

Enhancement of oxygen surface exchange on epitaxial $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ thin films using advanced heterostructured oxide interface engineering

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Abstract

Engineering of a novel heterostructured oxide interface was used to enhance the oxygen surface exchange kinetics of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF₁₁₃) thin films. A single-layer decoration of mixed $(\text{LaSr})_2\text{CoO}_{4\pm\delta}$ (LSC₂₁₄) and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC₁₁₃) and a double-layer decoration of stacked LSC₂₁₄ and LSC₁₁₃ grown on the LSCF₁₁₃ markedly enhanced the surface exchange coefficients of the LSCF₁₁₃ by up to ~1.5 orders of magnitude relative to the undecorated LSCF₁₁₃. It is hypothesized that two different types of surface decorations can enable Sr segregation at the interface and surfaces of LSC₁₁₃ and LSC₂₁₄, leading to enhancement of the oxygen surface exchange kinetics of decorated LSCF₁₁₃.

The development of highly active cathode materials is essential to lower the operating temperature of solid oxide fuel cells (SOFCs), where the slow kinetics of the oxygen surface exchange on the cathode surface limits the efficiency of SOFCs at intermediate temperatures (500–750 °C).^[1,2] Current cathode materials such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM₁₁₃)^[3–5] with high electronic conductivity but low ionic conductivity^[6] are inadequate for the usage in the intermediate temperature range due to insufficient surface activity.

$\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ (LSCF₁₁₃), which has beneficial materials properties such as high ionic and electronic conductivity,^[7] and fast oxygen surface exchange,^[8] therefore, has been developed as one of the most promising commercial cathode materials for intermediate temperature SOFCs. In particular, a solution infiltration process, in which a phase transition occurs from a liquid into a solid has been widely used to further enhance the surface activity of LSCF₁₁₃.^[9–12] Utilizing infiltrated LSM₁₁₃ coatings, it has been shown the enhanced electrocatalytic activity of LSCF₁₁₃ cathodes.^[11,12] Infiltrated $\text{La}_{0.4875}\text{Ca}_{0.0125}\text{Ce}_{0.5}\text{O}_{2-\delta}$ (LCC)^[9] and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC)^[10] coatings have also been used for better stability and activity of LSCF₁₁₃ electrodes. Although many studies have shown the enhanced cathodic performance of LSCF₁₁₃ by surface modification through a solution-based infiltration process,

the origin responsible for the enhanced stability and activity of decorated LSCF₁₁₃ cathode is poorly understood.

Ruddlesden-Popper (RP) phases ($A_2\text{BO}_4$) have been utilized as a material for the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC₁₁₃) surface modification, which results in the enhanced surface activity of LSC₁₁₃ significantly due to the formation of heterostructured oxide interfaces.^[13–18] Using well-defined epitaxial thin film systems, remarkably enhanced oxygen surface exchange kinetics (up to ~2 orders of magnitude) of LSC₁₁₃ has been reported by decorating $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_{4\pm\delta}$ (LSC₂₁₄) phase on the LSC₁₁₃ surface.^[13,19] Coherent Bragg rod analysis (COBRA) and density functional theory (DFT) have suggested that the enhanced oxygen surface exchange kinetics may be attributed to the Sr segregation at the LSC₂₁₄–LSC₁₁₃ interface and the LSC₂₁₄ surface, resulting from a large driving force for A-site cation interdiffusion across the heterostructured interface.^[14,15,20] In addition, the enhanced activity of LSC₁₁₃ may also be attributed to the stabilized LSC₁₁₃ surface by LSC₂₁₄ phase, which suppresses the formation of Sr-enriched secondary particles on the LSC₁₁₃ surface after a long-time annealing.^[17] However, the heterostructured oxide interfaces formed by decorating LSC₂₁₄ on LSCF₁₁₃ perovskites have shown negligible enhancement (up to two times) of the oxygen surface exchange kinetics of LSCF₁₁₃,^[17] which can be attributed to no further

