Oxygen Surface Exchange Kinetics on Sr-Substituted Lanthanum Manganite and Ferrite Thin-Film Microelectrodes

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Oxygen Surface Exchange Kinetics on Sr-Substituted Lanthanum Manganese and Ferrite Thin-Film Microelectrodes

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The surface oxygen exchange kinetics occurring on dense La$_{0.8}$Sr$_{0.2}$MnO$_3$ (65 nm thick) and La$_{0.8}$Sr$_{0.2}$FeO$_3$ (110 nm thick) thin films were investigated by electrochemical impedance spectroscopy (EIS). Rutherford backscattering spectroscopy revealed that the bulk film compositions were consistent with the nominal stoichiometry, with La$_{0.8}$Sr$_{0.2}$FeO$_3$ having a slight Fe deficiency. Surface compositions of La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.8}$Sr$_{0.2}$FeO$_3$ were enriched in La using X-ray photoelectron spectroscopy and Auger electron spectroscopy. EIS data were utilized to determine the surface oxygen exchange coefficients, $k^*$ and $k_{chem}$ in the range of temperatures from 790 to 660°C and oxygen partial pressures from 10$^{-5}$ to 1 atm. The magnitudes of $k^*$ and $k_{chem}$ were found comparable for both La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.8}$Sr$_{0.2}$FeO$_3$, and a $P_O_2$ dependence $m$ fell in the range from ~0.2 to ~0.3. The thermodynamic enhancement factor $\gamma$ was consistently higher for La$_{0.8}$Sr$_{0.2}$MnO$_3$ than La$_{0.8}$Sr$_{0.2}$FeO$_3$, which was in reasonable agreement with estimates based on thermogravimetric data of powder materials reported previously. The chemical capacitance for La$_{0.8}$Sr$_{0.2}$MnO$_3$ was approximately 1 order of magnitude larger than La$_{0.8}$Sr$_{0.2}$FeO$_3$, which indicates a larger oxygen vacancy content. The rate-limiting steps of surface oxygen exchange on La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.8}$Sr$_{0.2}$FeO$_3$ were discussed with regard to previously proposed models.

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Surface oxygen exchange and diffusion of oxygen ions are the two key processes that control the oxygen reduction reaction (ORR) through mixed ionic and electronic conducting (MIEC) cathodes. The diffusion of oxygen in the lattice of many perovskite-based MIECs is relatively well characterized due to the tremendous technological implications for these in applications such as oxygen separation membranes, solid oxide fuel cell (SOFC) cathodes, and gas sensors, to name a few.\(^4,5\) However, below a critical thickness $L_c$, defined as the ratio of the oxygen diffusion coefficient ($D$ in cm$^2$/s) and the surface oxygen exchange coefficient ($k$ in cm/s) (where $L_c = D/k$), surface exchange will start to limit ORR kinetics, where any further reduction of MIEC cathode thickness would provide no additional enhancement. Surface oxygen exchange on oxides is poorly understood. A variation of techniques had been used to quantify $k$ and $D$ and determine $L_c$, such as (i) $^{18}$O tracer gas for ion exchange depth profile (IEDP) with secondary-ion mass spectrometry (SIMS),\(^6,7,9\) (ii) conductivity relaxation methods,\(^10,11\) (iii) oxygen permeation studies,\(^12,13\) and, more recently, (iv) electrochemical impedance spectroscopy (EIS).\(^14,15\) A number of earlier studies using IEDP/SIMS techniques have shown empirical correlations of tracer surface oxygen exchange $(k^*)$ with oxygen tracer diffusion coefficient $(D^*)$, which suggests the importance of oxygen vacancies for oxygen exchange.\(^7,14,15\) However, the influence of oxygen vacancies on $k^*$ is shown to be much smaller than that on $D^*$ because $k^*$ values of MIEC cathodes $^{10,11}$ such as La$_{1-x}$Sr$_x$Fe$_{1-y}$Co$_y$O$_{3-y}$ (LSCF) and La$_{1-x}$Sr$_x$MnO$_3$ (LSM)\(^12,16\) differ by 1–2 orders of magnitude, while $D^*$ of LSM is 4–5 orders of magnitude lower than that of MIEC cathodes. More recently, De Souza\(^17\) proposed that the availability of electronic species governs the rate of oxygen surface exchange, where low concentrations of oxygen vacancies and high concentrations of charge carriers are needed for high exchange rates. This previous model\(^18\) is largely in agreement with mechanisms reported by Adler et al.\(^19\) where a metallic band structure is considered important in surface oxygen exchange. Using this concept, one would expect that the surface exchange rate on LSM with higher electronic conductivity\(^20\) but lower oxygen ion conductivity\(^21\) is higher than that on La$_{1-x}$Sr$_x$FeO$_{3-y}$ (LSF). The focus of this study is to examine and compare the kinetics of surface oxygen exchange of LSM and LSF as a function of oxygen partial pressure ($P_O_2$) and temperature.

For materials with very poor oxygen diffusion and limited oxygen nonstoichiometry in bulk, such as LSM, significant challenges remain in accurately measuring $k^*$ and $P_O_2$ dependence, particularly at $P_O_2$ less relevant to SOFC cathode operation. Using IEDP/SIMS, the $^{18}$O isotope fractions in the gas phase approach those on the surface of the LSM cathode, which results in large errors of 2 orders of magnitude or more in fitting $k^*$ at $P_O_2$ of $>10^{-3}$ atm.\(^20\) For oxygen permeation studies, given the extremely small $L_c$ for LSM,\(^2\) estimated to be ~10 nm at 720°C (using $D^* \sim 10^{-14}$ cm$^2$/s and $k^* \sim 10^{-6}$ cm/s), the fabrication of sub-100 nm freestanding membranes poses a significant challenge.\(^21\) An alternative method demonstrated by Jacobson and co-workers\(^22,23\) and by Maier\(^24\) is to determine the chemical surface oxygen exchange coefficient ($k_{chem}$) and the electrical surface oxygen exchange coefficient ($k^*$) from EIS measurements that is approximately equivalent to $k^*$ from tracer experiments.\(^25\) In this study, we examine the surface oxygen exchange kinetics on La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM80-20) and La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF80-20) thin-film microelectrodes using EIS. The chemical compositions on the surface of these microelectrodes is determined using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), while the bulk composition is analyzed using Rutherford backscattering spectroscopy (RBS). Surface exchange rates of $k^*$ and $k_{chem}$ of LSM80-20 obtained from EIS measurements are comparable to those of LSF80-20, from which insights into the influence of electronic properties and oxygen vacancies on the surface exchange rate is discussed.

