Chemically Driven Enhancement of Oxygen Reduction Electrocatalysis in Supported Perovskite Oxides

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Supporting Information

ABSTRACT: Perovskite oxides have the capacity to efficiently catalyze the oxygen reduction reaction (ORR), which is of fundamental importance for electrochemical energy conversion. While the perovskite catalysts have been generally utilized with a support, the role of the supports, regarded as inert toward the ORR, has been emphasized mostly in terms of the thermal stability of the catalyst system and as an ancillary transport channel for oxygen ions during the ORR. We demonstrate a novel approach to improving the catalytic activity of perovskite oxides for solid oxide fuel cells by controlling the oxygen-ion conducting oxide supports. Catalytic activities of (La0.8Sr0.2)0.95MnO3 perovskite thin-film placed on different oxide supports are characterized by electrochemical impedance spectroscopy and X-ray absorption spectroscopy. These analyses confirm that the strong atomic orbital interactions between the support and the perovskite catalyst enhance the surface exchange kinetics by ∼2.4 times, in turn, improving the overall ORR activity.

The development of renewable energy sources and highly efficient energy storage media is of high priority in the effort to overcome global warming and the depletion of petroleum sources. Electrochemical energy conversion devices such as metal–air batteries, electrolytic water splitters, and fuel cells have been regarded as some of the most promising candidates in this objective due to their high efficiency and sustainability. Among these technologies, solid oxide fuel cells (SOFCs) exhibit the highest energy efficiency and also offer fuel flexibility; that is to say that SOFCs can utilize any type of fuel, from hydrogen and hydrocarbons to even carbon, owing to the enhanced electrocatalytic oxidation activity of the oxygen ions. In contrast, other technologies generally require the use of hydrogen fuels, noble-metal catalysts, or proton conductors. For these reasons, SOFCs could be adopted readily into the current energy-generating system based on the existing hydrocarbon fuel infrastructure, and their use would reduce both the cost and the level of pollution as a result of their high efficiency. One of the main goals of the cutting-edge fuel-cell research is to establish reliable guidelines for the design of more efficient electrocatalysts that will enhance the efficiency of fuel-cell systems. In particular, the development of highly active electrochemical catalysts for the oxygen reduction reaction (ORR) is key to achieving improvements in the efficiency of fuel cells.

The major constituents in the electrocatalyst systems for ORR are transition metal-based perovskites with the general chemical formula ABO3, where A is a rare or alkaline earth metal, such as La or Sr, and B is a transition metal, such as Mn, Co, or Fe, or a mixture thereof. The octahedral symmetry around the transition metal promotes a metallic or semiconducting band structure at high temperatures, facilitating the retention of high electronic conduction, even at high temperatures. Perovskite-based catalysts have an excellent ability to reversibly adsorb and desorb oxygen through continuous changes in the oxidation state of the B transition-metal cation. The electrochemically active sites for the ORR, where the catalyst, oxygen-ion conducting support, and gaseous oxygen meet, are termed as triple phase boundaries (TPBs). The preparation of composite materials from a perovskite catalyst and an oxygen-ion conducting support leads to an increase in the density of TPB sites, thereby enhancing the performance of the composite electrodes. Increased capacity of oxygen ions to diffuse away from the reaction sites can accelerate the overall kinetics of the ORR. In this regard, the role of the oxygen-ion conducting supports used in composite electrodes has mainly been considered in terms of...
the ionic conductivity.\textsuperscript{13,14} Thermally stable oxygen-ion-conducting supports can also play a role as a structural inhibitor in composite electrodes, preventing the aggregation and sintering of unstable catalyst nanoparticles.\textsuperscript{15−17} Thus the development of efficient ORR catalysts is generally based on finding appropriate dopants for the perovskites to enhance their catalytic activity.