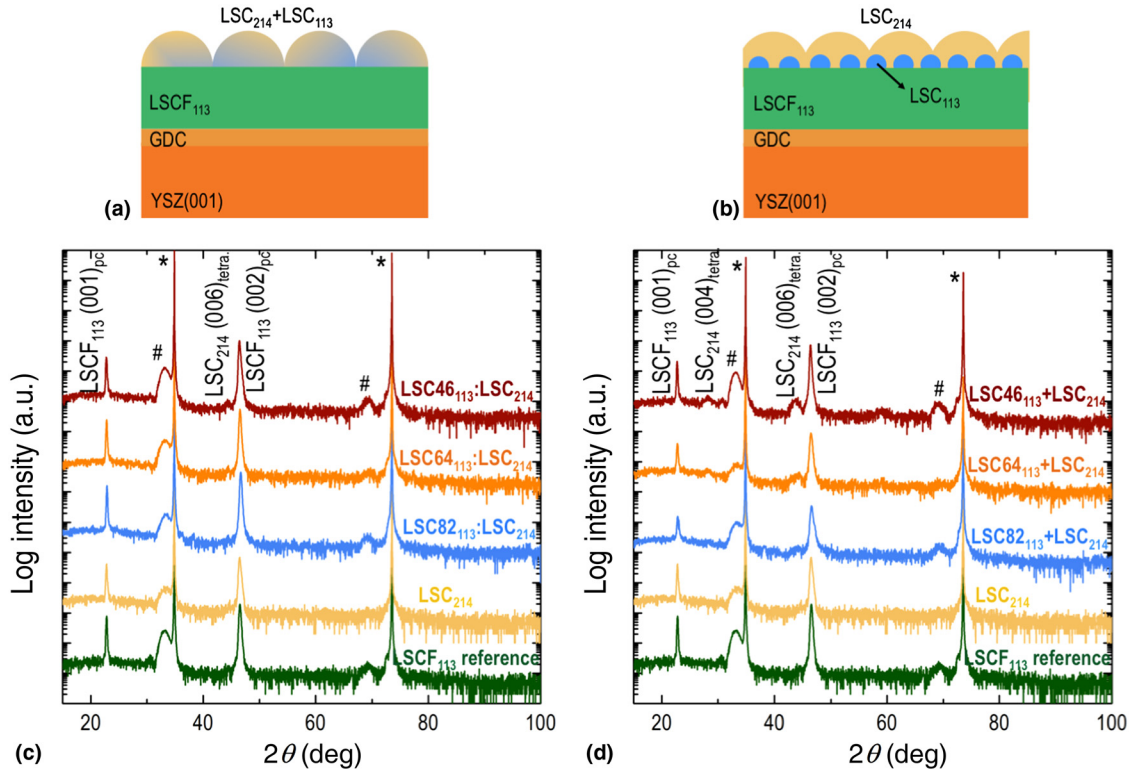


Figure 1. Schematic representation of (a) the LSCF_{113} with single-layer decoration of mixed LSC_{214} and LSC_{113} , and (b) with double-layer decoration of stacked LSC_{214} and LSC_{113} epitaxial thin films. High-resolution XRD analysis of (c) the ~ 65 nm LSCF_{113} reference (green), the ~ 3 nm LSC_{214} -decorated LSCF_{113} (yellow), and the LSCF_{113} with ~ 3 nm single-layer decorations of mixed LSC_{214} and LSC_{82113} (blue), LSC_{64113} (orange), and LSC_{46113} (red), and (d) the ~ 65 nm LSCF_{113} reference (green), the ~ 3 nm LSC_{214} -decorated LSCF_{113} (yellow), and the LSCF_{113} with double-layer decorations of stacked ~ 3 nm LSC_{214} and ~ 0.5 nm LSC_{82113} (blue), ~ 0.5 nm LSC_{64113} (orange), and ~ 0.5 nm LSC_{46113} (red) epitaxial thin films on (001) YSZ substrates with GDC buffer layer. YSZ substrate and GDC peaks are indicated with pounds (#) and asterisks (*), respectively.