In this study, it is of great interest to compare the $P_O_2$ dependence on the surface exchange rates of LSM80-20 and LSF80-20. Ambiguities exist in the rate-limiting step for surface oxygen exchange in the literature, which is largely derived from experimentally observed $P_O_2$ dependence on surface exchange rates. Three different rate-limiting steps for surface oxygen exchange have been reported for perovskites. De Souza\(^17\) suggested that the rate-limiting step involves the combination of atomic oxygen species and electrons (charge transfer) for both electron-poor and electron-rich perovskites. Adler and co-workers\(^26\) reported that a dissociative adsorption step was the rate-limiting step for metallic La$_{1-x}$Sr$_x$CoO$_{3-y}$ (LSC), while chemisorption was the rate-limiting step for p-type semiconductor LSF. More recently, Fleig et al.\(^27\) showed that electron-transfer steps such as $O_{ad}^\bullet + e^- \rightarrow O_{ad}^\bullet$ and $O_{ad}^\bullet + e^- \rightarrow O_d^\bullet$ are the rate-limiting step on materials with $P_O_2$-independent hole concentrations and materials having electronic carrier concentrations with $P_O_2$ dependence of $\frac{1}{2}$ in the $P_O_2$ and temperature relevant to SOFC operation (from $10^{-3}$ to 1 atm at

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Experimental

An 8 mol % yttria-stabilized zirconia (YSZ) electrolyte (Praxair Specialty Ceramics, USA) was initially sputtered onto alumina (Al₂O₃) substrates for 3 h at 400 W with an argon (Ar) to oxygen (O₂) atmosphere ratio of 7.5:1. The deposited films were then annealed in air at 800°C for 3 h. Cathode targets with LSM80-20 composition were deposited subsequently on top of the YSZ film by sputtering at 300 W, with the substrate heated to ~550°C under an identical Ar to O₂ ratio, from which LSM80-20 films with a thickness of 65 nm were obtained. Pulsed laser deposition was used to deposit LSF80-20 from a 1 in. diameter target with a repetition rate of 110 nm were obtained after a deposition of 2 h using an excimer laser operating at a wavelength of 248 nm, a 10 Hz repetition rate, an energy of 500 mJ/pulse, and a substrate heating at 800°C. LSM80-20 and LSF80-20 film thickness was verified using a Dektak profilometer and a RBS setup. A scan rate of 60 s/frame was used in the 2θ range from 20 to 65°. All diffraction patterns were analyzed using the Jade software package (Materials Data, Inc., Version 7).

The surface chemical compositions of the samples were measured using AES and XPS. LSM80-20 and LSF80-20 thin films were examined in the “annealed” state (800°C for 10 h and slowly cooled at a rate of 5°C/min to room temperature). Patterned microelectrodes of identical samples were, in contrast, examined in the “quenched” state after heating the annealed sample to ~700°C and quenching from ~700°C to room temperature in <5 s. AES was performed on a Physical Electronics model 660 scanning Auger microscope (Chanhassen, MN) with a lanthanum hexaboride (LaB₆) filament operating at an accelerating voltage of 10 keV. Analysis areas were limited to a 10 × 10 μm dimension on the LSM microelectrodes. In AES, the obtained energy spectrum for a particular element is always situated on a large background (low signal-to-noise ratio), which arises from the vast number of so-called secondary electrons generated by a multitude of inelastic scattering processes. To obtain better sensitivity for the detection of the elemental peak positions, the AES spectra from this study were presented in the differentiated form. Elemental quantification of AES spectra utilized relative sensitivity factors (RSFs) of 0.019, 0.027, 0.161, and 0.212 for La, Sr, Mn, and O, respectively, as supplied by the AES manufacturer (Physical Electronics). XPS was performed on a Kratos Axis Ultra spectrometer (Manchester, U.K.) with a monochromatized aluminum X-ray source (Al Kα). The analysis area was set to a minimum size of 1.1 mm diameter spot, and survey spectra were initially collected at low resolution. Higher resolution spectra were then obtained for quantitative analysis of elemental contents of LSM80-20 and LSF80-20, with each spectrum consisting of at least 20 cycles. To compensate for sample charging effects, all spectra were calibrated with the carbon (C 1s) photoemission line at 284.6 eV. RFS values of 9.122, 1.843, 2.659, and 0.78 for La₃d₅, Sr₃d₅, Mn₃d₅, and O₁s, respectively, were utilized as supplied by the XPS manufacturer (Kratos Analytical). RBS (Evans Analytical Group, Sunnyvale, CA) was performed on annealed LSM80-20 films to determine the elemental composition of the entire film using a He⁺ ion beam with a 2.275 MeV energy and a detector angle of 160° for the normal angle and a shallow grazing angle of 112°.

EIS measurements of annealed microelectrodes from ~130 to ~190 μm were performed using a microprobe station (Karl Suss, Germany) equipped with an optical microscope (Mitutoyo FS-70, Japan) and a temperature-controlled heating stage (Linkam TS1500, U.K.). The microelectrodes were coated by Pt-coated, tungsten carbide probes having a radius of 7 μm. EIS measurements were conducted with a Solartron 1260 frequency response analyzer connected to a Solartron 1296 dielectric interface. EIS data were collected in the frequency range from ~1 MHz to ~100 μHz using an ac voltage amplitude of 10 mV in the temperature range of 770–570°C in air. Actual microelectrode surface temperatures were calibrated using a thermocouple contacting the thin-film surface to have a deviation of ±5°C for each temperature setpoint. EIS experiments to probe surface exchange were carried out under varying nitrogen (N₂) to O₂ mixtures with a P(O₂) range of 10⁻²–1 atm. ZView software (from Scribner Associates, USA) was used to construct the equivalent circuit and perform a complex least-squares fitting to deconvolute the impedance response and extract resistance and capacitance values of different processes.

