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Oxygen Exchange and Transport in (La$_{0.6}$Sr$_{0.4}$)$_{0.98}$FeO$_3$–d – Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ Dual-Phase Composites

Simona Ovtar, a Martin Søgaard, a Kion Norrman, and Peter Vang Hendriksen a

Department of Energy Conversion and Storage, Technical University of Denmark, Risø Campus, 4000 Roskilde, Denmark

The chemical diffusion coefficient and the effective surface exchange coefficient ($k_{ex}$) of dual-phase (La$_{0.6}$Sr$_{0.4}$)$_{0.98}$FeO$_3$ (LSF) – Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO) composites containing between 30 and 70 vol.% of CGO were determined by electrical conductivity relaxation (ECR) at high oxygen partial pressures ($10^{-3}$ < $p_{O2}$ < 1 atm) and at temperatures between 600 °C and 900 °C. The surface impurity segregation was detected by TOF-SIMS analysis. A large enhancement of $k_{ex}$ was observed with increasing CGO fraction in the composite. $k_{ex}$ was increased from 3.51 × 10^{-3} cm/s for a pure LSF to 1.86 × 10^{-2} cm/s for a 70 vol.% of CGO in the composite at 750 °C for a $p_{O2}$ change from 0.2 to 1.0 atm. The experiments demonstrate that the $k_{ex}$ is enhanced due to a synergistic effect between the two phases, and suggest a direct involvement of CGO phase in the oxygen surface exchange reaction. Possible mechanisms that could account for the synergy are the oxygen exchange process occurs also on the CGO surface, for example a spillover of absorbed oxygen ions from the LSF surface to the CGO surface and scavenging of impurities from one phase to another, thereby improving the oxygen exchange properties of the cleaned phase.

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Perovskites within the (La,Sr)(Fe,Co)O$_3$ class of materials can potentially find application as catalysts, electrode materials in solid oxide fuel cells (SOFC) or solid oxide electrolysis cells (SOEC), in gas sensors and in oxygen transport membranes. Both end members of the class; the iron free one (strontium doped lanthanum cobaltate) as well as the cobalt free one (strontium doped lanthanum ferrite) have been intensively studied. A large focus has also been on the specific composition La$_{0.6}$Sr$_{0.4}$Fe$_{1-x}$O$_3$ (LSF), which is a mixed ionic electronic conductor (MIEC). The total conductivity of the strontium doped lanthanum ferrite depends on the oxygen non-stoichiometry and involves at least an oxygen molecule and a vacant oxygen site at the surface and that for LSCF the rate limiting step is dissociation of the oxygen species involving two oxygen vacancies. However, for the studies on thin films the activation energy and total reaction rate were different from what is observed on bulk LSF and composite electrodes and hence the mechanism deduced from these thin films does not necessarily represent the situation here. Deviations in behavior between studies on thin films and bulk/composite samples can be due to differences in stress state, structure and most importantly surface composition.

For most MIECs the concentration of oxygen vacancies and electron holes strongly depends on temperature and $p_{O2}$, which results in a variety of reported $p_{O2}$ dependencies of $k_{ex}$ for this class of materials.8–10,12,18–22 During the process, several different oxygen species may occur as intermediates $[O_{2ads}, O^{+}_2ads, O^{2+}_2ads, O^{3+}_2ads]$ and for different perovskite materials different species may be involved in the rate determining step (rds). The variation of the $k_{ex}$ with $p_{O2}$ can in some cases elucidate the rds of the overall oxygen exchange reaction. Different mechanisms of the oxygen exchange on perovskite materials have been discussed.7,10,18,19,23,24 Merkle et al.18 proposed for the experimental findings on Fe doped SrTiO$_3$ that the rds contains the dissociation of molecular oxygen species with or without electron transfer. ten Elshof et al.19 proposed on the basis of $p_{O2}$ dependencies of $k_{ex}$ for LSF that the rds involves at least an oxygen molecule and a vacant oxygen site at the surface and that for LSCF the rds involves molecular oxygen. Mosleh et al.1 proposed for experimental studies carried out on LSF thin films prepared with PLD point to that the first step is the oxygen adsorption and the rate limiting step is dissociation of the oxygen species involving two oxygen vacancies. However, for the studies on thin films the activation energy and total reaction rate were different from what is observed on bulk LSF and composite electrodes and hence the mechanism deduced from these thin films does not necessarily represent the situation here. Deviations in behavior between studies on thin films and bulk/composite samples can be due to differences in stress state, structure and most importantly surface composition.

Perovskites have been used in catalysis, electrocatalysis, and as electrode materials in solid oxide fuel cells (SOFCs) or solid oxide electrolysis cells (SOECs). The oxygen transport in oxygen deficient perovskites is generally considered to occur via a vacancy hopping mechanism and the rate of the transport is related to the vacancy concentration and mobility. A strong correlation between $D_v$ and $k_{ex}$ for many of oxygen deficient MEIC perovskites has been reported.26–28 From this it was proposed that the same mechanisms are operative for the whole class of materials and that oxygen vacancies play a major role in the oxygen exchange of these materials. Furthermore, high mobility and high concentration of oxygen vacancies are criteria for fast oxygen exchange kinetics, as highlighted by Wang et al. The presence of phases with higher oxygen exchange of high mobility vacancy concentrations in proximity to a MIEC perovskite could be speculated to...
locally improve the oxygen exchange rate. This is certainly the case for triple-phase boundary-type composite electrodes of an electro-catalyst like strontium doped lanthanum manganite (LSM) and an ionic conductor like ceria or zirconia.\textsuperscript{31,32} There, the electrode reaction relies on the incorporation of oxygen into the ionic conductor in the proximity of the electro-catalyst.\textsuperscript{31–33} The reaction zone in these composites is limited to narrow zone at the triple-phase boundary (TPB) and the overall oxygen exchange increases with the increase of the TPB length.\textsuperscript{31–33}

