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LaNi$_{1-x}$Fe$_x$O$_3$ solid solutions are an interesting system exhibiting a composition-controlled metal-insulator transition and are also potential cathode materials for solid oxide fuel cells, but the composition dependence of their electrical conductivity is still an open question due to the difficulty in synthesis and sintering. Here, in contrast to previous studies, it is demonstrated that the electrical conductivity of LaNi$_{1-x}$Fe$_x$O$_3$ monotonically increases with decreasing $x$ (increasing Ni content), reaching as high as $1.0 \times 10^2$ S cm$^{-1}$ at room temperature and $2.5 \times 10^3$ S cm$^{-1}$ at 800 °C in 0.2 bar O$_2$ when $x = 0$. The accurate electrical conductivity measurements of LaNi$_{1-x}$Fe$_x$O$_3$ with high Ni contents (0 ≤ $x$ ≤ 0.4) are realized using solely dense single-phase polycrystalline samples prepared by the post-sintering oxidation process. The results suggest that LaNi$_{1-x}$Fe$_x$O$_3$ with a higher Ni content might be more suitable as the cathodes than the widely-studied composition LaNi$_{0.6}$Fe$_{0.4}$O$_3$. Furthermore, LaNiO$_3$ is now considered to have the highest electrical conductivity among precious-metal-free oxides in high-temperature oxidizing atmospheres and can find more applications.

LaNiO$_3$, LaFeO$_3$, and their solid solutions LaNi$_{1-x}$Fe$_x$O$_3$ (LNF, 0 ≤ $x$ ≤ 1) have been extensively studied in the field of solid state chemistry/physics for over 50 years owing to their interesting chemistry/physics for over 50 years owing to their interesting properties. 1,2,3,4,5,6,7,8,9,10, 11,12,13,14,15,16,17,18,19,20, 21 LaNi$_3$ is a metallic oxide with high electrical conductivity, which is rather unusual for undoped 3d-transition-metal-based perovskite oxides. 6,10 LaNiO$_3$ contains a low-spin configuration of Ni$^{3+}$ (t$_{2g}^3$e$_g^1$). 1,7,8,11 Due to the strong covalent bonding between Ni$^{3+}$ and O$^{2-}$, the $e_g$ orbitals are transformed into one-quarter filled itinerant $\sigma^*$ band states, and it results in the metallic behaviors. By contrast, LaFeO$_3$ is a charge-transfer insulator which contains a high-spin, localized electron configuration of Fe$^{3+}$ (t$_{2g}^3$e$_g^2$). 1,11 Consequently the LaNi$_{1-x}$Fe$_x$O$_3$ system exhibits a composition-controlled metal-insulator (m-i) transition at $x = 0.3$. 2,3,4,5,13,14,15,22,23 Although no existing theory is sufficient to describe entirely the evolution of the electronic structure across the transition, a number of experimental and theoretical studies suggest that the metal-insulator transition is driven by increasing disorder effects arising from the random substitution for Ni with Fe in a metallic system with long-range Coulomb interactions. 12,16

In recent decades, LaNi$_{1-x}$Fe$_x$O$_3$ (in particular $x = 0.4$) has also been recognized as a promising cathode material for solid oxide fuel cells (SOFCs) 22,23,24,25,26,27,28,29,30,31, 32,33,34,35,36,37,38,39,40,41, 42 because of its high electrical conductivity, 22,23,24,25,26,28,32,34,37 good catalytic activity for oxygen reduction reaction, 24,27,29,40 high durability against chromium poisoning, 30 and thermal expansion coefficient (TEC) close to those of typical electrolyte materials. 24,25,26,28,31,32,33,37