While there is no consensus regarding the complete atomistic mechanism of ORR, it has been demonstrated that adjusting the d-band center of the ORR catalyst can allow the exploitation of novel platinum-based ORR catalysts proton exchange membrane fuel cells, capable of operating at room temperature.\textsuperscript{18,19} Likewise, Suntivich et al. found that the occupation of the $\sigma^*$-antibonding ($e_g$) orbital of the transition-metal ions in perovskites can serve as a descriptor of the ORR activity for perovskite oxide catalysts.\textsuperscript{20} Similar approaches for the theoretical prediction of ORR activity using activity descriptors have been introduced for SOFC cathodes operating at elevated temperatures above 650 °C by first-principles calculations, in which the d-band structure of the perovskite B ions predetermines the ORR activity.\textsuperscript{21,22} Theoretical studies confirmed that the electronic structure of the d-band of the B metal cation affects the hybridized O p-bands. This interaction governs the formation of oxygen vacancies and, in turn, determines the overall ORR activity.\textsuperscript{21,22} Despite the theoretical in-depth understanding of the catalytic ORR activity, experimental demonstrations of tuning the d-band state in perovskites for enhanced ORR activity remain challenging.

Controlling the d-band of the perovskite transition-metal cation without degrading the phase stability is extremely challenging. It is generally accepted, in fact, that the phase stability of perovskites and their catalytic activity trade off each other.\textsuperscript{10,11} Therefore, it is not only inherently difficult to determine the type and content of a dopant to use in the perovskite to control the d-band structure but also difficult to predict whether the doped perovskite will retain its phase stability, especially during long-term operation at high temperatures. For this reason, tuning the d-band structure of perovskites by heterostructuring with a different oxide in a heterogeneous electrochemical catalyst system presents an attractive alternative. Recent studies on La$_{0.8}$Sr$_{0.2}$CoO$_3$ / (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_4$ (LSC$_{113}$/214) heterostructures demonstrated the possibility of activating the electronic structure of LSC$_{214}$ by mixing it with LSC$_{113}$ for enhanced ORR activity.\textsuperscript{23−26} Strain-induced tuning of the M−O bond in heteroepitaxially grown LaCoO$_3$ thin films has also demonstrated that the physical and catalytic properties of perovskites can be altered by modulating the electronic configuration in perovskite oxides.\textsuperscript{27,28} These findings highlight the novel and alternative approaches of interfacial engineering compared with the conventional doping approaches.\textsuperscript{25,26} These observations underscore the potential of interfacial engineering, in which the atomic orbitals of perovskites can be readily modulated by strain-coupling or heterostructuring. Likewise, it might be possible that the oxygen-ion-conducting supports, employed in the composite electrodes of electrochemical cells, could also play a role as an electronic modifier if the perovskite interacts with the oxide.
Figure 2. ORR activities of LSM thin-film electrodes analyzed by EIS: LSM/YSZ (black), LSM/ScSZ (orange), and LSM/SDC (blue). (a) Total electrode polarization resistance as a function of temperature measured under a pO₂ of 0.2 atm. (b) LSM bulk diffusion resistance (R_D) and (c) surface reaction resistance (R_s) plotted as a function of pO₂. The error bars in panel a represent the standard deviations from the measurements of three different cells for each configuration, while those in panels b and c denote the fitting error of the representative plot for each configuration.

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support. Therefore, the oxygen supports could enhance the catalytic activity of the neighboring perovskite catalyst while simultaneously maintaining its phase stability without doping for the perovskites. The control over the chemical interactions at the interface between the perovskite catalysts and oxygen-ion conducting supports, that is, the control over the TPBs, is particularly important in determining the electrochemical ORR activity. Furthermore, if the perovskite-support interaction is chemical, that is to say that the specific elements in the perovskite and oxide support interact with each other, this strategy can be easily applied to practical SOFC cathodes as the form of composite without the need for delicate strain coupling or heterostructuring.

We suggest a novel approach to enhancing the catalytic activity of a (La₀.₇Sr₀.₃)₀.₉MnO₃ (LSM) perovskite oxide catalyst by controlling the type of employed oxygen-ion-conducting oxide supports. To date, LSM is the most widely used SOFC cathode material, and its chemical/mechanical properties and phase stability have been well established. It is generally recognized that LSM is thermodynamically more stable than cobaltite- or ferrite-mixed conducting perovskites. We show that it is possible to control the ORR activity of LSM by inducing different electronic interactions between the LSM and different conventional oxygen-ion conducting supports, including YₓSr₁₋ₓO₁.₉₁ (yttria-stabilized zirconia, or YSZ), ScₓZr₁₋ₓO₁.₉₁ (scandia-stabilized zirconia, or ScSZ), and SmₓCe₀.₅O₁.₉₄ (samaria-doped ceria, or SDC). Using electrochemical impedance spectroscopy (EIS), we decouple the contribution of the surface reaction kinetics of thin-film electrodes from the overall polarization behavior and relate these kinetics to the d-band structures of the Mn ions. Through a combination of experimental and theoretical studies examining the relationship between the kinetics of ORR and the catalyst-support interactions, we successfully demonstrate a new aspect for the development of the supported perovskite oxide catalysts.

