Long-Term Chemical Stability of LaNi(Fe)O$_3$ as a Cathode Material in Solid Oxide Fuel Cells

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Chemical reactivity of LaNi$_{0.6}$Fe$_{0.4}$O$_3$ (LNF) with Cr$_2$O$_3$ has been investigated in order to examine the long-term stability of the LNF phase at 1073 K, which shows a high performance as the cathode of intermediate-temperature solid oxide fuel cells (IT-SOFCs). The chemical stability of LNF was compared with that of La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) under the existence of Cr$_2$O$_3$. The LNF powder, a powder mixture of LNF and Cr$_2$O$_3$, and a powder mixture of LSM and Cr$_2$O$_3$ were, respectively, heated at 1073 K, and they are analyzed by X-ray powder diffraction with the Rietveld refinement. We found that the LNF phase maintains the hexagonal crystal system heated in air up to 1000 h. In the LNF-Cr$_2$O$_3$ mixture, the LNF phase kept its pristine crystal structure while a new phase, NiCr$_2$O$_4$, was detected, which was produced by the reaction between Cr$_2$O$_3$ and the residual NiO contained in the starting LNF powder. In the LSM-Cr$_2$O$_3$ mixture, LSM reacted with Cr$_2$O$_3$ and produced a significant amount of MnCr$_2$O$_4$. LNF showed a much better chemical stability against Cr$_2$O$_3$ than LSM. LNF can serve as a long-life cathode in the IT-SOFC system.
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Intermediate-temperature ($<$1073 K) solid oxide fuel cells (SOFCs) have recently attracted much attention because they can use metallic alloys as separators, which reduces material costs. However, it has been reported that Cr poisoning degrades the electrochemical properties of the cathode in SOFCs using metallic separators.[1-3] Furthermore, intermediate-temperature operation may lower the electrochemical performance of the SOFCs. Sr-doped LaMnO$_3$ (LSM) has been widely used as a cathode material in intermediate-temperature SOFCs, but, when the operating temperature is reduced, the electrode performance of LSM considerably decreases. Therefore, achieving high performance in SOFC requires a cathode material that has high electronic conductivity, high electrochemical activity for oxygen reduction, and good stability against Cr poisoning.

We have examined LaNi(Fe)O$_3$ as a cathode material for intermediate-temperature SOFCs.[4-6] LaNi$_{1-x}$Fe$_x$O$_3$ has an orthorhombic or hexagonal perovskite structure at room temperature when $x > 0.5$ or $x = 0.4$, respectively. For $x < 0.4$, two-phase mixtures were observed.[4] LaNi$_{0.6}$Fe$_{0.4}$O$_3$ (LNF) was found to have the highest electronic conductivity of 580 S/cm at 1073 K, which is more than three times as high as that of the LSM (La$_{0.8}$Sr$_{0.2}$MnO$_3$) (180 S/cm).[4] The SOFC using LNF as the cathode material shows high performance for electric power generation, with the maximum power density of 1.56 W/cm^2 at 1073 K.[5] We have investigated the effect of Cr poisoning on various cells, consisting of either LNF or LSM as a cathode.[6] As shown in Fig. 1, it was found that the cathodic overvoltage was almost the same for cells with LNF cathodes, either in the presence or absence of Cr-containing alloy. On the other hand, in the presence of the alloy, voltage curves for the cell with LSM cathodes seriously degrade after applying the current.[6] It was thus demonstrated the cells with LNF cathodes are more stable against Cr poisoning than those with LSM cathodes. These results indicate that LNF is a promising material for the intermediate-temperature SOFC cathode. However, to our knowledge, the stability of LNF has not been thoroughly examined. It is important to examine the thermal stability of LNF because the basic framework of LNF is LaNiO$_3$, which is unstable at temperatures above 1053 K in air.[7] It is also important to know whether LNF is chemically stable against Cr$_2$O$_3$ from the viewpoint of Cr poisoning.

Estimation of the long-term stability of LNF may provide detailed knowledge about the lifetime of the SOFC using the LNF cathode. Therefore, in this work, we examined thermal stability of LNF and its chemical stability against Cr$_2$O$_3$ at 1073 K for 0–1000 h by means of X-ray diffraction measurements and a Rietveld refinement analysis.