Results and Discussion

Crystal structure, surface microstructure, and chemical compositions.— XRD results showed that both LSM80-20 and LSF80-20 films were crystalline and single phase after annealing, as shown in Fig. 1. LSM80-20 films had a perovskite structure with rhombohedral symmetry (space group R₃c) and slight peak shifts toward higher 2θ angles, which indicates changes in the lattice parameters of Δa = −0.340% and Δc = + 0.325%. (a = 5.51 Å, c...
Standards. Interatomic distances in the YSZ listed in the Joint Committee on Powder Diffraction were in good agreement with those of the YSZ sputtering target and compound. Some preferred orientation was noted for the compound. A preferred orientation was also observed for the similar La enrichment with a cation chemical formula of La0.80Sr0.20Fe0.33 from the surface of LSM80-20 after annealing and quenching revealed a bulk composition of La0.80Sr0.20Fe0.33 from the surface of LSM80-20 films. The XPS analysis of LSM80-20 films, in contrast, revealed a similar La enrichment with a cation chemical formula of La0.80Sr0.20Fe0.33 from the surface of LSM80-20 films. The AES analysis of annealed and quenched LSF80-20 also showed significant La enrichment with a cation stoichiometry of La0.80Sr0.20Fe0.33 from the surface of LSF80-20 films. The AES analysis of annealed and quenched LSF80-20 showed a similar La enrichment with a cation stoichiometry of La0.80Sr0.20Fe0.33 from nominal LSF80-20. These surface analysis results represented almost nominal La/Sr ratios. However, the surface La/Fe ratio was higher than the nominal LSF80-20 composition. Evidence of La surface segregation found in this study was in agreement with the study by Baumann et al., which showed La/(Co + Fe) and La/Sr atomic concentration ratios that were higher than nominal ratios on the surface of dense LSCF thin-film microelectrodes. The selection of RSF factors for La, Mn, and Sr in the elemental quantification of XPS and AES data may influence the extent of surface La enrichment and Mn deficiency determined from these techniques. 

Table I. Elemental atomic concentration (%) of La, Sr, Mn, and Fe from the surface of LSM80-20 and LSF80-20 thin films as obtained from XPS, AES, and RBS analyses.

<table>
<thead>
<tr>
<th>Atomic concentration (%)</th>
<th>Nominal composition</th>
<th>RBS</th>
<th>XPS</th>
<th>AES</th>
</tr>
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<td>15.5</td>
<td>13.2</td>
<td>43.6</td>
</tr>
<tr>
<td>Sr</td>
<td>4</td>
<td>5.5</td>
<td>1.9</td>
<td>4.5</td>
</tr>
<tr>
<td>Mn/Fe</td>
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<td>19.0</td>
<td>5.0</td>
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<td>O</td>
<td>60</td>
<td>60.0</td>
<td>61.8</td>
<td>46.8</td>
</tr>
<tr>
<td>Cations only*</td>
<td>La0.80Sr0.20Fe0.33</td>
<td></td>
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<td></td>
<td>La0.80Sr0.20Fe0.33</td>
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*Normalizing with nominal La content of 0.8.

= 13.41 Å, and V = 352.68 Å³ in comparison to the stoichiometric compound. Some preferred orientation was noted for the (012) Bragg reflection, which was equivalent to the (100) plane in the cubic perovskite structure. The XRD analysis of LSF80-20 revealed that the expected orthorhombic structure (space group Pbnm) has slight peak shifts to higher 2θ angles, which indicates changes in the lattice parameters of Δa = +0.540%, Δb = -0.690%, and Δc = +0.969% (a = 5.58 Å, b = 5.47 Å, c = 7.92 Å, and V = 243.31 Å³) in comparison to the stoichiometric reference compound. A preferred orientation was also observed for the (012) Bragg reflection of LSF80-20. XRD peaks of the YSZ films after annealing (space group Fm̅3m, a = 5.160 Å, and V = 137.39 Å³) were in good agreement with those of the YSZ sputtering target and YSZ listed in the Joint Committee on Powder Diffraction Standards. Interatomic distances in the (012) plane of LSM80-20 were ~6% larger than those of YSZ (110), while interatomic distances in the (200) planes of LSF80-20 were ~6% larger than those of YSZ (110). Bulk elemental analysis results using RBS on LSM80-20 and LSF80-20 are summarized in Table I. The RBS analysis of sputtered and annealed LSM80-20 revealed a bulk composition of La 15.5 ± 1 atom %, Sr 5.5 ± 1 atom %, Mn 20 ± 2 atom %, and O 59 ± 6 atom %, which was close to the nominal stoichiometry of La 16 atom %, Sr 4 atom %, Mn 20 atom %, and O 60 atom %. The RBS analysis on laser-ablated and annealed LSM80-20 revealed a bulk composition of La 17.5 ± 1 atom %, Sr 5.0 ± 1 atom %, Fe 15.0 ± 2 atom %, and O 62.5 ± 6 atom %, which contained some Fe deficiencies in comparison to the nominal composition of La 16 atom %, Sr 4 atom %, Fe 20 atom %, and O 60 atom %. Therefore, a higher 2θ peak shift for both LSM80-20 and LSF80-20 may arise from (i) compressive strains associated with partial coherency between LSM80-20 or LSF80-20 and YSZ surfaces, and (ii) LSF80-20 deviation from nominal stoichiometry. SEM and atomic force microscopy (AFM) analyses of LSM80-20 and LSF80-20 microelectrodes revealed that they were dense and crack-free before EIS testing, as shown in Fig. 2a-d. AFM analysis revealed smooth LSM80-20 sputtered surfaces with root-mean-square (rms) surface roughness of ~3 nm in the quenched sample, as shown in Fig. 2b. AFM analysis on LSF80-20, presented in Fig. 2d, revealed a similar smooth surface with rms surface roughness of ~8 nm.

