~2 orders of magnitude relative to the reference LSC60-4013 film, having low coverage of 0.1 and 0.8 nm exhibiting the highest \( k^s \) values, as shown in Figure 5a. At \( p(O_2) \) greater than 10^-2 atm, the enhancement with surface coverage was ~1 order of magnitude. At these high \( p(O_2) \) conditions, the very high \( k^s \) values (∼10^-6 cm·s^-1 or higher) can decrease the critical thickness assuming a constant diffusion coefficient, and thus lead to ORR impedance to be influenced by bulk oxygen ion diffusion in addition to surface oxygen exchange. The much decreased \( p(O_2) \) dependency of \( k^s \) for LSC214-decorated LSC60-4013 films with low coverage at these high \( p(O_2) \) further supports that ORR kinetics are limited also by bulk oxygen ion diffusion in the films of ~90 nm as typically oxygen ion diffusion is inversely proportional to \( p(O_2) \). Therefore, EIS measurements in the low \( p(O_2) \) range from 1·10^-4 to 1·10^-2 atm better reflect the enhancement in the surface exchange kinetics associated with LSC214-decoration. The \( k^s \) values of LSC214-decorated LSC60-4013 films (0.1 nm) obtained from this study is ~2–3 orders of magnitude higher than that of bulk LSC60-4013.9,14 Interestingly, the LSC214-decorated LSC60-4013 films have comparable surface exchange coefficients to that estimated for the interfaces between bulk La0.6Sr0.4CoO3 (LSC60-4013) grains and secondary (La,Sr)2CoO4 precipitates relative at 500°C and 0.2 atm. Such high surface oxygen kinetics is comparable to those of the most active
cathode materials such as thin-film Ba$_0$Si$_2$Co$_3$Fe$_{12}$CoO$_{13}$ [\(k^* = ~1 \cdot 10^{-6} \text{ cm} \cdot \text{s}^{-1}\)] at 500°C and 0.5 bar of (O$_2$), and bulk La$_3$Co$_2$O$_4$ [\(k^* = 3 \cdot 10^{-6} \text{ cm} \cdot \text{s}^{-1}\)] at 500°C and 0.2 bar of (O$_2$). Moreover, the ORR area specific resistance (\(R_{\text{ORR}} \cdot \text{Area}[\text{electrode}]\)) of these LSC$_{214}$-decorated LSC60-40113 films (Figure 5b) at 550°C are smaller than the (001)-oriented epitaxial LSC60-40113 films [\((\sim 15 \text{ nm})\)] at 0.1 atm and greater, which are among the lowest reported to date.\(^5\)

The (O$_2$) dependency of \(k (k \propto P_{\text{O}_2}^{\alpha})\) can be indicative of the rate-limiting step of ORR.\(^{33,34}\) The (O$_2$) dependency of \(k^*\) for the LSC60-40113 films of different thicknesses was found comparable, having \(m_{\text{O}_2}\text{atm} = 0.72, m_{\text{O}_2}\text{thm} = 0.76.\) Similar values were found for \(k_{\text{chem}}\): \(m_{\text{O}_2}\text{atm} = 0.80, \text{and } m_{\text{O}_2}\text{thm} = 0.85.\) The obtained dependencies for \(k^*\) are in good agreement with those reported for bulk La$_{3}\text{Sr}_{2}\text{CoO}_4$ and La$_0.5\text{Sr}_{0.5}\text{CoO}_3$.\(^{32}\) Interestingly, the (O$_2$) dependencies of \(k^*\) for the LSC$_{214}$-decorated LSC60-40113 films in the range from 1 - 10$^{-4}$ to 1 - 10$^{-2}$ atm, having \(m_{\text{O}_2}\text{atm} = 0.42, m_{\text{O}_2}\text{thm} = 0.60, m_{\text{O}_2}\text{thm} = 0.61, \text{and } m_{\text{O}_2}\text{thm} = 0.53,\) are lower than the LSC60-40113 films and reference sample (\(m_{\text{O}_2} = 0.90\)). It should also be mentioned that these (O$_2$) dependencies are lower than that of LSC$_{214}$-decorated LSC80-20113 (\(m \sim 0.90\)) reported previously.\(^3\) Following the work of Adler et al.,\(^2\) such (O$_2$) dependencies suggest that the ORR rate-limiting step for LSC60-40113 is dissociative adsorption (m between 0.43 and 0.92).