increase in Sr concentration at the surface of LSCF_{113} induced by LSC_{214} decoration. While growing a more Sr-rich LSC_{214} on LSCF_{113} might yield enhancement due to the high oxygen surface exchange kinetics of LSC_{214} ($x_{\text{Sr}} > 1.0$),^[15,21] such an approach is inhibited by difficulties in the synthesis of RP phase with high Sr substitution.^[22,23]

In this study, we have developed the heterostructured oxide decoration on LSCF_{113} , which leads to the enhancement of the surface activity of the LSCF_{113} . Utilizing pulsed laser deposition (PLD), we employ two different types of surface decorations on the epitaxial LSCF_{113} thin films, which are the single-layer decoration of mixed LSC_{214} and LSC_{113} and the double-layer decoration of stacked LSC_{214} and LSC_{113} . These structures stabilize the LSC_{113} phase, providing sufficient Sr sources and thermodynamic driving force for the Sr interdiffusion between LSC_{214} and LSC_{113} . Electrochemical impedance spectroscopy (EIS) study reveals that the oxygen surface exchange coefficients (k^j) of the LSCF_{113} thin films can be significantly enhanced up to ~ 1.5 orders of magnitudes higher than those of the undecorated LSCF_{113} by the heterostructured oxide interface engineering. In addition, the LSC_{113} with higher Sr content relative to the LSC_{214} single

phase in both single-layer and double-layer decoration leads to higher enhancement in the surface exchange kinetics of the LSCF_{113} , which suggests that the enhancement of the surface exchange kinetics of the LSCF_{113} can be attributed to an increase of Sr concentration on the multiphase heterostructured interface.

PLD was used to deposit the epitaxial ~ 65 nm LSCF_{113} thin films with the ~ 3 nm single-layer decoration of mixed LSC_{214} and LSC_{113} [Fig. 1(a)] and the double-layer decoration of stacked ~ 3 nm LSC_{214} and ~ 0.5 nm LSC_{113} [Fig. 1(b)] on an yttria-stabilized zirconia (YSZ) (001) substrate with a Gd-doped ceria (GDC) buffer layer. Out-of-plane x-ray diffraction (XRD) results [Figs. 1(c) and 1(d)] of the undecorated LSCF_{113} , LSC_{214} -decorated LSCF_{113} , the LSCF_{113} with the single-layer decoration of mixed LSC_{214} and LSC_{113} thin films, and the LSCF_{113} with the double-layer decoration of stacked LSC_{214} and LSC_{113} thin films clearly show the presence of the $(00l)_{\text{pc}}$ (l is integer) peaks of LSCF_{113} and $(00l)_{\text{cubic}}$ (l is even) peaks of GDC and YSZ, indicating that the LSCF_{113} film was grown epitaxially with the following epitaxial relationships: $(001)_{\text{pc}}\text{LSCF}_{113} // (001)_{\text{cubic}}\text{GDC} // (001)_{\text{cubic}}\text{YSZ}$ (where “pc” denotes the pseudocubic notation).