Surface elemental analysis results using XPS and AES on LSM80-20 and LSF80-20 are summarized in Table I. Surface analysis using XPS of annealed LSM80-20 films, in contrast, revealed significant La enrichment with a cation chemical formula of La0.80Sr0.20Fe0.33 after normalizing with a nominal La content. AES analysis of LSM80-20 after annealing and quenching revealed a similar La enrichment with a cation chemical formula of La0.80Sr0.20Fe0.33. Both XPS and AES revealed that the surface La/Sr and La/Mn ratios were higher than the nominal LSM80-20 composition. The XPS analysis of annealed LSF80-20 also showed significant La enrichment with a cation stoichiometry of La0.80Sr0.20Fe0.33 after normalizing with a nominal La content. The AES analysis of annealed and quenched LSF80-20 showed a similar La enrichment with a cation stoichiometry of La0.80Sr0.20Fe0.33 from nominal LSF80-20. These surface analysis results represented almost nominal La/Sr ratios. However, the surface La/Fe ratio was higher than the nominal LSF80-20 composition. Evidence of La surface segregation found in this study was in agreement with the study by Baumann et al., which showed La/(Co + Fe) and La/Sr atomic concentration ratios that were higher than nominal ratios on the surface of dense LSCF thin-film microelectrodes. The selection of RSF factors for La, Mn, and Sr in the elemental quantification of XPS and AES data may influence the extent of surface La enrichment and Mn deficiency determined from these techniques.

Figure 2. (Color online) SEM and AFM of dense and patterned films of (a) and (b) sputtered LSM80-20 and (c) and (d) laser-ablation-deposited LSF80-20 after quenching at ~700°C. Both electrodes were fully dense and crack-free before and after electrochemical testing. AFM images are shown with a maximum height of 70 nm. AFM measurements revealed the LSM80-20 and LSF80-20 films' surface rms roughness of ~3 and ~8 nm, respectively.
correction factors are being calibrated with single-crystal, stoichiometric LSM80-20 thin films, which will be reported in future studies.

**ORR impedance data of LSM80-20 and LSF80-20 microelectrodes.**—The LSM80-20 microelectrodes were tested using an in-plane configuration, as shown in the schematic in Fig. 3a inset. Typical EIS data from LSM80-20 microelectrodes with a thickness of 65 nm at 750°C showed one low frequency semicircle, identified as LF1, and the impedance of LF1 decreasing with increasing $P_{O_2}$ from $10^{-5}$ to 1 atm, as shown in Fig. 3a. A shift in the peak frequency from $-5$ Hz at $P_{O_2} = 1$ atm to $-20$ mHz at $P_{O_2} = 10^{-5}$ atm was observed in the plot of the imaginary impedance ($-Z_{im}$) as a function of frequency, as presented in Fig. 3b. An equivalent circuit presented in Fig. 3b inset with resistors ($R_{ALO-HF}$, $R_{LF1}$), finite-length Warburg ($W_{ALO-W}$), and constant-phase elements (CPE_{LF1}) was used to deconvolute the impedance response as a function of $P_{O_2}$ and temperature. The ORR impedance (LF1 impedance) was found to increase with decreasing $P_{O_2}$, which suggests that the kinetics of ORR was limited by surface chemical processes such as surface oxygen exchange. Although previous IEDP/SIMS studies of LSM80-20 micrometer-sized particles suggested that the critical thickness for surface-controlled ORR, $L_c$, is $\sim 10$ nm at 720°C, our recent studies showed that the impedance associated with the three-phase boundary/bulk charge transfer vanishes at the microelectrode thickness of 65 nm at 750°C. Our findings were in agreement with those of Fleig et al., where a critical thickness of $\sim 200$ nm was recently extrapolated for LSM80-20 microelectrodes in $P_{O_2}$ of 0.2 atm at 800°C. As grain boundaries in LSM were reported to have $10^5$ higher diffusivity than bulk LSM, it was proposed that LSM thin-film microelectrodes prepared by sputtering and annealing, which have nanometer-scale columnar grains with a width in the range of $\sim 20$–$70$ nm, have much enhanced oxygen-ion diffusion relative to bulk LSM. Therefore, LSM80-20 microelectrodes with a thickness of 65 nm can have the kinetics of ORR governed by surface oxygen exchange.

Representative EIS data collected from LSF80-20 microelectrodes with a thickness of 110 nm at 750°C are shown in Fig. 4a, where a single semicircle impedance response was found at low frequencies. Similar to LSM80-20, both real impedance and peak frequency were noted to decrease and increase with increasing $P_{O_2}$ from $10^{-5}$ to 1 atm, as shown in Fig. 4a and b, respectively. This observation suggests that ORR kinetics on LSF80-20 (110 nm) is limited by surface oxygen exchange, which is in good agreement with the critical thickness reported for bulk LSF ($\sim 80$ μm at 720°C). The overall real impedance of LSF80-20 microelectrodes was smaller than that of LSM80-20 at all $P_{O_2}$ levels, which was expected as oxygen-ion diffusion in LSF80-20 was much greater than that in LSM. However, the peak frequencies found for LSF80-20, shown in Fig. 4b, were in the range from $-1$ Hz at $P_{O_2} = 1$ atm to $-2$ mHz at $P_{O_2} = 10^{-5}$ atm, which was considerably lower than those of LSM80-20 (5–10 times).

**Estimation of oxygen surface exchange coefficients from ORR impedance data.**—The $k^4$ and $k_{chem}$ of LSM80-20 and LSF80-20 microelectrodes were obtained from EIS data as a function of $P_{O_2}$ and temperature. $k^4$ was determined using the expression reported previously.

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**Figure 3.** (Color online) (a) Typical EIS spectra at 750°C from LSM80-20 microelectrode, $\sim 190$ μm in size and 65 nm thick, showing the variation of impedance with different $P_{O_2}$ from $10^{-5}$ to 1 atm at 750°C. The in-plane testing configuration is shown in the inset. (b) Plot of $-Z_{im}$ vs frequency showing the change in peak frequency as a function of $P_{O_2}$. At $P_{O_2} = 1$ atm, the peak frequency approaches 5 Hz. At $P_{O_2} = 10^{-5}$ atm, the peak frequency approaches 20 mHz. The equivalent circuit used to deconvolute the single-orthogonal impedance spectra is shown in the inset.