Experimental

Sample preparation.— LaNi$_{0.6}$Fe$_{0.4}$O$_3$ powder (Powlex, Japan) was used as a sample for the evaluation of thermal stability. For the evaluation of the chemical stability of LNF against Cr$_2$O$_3$, we used a mixture of the LNF and Cr$_2$O$_3$ (Kojundo Chemical Laboratory, Japan) powders. The weight ratio of LNF to Cr$_2$O$_3$ in the mixed powder was 10:1. Similarly, La$_{0.8}$Sr$_{0.2}$MnO$_3$ powder (Seimi Chemical, Japan) was also mixed with the Cr$_2$O$_3$ powder in the same ratio. The weight ratio of LSM to Cr$_2$O$_3$ in the mixed powder was 10:1. These mixtures were heated at 1073 K in air for 100, 200, 400, 800, and 1000 h. The heating/cooling rate was 100 K/h.

X-Ray diffraction measurements and Rietveld refinement analysis.— X-ray diffraction (XRD) patterns of the powder samples were measured with an XRD instrument (Rigaku, RINT2000) powered at 100 kV and 30 mA using Cu Ka radiation in air at room
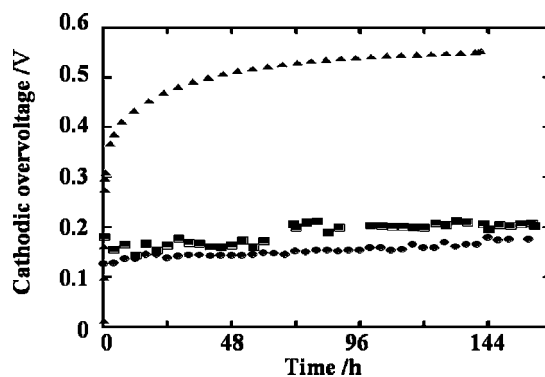

Figure 1. Cathodic overvoltage for cells as a function of time at 1073 K (derived from Ref. 6). ($\bullet$) The cell using LNF cathode with the alloy at 0.7 A/cm^2. ($\blacksquare$) The cell using LNF cathode without the alloy at 0.7 A/cm^2. ($\blacktriangle$) The cell using LSM cathode with the alloy at 0.076 A/cm^2.

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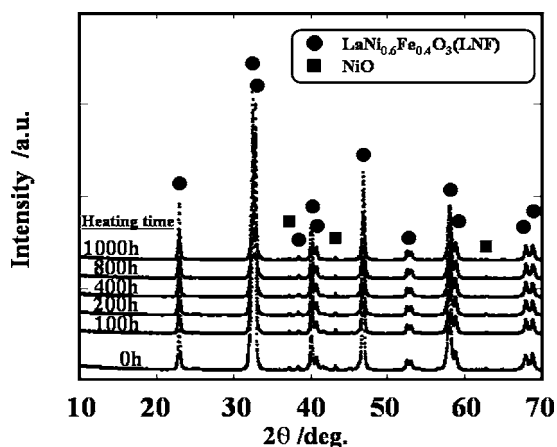z E-mail: takeshi@aecl.ntt.co.jp

Figure 2. XRD patterns of LNF powder. The samples were heated to 1073 K.
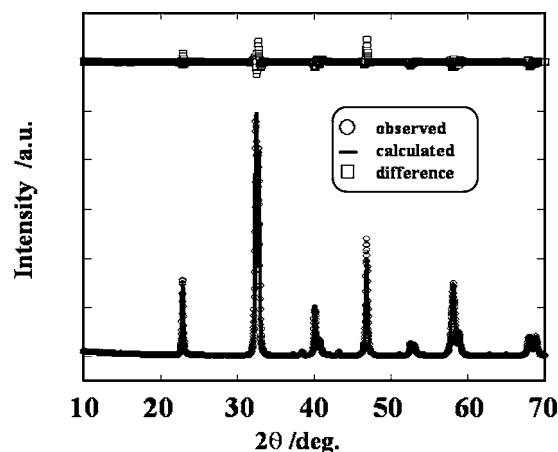

Figure 3. Rietveld refinement of the XRD pattern for LNF powder. The sample was heated for 1000 h at 1073 K.

temperature. The diffraction intensity was measured stepwise every 0.02° in the diffraction angle 2Θ range between 10° and 70°. Phase identification of the samples was made from the measured XRD pattern based on the International Center for Diffraction Data (ICDD) database. The molar ratio and lattice constant of each phase in the samples were evaluated by Rietveld analysis (RIQAS, Materials Data Inc. Company). The crystal system and initial unit cell parameters of the phases were taken from the ICDD database and the literature.