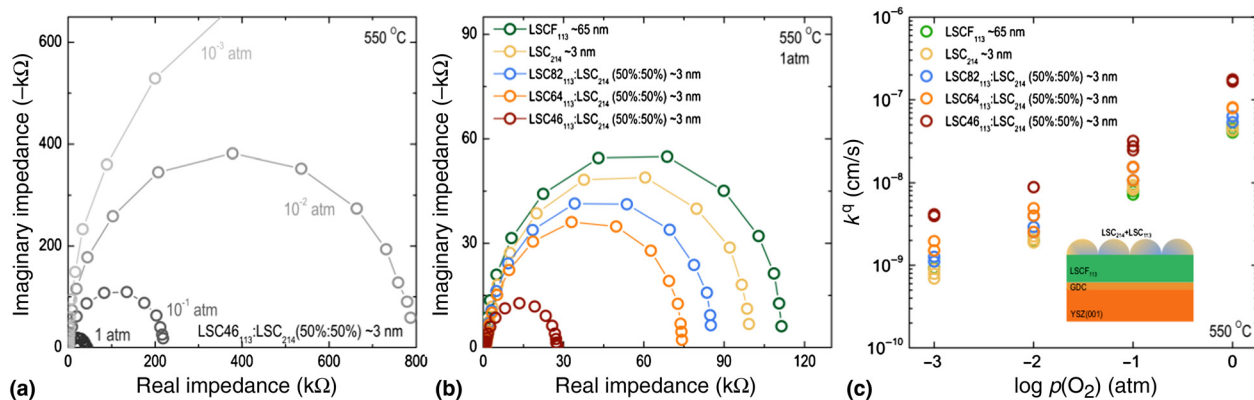


Figure 2. EIS results of microelectrodes (200 μm in diameter) for the epitaxial LSCF_{113} thin films with LSC_{214} decoration, and single-layer decorations of mixed LSC_{214} and LSC_{113} on YSZ (001) with a GDC buffer layer at 550 $^{\circ}\text{C}$. (a) Nyquist plot at 550 $^{\circ}\text{C}$ as a function of oxygen partial pressure, $p(\text{O}_2)$, of the LSCF_{113} thin films with single-layer decoration of mixed LSC_{214} and LSC_{46113} . (b) Nyquist plot at 550 $^{\circ}\text{C}$ with an 1 atm of $p(\text{O}_2)$ of the LSCF_{113} (green), the LSC_{214} -decorated LSCF_{113} (yellow), and the LSCF_{113} with ~ 3 nm single-layer decoration of mixed LSC_{214} and LSC_{82113} (blue), LSC_{64113} (orange), and LSC_{46113} (red) thin films. (c) $p(\text{O}_2)$ dependency of the surface exchange coefficients ($k^f < 1$) of the LSCF_{113} (green), the LSC_{214} -decorated LSCF_{113} (yellow), and the LSCF_{113} with ~ 3 nm single-layer decoration of mixed LSC_{214} and LSC_{82113} (blue), LSC_{64113} (orange), and LSC_{46113} (red) thin films. All EIS spectra were collected at 550 $^{\circ}\text{C}$.

With higher Sr content of LSC_{113} in the single- and double-layer decorations, the (001)_{tetra} (l is the integer) peaks of LSC_{214} become visible, which represents (001)_{tetra}. LSC_{214} //(001)_{pc}. LSCF_{113} //(001)_{cubic}.GDC//(001)_{cubic}.YSZ. The subscript “tetra.” denotes the tetragonal notation.^[24,25] Off-normal phi-scan analysis of the undecorated LSCF_{113} and LSC_{214} -decorated LSCF_{113} films shows that LSC_{214} {103}_{tetra}, LSCF_{113} {202}_{pc}, GDC {202}_{cubic}, and YSZ {202}_{cubic} have strong peaks with fourfold cubic symmetry (Fig. S1†). This reveals the in-plane crystallographic relationships between GDC and YSZ (a cube-on-cube alignment), LSCF_{113} and GDC (an in-plane 45 $^{\circ}$ rotation with [100]_{pc}. LSCF_{113} //[110]_{cubic}.GDC//[110]_{cubic}.YSZ), and LSCF_{113} and LSC_{214} (no rotation with [100]_{pc}. LSCF_{113} //[100]_{tetra}. LSC_{214}). Similar to our previous studies,^[13,14,17,19] the relaxed lattice parameters, \hat{a} of the epitaxial LSCF_{113} films with and without surface decoration in this study at room temperature did not change significantly, ranging from 3.898–3.904 \AA (Table S1†). As shown in Table S1†, both in-plane and out-of-plane strains of LSCF_{113} films were not strongly influenced by the surface decoration, which is supported by the fact that the lattice constant of LSC_{214} (a_{tetra} , ≈ 3.819 \AA for LSC_{214} bulk^[26]) is very close to that of LSCF_{113} (a_{pc} ≈ 3.885 \AA for the LSCF_{113} bulk^[27]) and LSC_{113} (a_{pc} ≈ 3.854 \AA for the LSC_{113} bulk^[28]). This observation is further supported by our recent work,^[14] where the LSC_{214} decoration has no influence on the in-plane and out-of-plane strains of the epitaxial LSC_{113} films at elevated temperatures. Details about deposition, lattice parameter calculation, and high-resolution XRD of LSC_{214} -decorated LSC_{113} film can be found in the ESI†.