**Figure 4.** (a) Typical EIS spectra at 750°C from LSF80-20 microelectrode, $\sim 170$ μm in size and 110 nm thick showing the variation of impedance with different $P_{O_2}$ from $10^{-5}$ to 1 atm. (b) Plot of $-Z_{im}$ vs frequency showing the change in peak frequency as a function of $P_{O_2}$ for LSF80-20. At $P_{O_2} = 1$ atm, the peak frequency approaches 1 Hz. At $P_{O_2} = 10^{-5}$ atm, the peak frequency approaches 2 mHz. Both the magnitude of impedance and the peak frequency of LSF80-20 in the entire $P_{O_2}$ range are lower than those of LSM80-20.
cm/s at 1 atm. As $k^q$ is approximately equivalent to the tracer surface exchange coefficient ($k^q = k^*$), we can compare these $k^q$ values of LSM80-20 from EIS measurements with available $k^*$ values\(^1\), of bulk LSM from IEDP/SIMS analysis. At $P_{O_2}$ equal to and lower than $10^{-2}$ atm, the $k^q$ values of LSM80-20 microelectrodes are in good agreement with $k^*$ values ($\sim 1 \times 10^{-8}$ cm/s at 750°C at $1 \times 10^{-3}$ atm) of bulk LSM estimated from previous studies\(^2,15\) provided that an activation energy of 1.32 $\pm$ 0.2 eV for $k^*$ was used for this $P_{O_2}$ range. However, the $k^q$ value of LSM80-20 ($\sim 5 \times 10^{-8}$ cm/s) at 1 atm found in this study was higher than the $k^*$ values\(^2,15\) of bulk LSM (in the range from $1 \times 10^{-8}$ to $10^{-5}$ cm/s between 700 and 800°C). It was hypothesized that the $k^q$ values of LSM80-20 microelectrodes in this study were higher than $k^*$ of bulk LSM. This increase can be attributed to (i) underestimation of $k^q$ values and large errors\(^1\) in $k^*$ values at $P_{O_2}$ greater than $10^{-3}$ atm in previous IEDP/SIMS studies as the oxygen stoichiometry of LSM80-20 is insensitive to changes in $P_{O_2}$ in this $P_{O_2}$ range; (ii) nanometer-scale microstructure (grains in the range of 20–70 nm) in the LSM80-20 microelectrodes can result in higher $k^q$ values than bulk LSM80-20, which is supported by the fact that grain boundaries in LSM have $\sim 10^3$ higher diffusivity than bulk LSM, and there is a strong correlation that exists between $D^*$ and $k^q$;\(^1,15\) and (iii) different surface chemistries of LSM80-20 that can strongly affect the surface exchange rates.\(^3,31\) The average $k^q$ ($4 \times 10^{-8}$ cm/s) of LSM80-20 in air at 750°C is higher than that obtained from a very recent study on thin-film LSM80-20 microelectrodes ($4 \times 10^{-9}$ cm/s) in air at approximately 800°C from EIS measurements.\(^34\) The difference in the surface oxygen exchange rate may be attributed to (i) dissimilar surface LSM80-20 chemistries and (ii) different strains for LSM80-20 thin films used in a previous study from this work.

$k^q$ values of LS80-20 microelectrodes ranging in size from $\sim 130$ to $\sim 190$ $\mu$m in the $P_{O_2}$ range from $10^{-3}$ to 1 atm at 750°C for (a) 65 nm thick LSF80-20 and (b) 110 nm thick LSF80-20. Microelectrode sizes tested here range from $\sim 130$ to $\sim 190$ $\mu$m. Data collected from four different microelectrodes were included to ensure data reproducibility. The slope dependence ($m$) of $k^q$ and $k^q_{chem}$ vs $P_{O_2}$ for LSF80-20 was $m_{ave} \sim 0.20$ and $m_{chem} \sim 0.28$. The slope dependence for LS80-20 was $m_{ave} \sim 0.31$ and $m_{chem} \sim 0.30$.

$$k^q = \frac{k_B T}{4 e^2 R_c e_o}$$

where $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $e$ is the elementary charge, $R_c$ is the area-specific resistance for surface reaction ($R_c = \text{electrode area} \times R_{i|f}$), and $e_o$ is the concentration of lattice oxygen. $k^q_{chem}$ was determined using the expression reported previously by Yang et al.\(^1\)

$$k^q_{chem} = \frac{I}{\tau}$$

where $I$ is the film thickness and $\tau$ is the relaxation time constant of the oxygen surface exchange, which is equal to the reciprocal of the peak frequency of the LF1 semicircle.

Figure 5. Calculated surface exchange coefficients, $k^q$ and $k^q_{chem}$, in the $P_{O_2}$ range from $10^{-3}$ to 1 atm at 750°C for (a) 65 nm thick LSF80-20 and (b) 110 nm thick LSF80-20. Microelectrode sizes tested here range from $\sim 130$ to $\sim 190$ $\mu$m. Data collected from four different microelectrodes were included to ensure data reproducibility. The slope dependence ($m$) of $k^q$ and $k^q_{chem}$ vs $P_{O_2}$ for LSF80-20 was $m_{ave} \sim 0.20$ and $m_{chem} \sim 0.28$. The slope dependence for LS80-20 was $m_{ave} \sim 0.31$ and $m_{chem} \sim 0.30$.
respectively, \( P_{O_2} \) range from \( 10^{-3} \) to 1 atm at 800°C. \( \gamma \) values of La\(_{0.75}\)Sr\(_{0.25}\)Fe\(_{0.9}\)O\(_{3}\)\(_{δ}\) fall in the range from \( 0.70 \) to \( 1.60 \) in the \( P_{O_2} \) range from \( 10^{-5} \) to 1 atm at 800°C, and which were consistent with \( \gamma \) values of typical MIEC oxides.\(^{4,14}\) Because \( c_{\text{aq}} \) is fairly constant over a wider range of \( P_{O_2} \) for LSF80-20 \(^{43}\) in comparison to La\(_{0.75}\)Sr\(_{0.25}\)Fe\(_{0.9}\)O\(_{3}\)\(_{δ}\) higher \( \gamma \) values are therefore expected for LSF80-20. \( \gamma \) values of LSF80-20 obtained from EIS measurements in this study were in reasonable agreement with those extracted from previously reported thermogravimetric data,\(^{43}\) while those of LSF80-20 microelectrodes obtained in this study were higher than those based on thermogravimetric data,\(^{55}\) which may be attributed to Fe deficiency in the LSF80-20 microelectrodes (Table I).

