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La(Ni,Fe)O₃ Stability in the Presence of Chromia—A Solid-State Reactivity Study

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The perovskite La(Ni_{0.6}Fe_{0.4})O₃ (LNF) is a candidate material for the electrochemically active cathode layer, the cathode current collecting layer, and/or the interconnect protective coating in intermediate temperature solid oxide fuel cells (IT-SOFCs) operated at 600–800°C. Since these operating temperatures enable the use of relatively cheap interconnect materials such as chromia-forming ferritic stainless steel, investigation of the chemical stability of LNF in the presence of chromium species is of importance. This study demonstrates that LNF is chemically unstable at 800°C when it is in direct contact with Cr₂O₃. It has been observed that Cr enters the perovskite phase, replacing first Ni and then Fe, already after 200 h. At 600°C, however, only minor reaction products were detected after 1000 h exposure to Cr₂O₃. Although this is a promising result, long-term testing under fuel cell operating conditions at 600°C is needed to prove that LNF is a viable IT-SOFC material.
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For intermediate temperature solid oxide fuel cells (IT-SOFCs), chromia-forming ferritic stainless steels can be used as bipolar plates, enhancing ease of fabrication, workability, and cost-effectiveness of the SOFC interconnects. However, the evaporation of Cr-oxide and oxy-hydroxide species from these metal separator plates in an oxygen-rich atmosphere is known to be highly detrimental to the functioning of common SOFC cathode materials such as (La,Sr)MnO₃ or (La,Sr)CoO₃ perovskite.^{1,2} This may be due to the poisoning of electrochemically active sites or the formation of secondary phases with low electrical conductivity.

It has recently been found that La(Ni,Fe)O₃-based cathodes have higher resistance to chromium poisoning.^{3,4} Of particular interest is La(Ni_{0.6}Fe_{0.4})O₃ (LNF) which exhibits high electronic conductivity and a thermal expansion coefficient matching that of zirconia, a common SOFC electrolyte material.⁵ Optimization of the microstructure of the LNF-cathode with respect to lateral conductivity and three phase boundaries at the electrode-electrolyte interface, has been shown to result in enhanced electrochemical performance.⁶ However, recent endurance test data obtained at ECN on SOFCs with an LNF cathode at operating temperatures of 800–850°C, showed degradation in cell performance when tested in combination with a chromium containing metallic interconnect,⁷ despite the claimed Cr-resistance of LNF in the literature.

Besides its application as a cathode material, LNF can be used as a cathode current collecting layer and/or an interconnect coating. Therefore, a thorough understanding of the true extent of LNF chemical stability in the presence of Cr species is vital for its application in SOFC systems when ferritic steel interconnects are used. The transport of Cr-species is known to take place along two pathways, through vapor phase transport or through solid-state diffusion.^{2,8} The present study deals with the solid-state reactivity between LNF and Cr₂O₃ in the IT-SOFC operating temperature range of 600–800°C. In addition, due to the gradient of the oxygen partial pressure throughout the cathode layer, caused by the applied overpotential under load, it is also important to investigate the reactivity at partial oxygen pressures lower than atmospheric. To this end, mixtures of LNF and Cr₂O₃ were heated at 600–800°C in a wide *p*O₂ range and possible changes in the phase composition of LNF were analyzed by means of X-ray diffraction (XRD).

Experimental

Powders of La(Ni_{0.6}Fe_{0.4})O₃ (Praxair, 99.9%) and Cr₂O₃ (Alfa Aesar, 99%) were used for the determination of the reactivity of Cr₂O₃ with La(Ni_{0.6}Fe_{0.4})O₃. The LNF raw material contained trace amounts of unreacted La₂O₃, which disappeared after heating at 800°C for 1 h in air. Therefore, in all experiments reported below this pretreated powder was used, and the abbreviation LNF used below refers to this pretreated powder.