LSM thin films were prepared on three different electrolytes, producing 2D interfaces (Figure 1a–c). Polycrystalline 160 nm thick LSM thin-film electrodes were deposited via pulsed laser deposition (PLD) on either (100) single-crystal YSZ, ScSZ/YSZ, or SDC/(100) single-crystal YSZ (Figure 1d–f). Well-defined thin-film electrodes permit elimination of geometrical irregularities such as porosity and tortuosity, thereby allowing the catalytic activities of electrodes to be evaluated solely with respect to the interfacial characteristics of the perovskite catalyst–oxide support. The specific thickness of the LSM thin film was selected so as to mimic the general dimensions of LSM in a powder-based realistic composite. It should be noted that LSM exhibits a sufficient ionic conductivity in this thickness range, allowing the surface exchange of oxygen ions and their transport to the electrolyte through the LSM to be characterized concurrently with the employed configuration (for details, see the Supporting Information). On the contrary, the polycrystalline structure of LSM mitigates the local mechanical strains that arise from lattice mismatches between LSM itself and the ion-conducting oxide substrates. High-resolution transmission electron microscopy (HRTEM) revealed that the ScSZ and SDC thin films grew as heterogeneous epitaxial single crystals on (100) YSZ, which possesses the same fluorite crystal structure as ScSZ and SDC. This observation was confirmed by the analysis of the selected area electron diffraction (SAED) patterns, shown in Figure S1. LSM thin-film electrodes, postannealed at 900 °C in air, exhibited a pseudocubic perovskite structure without any secondary phase, as shown in Figure S2. In the past, the contact between LSM and stabilized zirconia or doped ceria has been shown to afford chemically stable interfaces at temperatures of 800–1000 °C, without the formation of any pyrochlore-type secondary phase such as La₂Zr₂O₇ or La₂CeO₃. The formation of such secondary phase commonly takes place at above 1200 °C and is accompanied by a significant diffusion of Mn ions into the fluorite lattices. Considering the thin-film deposition temperature of 600 °C and subsequent postannealing at 900 °C, it is reasonable to assume that there are no secondary phase at the interface of LSM thin films and the oxide supports.