Oxygen partial pressure dependence of surface oxygen exchange coefficients.— Examination of the dependence (m) of \( P_{O_2} \) on surface exchange coefficients (\( k^i, k_{\text{chem}} \)) can provide insights into the species involved in the rate-limiting step for surface oxygen exchange.\(^{5,14,5,46}\) The \( k^i \) and \( k_{\text{chem}} \) values of LSF80-20 shown in Fig. 5a increase with increasing \( P_{O_2} \), having a dependence of \( m_{\text{aq}} = 0.20 \) and \( m_{\text{chem}} = 0.28 \) in the \( P_{O_2} \) range from \( 10^{-5} \) to 1 atm, respectively. There is no reliable \( P_{O_2} \) dependence of surface exchange on bulk LSF80-20 from previous isotope studies\(^{19}\) due to the large errors in \( k^i \) at high \( P_{O_2} \). The \( P_{O_2} \) dependence of \( m_{\text{aq}} \) for \( k^i \) in the range of \( 10^{-4} \)–\( 10^{-2} \) atm can be estimated from the results of LSF80-20 microelectrodes (250 nm) reported by Fleig et al.,\(^{34}\) which were considerably higher than that (\( \sim 0.25 \)) of our electrodes in the same \( P_{O_2} \) range. Similarly, the \( k^i \) and \( k_{\text{chem}} \) values of LSF80-20 presented in Fig. 5b have a \( P_{O_2} \) dependence of \( m_{\text{aq}} = 0.31 \) and \( m_{\text{chem}} = 0.30 \) in the \( P_{O_2} \) range from \( 10^{-5} \) to 1 atm, respectively. The observed \( P_{O_2} \) dependence in this study was considerably lower than those reported by ten Elshof et al.,\(^{35}\) where \( m_{\text{chem}} = 0.75–0.95 \) and \( m_{\text{aq}} = 0.65–0.85 \) have been noted for LSF \((x_{\text{Sr}} = 0.1 \) and 0.4), and the dependencies do not change greatly with Sr content nor with temperature in the range from 650 to 950°C. However, the \( P_{O_2} \) dependence of LSF \((x_{\text{Sr}} = 0.5)\) reported by Yeo et al.,\(^{36}\) varied from \( m = 0.21 \) to \( m = 0.51 \) for \( k_{\text{chem}} \) in the \( P_{O_2} \) range from \( 10^{-5} \) to \( 5 \times 10^{-2} \) atm between 780 and 950°C, which cannot be explained consistently by the work of ten Elshof et al.,\(^{35}\) due to the compositional similarity of LSF \((x_{\text{Sr}} = 0.5 \) vs 0.4). The \( P_{O_2} \) dependence of ORR polarization \((R = P_{O_2}^{m})\) can be related to the oxygen species involved in the rate-limiting reaction. Consider the following three processes,\(^{30,32}\) where

\[
\begin{align*}
  m & = 1 \quad \text{O}_2,\text{gas} \leftrightarrow \text{O}_2,\text{ads} \quad [4] \\
  m & = \frac{1}{2} \quad \text{O}_2,\text{ads} \leftrightarrow 2\text{e}^- + V_0 \leftrightarrow \text{O}_0^\dagger \quad [5] \\
  m & = \frac{1}{4} \quad \text{O}_2 + 2\text{e}^- + V_0 \leftrightarrow \text{O}_0^\dagger \quad [6]
\end{align*}
\]

Using this simple model, charge transfer with incorporation (Eq. 6) may be considered as the rate-limiting step for surface oxygen exchange on LSM80-20 and LSF80-20. However, this assignment is not unique as many elementary reaction steps can give rise to a \( P_{O_2} \) dependence of \( \frac{1}{4} \).

Here we discuss the observed \( P_{O_2} \) dependence of \( k^i \) in the context of three recently proposed mechanisms for oxygen surface exchange, which provides some insights into the underlying rate-limiting step of surface exchange. First, De Souza\(^{19}\) derived an empirical, atomistic expression for \( k^i \) based on the \( P_{O_2} \) dependence for electron-poor materials \((m \sim 0.23)\) such as La\(_{0.75}\)Sr\(_{0.25}\)Fe\(_{0.9}\)O\(_{3}\)\(_{δ}\) and for electron-rich materials \((m \sim 0.39)\) such as LSCF, where the charge transfer of one electron to an adsorbed oxygen was considered as the rate-limiting step for both types of materials. The observed \( P_{O_2} \) dependence of LSF80-20 \((m \sim 0.20)\) at 750°C in this study was considerably lower than that