Results and Discussion

Chemical stability of LNF.— Figure 2 shows XRD patterns of the LNF ($LaNi_{0.6}Fe_{0.4}O_3$) powder that had been heated at 1073 K for 0–1000 h. LNF (ICDD:88-0637)[4] and NiO (ICDD:73-1519)[8] were identified in these XRD patterns. Other phases, such as La_2O_3, Fe_2O_3, $LaNiO_3$, and $LaFeO_3$, were not observed. Weak NiO peaks were observed in the XRD pattern of the as-received powder; this indicates that a small amount of NiO existed as an impurity phase in the as-prepared condition.

Assuming that only the identified phases ($LaNi_{0.6}Fe_{0.4}O_3$ and NiO) existed in each LNF powder, the XRD patterns were analyzed by means of the Rietveld method. $LaNi_{1-x}Fe_xO_3$ is either a hexagonal or orthorhombic system, depending on the composition ratio between Ni and Fe.[4,9,10] As an initial condition, we assumed that the crystal system (space group) of LNF was either the hexagonal system $[R\bar{3}c(167)]$[4] or orthorhombic system (P*nma*).[4] The cubic system $[Fm\bar{3}m(225)]$[8] was assumed for NiO. Initial unit cell parameters of LNF[4,9] and NiO[8,11] were taken from the literature.

For LNF in the hexagonal system, the Rietveld refinement for all samples gave reliable factor (R_{wp}) values between 13 and 17, whereas no convergence was attained when the orthorhombic systems were applied. Therefore, the hexagonal system is suitable for the LNF crystal structure. Figure 3 shows an example of Rietveld refinement for the sample heated at 1073 K for 1000 h. The observed and calculated patterns agree very well. We believe that the R_{wp} values are acceptable as they are similar to the values obtained by Fálcon et al. in their study of the crystal structure of LNF by Rietveld refinement.[9] The same refinement analysis was also conducted on other samples. It was found that LNF maintained the hexagonal system in the powder during heating at 1073 K for 0–1000 h. The change in the molar amount and lattice constant of the LNF phase was calculated from a series of Rietveld refinement.

The heating-time dependence of the refined lattice constants for the LNF phase is shown in Fig. 4. By increasing the heating time from 0–1000 h, both lattice constants slightly decreased. Figure 5 shows the molar ratio of LNF phase and NiO in the LNF powder as

a function of heating time at 1073 K, obtained by the Rietveld refinement. The molar ratio of the LNF phase increases slightly with time and simultaneously the molar ratio of NiO decreases. This behavior could be explained as follows. If NiO is taken into the LNF matrix as a solid solution, the relative amount of LNF would increase and x in the $LaNi_{1-x}Fe_xO_3$ system would decrease. Then, the lattice constants a and c would decrease because, as Chiba et al. and Fálcon et al. have reported, the radius of Ni^{2+} ion is smaller than that
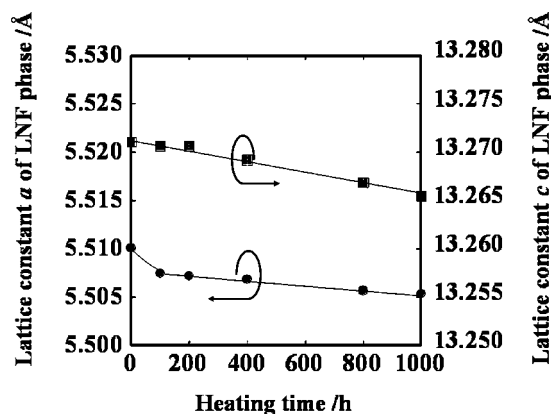