EIS results of geometrically well-defined microelectrodes (200 μm in diameter), measured at 550 $^{\circ}\text{C}$ are shown in Fig. 2. These microelectrodes were fabricated by photolithography and acid etched for the epitaxial LSCF_{113} thin films with

LSC_{214} decoration and single-layer decorations of mixed LSC_{214} and three different Sr contents of LSC_{113} (Sr = 0.2, 0.4, and 0.6). The predominant semicircle was found to increase with decreasing oxygen partial pressure [Fig. 2(a)], where EIS data of all samples used in this study showed nearly perfect semicircle impedances.^[6] Considering the fact that the film thicknesses are much smaller than the critical thickness for bulk transport limitation (estimated to 3.28 μm for bulk LSCF_{113} at 550 $^{\circ}\text{C}$ ^[29]), the oxygen partial pressure [$p(\text{O}_2)$]-dependent impedance responses suggest that the oxygen surface exchange kinetics governs the oxygen electrocatalysis on the film surface. In Fig. 2(b), the real part of the impedance of the predominant semicircle decreased with increasing Sr content of LSC_{113} in the single-layer decoration of mixed LSC_{214} and LSC_{113} , where the oxygen surface exchange coefficient (k^f) of the LSCF_{113} with mixed LSC_{214} and $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ (LSC_{46113}) decoration was found to be ~ 7 times higher than that of undecorated LSCF_{113} and LSC_{214} -decorated LSCF_{113} . This observation indicates that higher Sr content in mixed LSC_{214} and LSC_{113} decoration can lead to higher surface exchange kinetics of the LSCF_{113} .

To further investigate the effect of Sr concentration in the mixed LSC_{214} and LSC_{113} phase on the surface exchange kinetics of the LSCF_{113} , a different ratio between LSC_{214} and LSC_{46113} was applied for decorating the surface of the LSCF_{113} . EIS data collected from the LSCF_{113} with and without the single-layer decoration of mixed LSC_{214} and LSC_{46113} thin films at 550 $^{\circ}\text{C}$ with an $p(\text{O}_2)$ of 1 atm is shown in Fig. 3 (a). It is noted that the k^f values of the LSCF_{113} with 75% of LSC_{214} and 25% of LSC_{46113} decoration were found to be ~ 1.1 orders of magnitude higher than those of the LSCF_{113} with and without LSC_{214} decoration, as shown in Fig. 3(b). To understand these changes we consider if the decorations may lead to the enhancement of Sr in the LSCF_{113} surface,