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**Figure 6.** (a) Thermodynamic enhancement factor (\( \gamma \)) as a function of \( P_{O_2} \) for 65 nm thick LSM80-20 and 110 nm thick LSF80-20 at 750°C. \( \gamma \) was calculated by taking the ratio of \( k_{\text{chem}}/k^i \) using four data sets of LSM80-20 and three data sets of LSF80-20 (shown in Fig. 5a and b). Microelectrodes ranging in size from \( 130 \) to \( 190 \) μm were tested between \( P_{O_2} \) of \( 10^{-5} \) and 1 atm. \( \gamma \) for LSF80-20 was found to range from \( 1000 \) to \( 4500 \), while \( \gamma \) for LSF80-20 was found to range between \( 200 \) and \( 400 \). (b) Thermodynamic factor (\( \gamma \)) obtained from single data sets for LMS80-20 as a function of temperature between 570 and 750°C at \( P_{O_2} \) of \( 10^{-2} \) and \( 10^{-2} \) atm and for LSF80-20 at \( P_{O_2} \) of 1 atm. \( \gamma \) was found to range between \( 200 \) and \( 300 \) for LSF80-20 and between \( 700 \) and \( 3000 \) for LSM80-20 in the temperature range examined.
(m = 0.46) predicted for LSM80-20 at 1000°C by De Souza,51 based on limited data at $P_{O_2}$ equal to and lower than 10⁻² atm. Although the observed $P_{O_2}$ dependence of LSM80-20 (m = 0.20) was close to that of electron-poor materials in this model, LSM80-20 is known to have high electronic conductivity,41 and microprobes placed on different locations on the LSM80-20 microelectrodes of this study show very small resistance. Therefore, the observed $P_{O_2}$ dependence of $k^a$ for LSM80-20 as well as that for LSF80-20 (m = 0.30) cannot be explained consistently by the model of De Souza. Second, Adler et al.20 modeled the experimental $P_{O_2}$ dependence of the chemical surface exchange rate ($k_{chem}$) of metallic LSC (having x = 0.2, 0.5, and 0.7) from the data of van der Haar et al.51 with m in the range from ~0.43 to ~0.92, from which a dissociative adsorption step was proposed as rate-limiting. For p-type semiconductors such as LSF, a chemisorption limitation or barrier to charge transfer is considered as the rate-limiting step in the range from m ~ 0.75 to m ~ 0.95 based on the experimental data of LSF (x = 0.1 and 0.4) from ten Elshof et al.24 The observed $P_{O_2}$ dependence of $k^a$ for LSM80-20 found in this study was too low for those expected for metallic and p-type semiconductor MIEC cathodes. The observed $P_{O_2}$ dependence of $k^a$ for LSF80-20 (m = −0.30) in this study was considerably lower than those of LSF (x = 0.1 and 0.4) reported by ten Elshof et al.25 but comparable to that of LSF (x = 0.5) reported by Yoo et al. Therefore, the $P_{O_2}$ dependence of $k^a$ for LSF80-20 microelectrodes cannot be compared consistently with the model reported for p-type semiconductors.20 Fe deficiency in the LSM80-20 microelectrodes may influence the $P_{O_2}$ dependence of $k^a$, the extent of which is not understood. Third, Fleig et al.26 showed that the rate-limiting step of electron transfer such as $O_{ad}^- + e^- → O_{ad}^0$ and $O_{ad}^0 + e^- → O_{ad}^{2-}$ can give rise to a $P_{O_2}$ dependence of $2m$ in the $P_{O_2}$ range from 10⁻⁵ to 1 atm at 1000 K, which corresponds to a high coverage of $O_{ad}^-$ or $O_{ad}^{2-}$ on materials with $P_{O_2}$-independent hole concentrations. As the observed $P_{O_2}$ dependence of LSF80-20 is close to $2m$ and LSF80-20 has a $P_{O_2}$-independent hole concentration above 10⁻¹⁰ atm at 800°C,21 it was hypothesized in this study that the electron transfer such as $O_{ad}^- + e^- → O_{ad}^0$ and $O_{ad}^0 + e^- → O_{ad}^{2-}$ can be rate-limiting for surface oxygen exchange on LSF80-20 microelectrodes. This previous study21 showed that a rate-limiting step of electron transfer to form $O_{ad}^0$ or $O_{ad}^{2-}$ can give rise to a $P_{O_2}$ dependence of $2m$ for materials having electronic carrier concentrations with $P_{O_2}$ dependence of $m$ in the $P_{O_2}$ range from 10⁻³ to 1 atm at 1000 K. Because the observed $P_{O_2}$ dependence of $k^a$ for LSF80-20 (m = −0.30) was between $\frac{1}{2}$ and $\frac{3}{2}$, and LSF80-20 has an $\frac{1}{2}$ $P_{O_2}$-dependent hole concentration below 1 atm at 800°C,21 it was proposed here that the electron transfer to form $O_{ad}^0$ or $O_{ad}^{2-}$ can be rate-limiting for surface oxygen exchange on LSF80-20. Further studies are needed to test these hypotheses on the proposed rate-limiting step on LSM80-20 and LSF80-20.

**Temperature dependence of surface exchange coefficients.**—The temperature dependence of $k^a$ and $k_{chem}$ for LSM80-20 was examined in the range between 660 and 770°C at two $P_{O_2}$ levels (10⁻² and 10⁻⁴ atm), as shown in Fig. 7a. The activation energy ($E_a$) for $k^a$ of LSM80-20 was 1.87 ± 0.02 and 2.01 ± 0.02 eV at 10⁻⁴ and 10⁻² atm, respectively. The $E_a$ of $k_{chem}$, in contrast, was 1.48 ± 0.01 and 2.06 ± 0.04 eV at 10⁻⁴ and 10⁻² atm, respectively. Previously De Souza et al.15 showed that the $E_a$ of $k^a$ in LSM80-20 is equal to 1.33 ± 0.20 eV between 700 and 1000°C at 1 atm. However, large errors and underestimation in $k^a$ values for LSM80-20 at a $P_{O_2}$ greater than 10⁻³ atm from the IEDP/SIMS measurements18,21 led to ambiguity in the reported activation energy, $E_a$ values for $k^a$ in this study were in good agreement with a hypothesis proposed by De Souza et al.,35 where $E_a$ for $k^a$ falls in the range from 0.4 to 0.7 eV of $D^*$ (~2.6–3.0 eV) in LSM.5,18