The ORR activity of LSM thin-film electrodes was measured using EIS in the 700–800 °C temperature range. Porous platinum electrodes were utilized as the counter electrode in each case, and a mixture of O₂/N₂ was supplied directly to both the working electrode and the counter electrode, thereby eliminating the influence of the gradients in oxygen partial pressure (pO₂) within the electrodes. Representative Nyquist plots of LSM thin-film electrodes, determined as a function of pO₂ measured at 750 °C, are shown in Figure S3a. The ohmic resistance, which corresponds to the first intercept on the x axis, represents the ionic conduction through the electrolyte, while the electrode polarization manifests as semicircular arcs in the Nyquist plots. Obviously, the total electrode polarization resistance of the thin-film electrode deposited on ScSZ exhibits the smallest value (Figure 2a) out of the three fabricated thin-film electrodes. The total polarization resistance of an LSM thin film on ScSZ at 700 °C under a pO₂ of 0.2 atm was determined as 52.79 ± 1.5 Ω, and those of LSM on YSZ or on SDC were...
measured as 103.69 ± 4.6 Ω and 90.66 ± 9.3 Ω, respectively. The activation energies of ORR in all LSM thin films were relatively similar, exhibiting almost identical slopes in the plots shown in Figure 2a. The smallest polarization resistance of the LSM on ScSZ thin film and the similarities in the activation energies of all three films imply that the ORR reaction mechanism is similar in all films, while the active-site density of LSM on ScSZ may be higher than the density of the remaining thin-film electrodes. The polarization resistance of LSM thin-film electrodes can be deconvoluted using a generalized transmission model, as depicted in Figure 3b.31,32,35 The polarization response of a thin-film electrode reflects the total polarization during each step of the ORR as well as the oxygen ion transport, including the surface exchange reaction of oxygen ions, ion transport through the electrode, and dielectric polarization at the electrode–electrolyte interface (due to the blocking of electrons by an ionic conductor, i.e., the electrolyte).31,32,35 The results of the equivalent circuit (EC) fitting and a more detailed discussion on the experimental setup can be found in Table S1 and Figure S4 of the Supporting Information, respectively. Note that the critical diffusion length ($L_c$) determined from the surface reaction resistance, $R_s$ and the LSM bulk diffusion resistance, $R_{bulk}$ ($L_c = AR_sσ_{bulk}$ where $A$ is the electrode area and $σ_{bulk}$ denotes the LSM bulk diffusion conductivity) was in the range of 198–265 nm for the thin films (Table S1). Therefore, the polarization response of the LSM thin films reflects both the LSM surface reaction and the bulk diffusion of oxygen ions in the LSM.31 The surface reaction is strongly correlated with the $p_{O2}$ while the oxygen ion diffusion in LSM is nearly independent of $p_{O2}$ indicating that $R_s$ and $R_{bulk}$ arise from separate electrode processes. The deconvoluted polarization resistances, $R_s$ and $R_{bulk}$ at 750 °C were plotted as a function of $p_{O2}$ (Figure 2b,c). The $R_{bulk}$ of thin-film electrodes was found to be the smallest for LSM/ScSZ. Nevertheless, the $R_{bulk}$ values and the $p_{O2}$ dependency were fairly similar across the three thin film samples, demonstrating that the crystallinity of all LSM thin films is nearly identical and diffusion occurs at a similar rate. In contrast, the value of $R_s$ was found to be distinctively lower for the LSM/ScSZ cell than for the other cells (Figure 2c). The surface exchange kinetics, proportional to the inverse of $R_s$ for LSM/ScSZ was faster than those of the others by ~2.4 times. The LSM films on SDC and YSZ exhibited similar $R_s$ values; therefore, it is possible to conclude that the smallest electrode polarization of LSM/ScSZ stems from the enhanced surface reaction kinetics. This observation implies that the surface reaction kinetics of the thin-film electrode on ScSZ is accelerated while maintaining its crystal structure and preserving its oxygen diffusion capacity. As mentioned before, the oxidation state of the transition metal ion has been used to explain the variation in the LSM surface exchange kinetics. Therefore, it is necessary to elucidate how the nature of the oxide support influences the electronic structure of the Mn cation in LSM and the subsequent effect of these changes on the surface reaction kinetics.

Mn K-edge spectra of LSM films deposited on three different oxide supports were measured by X-ray absorption near edge structure (XANES), allowing us to study the variation in the electronic structure of Mn ions. The main absorption edges of Mn K-edge spectra for the three samples exhibited similar profiles without any distinct energy shifts. The main edge of all three samples was measured at 6556.4 eV (Figure 3a). The main edge predominantly represents the electronic transitions from the Mn 1s orbital to the empty Mn $p$ orbital. For the manganites, the local spin density approximation and multiple scattering calculations have shown that the energy level of the main edge structure is sensitive to the Mn–O bond length.36–38 These calculations revealed that the shift of the main edge to a lower energy occurs when the Mn–O bond is elongated, whereas a shortened Mn–O bond induces a shift of the main edge structure to a higher energy. This observation demonstrates that the Jahn–Teller effect in all samples is similar: the average Mn–O bond length in the LSM deposited on different oxide supports is identical, and the Mn$^{3+}$/Mn$^{4+}$ states are evenly distributed regardless of the oxide support type.