Studies on dense MIEC dual-phase composites like La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Sm\textsubscript{0.2}O\textsubscript{3–d},\textsuperscript{37} La\textsubscript{0.6}Sr\textsubscript{0.4}Fe\textsubscript{1.5}Mo\textsubscript{0.5}O\textsubscript{6} \textsuperscript{38}COSO, where the rate limiting process for the oxygen transport at 750 °C and high pO\textsubscript{2} is the oxygen exchange, the effective surface exchange rate can be increased by increasing the volume fraction of CSO, which was ascribed to an TPB length increase.\textsuperscript{21}

Even for single phases like La\textsubscript{0.6}Sr\textsubscript{0.4}FeO\textsubscript{3–d},\textsuperscript{41} La\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3–d} and Ce\textsubscript{0.9}Gd\textsubscript{0.1}O\textsubscript{2}–d (CGO), compared to the bare MIEC. Recently, it was also shown that for dual-phase composites of SrFe\textsubscript{1.5}Mo\textsubscript{0.5}O\textsubscript{6} (CSO) or Ce\textsubscript{0.9}Gd\textsubscript{0.1}O\textsubscript{3–d} (CGO), the reaction occurring at the TPB and that the surface exchange rate must be substantially higher than that on the “pure” LSCF surface.

The aim of this study is to characterize the oxygen transport properties of a dual-phase composite system as a function of temperature and to elucidate the origin of the enhancement of the oxygen surface exchange reaction occurring with increasing the amount of the ionic conductor. The study contains two parts. In the first part, the oxygen transport properties of samples with different volume fractions of (La\textsubscript{0.6}Sr\textsubscript{0.4})\textsubscript{0.98}FeO\textsubscript{3–d} (LSF) and Ce\textsubscript{0.9}Gd\textsubscript{0.1}O\textsubscript{3–d} (CGO) are discussed based on ECR measurements. In the second part, a sample with 70 vol.% of CGO and 30 vol.% of LSF and with adjusted microstructure was investigated by of time-of-flight secondary ion mass spectrometry (TOF-SIMS) to investigate surface impurities segregation on the dual-phase composite.

### Possible Mechanisms of Oxygen Exchange for Dual Phase Composites

Oxygen exchange on dual-phase composites have been discussed by several groups as mentioned in the introduction. Different involvements of the two phases in the oxygen exchange were proposed. The predicted conductivity relaxation curve after a sudden step change of pO\textsubscript{2} for dual phase composites for different assumptions regarding the active surface is illustrated in Figure 1. The following assumptions are made; i) random distribution of phases, ii) oxygen exchange is much slower than bulk transport in the material, iii) the oxygen concentration changes only in the P1 phase, and iv) the surface area fraction (f\textsubscript{S1}) and volume fraction (f\textsubscript{V1}) of the P1 phase are equal. In this case, the normalized conductivity change can be described by Eq. 1:

\[
f(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(0)} = \exp \left( -t \cdot \frac{S_1}{V_1} \cdot k_1 \right) \tag{1}
\]

Where \(\sigma(0)\) is the conductivity at the new equilibrium, \(\sigma(t)\) is the conductivity at time \(t\) during the relaxation and \(\sigma(0)\) is the conductivity before the step change in pO\textsubscript{2}. \(S_1\) is the surface area of the P1 phase, \(V_1\) is the volume of P1, \(t\) is time and \(k_1\) is the efficient surface exchange coefficient of the P1 phase. This simplification gives a direct illustration of the influence of surface area and volume of the phases, where the oxygen content varies, on the shape of a relaxation curve. In dual-phase composites where only one phase (P1) changes oxygen concentration (like LSF in the here studied case), and in a case that this phase is also the only one active for the oxygen exchange, the conductivity relaxation curve will for a constant \(S_1/V_1\) ratio not be affected by the change in the phase ratio (P1: P2), as illustrated in Figure 1. Contrary, for equal involvement of both phases (P1 and P2) in the oxygen exchange, and if only the P1 phase can take up/release oxygen, increasing the amount of the P2 phase will result in shorter relaxation times. In this case Eq. 2 needs to be used to fit the model to the experimental relaxation data.

\[
f(t) = \exp \left( -t \cdot \frac{S}{V} \cdot \left( f_{S1} k_1 + f_{S2} k_2 \right) \right)
\]

Here \(k_1\) and \(k_2\) represent the surface exchange coefficients on the P1 and P2 phases, respectively. \(f_{S1}\) and \(f_{S2}\) are the surface area fraction of the P1 phase and the P2 phase, for which holds that \(f_{S1} + f_{S2} = 1\). The right part of the equation is derived by assumption that \(f_{S1} = f_{V1}\) and \(f_{S2} = f_{V2}\). \(S\) represents the total surface of the sample and \(V\) represents the total volume of the sample.

Besides, as described above, considering the general involvement of the two phases in the oxygen exchange, one has to account for different possibilities where the surface exchange and oxygen incorporation will take place. Different steps and possible routes of oxygen surface exchange reaction in the composite are illustrated in Figure 2. In the following specific limiting cases that can be correlated to the findings reported in the here presented study will be considered (in the sections Fast oxygen exchange on LSF – Involvement of CGO in the oxygen surface exchange reaction), with the aim to describe the dependence of the effective surface exchange coefficient on bulk properties of the composite.

### Fast oxygen exchange on LSF—The effective surface exchange coefficient can for the dual-phase LSF-CGO composite be described by:

\[
k_{S1\text{sample}} = k_{S1\text{LSF}} + \frac{f_{S2}}{1 - f_{S2}} k_{S1\text{CGO}} \tag{3}
\]

Where, \(f_{S2}\) represents the surface area fraction of the CGO phase in the composite, \(k_{S1\text{sample}}\) is the effective surface exchange coefficient.
Figure 2. Schematic presentation of possible routes of oxygen exchange with different locations of the oxygen incorporation; I) independently occurring on LSF and CGO, II) primarily occurring on grain boundaries, III) occurring on LSF and CGO, with spillover mechanism.

of the composite, \( k_{ex}(LSF) \) is the surface exchange coefficient of the LSF phase and \( k_{ex}(CGO) \) is the surface exchange coefficient of the CGO phase.

