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**Electrical Conductivity and Oxygen Exchange Kinetics of \( \text{La}_2\text{NiO}_4^{+\delta} \) Thin Films Grown by Chemical Vapor Deposition**

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dated to the planar geometry necessary to tackle practical applications. In the last decades, transition metal oxides with perovskite-related structures such as \( \text{La}_2\text{NiO}_4^{+\delta} \) (LNO) have shown high oxygen diffusivities and high electronic conductivities at high temperatures, 18 making them attractive candidates for their use in electrochemical devices. Actually, LNO presents the advantage of having a thermal expansion coefficient close to the commonly used SOFC electrolytes, such as yttria-stabilized zirconia, \( \text{La}_2\text{Sr}_2\text{MgO}_6 \), and gadolinia-doped ceria. \( \text{La}_2\text{NiO}_4^{+\delta} \) with a \( \text{K}_2\text{NiF}_4 \) structure, can be described as a sequence of perovskite \( \text{LaNiO}_3 \) layers alternated with rock-salt-type \( \text{LaO} \) layers along the \( c \) axis. The enhanced oxygen conductivity of such structures was found to be related to their high oxygen hyperstoichiometry \( (0 ≤ \delta ≤ 0.2) \), resulting from the incorporation of interstitial oxygen anions into the rock-salt-type layers. 9 Because oxygen ionic transport in such compounds occurs mainly via diffusion along the interstitial sites, higher transport is expected along the \( c \) axis perpendicular to the substrate surface. Planar electrical conductivity measurements along with conductivity relaxation experiments at high temperature were performed in order to analyze the oxygen exchange kinetics. Results are discussed as a function of temperature and film thickness.

**Experimental**

Films were grown in a PIMOCVD setup using solid \( \beta \)-diketonates \( \text{La(tfd)}_3 \) and \( \text{Ni(tfd)}_3 \) \(( \text{tfd} = 2,2,6,6\text{-tetramethylheptane-3,5-dionate}) \) precursors from Sterm Chemicals dissolved in 1,2-dimethoxyethane. The total concentration of the solution was 0.02 M, while the molar ratio \( \text{La/Ni} \) in the precursor solution was equal to 3. The evaporation and deposition temperatures were fixed at 280 and 750°C, respectively, and the total gas flow was maintained at 1 L/h with a 1:1 ratio of oxygen and argon. The opening time of the injector was 2 ms with a pulse frequency of 1 Hz. Films were deposited on \( \text{SrTiO}_3 \) (100) substrates which were introduced in the reactor at room temperature. The substrate temperature was increased to 700°C in 3 min, and subsequently the gas atmosphere was abruptly switched to a \( 98 \% \text{O}_2 + 2 \% \text{H}_2 \) mixture at 1400°C for 30 min. The films were cooled with a rate of 16°C/min down to room temperature. The corresponding change of conductivity along the \( a-b \) plane was determined using an HP 4192A impedance analyzer at 1 kHz frequency during the cooling process from 1015 K to room temperature and at 1 atm of pure oxygen. Two parallel Ag contacts were painted on the surface of the films and membranes as probe contacts. In the electrical conductivity relaxation (ECR) experiments, for a constant temperature the sample was held at equilibrium under an initial oxygen partial pressure and subsequently the gas atmosphere was abruptly switched to a different chosen oxygen partial pressure. The corresponding change in the conductivity of the sample, which reflects the change in its oxygen content, was recorded until a new equilibrium was established. By analyzing the normalized conductivity as a function of time \( \sigma(t) \)

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where \( \sigma_0, \sigma_x, \text{ and } \sigma(t) \) are the initial, final, and time \( t \) conductivity values, respectively, and solving Fick’s second law for the given initial and boundary conditions, we obtained the chemical surface exchange coefficient, \( k_{Ex} \). In the case of surface exchange reaction control of the oxygen transport, according to the mass conversation law and assuming linear surface exchange kinetics, we have

\[
\frac{\partial c(t)}{\partial t} = -\frac{S}{V} k_{Ex} [c(t) - c(\infty)]
\]

with

\[
\tau = \frac{l}{k_{Ex}}
\]

where \( \tau \) is the time constant and \( l \) is the film thickness.