Distinguishable features were instead observed in the pre-edge region, where only the LSM/ScSZ displayed a clear splitting of $A_g$–$A_g$ subpeaks, while LSM/YSZ and LSM/SDC each exhibited a single broad peak (Figure 3b). Taking into consideration the micrometer-scale penetration depth of moderately hard X-rays with a photon energy of 6 to 7 keV, the pre-edge structures of LSM thin films reflect the electronic structures of the entire LSM thin films. For many of the transition elements, the pre-edge structures provide detailed information about the d-band structure. The two or three pre-edge subpeaks (denoted as $A_g$) that appeared well below the main edge (usually 15 eV below) can be assigned to the transition of 1s electrons to empty states in the d orbitals, that is, the transition from 1s to 3d$^m$(1$s^1$), where $n$ is the initial number of d orbital electrons and $n+1$ represents the number of excited electrons in the final state. Splitting of $A_g$–$A_g$ subpeaks occurs when the d orbitals are split into $t_{2g}$ and $e_g$ levels, as for example, in the octahedral environment of MnO$_6$. Subsequently, the $e_g$ levels can be split further into nondegenerate $e_g$ levels by the Jahn–Teller effect. This demonstrated that the rich concentration of the lower valence state of Mn in perovskites (Mn$^{3+}$, i.e., a singly occupied $e_g$ state) facilitates the $A_g$–$A_g$ splitting, which is frequently observed in LaMnO$_3$, in which the nominal valence of Mn is 3+.38 These phenomena have to accompany the shift in the main edge position as a result of the Jahn–Teller effect, which leads to a tetragonal distortion of the MnO$_6$ octahedron. However, the shift in the main edge structures was not observed in our samples. Therefore, the splitting of the $A_g$–$A_g$ subpeaks can be explained by the dipole-allowed transition of Mn 1s electrons to 4$p$ orbitals, mediated by the hybridization with the 3d states of the neighboring cations. Hybridization introduces new levels with $p$- and d-orbital character, resulting in the splitting of $A_g$–$A_g$ subpeaks, without the Jahn–Teller distortion.40 Such hybridization generates holes in the $e_g$ level of Mn, thereby enabling further hybridization between 3d orbitals of Mn and the 2$p$ orbitals of O, which accounts for the strongly covalent nature of Mn–O bonds.
Mn−O bonds. On the basis of this explanation, the splitting of $A_1−A_2$ subpeaks observed only in the LSM on ScSZ thin film is indicative of (i) significant hybridization of the 4p orbitals of Mn with the 3d states of the neighboring cations and (ii) the greater covalency of Mn−O bonds in the LSM/ScSZ system than in either LSM/YSZ or LSM/SDC. Considering the identical probability of Mn 3d-Mn 4p hybridization in all samples, it is possible that the distinctively augmented subpeak $A_1$ in LSM/ScSZ is triggered by a strong hybridization of Mn 4p orbital with the Sc 3d state, a unique element present at the interface in ScSZ only. Subsequently, the hybridized pd orbital induces knock-on hybridizations with the Mn 4p levels in the outer-planes of LSM, resulting in a strong $A_1$ subpeak for the entire film.

Multiscattering XANES simulations enable us to understand the influence of the oxide support on the hybridization of the Mn 4p orbitals. Using a finite difference multiscattering calculation, we performed a series of simulations based on the octahedral Mn−O ligand model. The XANES spectra were simulated mainly for the Mn−O ligands, with the dopant cations located in the support oxides, an element unique to each oxide support. We hypothesized that the influence of the shared elements such as Zr, Ce, or Mn would be negligible compared with that of the dopant cations. The simulated XANES spectra for the interactions between MnO$_6$ and either Zr, Ce, or Mn ions exhibited insignificant splitting in the pre-edge structures and much lower electronic densities in the pre-edge region than that determined for MnO$_6$−Sc (Figure S5), confirming the validity of our hypotheses. The results of the XANES simulations showed a clear $A_1−A_2$ splitting in MnO$_6$−Sc (Figure 4a). These results are consistent with the experimental XANES spectra (Figure 3b). The electron density of the occupied Sc 3d orbitals is indicative of strong hybridization of the Sc 3d orbitals with the Mn 4p orbitals (Figure 4b). The Sc 3d states have the greatest occupancy at the energy level of the $A_1$ subpeak, suggesting strong hybridization between the 4p states of Mn and 3d states of Sc. The Y 3d and Sm 3d states are significantly less occupied than the Sc 3d states, suggesting much weaker hybridization with Mn 4p orbitals. The theoretical calculations in conjunction with the experimental evidence allow us to conclude that the electronic structure of the Mn d-bands in LSM on ScSZ is modified by the presence of the neighboring Sc atoms, which subsequently triggers changes in the d-band structure of the entire LSM film.