Several studies of \( k_{ex} \) on LSF by conductivity relaxation are available in literature.\(^{7,9,11,26}\) For CGO data is scarcer. Two different hypotheses can be postulated on base of the reported oxygen exchange properties of doped ceria; a) the CGO is inactive for oxygen surface exchange at high \( p_{O_2} \) (compared to LSF) and b) CGO surface is active for oxygen surface exchange.

a) In support of this, very low oxygen surface exchange coefficients (\( k_{ex} \)) of CGO have been reported at various conditions.\(^{43,44}\) The experimental investigations show that \( k_{ex}(CGO) = 1.1 \times 10^{-8} \text{ cm/s} \) at 700 °C\(^{45}\) whereas exchange is a 1000 times faster on LSF; \( k_{ex}(LSF) = 4.0 \times 10^{-5} \text{ cm/s} \) at 750 °C,\(^{46}\) as determined from \(^{18}O \) isotope diffusion profiles. Thus, most of the oxygen reduction will occur at the LSF surface. If the two materials in the composite behave independently with respect to the oxygen exchange, the addition of a doped ceria (with constant oxygen stoichiometry) will increase the oxygen diffusion coefficient but the overall surface exchange coefficient will for a constant \( S_{1}/V_{1} \) ratio remain constant.

b) Recently, relatively fast surface exchange (\( k_{ex} \)) has been reported on a similar system, \( \text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{2-x} \),\(^{47}\) measured by ECR, which hints that the doped ceria can be active for oxygen exchange also at a high \( p_{O_2} \). In this case, the both surfaces LSF and CGO can in principle be active for the oxygen surface exchange reaction as illustrated in Figure 2I. The addition of doped ceria will speed up not only oxygen diffusion but also oxygen exchange.

**Fast oxygen exchange on grain boundaries.**—In case that the \( nds \) involves a vacant oxygen site at the surface (for adsorption as proposed by ten Elshof et al.,\(^{48}\) or for dissociation of oxygen molecules, as proposed by Mosleh et al.,\(^{49}\) or for oxygen incorporation into the oxide crystal lattice) the increase of the oxygen vacancies mobility and their concentration should result in an increased \( k_{ex} \). Grain boundaries could possibly be fast reduction and dissociation sites with a higher concentration of defects. The here studied composites have two different types of grain boundaries; a single phase grain boundary (GB) and a dual-phase grain boundary (TPB).

For a GB in CSO (10^{-30} \text{ atm} < \rho_{O_2} < 10^{-18} \text{ atm}) it has been reported that at low temperature the surface exchange rate depends on the grain size of the studied material. This is likely associated with the concentration of oxygen vacancies being significantly higher at the grain boundary than on the surface of CSO grains, while at \( \geq 800^\circ \text{C} \) the oxygen exchange was independent on grain size.\(^{46}\) Contribution of gains and grain boundaries to the oxygen exchange and the oxygen diffusion in LSM thin films with controlled grain sizes ranging from 30 nm to 75 nm was reported by Navickas et al.\(^{46}\) In that case, the grain boundary diffusion and the grain boundary surface exchange were approximately two to three orders of magnitude larger than those of the grains.

For a TPB in dual-phase \( \text{Sr}_{2}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6} - \text{CSO} \) composites it was from relaxation results suggested that more than 90% of the overall oxygen uptake occurs at the TPB, for a TPB length between 0.50 × 10^{-3} \text{ and} 1.46 \times 10^{-4} \text{ m} \text{-}^{-1} \text{.}\(^{21}\) Similar conclusions were reached for a \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3} - \text{CSO} \) composite, where 70% of the oxygen uptake at 650–800 °C was reported to occur at the TPB.\(^{37}\) Inspired by these observations it is hypothesized that also for the here studied LSF-CGO composite the grain boundaries could act as zones of fast dissociation/incorporation. It would then be expected that \( k_{ex} \) will be enhanced by increasing the GB or/and TPB lengths. The effective surface exchange coefficient can for this case be written

\[
k_{ex\text{(sample)}} = k_{ex\text{(LSF)}} + \frac{f_{LSF}\cdot k_{ex\text{(LSF}\text{GB})}}{f_{1}} + \frac{f_{CGO}\cdot k_{ex\text{(CGO}\text{GB})}}{f_{1}} + \frac{f_{TPB}\cdot k_{ex\text{(TPB)}}}{f_{1}} \tag{4}
\]

The \( f_{GB} \) represents the surface area fraction of single phase grain boundaries (\( i = \text{LSF} \) or \( \text{CGO} \)), and \( f_{TPB} \) the surface area fraction of dual-phase boundaries. The \( k_{ex\text{(LSF}\text{GB})} \) and \( k_{ex\text{(CGO}\text{GB})} \) are the effective surface exchange coefficient on the single-phase grain boundaries and \( k_{ex\text{(TPB)}} \) is the effective surface exchange coefficient on the dual-phase grain boundaries (as illustrated in Figure 2II).

**Involvement of CGO in the oxygen surface exchange reaction.**—

Besides, the two previously presented limiting cases of exchange occurring independently on the LSF and CGO surfaces, or enhanced exchange at the GB/TPB a third possibility of synergy between the two phases is schematically illustrated in Figure 2III. Possibly the CGO surface could contribute by incorporating oxygen ions (\( O^2- \)) to \( O^2- \) ion and incorporation into the oxide crystal lattice occurs at the CGO surface. The final ionization of \( O^2- \) to \( O^2- \) in the mixed conductors is assumed to be fast,\(^{22}\) therefore the low, but non-negligible electronic conductivity of CGO (8 \times 10^{-4} S/cm at 900 °C and 0.21 atm),\(^{50}\) is speculated to be high enough that electron transfer can occur during the incorporation reaction at CGO. In this case the addition of better ionic conductor (CGO) will improve both the oxygen diffusion and the effective surface exchange rate, which can be described with Eq. 3.

Another synergistic effect was recently reported, namely that a transition metal perovskite in the vicinity of the CGO surface may act to remove impurities from the CGO surface. The oxygen exchange on the “cleaned” CGO surface appears to be very fast,\(^{23}\) and possibly, in the older SIMS studies of single phase CGO the exchange reaction has been impeded by unintended impurities on CGO surface.