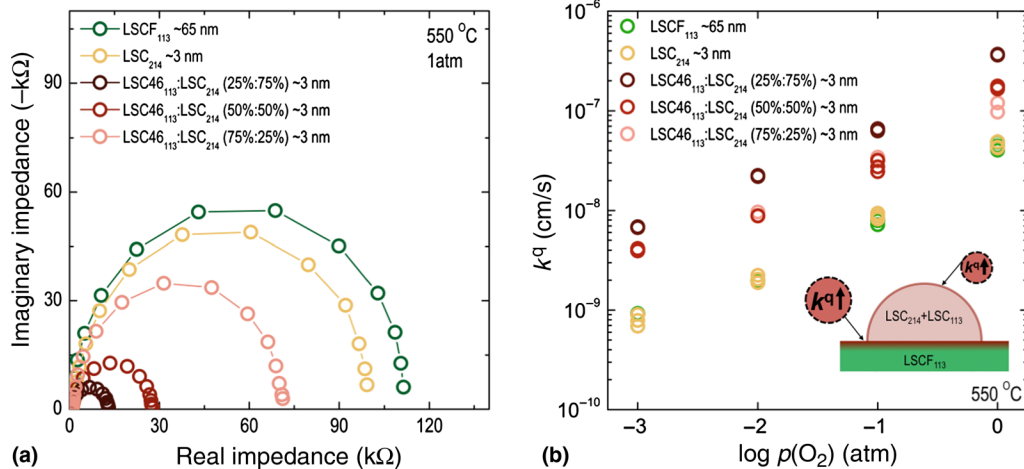


Figure 3. EIS results of microelectrodes (200 μm in diameter) for the epitaxial LSCF₁₁₃ thin films with LSC₂₁₄ decoration, and single-layer decorations of mixed LSC₂₁₄ and LSC46₁₁₃ on YSZ (001) with a GDC buffer layer at 550 °C. (a) Nyquist plot at 550 °C with an 1 atm of $p(O_2)$ of the LSCF₁₁₃ (green), the LSC₂₁₄-decorated LSCF₁₁₃ (yellow), and the LSCF₁₁₃ with ~ 3 nm single-layer decoration of mixed LSC₂₁₄ and LSC64₁₁₃ (75%:25%) (dark red), LSC₂₁₄ and LSC64₁₁₃ (50%:50%) (red), and LSC₂₁₄ and LSC64₁₁₃ (25%:75%) (light red) thin films. (b) $p(O_2)$ dependency of k^q calculated from EIS spectra collected at 550 °C of the LSCF₁₁₃ (green), the LSC₂₁₄-decorated LSCF₁₁₃ (yellow), and the LSCF₁₁₃ with ~ 3 nm single-layer decoration of mixed LSC₂₁₄ and LSC64₁₁₃ (75%:25%) (dark red), LSC₂₁₄ and LSC64₁₁₃ (50%:50%) (red), and LSC₂₁₄ and LSC64₁₁₃ (25%:75%) (light red) thin films. Inset shows a hypothetical model: enhancement of the Sr content at the top surface of the LSCF₁₁₃ due to adding LSC₁₁₃ to LSC₂₁₄.

which would be expected to increase the oxygen $2p$ band center relative to the Fermi level,^[17] which in turn is expected to correlate with the enhancement of the oxygen surface exchange kinetics.^[17,20,30] In the case of the LSC₂₁₄ decorated LSCF₁₁₃, it has been proposed that low enhancement is observed because there is a negligible change of the surface Sr concentration at the heterostructured interface due to the initially high Sr surface concentration ($\sim 100\%$) of the stable LSCF₁₁₃ (001) surface. This high Sr concentration cannot be easily increased. In contrast, the addition of the LSC₁₁₃ phase into the LSC₂₁₄ can provide the increased Sr content in LSC₂₁₄ and associated thermodynamic driving force for Sr interdiffusion from the LSC₁₁₃ into the LSC₂₁₄. We propose that this driving force is large enough to result in higher Sr concentration in the surface decoration layer of mixed LSC₂₁₄ and LSC₁₁₃ on the LSCF₁₁₃ surface. Accordingly, this Sr enrichment is expected to uplift the oxygen $2p$ band center (relative to the Fermi level) of the LSCF₁₁₃ interface layer and enhance the oxygen exchange kinetics of the LSCF₁₁₃, as reported previously.^[17] Interestingly, the enhancement in the surface exchange kinetics of the LSCF₁₁₃ was found to decrease with increasing the LSC46₁₁₃ ratio in the LSC₂₁₄ phase. This can be explained by the fact that the LSC₂₁₄ phase becomes unstable with increasing LSC46₁₁₃, which can be supported by the reduced intensity of LSC₂₁₄ (001)_{tetra} peak in Fig. S2†. Although a detailed study of the electronic structure changes is needed, the enhanced Sr concentration in the LSC₂₁₄ by mixing with LSC₁₁₃ may be responsible for enhancing the surface exchange kinetics of the LSCF₁₁₃.