To probe the influence of the orbital hybridization on the surface region of LSM, the surface-sensitive techniques of X-ray photoelectron spectroscopy (XPS) and soft-XAS have been conducted to characterize the electronic configuration and stoichiometry of the surface region. Both techniques count the photoelectrons or secondary electrons excited by soft X-rays with photon energy below 1.5 keV so that the information depth is generally estimated to 10 nm from the surface. Figure S5a,b represents the Mn-L$_{3,2}$ and O−K edge spectra obtained by soft-XAS with a total electron yield (TEY) mode. The hybridization of Mn 4p and neighboring Sc 3d states results in the modulation of Mn 3d structures, generating new density-of-states (DOS), as observed in the preedge structure of Mn−K edge spectra. However, the unoccupied DOS cannot be characterized in Mn-L$_{3,2}$ spectra because of the strong atomic
multielectron effect in 3d-transition metals, by which Mn-4s, 4p, and 4d states, we can infer that the oxygen-ion-conducting oxide supports.

This hybridization propagates along the Mn–O bonding direction, giving rise to a serial hybridization of Mn 4p and σ\(^*\)pd states, thereby introducing σ\(^*\)pd states throughout the film and the surface. In this situation, the generation of the oxygen vacancies becomes more favorable as a result of the higher probability of the antibonding orbital occupancy. The facile formation of oxygen vacancies in LSM as a result of the interfacial interactions of the Mn ion with the oxide support will enhance its surface reaction kinetics efficiently. On the basis of these conjectures, we can conclude that the facile oxygen vacancy formation, stemming from the generation of low-lying antibonding orbitals (σ\(^*\)pd) near the LSM–ScSZ interface, results in higher surface exchange kinetics of LSM–ScSZ. A systematic work examining a wide range of interactions between perovskites and oxide supports and the correlation between hybridization and oxygen vacancy formation is currently underway in our laboratory.

We have presented a novel approach to enhance the ORR activities of LSM cathodes by controlling the previously unexplored interactions between the LSM catalyst and the oxygen-ion-conducting oxide supports. EIS measurements demonstrated that the surface-exchange kinetics of LSM/ScSZ are faster than those of LSM/YSZ and LSM/SDC by ~2.4 times. XAS studies allowed us to observe distinctive splitting of A1g–A2g subpeaks in the K pre-edge structure of Mn in LSM/ScSZ, while only a single broad A2g subpeak was observed in both LSM/YSZ and LSM/SDC. Simulated XANES spectra confirmed that the A1g–A2g splitting arises as a result of the strong hybridization of Mn 4p levels with Sc 3d levels, thereby creating an additional antibonding state in Mn atoms. This antibonding state resulted in the weakening of the Mn–O bonds, thus enabling oxygen vacancies to form more easily in the LSM and enhancing the surface exchange kinetics. We believe that this unprecedented strategy can be extended to the bulk composite cathodes utilized in practical SOFC applications by selection of orbital-modulating elements in the oxide supports without the need for careful strain coupling or heterostructuring. Furthermore, we believe that this simple interface-controlled enhancement method might provide an alternative approach to the development of highly efficient catalysts based on an appropriate combination of well-known conventional catalysts and supports.

### EXPERIMENTAL SECTION

Fabrication and Characterization of Thin-Film Cells. Single-crystal 9.5 mol % YSZ (001) wafers with dimensions of 10 x 10 × 0.5 mm (Princeton Scientific, USA) were employed as a substrate for the fabrication of the LSM thin-film electrodes. Thin films of ScSZ and of SDC were first grown epitaxially on YSZ (001) wafers via PLD (Pioneer 180, Nocerco, USA) to serve as the oxide supports. Subsequently, LSM thin films were grown by PLD on each of these substrates: (i) a bare YSZ (001) wafer and YSZ wafers with deposited thin films of (ii) ScSZ or (iii) SDC. These PLD depositions were conducted using a KrF excimer laser at λ = 248 nm, 10 Hz pulse rate, and 50 ml pulse energy at 600 °C, under a pO\(_2\) of 10 mTorr. After deposition, the samples were annealed at 900 °C for 1 h under ambient atmosphere. Each target for PLD was prepared by uniaxial pressing of commercial powders of either LSM (LSM20-P, Fuel Cell Materials, USA), ScSZ (89 mol % ZrO\(_2\), 10 mol % Sc\(_2\)O\(_3\), 1 mol % Al\(_2\)O\(_3\), Seimi Chemical, Japan), or SDC (SDC20-P, Fuel Cell Materials, USA), followed by sintering. The microstructures of the fabricated thin films were characterized by