Figure 4. Lattice constants of the LNF phase during heating at 1073 K for 0–1000 h.
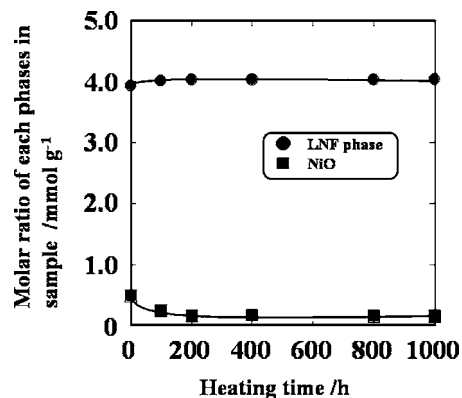

Figure 5. Molar ratio of each phase in LNF powder during heating at 1073 K for 0–1000 h.
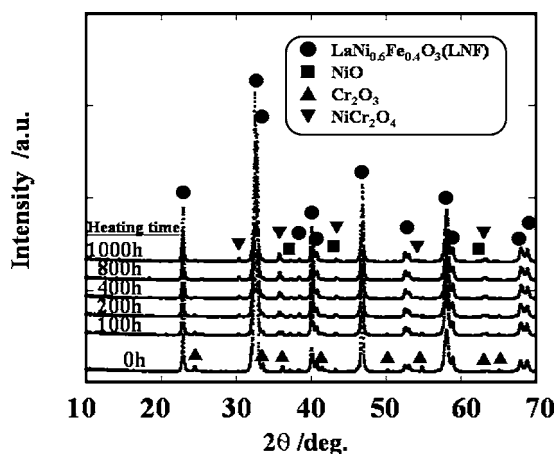
Figure 6. XRD patterns of LNF-Cr_2O_3 mixture powder. The samples were heated to 1073 K.

Figure 8. Molar ratio of phases in LNF-Cr_2O_3 mixture powder during heating at 1073 K for 0–1000 h.

of Fe^{3+} ions.[4,9] Another possible reason for the lattice constant changes is oxygen nonstoichiometry of the LNF phase. Prado et al. have reported that oxygen nonstoichiometry of $LaMnO_{3\pm\delta}$ perovskite-type oxide, which has a crystal structure similar to the LNF phase, is related to the change of the lattice constants.[11] The LNF phase could exhibit the similar behavior. As we have currently no information on the oxygen nonstoichiometry of our LNF phase, the detailed mechanism for the small change in the lattice constants is still unclear and may be a topic for future research.

Nevertheless, we have clarified that the LNF phase remains a hexagonal system and we observed no phase decomposition during heating between 0 and 1000 h. We therefore conclude that LNF is chemically stable at least below 1073 K.

Chemical stability against Cr_2O_3 of LNF.— The XRD patterns of the LNF-Cr_2O_3 mixture that had been heated at 1073 K in air for 0–1000 h were measured. Figure 6 shows the XRD patterns obtained from the mixture powder. $NiCr_2O_4$ (ICDD:75-0198)[12] was identified in the XRD patterns in addition to the raw materials, namely, LNF, NiO, and Cr_2O_3 (ICDD:38-1479).[13] The peaks for other phases, such as $LaCrO_3$, were not observed, suggesting that the reactivity of LNF phase with Cr_2O_3 was low.[14]