**Experimental**

**Sample preparation.**—CGO (\( \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-x} \), Rhodia) and LSF (\( \text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3} \), Kusaka, Japan) were mixed in the following volume ratios CGO:LSF = 70:30 (CGO70), 50:50 (CGO50), 30:70 (CGO30). The powder mixtures and pure LSF were ball milled in ethanol using \( \text{ZrO}_2 \) balls for 24 h at 50 rpm (with volume ratio;
1/4 powder, 1/4 ethanol and 1/2 of ZrO2 balls). The slurries were dried and the mixtures of CGO and LSF powders and pure LSF were pressed uniaxially into rectangular bars with a pressure of 30 MPa. The bars were further compressed isostatically at 325 MPa and were subsequently sintered at 1300°C for 2 h. To increase the TPB length for the CGO:LSF = 70:30 composition the LSF and CGO powders were ball milled for 3 days (CGO70-3 M) which significantly reduced the particle size. Geometrical densities of all samples were larger than 95% of the theoretical density, as is listed in Table I. All surfaces of the bars were ground and polished with 1 μm diamond polishing agent to obtain bars with size of 2.5 × 1.5 × 20 mm3. After polishing, the bars were re-annealed in air at 1000°C for 12 h.

A sample (LSF-1200+CGO sample) with a microstructure adjusted to the spatial resolution of TOF-SIMS was prepared from the LSF powder that was pre-calcined at 1200°C for 3 h and the as-received CGO powder. The sample was sintered at 1300°C for 10 h to reach 97.4% of the theoretical density, polished and re-annealed at 1000°C.

Characterizations.—Phase purity of sintered and annealed bars before the relaxation measurements was determined using a BrukerD8 X-ray diffractrometer with CuKa radiation (λ = 1.5406 Å). The microstructure of the re-annealed samples was investigated by scanning electron microscopy (SEM, SUPRA Zeiss). The length of the TPB from the effective vacancy diffusion coefficient of a dual-phase problem is used in the fitting because the conductivity is measured also applied at other temperatures. pO2 was monitored in the inlet and outlet gasses using an in-house constructed zirconia-based oxygen sensor. The analysis of data of the oxygen transport properties for pO2 < 0.01 atm was done by taking gas concentration polarization into consideration, due to the uptake/release of oxygen from the sample.51

Fitting parameters.—ECR is a well-established method to determine the oxygen transport properties of MIECs.10,11 ECR measures a change of the conductivity of a sample being subjected to a step change in the surrounding pO2. At t = 0 the pO2 is abruptly changed to a new value, which leads to a new equilibrium concentration of oxygen vacancies in the material. As the conductivity of the MIEC depends on the concentration of charge carriers via the electroneutrality condition the change of conductivity after a change in the pO2 can, for well-defined geometries, be correlated to the oxygen transport properties of the material. By fitting the conductivity change using Fick’s law of diffusion with appropriate boundary conditions, the values of kex and Dchem can be obtained. Assumptions used in the data analysis include: i) local electro-neutrality, ii) linear surface exchange kinetics, iii) a linear relationship between the conductivity and the oxygen vacancy concentration, iv) a constant value of Dchem and kex during the relaxation, and v) that for a two-dimensional system the oxide ion concentration is in local equilibrium in x and y direction. The two-dimensional diffusion problem with a first order surface reaction can be described using Eq. 5, which was used for fitting the normalized conductivity.11

\[
\begin{align*}
    f(t) &= \frac{\sigma_{\infty} - \sigma(t)}{\sigma_{\infty} - \sigma(t_0)} = \sum_{n=1}^{\infty} 2L_x^2 \exp \left( \frac{-\beta_{n,0}^2 D_{chem}}{k_x^2} \right) \\
    &\times \sum_{n=1}^{\infty} 2L_y^2 \exp \left( \frac{-\beta_{n,0}^2 D_{chem}}{k_y^2} \right)
\end{align*}
\]

\[
\beta_{n,0}^3 \tan \beta_{n,0}^2 L_y = L_x \qquad L_y = \frac{l_k \sigma_{ex}}{D_{chem}} \qquad \beta_{n,0}^3 \tan \beta_{n,0}^2 L_x = L_y \qquad L_x = \frac{l_k \sigma_{ex}}{D_{chem}}
\]

2Lx and 2Ly are the width and thickness of the sample. For accurate ECR results the sample dimensions should fulfill the criteria of l_k ≈ l_x < l_y, where z is the direction of the electrical current and 2l_y the length of the sample. A two-dimensional solution of the diffusion problem is used in the fitting because the conductivity is measured over a short distance close to the center of a long rectangular bar. Details relating to the fitting can be found elsewhere.52 The error bars shown in the later figures represent Dchem and kex values within the 5% of standard deviation from the best fit values. For the dual-phase LSF-CGO composites it was additionally assumed that i) the conductivity change after pO2 step reflects only a change of oxygen concentration in LSF (since for the studied temperature and pO2 range the oxygen stoichiometry of CGO is known to be virtually constant in the air) and ii) the phases are randomly distributed in the composite.

The measured Dchem was fitted with theoretically calculated Dchem from the effective vacancy diffusion coefficient of a dual-phase