Both LNF and Cr₂O₃ powders were thoroughly mixed in weight ratios of 10:1, 10:3, and 10:5. The mixing procedure included overnight rolling of polyethylene bottles containing the powder mixture and zirconia milling balls. Subsequently, these powder mixtures were heated at 800°C for 200 h and at 600°C for 200 or 1000 h. The heating was conducted either in ambient air or in a flowing gas mixture of O₂, N₂, or Ar of the desired *p*O₂ level (2×10^{-2} , 4×10^{-3} , 6×10^{-5} atm) which was monitored using a zirconia oxygen analyzer (Systech, model ZR 893/4). The heating and cooling rates were 100°C/h. The resulting samples were examined at room temperature by powder XRD using a Philips X'Pert diffractometer, equipped with a X'Celerator, operating with Cu K α radiation in steps of 0.02° (2 θ) and 10 s counting time in a 2 θ range between 10 and 140°. The lattice parameters were obtained by fitting the XRD spectra using the Le Bail method⁹ implemented in the LHPM-RIETICA software.¹⁰

As a reference, the thermal stability of pure LNF was investigated by means of prolonged heating at 600–800°C in a wide *p*O₂ range followed by XRD-analysis and by in-situ high temperature-XRD using a Bruker D8 Advance diffractometer equipped with an MRI chamber as the heating device and operating in Bragg Brentano mode.

To check whether full thermodynamic equilibrium had been reached in some heated LNF-Cr₂O₃ powder mixtures, additional heat-treatments were conducted on selected samples in air at 1400°C for 24 h. For the same reason, some perovskite compositions in the La(Ni,Fe,Cr)O₃ system were prepared via a standard solid-state reaction method and sintered in air at 1400°C for 24 h.

Results and Discussion

The following sections describe the results concerning the stability of LNF in direct solid-state contact with Cr₂O₃-powder at 800 and 600°C in a wide *p*O₂ range. The thermal stability of pure LNF is discussed first, followed by the XRD analysis of the reactivity between LNF and Cr₂O₃ at 800 and 600°C, respectively.

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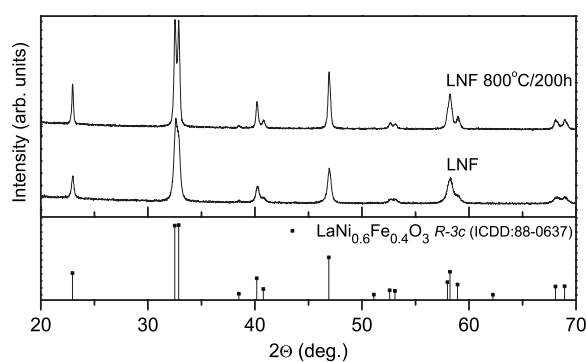


Figure 1. X-ray powder diffraction patterns of $\text{La}(\text{Ni}_{0.6}\text{Fe}_{0.4})\text{O}_3$ compound (initial LNF and LNF heated at 800°C in air for 200 h).

Thermal stability of pure LNF.—Figure 1 and Table I show the XRD patterns and cell parameters of the starting LNF material and LNF material after heating at 800°C in air for 200 h. Prolonged heating in air resulted in enhanced crystallinity as compared with the starting LNF material (Fig. 1). Double splitting of the main reflection, characterizing the rhombohedral distortion of the ideal perovskite structure, was clearly visible at $32^\circ < 2\theta < 33^\circ$ for the LNF sample heated at 800°C in air for 200 h. The resulting fitted cell parameters of both LNF samples were identical within the given errors (Table I) and comparable to previously reported values,¹¹ demonstrating that LNF remains the same phase after prolonged heating in air. High temperature XRD analysis in the $800\text{--}1200^\circ\text{C}$ range in air shows that $\text{La}(\text{Ni}_{0.6}\text{Fe}_{0.4})\text{O}_3$ also remained in the *R-3c* rhombohedral structure, indicating the stability of the LNF phase in the given temperature regime. In all cases, neither impurities (such as NiO) nor other phases were found, which further proves the intrinsic thermal stability of the LNF compound.