![Figure 5. XAS spectra of the LSM films placed on three different oxide supports. (a) Mn-L\(_{2,3}\) edge spectra and (b) O-K edge spectra.](image)
XANES calculations were conducted using the FDMNES to the reference energy of the Mn K-edge, 6539 eV. Ab initio spectra were calibrated by setting the maximum in element Ge array detector in the 8C beamline using a monochromatic radiation and a seven-element Ge array detector in the fluorescence mode. The spectra were calibrated by setting the maximum in the active area of the electrochemical cells, which was 0.50 cm² for all samples. The polarization of thin-film cells was analyzed in the frequency range of 100 kHz to 0.1 Hz with an AC amplitude of 10 mV by using a potentiostat (1287A, Solartron, U.K.) and a frequency analyzer (1260, Solartron, U.K.).

X-ray Spectroscopies and Simulations of Spectra. XAS experiments were carried out at the Pohang Light Source (PLS, Republic of Korea). K-edge spectra of Mn were obtained at the 8C beamline using a monochromatic radiation and a seven-element Ge array detector in the fluorescence mode. The spectra were calibrated by setting the maximum inflection point to the reference energy of the Mn K-edge, 6539 eV. Ab initio XANES calculations were conducted using the FDMNES program (Centre National de la Recherche Scientifique, France). The electronic structure around the absorbing atoms was calculated by solving the Schrödinger equation using a finite difference method based on a monoelectronic approach. The absorption was convoluted to a Lorentzian with an energy-dependent width to take into account the core and final-state lifetimes. The absorption was convoluted to a Gaussian to mimic the experimental energy resolution. The Mn K-edge XANES spectra were calculated with a neighboring transition metal (i.e., Y, Sc, or Sm) atom attached to a minimalistic cluster of MnO₂ along the Mn-O bond. The XAS Mn-L₃,₂ spectra were collected at the 10D beamline in the total electron yield mode under the basal pressure of 5.3 × 10⁻⁸ Torr. The XPS spectra were calibrated by setting the position of C 1s spectra to 284.5 eV.

**Author Contributions**

The manuscript was written through the contribution of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02503.

SAED patterns of oxide supports, XRD patterns of LSM thin films, equivalent circuit model and Nyquist plots of LSM/ScSZ, fitting parameters obtained from the fitting of LSM/ScSZ data, details of experimental setup employed for the electrochemical characterizations, schematic illustration of the experimental setup, simulated XANES spectra of MnO₂ ligand complexes with various cations, and XPS analysis results of the LSM thin films. (PDF)

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Supporting Information:

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Figure S1. SAED patterns of oxide supports grown on a YSZ (100) single crystal, obtained through the Fourier transformation of the HRTEM images shown in Figure 1. (a) YSZ (100) single crystal substrate, (b) ScSZ grown epitaxially on a YSZ (100) single crystal, and (c) SDC thin film grown on a YSZ (100) single crystal.
**Figure S2.** XRD patterns of LSM thin films deposited on oxide supports via PLD: LSM on SDC (blue), LSM on ScSZ (orange), and LSM on YSZ (black).
Figure S3. The equivalent circuit (EC) model employed in the fitting of EIS spectra, and Nyquist plots of LSM/ScSZ at 750 °C. (a) The generalized transmission model in which $R_0$, $R_s$, $R_{\text{ion}}$, $C_s$, $C_{\text{chem}}$, $C_{\text{dl}}$ and $N$ denote the ohmic resistance of the electrolyte, the LSM surface reaction resistance, the LSM bulk diffusion resistance, the LSM surface reaction capacitance, the LSM chemical capacitance, the dielectric capacitance of electron blocking at the LSM-YSZ interface, and the number of conducting units in LSM, respectively. The capacitors were replaced with a constant phase element, a pseudo-capacitor, to improve the fitting accuracy. (b) Nyquist plots of LSM/ScSZ determined as a function of $pO_2$. 