\[
\begin{array}{c|c|c|c|c|c|c|c}
\text{Sample} & t_{sintering} [h] & \text{Surface area LSF} & \text{Surface area CGO} & \text{TD} & \text{Length of TPB} [\mu m/m^2] & \text{Conductivity at 750°C in air [S/cm]} \\
\hline
\text{LSF} & 2 & 1 & 0 & 98.7 & / & 4.4 \\
\text{CGO30} & 2 & 0.69 & 0.31 & 99.7 & 2.8 ± 0.1 & 90 \\
\text{CGO50} & 2 & 0.46 & 0.54 & 96.9 & 2.7 ± 0.1 & 35 \\
\text{CGO70} & 2 & 0.26 & 0.74 & 99.3 & 2.1 ± 0.1 & 4.0 \\
\text{CGO70-3M} & 3 & 0.25 & 0.75 & 100.0 & 2.3 ± 0.1 & 4.6 \\
\text{LSF-1200+CGO} & 10 & 0.29 & 0.71 & 97.4 & 0.16 ± 0.03 & 0.2 \\
\end{array}
\]
calculate tortuosities and sintering at 1300 °C of the pure LSF, the dual-phase LSF-CGO composites after thermally annealed pure LSF sample. The average grain size determined from image analysis was 2.0 ± 0.2 μm and the dark phase is LSF with the average grain size of 0.50 ± 0.26 μm. The surface areas of LSF and CGO derived from the SEM micrographs for the composites are listed in Table I. As expected, the measured surface area ratios are similar to the volume fraction used for preparation of the composites. The TPB length, also derived from SEM micrographs, decreases with the increasing CGO volume fraction. There is however no clear maximum at the expected 50 vol.% LSF; 50 vol.% CGO composite. The variation from CGO30 to CGO50 and CGO70 seems to be more controlled by small unattended differences in the grain sizes of the CGO and LSF grains and difference in agglomeration of each phase than by the volume ratio (Table I).

Morphology variation.—With a longer milling time of the powders the final grain size of the sintered composite was slightly decreased to 0.45 ± 0.22 μm for the CGO grains and to 0.35 ± 0.17 μm for the LSF grains (Figure 5A), compared to the grain size of the sintered as-received powders (Volume fraction variation section). The TPB length of the CGO70-3 M sample was slightly increased (Table I).

For the composite with the pre-calcined powder the average grain sizes were 0.9 ± 0.6 μm and 1.1 ± 0.8 μm for CGO and LSF, respectively (Figure 5B) and were approx. twice larger than for the composites prepared from the as-received powders. The LSF-1200+CGO sample consists of large multi-grain LSF islands in range of 10’s μm in a CGO matrix.

Electrical conductivity.—The samples’ total conductivity includes both an electronic and an ionic contribution. However, for pure LSF and the LSF-CGO composites studied here the ionic contribution to the total conductivity is small (σi < σel/100) and the major contribution to the measured total conductivity comes from electronic conductivity of LSF. The conductivity of the pure LSF and the LSF-CGO composites increases with temperature, goes through a broad maximum and then decreases. Below 600 °C the activation energy of the conductivity of LSF as well as the composites is in the range of 5.8 to 7.7 kJ/mol. The temperature dependence of the LSF conductivity found in the present study as well as the activation energies are in good agreement with values that can be found in the literature.

The total conductivity of the composites is lower than that of the pure LSF, due to much lower total conductivity of CGO (Table I). The total conductivity in air at 750 °C for the CGO70 is only 4.0 S/cm compared to 250 S/cm for the pure LSF. However, even at 70 vol.% of CGO in the composite the microstructure still enables percolation of the electronically conductive phase and the total conductivity is around 40 times higher than for the pure CGO. The microstructure of the composites also strongly influences the total conductivity, as it is evident from the 70 vol.% of CGO composites in Table I. Formation of larger LSF islands in the CGO matrix (LSF-1200+CGO sample) strongly reduces the electrical conductivity, due to a decreased fraction of the percolating LSF grains.

The total conductivity of LSF decreases with decreasing PO2 as a consequence of an increased concentration of oxygen vacancies and the associated reduction of the electron hole concentration. The PO2 dependence of the total conductivity of LSF increases with temperature and for the highest temperature (900 °C) in Figure 6A the slope approaches 1/2, which is expected when the material is becoming gradually more non-stoichiometric. At lower temperature, the PO2 dependence of the total conductivity is smaller (see Figure 6C). As the temperature decreases, the concentration of oxygen vacancies in LSF decreases. Consequently, at low temperature the dopant (Sr2+), is mostly electronically compensated, which results in the weaker PO2 dependence. The observed PO2 dependence of the total conductivity of the composite is the same as that observed for the pure LSF sample (Figure 6), further illustrating that the conductivity of the composites is completely dominated by the electronic conductivity of LSF.
Oxygen exchange kinetics.—Figures 7A–7C shows the relaxation of the normalized conductivity and corresponding fitting curves (Eq. 5) after an instantaneous change of the oxygen pressure from 0.2 atm to 1.0 atm at 900°C, 750°C and 600°C, respectively. The addition of CGO to the LSF reduces the time of equilibration with the atmosphere, as is clearly seen in Figures 7A–7C, where all samples have a very similar size. The equilibration time decreases with an increased volume fraction of CGO and for the CGO70 it is 1 min, 13 min and 5 h at 900°C, 750°C and 600°C, respectively.

The decrease of the relaxation time by a factor of 5 reported in this study is smaller than the factor of 30 reported for Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$–Ce$_{0.8}$Sm$_{0.2}$O$_{2–x}$ composites, but is well in line with values reported for coated surface of dense LSCF bars with CSO, where a 6.5 times reduction of overall relaxation time was observed. The decreased relaxation time points to the existence of synergistic effect between the LSF and CGO phases in the composite.

It should be noted that the faster equilibration cannot be ascribed to just being an effect of that less oxygen is exchanged with increasing the CGO fraction. When the LSF fraction is decreased in the composite, the amount of exchanged oxygen on a p$_{O_2}$ change is decreased but also the LSF surface area is decreased (both to the same degree). Hence, if the CGO is totally inert in the oxygen surface exchange process the relaxation time should be unaltered (if the effect of tortuosity in oxygen incorporation path is neglected), as presented in Figure 1.

Fitting of the relaxation curves with Eq. 5 allows extraction of the $D_{chem}$ and $k_{ex}$ values. Figure 7D shows measured values for a CGO50 composite and different fitting curves assuming different sets of $D_{chem}$ and $k_{ex}$ values. The mismatch between measured and calculated curves shows that, when the $k_{ex}$ value determined for LSF at the same measurement conditions ($3.51 \times 10^{-5}$ cm/s) is used for the composite (CGO50), the curve cannot be fitted by varying $D_{chem}$ only (Figure 7D). The obvious conclusion is that not only $D_{chem}$ is enhanced when introducing CGO, but also $k_{ex}$ is enhanced in the composites compared to the pure LSF sample.