Interestingly, 200 h heating of LNF in a $p\text{O}_2$ as low as 6×10^{-5} atm at 800°C did not result in perovskite phase decomposition. Moreover, the fitted lattice parameters of all rhombohedral LNF samples heat-treated at 800°C in a wide $p\text{O}_2$ range exhibited comparable values within the range of one to three standard deviations.

LNF and Cr_2O_3 reactivity at 800°C .—Mixture 10LNF + $1\text{Cr}_2\text{O}_3$.—For the mixture of 10LNF + $1\text{Cr}_2\text{O}_3$ heated at 800°C in air for 200 h, the analysis of the XRD spectra revealed NiO and two perovskite phases: orthorhombic *Pbnm* and rhombohedral *R-3c* (Fig. 2). No presence of Cr_2O_3 was observed, suggesting that it had

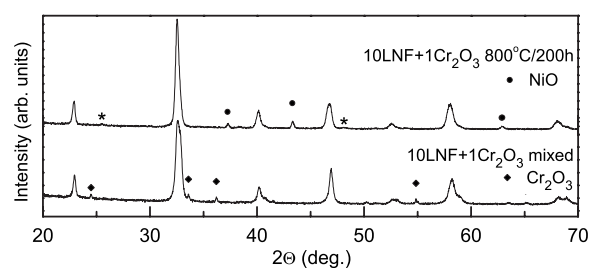


Figure 2. X-ray powder diffraction patterns of the mixture 10LNF + $1\text{Cr}_2\text{O}_3$ (only mixed and heated at 800°C in air for 200 h). The presence of the orthorhombic *Pbnm* phase is marked by * at the distinctive reflection angles where the specific Bragg reflections for the orthorhombic phase are visible.

completely reacted with LNF. The fitted cell parameters of the two perovskite phases are summarized in Table I. This table shows that the rhombohedral phase has comparable cell parameters as LNF, suggesting that LNF was still present in the mixture. The coexistence of the two perovskite phases is supported by the fact that the fit with only an orthorhombic or a rhombohedral phase resulted in the inferior reliability factors and worse accuracy of the fit. The presence of NiO, LNF, as well as the absence of Cr_2O_3 , implies that Ni was partially extracted from the LNF perovskite lattice, whereas Cr was incorporated, most likely to form an orthorhombic $\text{La}(\text{Ni},\text{Fe},\text{Cr})\text{O}_3$ phase.

The observed reactivity of LNF with Cr_2O_3 is in agreement with thermodynamic calculations,¹² which predict the instability of LNF in combination with Cr_2O_3 and the precipitation of NiO. However, a similar study¹³ suggests that only the rhombohedral LNF and NiCr_2O_4 were formed. The difference in results with Ref. 13 is hard to explain, but might have resulted from NiO-impurity that was reported in their initial LNF.

To investigate whether the 10LNF + $1\text{Cr}_2\text{O}_3$ -mixture had reached thermodynamic equilibrium at 800°C , the same mixture was heated in air at 1400°C for 24 h in order to accelerate the reaction between the two components. Figure 3 shows X-ray diffraction peaks evolution in the 2θ range of $39\text{--}41^\circ$ of LNF and the mixture of 10LNF + $1\text{Cr}_2\text{O}_3$ heated at different temperatures. The chosen 2θ range of $39\text{--}41^\circ$ is characteristic for the detection of the presence of rhombohedral and orthorhombic perovskite phases.¹⁴ For the pure LNF, heated at 800°C in air for 200 h, two single peaks appearing in the studied 2θ range can be indexed as $(202)_r$ and $(006)_r$ of the rhombohedral phase. In the sample 10LNF + $1\text{Cr}_2\text{O}_3$