As the measured \( \text{La}_2\text{NiO}_4^{+} \) films were relatively thin (<350 nm) and largely below the characteristic thickness of the material determined by Kim et al., it was reasonable to assume that the \( \text{La}_2\text{NiO}_4^{+} \) transport was mainly controlled by the surface exchange rate. For a single surface reaction and a small oxygen pressure change, the normalized conductivity of a plane sheet is

\[
g(t) = 1 - \exp\left(-\frac{t}{\tau}\right)
\]

phases, showing for films deposited around 750°C the narrowest XRD peaks and the best surface morphology uniformity. Films with different thickness were prepared, at these optimized conditions, by simply varying the number of droplets injected into the reactor. Film thickness was measured by X-ray reflectometry and the growth rate was estimated in 305 nm/h. The highly \( c \)-axis orientation of the layers was confirmed by XRD, as shown in the patterns in Fig. 1, in which, together with the substrate reflections, only the 00l \( \text{LNO} \) reflections were detected. The narrow rocking curves [full width at half maximum (fwhm) = 0.2°] of the 008 reflection (Fig. 2a), that slightly broaden with film thickness, confirmed the high degree of

**Results and Discussion**

The general experimental conditions for the film deposition (total pressure of 10 Torr, valve opening time of 2 ms, and injection frequency of 1 Hz) were established by former studies performed with the same PIMOCVD equipment. Initial deposition tests starting from a \( \text{La}_2\text{Ni} \) solution ratio of 2.33 showed after wavelength-dispersive spectrometry analysis that \( \text{La}_2\text{Ni} \) in the solution had to be increased up to 3 to reach the expected \( \text{La}_2\text{Ni} \) value of 2 in the solid phase. The \( \text{La}_2\text{Ni} \) ratio optimization details, as well as the XRD patterns of the different phases obtained by varying the \( \text{La}_2\text{Ni} \) ratio in an extreme range, are described elsewhere. The deviation in the composition transfer between vapor and condensed phases is typical for MOCVD processes and occurs because each individual precursor has a different decomposition temperature which induces a different deposition yield for each element. The deposited lanthanum nickelates were nickel-rich compared with the injected precursor solution, as previously observed by Lane et al. in \( \text{La}_2\text{NiO}_4^{+} \) layers and by Faucheur et al. in \( \text{La}_2\text{NiO}_4^{+} \) layers. Increasing the deposition temperature gave rise to highly \( c \)-axis oriented \( \text{La}_2\text{NiO}_4^{+} \)

![Figure 1. XRD patterns of thin films deposited on STO and NGO under the selected optimal conditions. The positions for substrate peaks: STO (squares) and NGO (circles) and of the 00l peaks corresponding to c-axis oriented LNO are indicated.](https://example.com/figure1)

![Figure 2. (a) X-ray rocking curve of the 008 reflection of a LNO layer grown on NGO of a thickness of 200 and 300 nm, and (b) phi-scan of 200 nm thick LNO/NGO 208 reflection superimposed to the phi-scan of the 204/024 substrate reflection.](https://example.com/figure2)
orientation in the perpendicular direction. The orientation of the film slightly decreases when the film is grown on STO, as evidenced by a wider rocking curve of the 008 reflection (fwhm = 0.78° for 325 nm thick films grown on STO compared to 0.63° for 300 nm thick films grown on NGO substrate), which induces lower intensities of all 00i diffraction peaks (Fig. 1). The fourfold symmetry observed in the phi-scan of the asymmetric 208 LNO reflection (Fig. 2b) and its relation with the 204 reflection phi-scan of the NGO substrate confirmed the perfect in-plane alignment of the film, which corresponded to the expected parallel arrangement of the perovskite blocks of the LNO structure onto those of the substrate. The surface roughness (roughness-mean-square) of the layers was relatively low, around 4 nm for the thin films and increased slightly up to 40 nm for the thicker films.