![Figure 7. Calculated surface exchange coefficients, $k^a$ and $k_{chem}$ for (a) LSM80-20, ~190 µm in size and 65 nm thick, between 770 and 660°C at two $P_{O_2}$ levels of 10⁻² and 10⁻⁴ atm. Activation energy for $k^a$ increases from 1.87 to 2.01 eV with increasing $P_{O_2}$. Activation energy for $k_{chem}$ also increased from 2.06 to 1.48 eV with increasing $P_{O_2}$. (b) Calculated surface exchange coefficients, $k^a$ and $k_{chem}$ for LSF80-20 obtained from three data sets, ~170 µm in size and 110 nm thick, between 770 and 570°C at 1 atm $P_{O_2}$. Activation energies for $k^a$ and $k_{chem}$ were 2.06 and 1.95 eV, respectively.](image)
Chemical capacitance estimated from ORR impedance data.— As the magnitude of chemical capacitance provides a good measure of bulk oxide involvement and, therefore, an indication of increased oxygen vacancy content, the chemical capacitance per unit area (F/cm²) and per unit volume (F/cm³) for LSM80-20 and LSF80-20 films was determined as a function of P_{O_2} at 750°C, as shown in Fig. 8a and b, respectively. These values were calculated from the expression by Fleig²⁶

$$C = \left( \frac{R_{\text{p0}}}{R_{\text{p1}}} \right)^{1/p} \left( \frac{\chi}{1 - \chi} \right)$$

[7]

where $R_{\text{p0}}$ is the parallel resistance value in the equivalent circuit, $\chi$ is the nonlinear “capacitance,” and $p$ is the nonideality factor used to fit the CPE. The area-specific and volumetric chemical capacitances of LSM80-20 at 750°C were fairly constant over the entire $P_{O_2}$ range and slightly decreased ($5 \times 10^{-2}$ to $2 \times 10^{-4}$ F/cm²) for area-specific capacitance vs $6 \times 10^{-3} \times 10^{-1}$ F/cm³ for volumetric capacitance) with increasing $P_{O_2}$ from $10^{-5}$ to 1 atm. These results are in good agreement with those of LSF80-20 microelectrodes, with a thickness of 250 nm, previously reported ($-5 \times 10^{-4}$ F/cm² for area-specific capacitance vs $\sim 2 \times 10^{1}$ F/cm³ for volumetric capacitance) in the $P_{O_2}$ range from $5 \times 10^{-4}$ to 1 atm at $\sim 800°C$.

As expected from the oxygen nonstoichiometry of LSM80-20 and LSF80-20 as a function of $P_{O_2}$, the area-specific (5 x 10^{-3} - 2 x 10^{-2} F/cm²) and volumetric (4 x 10^{-2} - 10^3 F/cm³) chemical capacitances for LSF80-20, despite its almost double microelectrode thickness, are approximately 1 order of magnitude greater than those for LSM80-20 at 750°C. A similar trend in the area-specific and volumetric capacitances as a function of $P_{O_2}$ for LSF80-20 was found for LSM80-20, which showed that the capacitances also slightly decreased with increasing $P_{O_2}$ from $10^{-2}$ to 1 atm. The area-specific and volumetric capacitance values of this study are approximately 1 order of magnitude smaller than those reported for 100 nm thick LS (Sr = 0.4) microelectrodes at 750°C in air reported by Baumann et al. (1.2 x 10^{-2} F/cm² for area-specific capacitance and 1.5 x 10^3 F/cm³ for volumetric capacitance). The reduced capacitance observed with LSF80-20 can be attributed to the lower Sr content in LSF80-20 relative to LS (Sr = 0.4), which decreases the inherent oxygen vacancy concentration in the perovskite.

The volume-specific chemical capacitance ($C = \left( \frac{8F^2}{V_{m}RT} \right) \delta \beta / d \ln P_{O_2}$, where $V_{m}$ is the molar volume of the oxide) estimated from thermogravimetric data of bulk LSM80-20 and LSF80-20 previously reported²⁴,³⁴ ranges from 200–1600 F/cm³ and 2000–4000 F/cm³, respectively, in the $P_{O_2}$ range measured in this study. These values are approximately 1 order of magnitude higher than those for the thin-film LSM80-20 and LSF80-20 microelectrodes of this study. A reduction in the volume-specific capacitance and oxygen vacancy concentration in thin-film LSC microelectrodes relative to bulk LSC has been observed previously.²⁵ It was proposed that the compressive strains and nanograins present in the 65 nm thick LSM80-20 microelectrodes of this study can modify the thermodynamic parameters and thus reduce the chemical capacitance of these microelectrodes relative to bulk LSM80-20, while the Fe deficiency and compressive strains and nanograins present in the 110 nm thick LSF80-20 microelectrodes may contribute to chemical capacitance reduction relative to bulk LSF80-20.

Conclusions

The EIS data of dense, thin-film LSM80-20 and LSF80-20 microelectrodes have been used to determine the (i) electrical ($k^3$) and chemical ($k_{\text{chem}}$) surface oxygen exchange coefficients, (ii) thermodynamic enhancement factor ($\gamma$), and (iii) chemical capacitance as a function of $P_{O_2}$ and temperature. While the oxygen-ion conductivity in bulk LSM80-20 is low, LSM microelectrodes with a thickness of 65 nm and nanometer-scale microstructure showed enhanced ion transport relative to bulk LSM, where ORR kinetics is limited by surface oxygen exchange. We demonstrated that $k^3$ and $k_{\text{chem}}$ on LSM80-20 at $P_{O_2} > 10^{-2}$ atm can be measured accurately in contrast to large errors in $k^3$ from conventional tracer measurements. Moreover, although the chemical capacitance for LSF80-20 is greater than that for LSM80-20, indicating a higher oxygen vacancy concentration for the iron-based perovskite, $k^3$ and $k_{\text{chem}}$ of LSM80-20 and LSF80-20 microelectrodes are shown to be comparable, which reveals the potential importance of electronic properties over oxygen vacancy content in determining the magnitude of surface oxygen exchange. The $P_{O_2}$ dependence of $k^3$ and $k_{\text{chem}}$ of LSF80-20 and LSM80-20 microelectrodes falls in the range from $-0.2$ to $-0.3$. This suggests a common rate-limiting reaction for surface oxygen exchange, namely, electron transfer to an adsorbed oxygen species based on the work of Fleig et al.²⁶ Further research that combines film structural analysis, surface science, EIS, and sur-
face exchange reaction modeling is needed to determine the nature of the rate-limiting step for surface oxygen exchange.

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