At 600°C and low p$_{O_2}$ the rate of the equilibration process is completely controlled by the surface exchange process. This is illustrated in Figure 7E, showing an experimental curve for the LSF and CGO50 samples measured at 600°C and p$_{O_2}$ (end) of 0.1 atm, where the best fit curves using both Eq. 1 and Eq. 5 are shown. The deviation between these two fitting curves is very small. Clearly, the data can be well fitted with only one parameter ($k_{ex}$), confirming the surface control. The direct comparison of the experimental data sets at these conditions, where oxygen exchange is completely oxygen exchange...
limited, again demonstrates that adding CGO enhances the oxygen exchange.

Figure 8 shows the $D_{\text{chem}}$ values deduced from reduction steps at different $pO_2$ values and different temperatures for the LSF-CGO composites. $D_{\text{chem}}$ decreases with temperature and is virtually independent on $pO_2$. Similar results have been reported for LSF in the literature. For a slightly different LSF powder same $D_{\text{chem}}$ of 1.8 $\times$ 10⁻⁵ cm²/s at 900°C has been reported by Søgaard et al. Dₜₚ increases with increasing volume fraction of CGO as expected, due to the high ionic conductivity of CGO compared to LSF. The effect of CGO addition is higher at lower temperatures, because of the increased difference between the ionic conductivities of CGO and LSF. The ionic conductivity of CGO and LSF are only a factor of three different at 900°C ($\sigma_{\text{CGO}} = 0.155$ S/cm⁴ and $\sigma_{\text{LSF}}(\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{3}) = 0.049$ S/cm) compared to at 750°C, where CGO is 20-times more conductive than LSF ($\sigma_{\text{CGO}} = 0.069$ S/cm⁴ and $\sigma_{\text{LSF}}(\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{3}) = 0.003$ S/cm). The theoretical values of $D_{\text{chem}}$ for the dual-phase composites have been calculated by Eq. 7 and are shown in Figure 8. For the calculation of $D_{\text{chem}}$ at 900°C a tortuosity $\tau_{\text{C}}$ of 1 was assumed. For the CGO30 sample a good agreement between calculated and measured $D_{\text{chem}}$ values is observed. The measured $D_{\text{chem}}$ values for the CGO50 sample were ~3 times higher than the calculated one and for the CGO70 were ~4-times higher. At 750°C the measured values correspond well to the calculated one with $\tau_{\text{C}}$ of 1 for the CGO70 sample, whereas $\tau_{\text{C}}$ of 2.5 and 20 were used for the CGO50 and CGO30 samples, respectively (Figure 8B) to match the measured and calculated $D_{\text{chem}}$ values. At 600°C it was not possible to determine $D_{\text{chem}}$ as oxygen transport in the samples is mainly limited by the oxygen surface exchange reaction.

Involvement of the CGO surface.—In Figure 10 the measured $k_{\text{ex}}$ values versus the fractions of CGO in the LSF-CGO composites at different temperatures and different $pO_2$ values are shown. The values presented in Figure 10 are obtained for two $pO_2$ steps from 0.05 atm to 0.1 atm and from 0.2 atm to 1.0 atm. The later $pO_2$ step is larger than for the results plotted in Figures 9A and 9B, but the same as was used for the relaxation measurement at 600°C (Figure 9C). A larger $pO_2$ step has been used at 600°C to get a significant change of conductivity. The highest $k_{\text{ex}}$ was measured for the CGO70 composite at all temperatures and $pO_2$'s and the smallest $k_{\text{ex}}$ was measured for the pure LSF. The $k_{\text{ex}}$ of the CGO70 for the $pO_2$ step from 0.2 to 1.0 atm at 750°C was 1.86 $\times$ 10⁻⁴ cm²/s whereas for the pure LSF 3.51 $\times$ 10⁻⁵ cm²/s was found. An even larger enhancement of $k_{\text{ex}}$ for the dual-phase composites of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_3$-CSO at 750°C from 1.4 $\times$ 10⁻⁵ cm²/s to 1.0 $\times$ 10⁻⁴ cm²/s has recently been reported. For the CGO50 sample a good agreement between calculated and measured $k_{\text{ex}}$ values is observed. The measured $k_{\text{ex}}$ values for the CGO50 sample were ~3 times higher than the calculated one and for the CGO70 were ~4-times higher. At 750°C the measured values correspond well to the calculated one with $\tau_{\text{C}}$ of 1 for the CGO70 sample, whereas $\tau_{\text{C}}$ of 2.5 and 20 were used for the CGO50 and CGO30 samples, respectively (Figure 8B) to match the measured and calculated $D_{\text{chem}}$ values. At 600°C it was not possible to determine $D_{\text{chem}}$ as oxygen transport in the samples is mainly limited by the oxygen surface exchange reaction.

Figure 9 shows $k_{\text{ex}}$ taken from the reduction step and oxidation step as a function of the final $pO_2$ at different temperatures for all samples. Common to all obtained results is that $k_{\text{ex}}$ increases with increased fraction of CGO and decreases with decreasing $pO_2$. The $n$ value of $k_{\text{ex}}$ a $pO_2^n$ is between 0.4 and 0.5 for pure LSF, CGO30 and CGO50 at 900°C. At 750°C the $n$ value for the CGO50 sample is 0.4 and for the LSF and CGO30 samples it is 0.7. For the CGO70 sample a smaller $pO_2$ dependence of $k_{\text{ex}}$ with $n = 0.3$ at both temperatures was observed. At 600°C only few measurements were done, due to a small and slow change of conductivity with $pO_2$, but the trend in Figure 9C shows that, the logarithmic $pO_2$ dependence of $k_{\text{ex}}$ for the reduction steps was close to 1. For LSF a similar $pO_2$ dependence of $k_{\text{ex}}$ was also reported in the literature. Søgaard et al. reported that the $k_{\text{ex}}$ value at 900°C in air is 5.3 $\times$ 10⁻⁵ cm²/s and that the $pO_2$ dependence of $k_{\text{ex}}$ could be described as $k_{\text{ex}} = a \cdot pO_2^n$, where $n$ was between 0.62 and 1.22 depending on the measurement temperature and ten Elshof et al. reported a $pO_2$ dependence of $k_{\text{ex}}$ of 0.75 < $n$ < 0.83 for a bulk LSF.