As films were c-axis oriented, the planar conductivity measurements reveal the transport properties along the a-b plane. We have selected two extreme thicknesses, 50 and 335 nm, deposited on STO and NGO substrates to study the influence of both thickness and strain on the total conductivity. The measured conductance of the substrates was found to be several orders of magnitude smaller than that in polycrystalline ceramic (with randomly oriented grains). Nevertheless, the physical phenomena giving rise to a conductivity larger than that in single crystals is still unknown. The high conductivity of very thin films in comparison with a-b plane, single-crystal conductivity could be an effect of the film strain induced by the substrate, as already observed in isostructural La2CuO4 phase, where superconducting properties are improved by the substrate-induced strain.37 In La2CuO4-related compounds, the intrinsic local mismatch between the perovskite and rock-salt slabs forming the structure modulates the Cu-O distance and is responsible for the electronic doping state and, consequently, the superconducting properties.38 In the case of epitaxial thin films of La2NiO4, both phenomena could thus also take place or coexist. Nevertheless, many other parameters can simultaneously and competitively affect the total transport properties of the LNO films, such as the microstructure and the oxygen content (b). Because we are not able to estimate the oxygen content of our samples because of the small volume/weight, added to the presence of an oxide substrate, the contribution of δ to the conductivity cannot be evaluated.

The conductivity measurements have been complemented with the determination of oxygen exchange parameters. As already described in the Experimental section, the oxygen exchange process of 50 and 335 nm thick LNO epitaxial films in oxygen atmosphere vs temperature.

![Figure 3](https://example.com/fig3.png) **Figure 3.** (Color online) Total conductivity measured during the cooling process of 50 and 335 nm thick LNO epitaxial films in oxygen atmosphere vs temperature.

![Figure 4](https://example.com/fig4.png) **Figure 4.** (Color online) Oxygen pressure and conductivity data for gas switches from 0.25 to 0.125, 0.125 to 0.25, 0.25 to 0.50, and 0.50 to 1 atm O2 at 480°C, and the three reduction plus the three oxidation steps at 580°C for the 335 nm LNO film grown on STO.
coefficients of thin (50 nm) and a thick (335 nm) films were measured by the electrical conductivity relaxation technique at different temperatures and with different oxygen partial pressure changes. In Fig. 4a and b we can see the conductivity evolution of the 335 nm LNO/STO film by stepping the oxygen partial pressure from 0.125 to 1 atm of O$_2$ at 480 and 580°C, respectively. We can observe that the conductivity curves do not have a simple exponential behavior. The presence of a slower diffusion process could be responsible for the apparent anomalies. Figure 5 shows one typical ECR normalized curve corresponding to the 1–0.50 atm of O$_2$ reduction step measured simultaneously, according to

$$g(t) = 1 - A_1 \exp\left(-\frac{t}{\tau_1}\right) - A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

with $A_1 + A_2 = 1$.