Assuming that the mixture consisted of LNF, NiO, Cr_2O_3, and $NiCr_2O_4$, we analyzed the XRD patterns by means of the Rietveld method. The initial unit cell parameters of LNF, NiO, Cr_2O_3[12,13] and $NiCr_2O_4$[13,15] were taken from the literature.
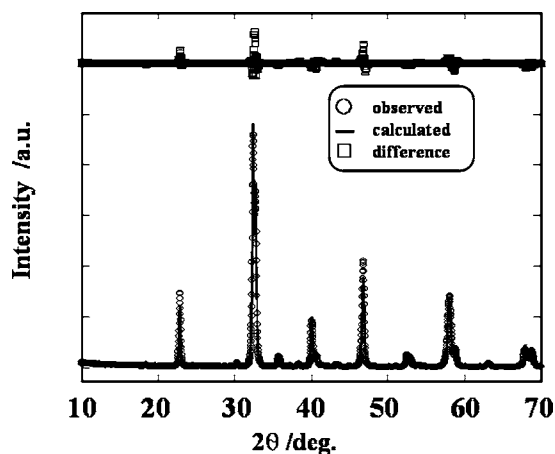
Figure 7 shows an example of the Rietveld refinement. Using the hexagonal setting for the LNF phase, the observed and calculated patterns agreed very well with the R_{wp} value of 16. The Rietveld refinement gave R_{wp} values between 13 and 17 for the LNF-Cr_2O_3 mixture. These values are similar to those of the Rietveld refinements of the LNF powder. These results suggest that the fitting for the mixture was again appropriate. It was found that the LNF phase remained a pristine hexagonal system even when there was Cr_2O_3 in the mixture.

Figure 8 shows the molar ratio of LNF, NiO, Cr_2O_3, and $NiCr_2O_4$ in the LNF-Cr_2O_3 mixture powder as a function of heating time at 1073 K. The molar ratio of LNF was nearly unchanged. On the other hand, the molar ratio of $NiCr_2O_4$ increased while that of NiO and Cr_2O_3 decreased, suggesting that $NiCr_2O_4$ was mainly caused by the reaction between NiO and Cr_2O_3. It was found that Cr_2O_3 still existed in the mixture after it had been heated for 1000 h.

For comparison, LSM-Cr_2O_3 mixture powder was heated to examine the reactivity of Cr_2O_3 with LSM. The XRD pattern of LSM-Cr_2O_3 mixture powder that had been heated at 1073 K for 1000 h was measured. LSM ($La_{0.8}Sr_{0.2}MnO_3$, ICDD:53-0058)[16] and $MnCr_2O_4$ (ICDD:75-1614)[17] were identified in the XRD patterns, but no Cr_2O_3 was found. It is obvious that Cr_2O_3 reacted with LSM and was consumed to form $MnCr_2O_4$. This confirms that LNF is less reactive with Cr_2O_3 than LSM is.

Conclusions

LNF powder was heated for 0–1000 h at 1073 K in air and analyzed by XRD measurements and the Rietveld refinement. It was found that the LNF phase kept its hexagonal system, and no reaction product was observed, which suggests that LNF is chemically stable itself.

Similarly, LNF-Cr_2O_3 and $La_{0.8}Sr_{0.2}MnO_3$(LSM)-Cr_2O_3 mixtures were heated at 1073 K in air. It was found that the LNF phase maintains its hexagonal system in the mixture powder at 1073 K during heating for 0–1000 h. $NiCr_2O_4$ was predominantly produced when the residual NiO in the LNF powder reacted with the Cr_2O_3 powder. We hardly observed peaks of other phases, such as $LaCrO_3$. From the viewpoint of the consumption of Cr_2O_3 in the mixtures, LNF powder was less reactive with Cr_2O_3 than LSM powder. Since LNF cathodes have high stability against Cr poisoning due to the low reactivity of LNF with Cr_2O_3, we can expect that LNF can serve as a long-life cathode in the SOFC systems compared with LSM.

Figure 7. Rietveld refinement of the XRD pattern for LNF-Cr_2O_3 mixture powder. The sample was heated for 1000 h at 1073 K.

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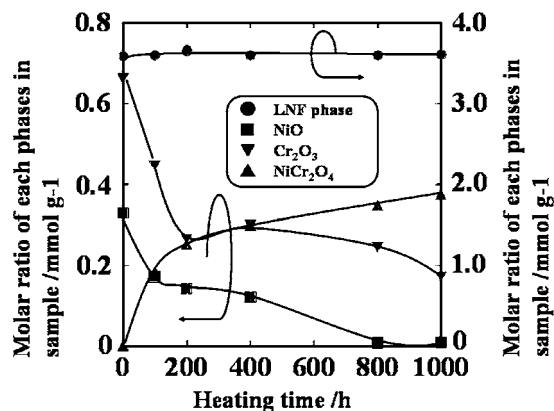
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