- 0.05 atm
- 0.2 atm
- 1 atm
- 1 atm
- EC fitting
Table S1. Fitting parameters obtained from the fitting of LSM/ScSZ data, plotted in Figure S3.

<table>
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Details of the experimental set-up employed in the electrochemical characterization

The ORR activity of an LSM thin film can be characterized by measuring the electrode polarization of an electrochemical cell consisting of the LSM thin film | solid electrolyte | Pt. The electrode polarization of the cell is induced by the ORR occurring on the LSM film (working electrode) and the oxygen evolution reaction (OER) on the Pt electrode (counter electrode). In order to be able to attribute the electrode polarization as ORR on the LSM, OER on the Pt electrode must be sufficiently fast. For this reason, the Pt electrode employed possesses a porous structure to maximize the number of the active sites for OER and the mass transport of oxygen. In fact, OER on Pt is not so fast relative to the ORR on Pt, so that Ir or Ru compounds are employed as the state-of-the-art OER electrode.\textsuperscript{1,2} Therefore, ensuring a steady-state of oxygen throughout the electrochemical cell is essential in order to be able to evaluate the ORR activity of the LSM accurately. Previous studies have utilized an instrument with a hot-plate, which is in direct contact with the electrochemical cell and allows the cell to be heated to the desired operation temperature, as shown in Figure S4a.\textsuperscript{3,4} In this configuration, the evolved oxygen cannot be emitted from the Pt electrode smoothly, resulting instead in a high localized $pO_2$ near the Pt electrode. This can result in the accumulation of oxygen ions near the Pt-electrolyte interface, thereby interfering with the equilibration of oxygen ions with the oxygen gas. In the set-up we employed for the ORR characterization, the samples were first loaded onto an alumina mount, placed between two alumina tubes with inner quartz gas channels, in which both electrodes were directly exposed to the flow of O$_2$ and N$_2$, as illustrated in Figure S4b. This set-up enables fast equilibration between the oxygen ions and the gas, allowing the steady state to be reached efficiently throughout the cell. To confirm the steady state of the cell, the open-circuit voltage (OCV) was carefully monitored during each measurement. These measurements showed ca. 4 times larger surface exchange kinetics of LSM thin films than any previous studies; the electrical surface exchange coefficient ($k_\text{s}$) for LSM/YSZ at 750 °C was determined as $1.68 \times 10^{-7}$ cm s$^{-1}$ in this study, while this coefficient was established as $4 \times 10^{-8}$ cm s$^{-1}$ by la’ O et al.\textsuperscript{4} On the other hand, the active cell area of micro-patterned electrodes employed in previous works (Figure S4c) contains both 2PB and 3PB sites, whereas the active cell area of the cell used in this work (Figure S4d) retains only 2PB sites on which ORR occurs.
**Figure S4.** Schematic illustration of the experimental set-up and cell configuration for the electrochemical characterizations: (a) the set-up employed in previous studies and (b) the set-up employed in this study. (c) The cell configuration used in previous studies with the microelectrodes, and (d) the cell configuration of this study. The Pt counter electrode is located in the opposite side to the thin film side, which covers the whole area of the substrate in previous studies, whereas the Pt electrode same as the Pt current collector at the top (Figure S4d) is aligned in the vertical direction at bottom of the cell in this work. The 3PB sites are marked as red dotted lines in the figure c and d. The active cell area for the microelectrodes is determined by the area of circular microelectrode, while that for this work is defined by the area of Pt counter electrode.

**Supplementary References**

Figure S5. Simulated XANES spectra of MnO$_6$ ligand complexes with various cations. (a) Pre-edge structures calculated using a finite difference method. (b) Electronic densities of hybridized atoms in their final states of multi-scattering. Results of ligand complexes with Y, Sc and Sm are also presented for comparison purpose.
Figure S6. The XPS analysis results of the LSM films placed on three different oxide supports. Quantitative elemental analyses of (a) Sr/(Sr+La) and (b) (La+Sr)/Mn in the LSM. (c) Mn 2p spectra. The error range was estimated to 10% for each spectrum from the average signal-to-noise ratio of the spectra.