Table I. Structural properties of investigated perovskites heated in air.

| Composition | Space group | a [Å] | b [Å] | c [Å] | V [Å] ³ |
|---|-------------|-----------|-----------|------------|--------------------|
| LNF ¹¹ | <i>R-3c</i> | 5.5047(1) | — | 13.2642(1) | 348.06 |
| LNF | <i>R-3c</i> | 5.5032(9) | — | 13.267(2) | 347.98(9) |
| LNF $800^\circ\text{C}/200$ h | <i>R-3c</i> | 5.5039(5) | — | 13.267(1) | 348.07(5) |
| 10LNF + $1\text{Cr}_2\text{O}_3$ $800^\circ\text{C}/200$ h | <i>R-3c</i> | 5.5015(4) | — | 13.274(9) | 347.94(4) |
| | <i>Pbnm</i> | 5.5273(4) | 5.4773(4) | 7.8145(5) | 236.58(3) |
| 10LNF + $1\text{Cr}_2\text{O}_3$ $1400^\circ\text{C}/24$ h | <i>Pbnm</i> | 5.5325(1) | 5.5101(1) | 7.7982(2) | 237.72(1) |
| $\text{La}(\text{Ni}_{0.28}\text{Fe}_{0.40}\text{Cr}_{0.32})\text{O}_3$ | <i>Pbnm</i> | 5.5311(1) | 5.5081(1) | 7.7958(2) | 237.51(1) |
| $\text{La}(\text{Ni}_{0.1}\text{Fe}_{0.4}\text{Cr}_{0.5})\text{O}_3$ | <i>Pbnm</i> | 5.5352(1) | 5.5163(1) | 7.8026(2) | 238.24(1) |
| $\text{La}(\text{Ni}_{0.5}\text{Fe}_{0.4}\text{Cr}_{0.1})\text{O}_3$ | <i>Pbnm</i> | 5.5326(1) | 5.4735(1) | 7.7574(2) | 234.44(1) |
| 10LNF + $3\text{Cr}_2\text{O}_3$ $800^\circ\text{C}/200$ h | <i>Pbnm</i> | 5.5132(4) | 5.4897(6) | 7.8070(4) | 236.29(3) |
| 10LNF + $5\text{Cr}_2\text{O}_3$ $800^\circ\text{C}/200$ h | <i>Pbnm</i> | 5.5066(5) | 5.4885(5) | 7.8093(7) | 236.02(4) |

Note: Le Bail full pattern decomposition method yielded in all cases the reliability factors of $R_p = 3\text{--}4\%$ and $R_{wp} = 5\text{--}6\%$ with accuracy of the fit $\chi^2 = 1.3\text{--}1.4$. The standard deviation of the last digit is given in parentheses.