To illustrate the range of the equivalent $k_{\text{O(CGO)}}$ values ($k_{\text{O(CGO)}}$ = $k_{\text{O(CGO)}}/\gamma_0$), they were calculated by using rough estimates of the thermodynamic enhancement factors ($\gamma_0$) for CGO calculated from the defect model reported in Ref. 50. Comparison to the measured $k_0$ values by 1⁰O isotope diffusion profiles is however very difficult, due to the large uncertainty on the $\gamma_0$ for the CGO in this $pO_2$ and temperature interval. The uncertainty is estimated to be in one or even two orders of magnitude. The roughly estimated $k_{\text{O(CGO)}}$ values are lower than the both reported $k_{\text{O(CGO)}}$ values measured on a CGO-LSFC composite.

**Figure 6.** The total conductivity of the pure LSF and the LSF-CGO composites at different $pO_2$ A) at 900°C, B) at 750°C and C) at 600°C.
Figure 7. Electrical conductivity relaxation recorded for a $pO_2$ change from 0.2 atm to 1.0 atm at A) 900°C, B) 750°C and C) 600°C for the pure LSF and the LSF-CGO composites with corresponding fitting curves (lines). D) Measured ECR with different fitting curves for CGO50 at 750°C (SSD is the sum of squared deviations). E) ECR plots of the LSF and CGO50 samples measured at 600°C with corresponding calculated relaxation curves by Eq. 1 and Eq. 5.

Table II. Surface exchange coefficient of the CGO at different temperatures and $pO_2$’s, obtained by fitting measured values by Eq. 3.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$k_{ex(GGO)}$ [cm s$^{-1}$] $pO_2$ = 0.2 atm</th>
<th>$k_{ex(GGO)}$ [cm s$^{-1}$] $pO_2$ = 0.1 atm</th>
<th>$k_{ex(GGO)}$ [cm s$^{-1}$] $pO_2$ = 0.05 atm</th>
<th>$k_{O(CGO)}$ [cm s$^{-1}$]</th>
<th>$K_{ex(LSF)}$ [cm s$^{-1}$] $pO_2$ = 0.2 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>$6.7 \times 10^{-4}$</td>
<td>$5.1 \times 10^{-4}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$6 \times 10^{-8}$ ($\gamma_O \sim 115000$)</td>
<td>$1.32 \times 10^{-3}$</td>
</tr>
<tr>
<td>750</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$6.8 \times 10^{-5}$</td>
<td>$3.4 \times 10^{-5}$</td>
<td>$4 \times 10^{-10}$ ($\gamma_O \sim 271000$)</td>
<td>$3.51 \times 10^{-5}$</td>
</tr>
<tr>
<td>600</td>
<td>$4.5 \times 10^{-6}$</td>
<td>/</td>
<td>/</td>
<td>$9 \times 10^{-12}$ ($\gamma_O \sim 512000$)</td>
<td>$1.25 \times 10^{-6}$</td>
</tr>
<tr>
<td>850</td>
<td>$8.5 \times 10^{-4}$</td>
<td>$10^{-3}$ atm, $pO_2$ = $10^{-3}$ atm, Ref. 47 *</td>
<td>$1.2 \times 10^{-6}$, CGO-LSCF, Isotope, Ref. 40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>$1.1 \times 10^{-8}$</td>
<td>$1.0 \times 10^{-8}$, CGO, Isotope, Ref. 45</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Ce$_{0.85}$Sm$_{0.15}$O$_2$-d.
by oxygen isotope diffusion profiles, and the reported values on a pure CGO surface, as listed in Table II.

In summary, it is thus possible to evaluate an apparent $k_{ex}$ value on the CGO phase in the composite from the measured relaxations and it is clear that the estimated values are significant and at low temperatures even faster than the LSF values. However, it is difficult to compare to the transport properties determined on CGO by more direct methods, such as isotope exchange measurements, due to high uncertainty on the thermodynamic enhancement factor.

Involvement of three phase boundaries.—Many studies on ionic conductor/MIEC composites have shown that the TPB (gas/ionic conductor/MIEC) plays a crucial role in oxygen surface exchange process. The contribution is mostly related to the concentration of oxygen vacancies, which is assumed to be higher at the TPB. Higher concentration can increase the surface exchange rate as stated in Fast oxygen exchange on grain boundaries section.

In Figure 11 the $k_{ex}$ values for all here studied composites as a function of the measured TPB length are shown. The highest $k_{ex}$ were measured for the composite with the shortest TPB lengths ($2.1 \mu m/\mu m^2$) and more or less it seems that $k_{ex}$ decreases with the TPB length. To exclude the effect of changed composition two composites with the same CGO/LSF ratio but different TPB lengths were compared. A slight decrease in the surface exchange coefficients was observed for the composites with longer TPB, with $k_{ex}$ being lower at the CGO70-3 M sample than at the CGO70 sample. However, there is no obvious correlation between TPB length and $k_{ex}$ in the range of here studied TPB lengths.

Surface impurities segregation.—The surface of the LSF-1200+CGO sample was characterized by TOF-SIMS, after exposing it to similar conditions as the samples have experienced during the ECR. Results are shown in Figure 12. The LSF phase is clearly associated with a higher amount of impurities compared to the CGO phase. Specifically, for the surface of the LSF phase higher amounts of K, Na, Ca and Cr compared to the CGO surface were observed.