Figure 4(b) shows the k^q values of the LSCF₁₁₃ with double-layer decoration of stacked LSC₂₁₄ and three different Sr

contents of LSC₁₁₃ (LSC82₁₁₃, LSC64₁₁₃, and LSC46₁₁₃) thin films, extracted from the EIS data [Fig. 4(a)]. As shown in Fig. 4(b), the k^q values of the LSCF₁₁₃ thin films were found to change with the additional LSC₁₁₃ phase between the LSCF₁₁₃ and LSC₂₁₄, which can be attributed to a change in the Sr concentration at the multiphase heterostructured interface. We hypothesize that the added LSC₁₁₃ phase provides sufficient Sr sources for surface Sr redistribution between LSC₁₁₃ and LSC₂₁₄, which results in increased Sr segregation on the LSCF interface layer. This hypothesis is consistent with our previous ab initio DFT calculations,^[17] which found that the thermodynamic driving force for Sr interdiffusion from La_{0.625}Sr_{0.375}Co_{0.25}Fe_{0.75}O₃ to (La_{0.5}Sr_{0.5})₂CoO₄ (-0.12 eV) is much weaker than that from La_{0.75}Sr_{0.25}CoO₃ to (La_{0.5}Sr_{0.5})₂CoO₄ (-0.7 eV). This driving force is likely responsible for different enhancements in the surface Sr content in the LSCF₁₁₃ films upon LSC₂₁₄ decoration, resulting in different surface exchange kinetics.

LSCF₁₁₃ with the double-layer decoration of stacked LSC₂₁₄ and LSC46₁₁₃ shows significantly higher k^q values up to ~ 1.5 orders of magnitude relative to the undecorated LSCF₁₁₃ and LSC₂₁₄-decorated LSCF₁₁₃. The enhancement can be attributed to Sr segregation at the interface between LSC₂₁₄ and LSC46₁₁₃ and on the LSC₂₁₄ surface at the expense of Sr in LSC46₁₁₃ in the double-layer decoration considering markedly enhanced activity of LSC₂₁₄-decorated LSC82₁₁₃ in the previous work.^[17]

In conclusion, we demonstrate that the oxygen surface exchange kinetics of the (001)-oriented epitaxial LSCF₁₁₃ thin films can be markedly improved by the advanced heterostructured oxide interface engineering using the single-layer