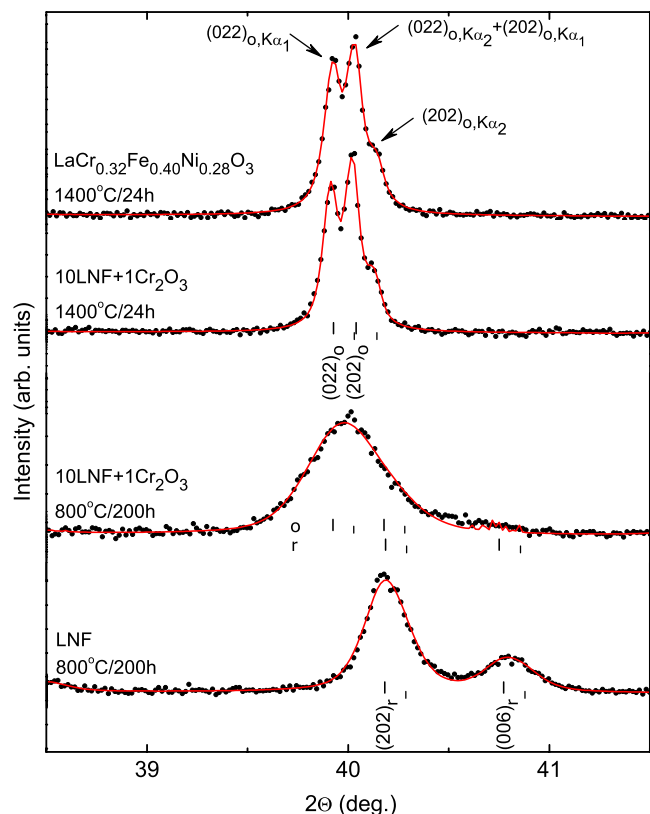


Figure 3. (Color online) X-ray diffraction peaks variation in the 2θ range $39\text{--}41^\circ$ of LNF and the mixture $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ heated in air at different temperatures. The continuous line is the Le Bail fit using the space group $R\text{-}3c$ and/or $Pbnm$. For a doublet peak $(022)_o$ and $(202)_o$, additional splitting due to $K\alpha_1$ and $K\alpha_2$ radiations is visible (denoted by arrows). In all cases the longer and shorter bars correspond to $K\alpha_1$ and $K\alpha_2$ radiations, respectively.

heated at 800°C in air for 200 h, the small $(006)_r$ peak was very weak and the single peak, $(202)_r$, began evolving into a doublet peak, indicating the presence of both rhombohedral and orthorhombic perovskite phases. This observation was supported by better reliability factors and higher accuracy of the fit obtained for a two perovskite system as compared to the fitting with only a single perovskite. For the same mixture of $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ but heated at 1400°C for 24 h, the single peak changed completely into a doublet peak indexed as $(022)_o$ and $(202)_o$ of the orthorhombic phase. No peak identified as rhombohedral phase was detected. Therefore, due to the fact that after cooling down from 1400°C to room temperature only a single orthorhombic phase was observed, it is very likely that the Cr containing orthorhombic perovskite is a thermodynamically stable phase over the whole temperature range of $20\text{--}1400^\circ\text{C}$. As a consequence, this indicates that the sample $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ heated at 800°C for 200 h has not yet reached thermodynamic equilibrium, most likely due to the slower reaction kinetics as compared to 1400°C . For the sample sintered at 1400°C for 24 h, the composition of the orthorhombic perovskite phase can be calculated by completely replacing Ni in the LNF lattice by chromium, resulting in the composition $\text{La}(\text{Ni}_{0.28}\text{Fe}_{0.40}\text{Cr}_{0.32})\text{O}_3$ (under the assumption that the amount of Cr lost due to the possible vaporization process is negligible, as indicated by a minor Cr weight change of less than 0.5 wt %). As a final check, this perovskite phase was prepared by means of a standard solid-state reaction method with a final sintering step in air at 1400°C for 24 h. The resulting X-ray pattern (see Fig. 3 and Table I) indicates that the composition $\text{La}(\text{Ni}_{0.28}\text{Fe}_{0.40}\text{Cr}_{0.32})\text{O}_3$ exists as a single phase with an orthorhombic $Pbnm$ structure.

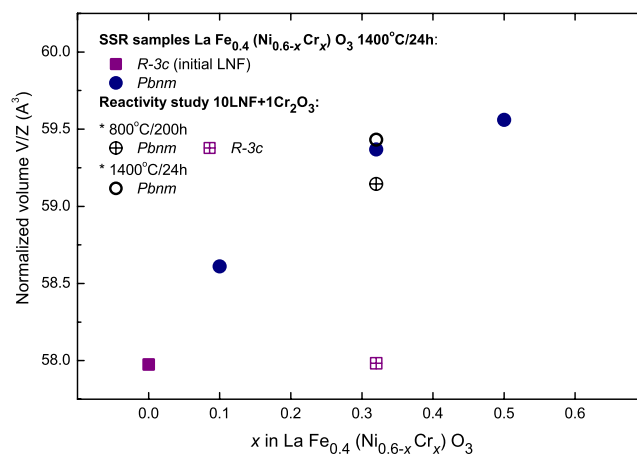


Figure 4. (Color online) Variation of the normalized cell volume as the function of Cr amount in the $\text{LaFe}_{0.4}(\text{Ni}_{0.6-x}\text{Cr}_x)\text{O}_3$ series. Additionally, values for $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ samples heated in air are included.