This double-exponential function fitting was more satisfactory, as can be seen in Fig. 5, and therefore two different time constants could be extracted. As an example, the time constants $\tau_1$ and $\tau_2$ for the 1–0.50 atm step are shown as a function of temperature in Fig. 6. Both $\tau_1$ and $\tau_2$ show an exponential dependence with reciprocal temperature, which is an indication of a thermally activated process. The apparent activation energy for the process associated to $\tau_1$ is about 0.27 eV, in agreement with values of about 0.38 eV reported for isotopic oxygen exchange for the same La$_2$NiO$_4$ films. The $\tau_2$ value is about two orders of magnitude higher than $\tau_1$ at low temperatures and one order of magnitude larger at high temperatures. We relate the short time constant $\tau_1$ to the film surface exchange process (fast), whereas the large time constant $\tau_2$ might be associated either to a slow process limiting the oxygen diffusion at the film–substrate interface or even to a material chemical degradation. Other authors have also used the double-exponential model to better fit the ECR data of (La$_{0.6}$Sr$_{0.4}$)$_2$FeO$_{2.9}$, PrBaCo$_2$O$_{4+\delta}$, and La$_2$NiO$_{4+\delta}$ thin films. For Sogaard, the most realistic interpretation of this second added time constant was related to a chemical diffusion process, and the argument was made that in some cases even a third time constant had to be added to correctly fit experimental results. Kim et al. attributed the double kinetic model to the existence of two independent regions in PrBaCo$_2$O$_{4+\delta}$ and La$_2$NiO$_{4+\delta}$ films, where the different exchange rates were related to different film microstructures that can induce different chemical reactions at the film surface. In the specific case of LNO films, Kim et al. considered their material formed by two regions of different surface morphology. The slow exchange kinetics was associated to the expected (001) surface of the c-axis oriented LNO films, while the faster exchange kinetics was assigned to the (110) and (100) LNO surface facets, which appeared after the ECR experiments, as detected by XRD.

In Fig. 7 we plot the $k_{\text{Ex}}$ values, extracted from the fast process with time constant $\tau_1$, as a function of temperature for both oxidation and reduction processes for the two film thicknesses. The four graphs correspond to the four different final oxygen pressures reached in the reaction chamber after gas switching. No substantial differences between the oxidation and the reduction surface exchange coefficients are observed. On the contrary, a clear difference between the two film thicknesses is detected, $k_{\text{Ex}}$ being higher in the thick than in the thin layer. The difference seems to increase as the final $p_{O_2}$ decreases. In fact, surface exchange coefficients of both thicknesses are similar at 1 atm of $O_2$. These differences could be basically explained in terms of the larger surface roughness observed in the thick film, which enhances the exchange rate. The increase of the roughness directly enlarges the effective surface. Besides, it could also enhance the oxygen exchange activity, either by the formation of kinks or by the exposure of the exchange gas, to more reactive faces of the LNO structure. The film strain and oxygen content may also vary with thickness; therefore, we cannot rule out an influence of these parameters on the oxygen surface exchange values. Some authors have found higher surface exchange coefficients for bulk ceramic samples in comparison with the same material prepared as thin films. This difference can be related to a different orientation present in polycrystalline materials, as also seems to be the case in the layers prepared by Kim et al., but also could relate to the influence of grain boundaries and even grain boundary impurities, which could act in some cases as preferential sites for surface oxygen exchange.

**Conclusions**

We have grown high-quality, epitaxial c-axis oriented La$_2$NiO$_{4+\delta}$ thin films by the PIMOCVD technique. We have prepared films with different thickness onto STO and NGO substrates. High-temperature electrical conductivity measurements have shown that decreasing film thickness enhances the electrical conductivity to values over those found for single crystal. In order to precisely correlate the relation between thickness, strain, microstructure, and conductivity enhancement detected in the present work, the preparation of thinner samples on different substrates and their characterization at different temperatures and oxygen partial pressures is underway. We have
also studied the chemical surface exchange coefficients by the electrical conductivity relaxation technique. As some ECR data could not be fitted with one single exponential function, we have introduced a double-exponential fitting model. The oxygen surface exchange coefficient is thermally activated and no major differences were found between the oxidation and reduction reaction steps. The thick LNO film presented higher surface exchange coefficient values than the thin one. This could either be an effect of the surface roughness or could be associated to the differences in cell parameters and δ associated to the different strain in the film, in the case of electrical conductivity.

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Figure 7. Surface exchange coefficient for the 335 nm LNO film on STO and the 50 nm LNO film on NGO as a function of temperature for gas switches, with final oxygen pressure of (a) 1, (b) 0.50, (c) 0.25, and (d) 0.125 atm. The dotted lines serve as eye guidelines for the data corresponding to each LNO film.