The results reported here are in agreement with observed scavenging effect on a CGO-LSCF composite, where none of the impurities (Na, Si, Ca) seen for the single phase CGO were evident when this material was a part of a composite. As reported by Druce et al., the presence of specific impurities; La-, Sr-, Fe- or Co-rich phases at the surface of CGO may also lead to a drastic improvement of the oxygen exchange on CGO. This have been speculated by the formation of a SrCeO$_3$ perovskite phase on the surface of CGO that is able to...
incorporate a wide variety of elements with different charge and atomic radii on both A and B sites. This SrCeO$_3$ perovskite islands then can scavenge exchange impeding impurities from the CGO surface and it results in fast oxygen exchange on the ceria.$^{45}$

In an opposite case, where a perovskite surface partially covered by ceria nanoparticles was studied, an enchantment of the exchange rate was also observed. LSCF bars decorated with CSO nanoparticles showed an increase in the surface exchange rate from $2.7 \times 10^{-3}$ cm/s (bare LSCF) to $4.6 \times 10^{-4}$ cm/s for the decorated sample as reported by Hong et al.$^{15}$ The improvement was ascribed to formation of a fast LSCF/CGO/O$_2$ interface. A large increase in surface exchange rate, up to 100 – times, was also observed for a Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$ surface decorated with CSO nanoparticles.$^{38}$

**Discussion**

In case of pure LSF the surface exchange reaction at high $pO_2$’s ($10^{-3} < pO_2 < 1$ atm), by assuming the involvement of oxygen vacancies in the oxygen surface exchange process,$^{10}$ will be strongly depended on the mobility and/or concentration of oxygen vacancies, while for pure CGO the oxygen exchange will be presumably limited by the electronic conductivity.$^{50}$ From the results reported here it is seen that combining LSF and CGO into a composite is beneficial and that the surface exchange rate is enhanced with increasing the fraction of CGO in the composite. The enhancement is larger at lower temperatures. The enhanced surface exchange coefficient with increasing amount of CGO indicates that the CGO is involved directly in the oxygen surface exchange reaction. In principle, as also discussed in Fast oxygen exchange on grain boundaries section, the increasing exchange rate could be due to the introduction of fast BG/TPB upon the introduction of CGO. However, as the enhancement does not scale with the observed TPB length, it does not seem the dominant effect in this system.

The observed CGO involvement in the oxygen surface exchange reaction could be speculated to occur via different routes, for example;

i) The CGO is involved in surface exchange reaction or in one of the oxygen exchange steps. For example; reduced oxygen species formed on the LSF surface could spill over to the CGO surface. In this case the CGO surface is active in the subsequent dissociation of partly reduced oxygen species to the atomic species and/or their incorporation. This will also act as removal of intermediate oxygen species formed on the LSF, which would otherwise impede the incorporation reaction. This agrees with the here reported experimental result that both CGO and LSF surfaces are active in the oxygen surface exchange reaction.

ii) One phase scavenges impurities from other, thereby making one of the phases much faster for oxygen exchange than when this phase is present alone. Indeed, here we found larger amount of alkali impurities on the LSF than on the CGO. Hence, it could be, that a cleaning of the CGO surface takes place via the presence of LSF, making the oxygen exchange on CGO much faster than when considering single phase CGO samples. This would be consistent with the observations here and with results on CGO and LSCF-CGO composites reported by Druce et al.$^{40,45}$ Additionally, the results reported by Gopal and Haile$^{47}$ on $k_{ex}$ of Sm doped CeO$_2$ surface studied as a single phase material also show that in some cases the oxygen surface exchange reaction at high $pO_2$ on doped ceria can be fast.

Although further studies are needed, e. g. replacing CGO with better or worse ionic or electronic conductors, to verify the influence of conductivities, we find that both routes involving spillover of oxygen species from one phase to the other and enhanced exchange on CGO itself due to impurity scavenging in LSF are supported by the presented data and both are likely possible. It should also be pointed out that these two mechanisms are not mutually exclusive and can act simultaneously.
Further, the $p_O^2$ dependence of $k_{\alpha n}$, which was observed to vary with the CGO fraction and the temperature, can point out different aspects of the mechanism of the oxygen exchange. Different $rds$ can be assumed depending on the observed exponent $n$ ($k_{\alpha n} \propto p_O^{n}$): i) $n \approx 1$ indicates that molecular oxygen participates in the $rds$, ii) $n \approx 0.5$ indicates the involvement of atomic oxygen species in the $rds$ and iii) $n \approx 0.25$ would indicate the involvement of electron transfer or oxygen incorporation in the $rds$.\(^{18}\)

For the LSF-CGO composites presented in this study the $n$ ($k_{\alpha n} \propto p_O^{n}$) was between 0.3 and 1.0 and varied with the composition and temperature. The broad range of observed $p_O$ dependences disables a decisive conclusion about the $rds$ of the oxygen surface exchange reaction. However, two trends are clear:

i) Firstly, that the $rds$ depends on the temperature. Higher $n$ values ($k_{\alpha n} \propto p_O^{n}$) are observed at lower temperature, which point toward the involvement of oxygen molecules in the $rds$, as also found by ten Elshof et al.\(^{10}\) At low temperature, it is expected that the adsorption/desorption reaction will be slower than at higher temperatures. Additionally, other strongly adsorbed molecules (e.g. CO$_2$) or intermediate oxygen species can contribute to even slower adsorption/desorption reaction of oxygen through covering of active sites. While, at high temperature overall $p_O$ dependence of $k_{\alpha n}$ points in the direction of atomic oxygen species being involved in the $rds$.

ii) Secondly, if oxygen vacancies are involved in the $rds$ the $p_O$ dependence of $k_{\alpha n}$ would be influenced by the composition of the composite. The vacancies in LSF respond differently to the temperature (900°C), where the ionic conductivity of CGO and LSF are more similar, and iii) increased fractions of CGO in a dual-phase composite (from 30% to 70%) enhances the oxygen surface exchange reaction and, (iv) the enhancement of $k_{\alpha n}$ does not scale with the TPB length. Considering all experimental data it is further suggested that the $rds$ is temperature and composition dependent. The involvement of CGO in the oxygen exchange can be through the spillover of oxygen ions, partly reduced oxygen species, from LSF to CGO, where they dissociate and/or incorporate. An alternative effect could be that the LSF scavenges impurities from CGO and thereby activates the CGO surface for the oxygen surface exchange reaction. Both proposed mechanism could account for the observations.

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ORCID

Simona Ovtar https://orcid.org/0000-0003-4588-2679

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