Until now, no crystallographic data concerning the perovskites belonging to the $\text{La}(\text{Ni},\text{Fe},\text{Cr})\text{O}_3$ system have been available. Therefore, three different compositions of the $\text{LaFe}_{0.4}(\text{Ni}_{0.6-x}\text{Cr}_x)\text{O}_3$ series were prepared to further confirm the existence of a perovskite solid solution phase where Ni is replaced by Cr in LNF. The X-ray diffraction analysis shows that the $\text{LaFe}_{0.4}(\text{Ni}_{0.6-x}\text{Cr}_x)\text{O}_3$ series samples with $x = 0.1, 0.32, 0.5$ adopt an orthorhombic structure with the space group $Pbnm$. An increase in cell parameters and cell volume following Vegard's law was observed on the successive replacement of the smaller nickel-ion by the larger chromium-ion. The standard six-coordinate ionic radii of Ni^{3+} and Cr^{3+} is 0.60 and 0.615 Å, respectively.¹⁵

Figure 4 shows the increase in normalized volume V/Z , where V is the unit cell volume and Z is the number of formulas per unit cell, with increasing Cr-content. This figure also provides the normalized volume data of the orthorhombic and rhombohedral perovskite phase of the $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ sample heated at 800°C in air for 200 h. It is observed that the normalized volume of the rhombohedral phase in the mixture is equal to the normalized volume of LNF. The orthorhombic phase in the mixture has a slightly lower normalized volume than the expected orthorhombic perovskite $\text{La}(\text{Ni}_{0.28}\text{Fe}_{0.40}\text{Cr}_{0.32})\text{O}_3$, indicating a lower Cr-content, which is in agreement with the fact that this mixture still contains the rhombohedral LNF and has not yet reached equilibrium.

Figure 4 also shows that an increase in the temperature to $1400^\circ\text{C}/24\text{ h}$ for the $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ mixture results in a perovskite cell volume corresponding with $\text{La}(\text{Ni}_{0.28}\text{Fe}_{0.40}\text{Cr}_{0.32})\text{O}_3$, which proves that all available Cr can be incorporated into the perovskite lattice. In sum, although the thermodynamic equilibrium was probably not yet reached for the sample $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ heated for 200 h at 800°C in air, the reactivity between LNF and Cr_2O_3 was clearly demonstrated.

In the case of the heated mixtures of $10\text{LNF} + 1\text{Cr}_2\text{O}_3$ at $p\text{O}_2$ lower than atmospheric (2×10^{-2} , 4×10^{-3} , 6×10^{-5} atm) the XRD analysis revealed exactly the same phases as observed in air. The obtained lattice parameters of both orthorhombic and rhombohedral phases of the mixtures heated under low oxygen partial pressures were comparable with the cell parameters of the perovskite phases in the mixtures heated in air within the range of one to three standard deviations. Consequently, lowering the oxygen partial pressure results in a similar reactivity between LNF and Cr_2O_3 (for the sample of 10:1 ratio) as observed in air, which means that Ni in LNF is substituted by Cr and the mixture has not yet reached equilibrium.