The \(k^*\) and \(k_{\text{chem}}\) values of (001)-oriented epitaxial LSC60-40113 films in this study are comparable to those of (001)-oriented epitaxial LSC80-20113 thin films reported previously,\(^5,12\) (the range of max. \(m^*\) and \(m_{\text{chem}}\) values shaded in blue in Figure 4a), where LSC60-40113 have activities toward the upper end of the activity spread of LSC80-20113 films. This is in contrast to the fact that bulk LSC60-40113\(^{33,34}\) has surface exchange coefficients significantly higher than LSC80-20113.\(^{33,34}\) The enhancement associated with LSC$_{214}$ decoration for LSC60-40113 is similar to that reported for LSC80-20113 coated with LSC$_{214}$,\(^{5,12}\) where LSC$_{214}$-decorated LSC60-40113 and LSC80-20113 surface have very comparable surface oxygen exchange kinetics (having similar \(k^*\) and \(k_{\text{chem}}\) values in Figure 5a).

We further show that LSC$_{214}$ decoration does not greatly influence the oxygen nonstoichiometry (\(\delta\)) in the LSC60-40113 films, which strongly depends on the La/Sr ratio in the perovskite structure. The oxygen nonstoichiometry (\(\delta\)) in the LSC60-40113 films at 520°C was estimated using volume-specific capacitance (VSC). VSCs, indicative of changes in the oxygen nonstoichiometry induced by changes in the electrical potential, were extracted from EIS data (Supporting Information).\(^{34}\) LSC60-40113 films of different thicknesses at 520°C had comparable VSCs (Figure 6a), which were smaller than those of bulk LSC60-40113 extrapolated from thermodynamic parameters.\(^3\) We can exclude the contribution of the interfacial capacitance\(^{36}\) to the VSCs.
of LSC60-40113 films as plotting the area specific capacitance (ASC) obtained from EIS data as a function of film thickness in Figure S7 yields zero intercept in ASC. Correspondingly, oxygen nonstoichiometry, $\delta$, of the LSC60-40113 films, which was calculated from the thermodynamic parameters (Table S2) of oxygen vacancy formation in the films based on the $p(O_2)$ dependency of VSC, was slightly smaller than that estimated for LSC60-40113 bulk, and was similar to that of polycrystalline LSC60-40113 films reported by Kawada et al. The lower oxygen nonstoichiometry of LSC60-40113 films at 520 °C is consistent with smaller relaxed unit cells of LSC60-40113 films than bulk LSC60-40113, at room temperature (Table 1). The (001)-oriented epitaxial LSC60-40113 films of this study had higher oxygen nonstoichiometry than similarly prepared LSC80-20113 films but the strong influence of the La/Sr ratio albeit its influence on the oxygen nonstoichiometry of the entire film. This study illustrates the potential of utilizing hetero-structured oxide surfaces/interfaces to develop highly active surface oxygen exchange materials for applications in the field of solid-state electrochemistry such as micro SOFC cathodes, solid-electrolyte-based sensors, and oxygen conducting membranes.

Figure 7. Oxygen partial pressure dependency of a) volume specific capacitance (VSC), b) average oxygen nonstoichiometry $\delta$ of LSC60-40113-reference and the ~82 nm LSC60-40113 films with ~0.1 nm, ~0.8 nm, ~5 nm, and ~15 nm LSC214 surface coverage at 550 °C. Blue shaded regions are the range of VSC and $\delta$ from LSC80-20113 with LSC214 decoration. Values of bulk LSC60-40113 and LSC80-20113 were calculated by using a method reported by Kawada et al.34

Conclusions

We show that the surface oxygen exchange kinetics and oxygen nonstoichiometry of (001)-oriented LSC60-40113 films grown epitaxially on YSZ are comparable to those of LSC60-40113 bulk. This is in contrast to (001)-oriented LSC80-20113 films with enhanced activities and oxygen nonstoichiometry relative to LSC80-20113 bulk reported previously. In addition, (001)-oriented epitaxial LSC60-40113 films have similar surface oxygen exchange coefficient to polycrystalline LSC60-40113 films reported previously. LSC214 surface decoration on the (001)-oriented LSC60-40113 films leads to ORR activity enhancement up to ~3 orders of magnitude with respect to bulk LSC60-40113. The enhancement associated with LSC214 decoration for LSC60-40113 is similar to that reported for LSC80-20113-covered LSC214, where LSC214-decorated LSC60-40113 and LSC60-40113 surfaces have very comparable surface oxygen exchange kinetics. Moreover, these LSC214-decorated LSC60-40113 films (Figure 5b) have the area specific resistance approaching ~0.45 cm$^2$ at 1 atm and 550 °C, which are among the lowest reported to date. While the enhancement in ORR kinetics cannot be attributed to changes in the oxygen vacancy concentration of the entire films and film strains measured at room temperature, it is proposed that interfacial LSC113/LSC214 regions are responsible for the observed ORR enhancement. Future studies are needed to elucidate the origin of enhanced ORR kinetics at interfacial LSC113/LSC214 regions. This study illustrates the potential of utilizing hetero-structured oxide surfaces/interfaces to develop highly active surface oxygen exchange materials for applications in the field of solid-state electrochemistry such as micro SOFC cathodes, solid-electrolyte-based sensors, and oxygen conducting membranes.
Acknowledgments

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