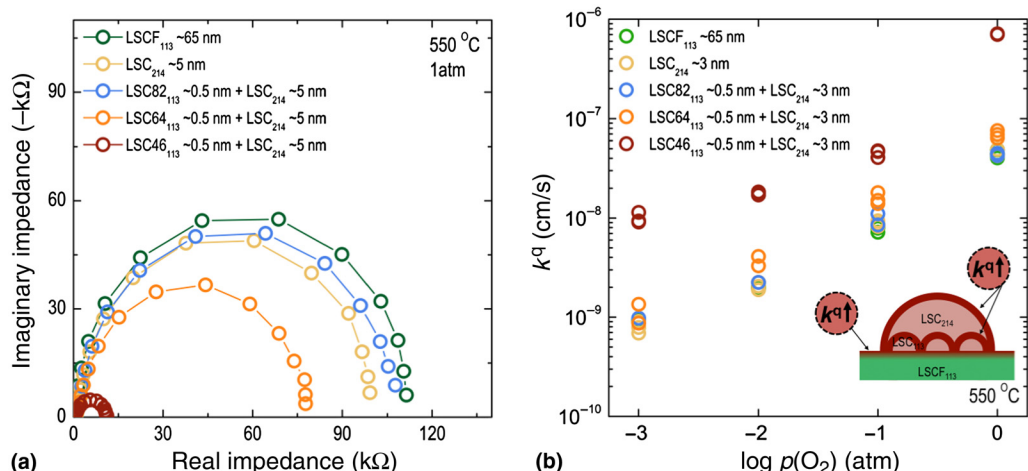


Figure 4. EIS results of microelectrodes (200 μm in diameter) for the epitaxial LSCF_{113} thin films with LSC_{214} decoration, and double-layer decorations of stacked LSC_{214} and LSC_{113} on YSZ (001) with a GDC buffer layer at 550 $^{\circ}\text{C}$. (a) Nyquist plot at 550 $^{\circ}\text{C}$ with an 1 atm of $p(\text{O}_2)$ of the LSCF_{113} (green), the LSC_{214} -decorated LSCF_{113} (yellow), and the LSCF_{113} with double-layer decoration of stacked ~ 3 nm LSC_{214} and ~ 0.5 nm $\text{LSC}_{82,113}$ (blue), ~ 0.5 nm $\text{LSC}_{64,113}$ (orange), and ~ 0.5 nm $\text{LSC}_{46,113}$ (red) thin films. (b) $p(\text{O}_2)$ of the k^a calculated from EIS spectra collected at 550 $^{\circ}\text{C}$ of the LSCF_{113} (green), the LSC_{214} -decorated LSCF_{113} (yellow), and the LSCF_{113} with double-layer decoration of stacked ~ 3 nm LSC_{214} and ~ 0.5 nm $\text{LSC}_{82,113}$ (blue), ~ 0.5 nm $\text{LSC}_{64,113}$ (orange), and ~ 0.5 nm $\text{LSC}_{46,113}$ (red) thin films. Inset shows a hypothetical model: enhancement of the Sr content at the interface between the LSCF_{113} and the LSC_{214} phase due to an increase in the Sr interdiffusion from LSC_{113} to LSC_{214} .

decoration of mixed LSC_{214} and LSC_{113} and double-layer decoration of stacked LSC_{214} and LSC_{113} . This result extends previous results,^[17] showing enhancement from decoration of LSC_{214} on LSC_{113} to the LSCF_{113} material, which is of significantly more interest for commercial applications than LSC_{113} . The oxygen surface exchange coefficients of the LSCF_{113} with single-layer decoration of mixed LSC_{214} and LSC_{113} are ~ 1.1 orders of magnitude greater than those of the undecorated LSCF_{113} and LSC_{214} -decorated LSCF_{113} . In addition, the oxygen surface exchange coefficients of the LSCF_{113} with double layer decoration of stacked LSC_{214} and LSC_{113} are ~ 1.5 orders of magnitude higher than those of the undecorated LSCF_{113} with and without LSC_{214} decoration. The previous work^[17] suggests a strong correlation between the O $2p$ band center and surface exchange kinetics, where surface Sr segregation in the perovskite structure and associated O $2p$ band uplift could increase the surface exchange rate. Therefore, we hypothesize that the decoration on the surface of LSCF_{113} provides Sr segregation at the interface LSC_{214} and LSC_{113} and on the surface of LSC_{214} , which can uplift in the position of the O $2p$ band center relative to Fermi energy of the LSCF interface layer in comparison to that of the LSCF_{113} surface. This work illustrates that heterostructured oxide interface engineering is a strategy, which can enhance multiple types of active oxide materials. Such approaches could potentially be utilized in the infiltration process for decorating cathodes to enhance the performance of SOFCs.

Supplementary material

The supplementary material for this article can be found at <http://dx.doi.org/10.1557/mrc.2016.28>

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