Mixture $10\text{LNF} + 3\text{Cr}_2\text{O}_3$ and $10\text{LNF} + 5\text{Cr}_2\text{O}_3$.— The X-ray diffraction analysis of the sample $10\text{LNF} + 3\text{Cr}_2\text{O}_3$ heated at 800°C

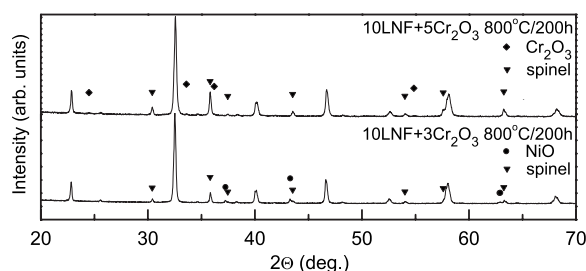


Figure 5. X-ray powder diffraction patterns of the mixtures 10LNF + 3Cr₂O₃ and 10LNF + 5Cr₂O₃ heated at 800°C for 200 h.

for 200 h in the pO_2 range of 2×10^{-1} – 6×10^{-5} atm showed the presence of an orthorhombic perovskite phase, a spinel phase, and NiO (Fig. 5). The initial rhombohedral LNF-phase was no longer observed, indicating a complete reaction of LNF with Cr₂O₃. Interestingly, in the samples heated at pO_2 above 4×10^{-3} atm no Cr₂O₃ was found, whereas trace amounts of Cr₂O₃ could be detected for the sample exposed to pO_2 as low as 6×10^{-5} atm. The presence of trace amounts of chromium oxide at a pO_2 of 6×10^{-5} atm suggests a lower reactivity of Cr₂O₃ under this condition, which might indicate that vapor phase transport of Cr-species plays a role in the reaction mechanism, given the fact that volatile chromium species are less present under low partial oxygen pressures.⁸

In the sample 10LNF + 5Cr₂O₃ heated at 800°C for 200 h in a wide pO_2 range, the main phase detected was an orthorhombic perovskite phase, resembling the Cr-rich La(Fe,Cr)O₃ phase (Table I). This result suggests that first Ni is being replaced by Cr, followed by the replacement of Fe by Cr. Next to this perovskite phase, for every partial oxygen pressure condition, a significant amount of a spinel phase was detected, together with a trace amount of unreacted Cr₂O₃, while NiO was not detected (Fig. 5). The spinel phase identified in the case of 10LNF + 3Cr₂O₃ and 10LNF + 5Cr₂O₃ mixtures can generally be described as (Ni,Fe)(Fe,Cr)₂O₄. In these samples, no rhombohedral LNF-phase was present, again indicating a complete reaction of LNF with Cr₂O₃.

For the discussed samples of 10LNF + x Cr₂O₃ ($x = 1,3,5$) heated at 800°C, the lower pO_2 exposure conditions did not influence either the reactivity or the lattice parameters, which were comparable with the variations in the range from one to three standard deviations.

The current study on the reactivity between LNF and Cr₂O₃ at 800°C demonstrates that chromium enters the perovskite phase, replacing first Ni and then Fe in the investigated pO_2 -range. The observed order of the precipitation (first Ni, then Fe) from the initial LNF perovskite phase correlates well with the relative thermodynamic stability of the perovskites: LaCrO₃ > LaFeO₃ > LaNiO₃.¹⁶

The substitution of Cr into the LNF lattice may result in a decrease of the electronic conductivity, similar to that reported for the La(Ni_{1-x}Cr_x)O₃ system.¹⁷ This might have significant implications for the ohmic losses across an LNF layer exposed to Cr during a fuel cell operation under the given conditions. Moreover, LNF crystal structure change from rhombohedral to orthorhombic induced by Cr might seriously affect the electrochemical activity of the LNF material. A comprehensive investigation of the lateral conductivity of the La(Ni,Fe)O₃ layer exposed to the Cr will be reported soon.¹⁸

LNF and Cr₂O₃ reactivity at 600°C.— The previous section showed that the thermodynamic equilibrium in a mixture of LNF and Cr₂O₃ depends on the temperature levels and the exposure time. Equilibrium was not reached after 200 h at 800°C, but increasing the temperature to 1400°C did result in an equilibrium composition. Consequently, lowering the temperature is expected to hinder the reactivity between LNF and Cr₂O₃. Therefore, a similar reactivity study was conducted at 600°C for 200 h and also for a prolonged period of 1000 h.

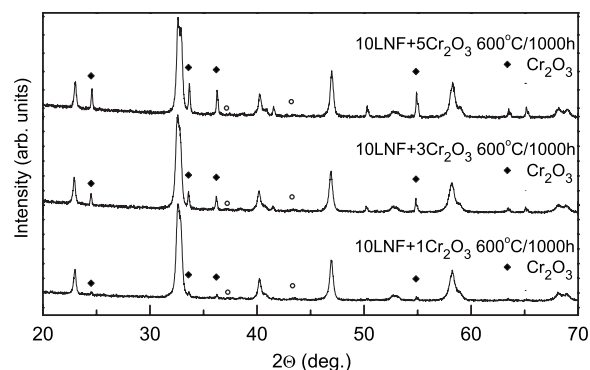


Figure 6. X-ray powder diffraction patterns of 10LNF + x Cr₂O₃ mixtures ($x = 1,3,5$) heated in air at 600°C for 1000 h. The presence of the trace amounts of NiO is marked by ° at the most intensive Bragg reflections.

The XRD-analysis of the 10LNF + x Cr₂O₃ mixtures ($x = 1,3,5$) heated in air at 600°C for 200 h and ultimately for 1000 h revealed no reaction between the two compounds: In all cases only rhombohedral LNF and unreacted Cr₂O₃ were found, however, trace amounts of NiO appeared (Fig. 6). Lowering the partial oxygen pressure gave the same results as obtained in the reactivity test in air. The fitted lattice parameters of all samples heat-treated at 600°C under all pO_2 conditions exhibited comparable values within the range of one to three standard deviations. However, the influence of Cr cannot be neglected even at 600°C as the minor appearance of NiO might indicate some influence of Cr on the phase composition. Presumably, some reaction between Cr and the perovskite could possibly take place at the surface of the LNF-grains. NiO may nucleate and form a minor second phase. The Cr-substitution into the LNF-perovskite might take place in a thin subsurface layer in the pure LNF grains creating a core-shell like structure. The formed reaction layer might be too thin to observe a change in the perovskite lattice parameters using XRD. This phenomenon needs further investigation.¹⁸

The application of LNF at 600°C as a Cr-resistant cathode or contact coating would seem to be feasible, but this ought to be tested under long-term fuel cell operating conditions.¹⁸ Such a low operating temperature of 600°C might require improvement of the LNF-cathode electrochemical activity possibly by means of composite structure or cathode infiltration.

Conclusions

This study demonstrates the intrinsic instability of the LNF cathode when it is in direct contact with Cr₂O₃ at 800°C. This situation may occur in the cathode compartment of a SOFC stack, where the Cr-containing metallic interconnect is in direct contact with this cathode or with a contact coating material. The rate of the chromium reaction with LNF has been demonstrated to depend on the temperature levels and the exposure time. Lowering the operating temperature to 600°C resulted in a very low chromium reactivity with LNF: No reaction was observed with XRD. Thus, LNF at 600°C would seem to offer promising opportunities concerning its use as a Cr-resistant cathode or contact coating. Nevertheless, further investigations remain necessary, especially under long-term fuel cell operation conditions.

The solid state reactivity between LNF and chromium oxide is not significantly influenced by the level of the pO_2 , at least not within the pO_2 range studied herein. This result might indicate that Cr-poisoning of LNF, by solid state diffusion and subsequent solid state reactivity, would be the same along the depth of the operating LNF cathode when only taking partial oxygen pressure gradients into account. However, gas diffusion of volatile chromium species may play an additional role in the actual distribution of Cr throughout the cathode layer.

Acknowledgments

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