Here, the structural and physical properties of LaNi$_{1-x}$Fe$_x$O$_3$ is briefly reviewed, which vary rather monotonically with iron content $x$. At room temperature, the solid solutions with 0 ≤ $x$ < 0.5 are isostructural with LaNiO$_3$ and have a rhombohedral perovskite structure, while those with composition 0.5 ≤ $x$ ≤ 1 are isostructural with LaFeO$_3$ and have an orthorhombic perovskite structure. 2,14,15,20,22,24,31,32,33,44 At 800 °C, the stable region of the rhombohedral phase extends up to $x = 0.9$. 31 The molar volume of LaNi$_{1-x}$Fe$_x$O$_3$ increases with $x$ due to the larger ionic radius of Fe$^{3+}$ compared with that of Ni$^{3+}$. 14,15,22,24,31,32,33,36,43 The thermal expansion coefficient is normally reported to be in the range of 8–14 × 10$^{-6}$ K$^{-1}$, close to those of typical electrolyte materials yttrium-stabilized zirconia (YSZ) and gadolinium-doped ceria (GDC), and it decreases with $x$. 24,25,26,28,31,32,33,37 LaNiO$_3$ decompose in air at around 1000 °C or higher to form phases with oxidation states of Ni below +3 according to the following equation 45:

$$4 \text{LaNiO}_3(s) \rightarrow \text{La}_2\text{Ni}_2\text{O}_7(s) + \text{NiO}(s) + 1/2 \text{O}_2(g).$$  (1)

This makes synthesis and sintering of LaNiO$_3$ difficult. The
decomposition temperature of LaNi_{1-x}Fe_{x}O_{3} becomes higher with x due to the higher stability of Fe^{3+} compared with Ni^{3+}, and thus LaNi_{0.5Fe_{0.5}O_{3}} (x = 0.4) is stable up to around 1200 °C in air. 

Despite many works to characterize LaNi_{1-x}Fe_{x}O_{3}, the composition dependence of the electrical conductivity of LaNi_{1-x}Fe_{x}O_{3} is still an open question. Some studies have shown a monotonic increase of the electrical conductivity with decreasing x (increasing Ni content), while other recent studies have indicated a conductivity maximum at x = 0.4. The overpotential of LaNi_{1-x}Fe_{x}O_{3} cathodes on scandia-stabilized zirconia electrolytes reached a minimum also at x = 0.4, which suggested a correlation between the electrical conductivity and the cathode performance. However, it is worth mentioning that the decrease in the electrical conductivity while entering into the metallic region (x < 0.3) is rather unusual. In this context, the origin of the apparent conductivity maximum has been suggested to be lower sintering density or decomposition of LaNi_{1-x}Fe_{x}O_{3} samples with x < 0.4 due to their poor thermal stability. Therefore, it is quite important to re-evaluate accurately the electrical conductivity of LaNi_{1-x}Fe_{x}O_{3} with x < 0.4 to validate the picture of the electronic conduction in the

Figure 1. Powder X-ray diffraction patterns and SEM images of LaNi_{1-x}Fe_{x}O_{3} samples (a) after sintered at 1300 °C in air or oxygen gas and (b) after HIP treatments at 1250 °C under pO{subscript}= 392 bar. The SEM images are those of fracture surfaces of the tablets. Their relative densities measured by the Archimedes method are indicated on the SEM images. The data of LaNi_{1-x}Fe_{x}O_{3} with x = 0 are from our previous work. Part of the figure was presented at conferences.

Figure 2. (a) Schematic of LaNi_{1-x}Fe_{x}O_{3} samples used for electrical conductivity measurements. (b) Photograph of a LaNi_{1-x}Fe_{x}O_{3} sample used for electrical conductivity measurements.
oxidizing a pre-sintered tablet composed of fine La$_3$NiO$_4$ and NiO grains as reported in our previous paper. Its XRD pattern in Figure 1 (b) confirms the almost single-phase nature. SEM images of the fracture surfaces of the samples with $x = 0, 0.2, 0.36, 0.4$, and their relative densities measured by the Archimedes method are also shown in Figure 1 (a) and (b). There are few pores in their fracture surfaces after the final heat treatments, and their relative densities finally exceeded 98%.

Electrical conductivity measurements using the dense LaNiO$_3$ sample revealed that the electrical conductivity of LaNiO$_3$ has been much underestimated in the literature due to insufficient sintering. The electrical conductivity measurements of LaNi$_{1-x}$Fe$_x$O$_3$ were carried out by the four-probe technique using bar-like tablets with silver electrodes (illustrated in Figure 2) in air or a mixture of O$_2$ and Ar gases. Figure 3 shows the electrical conductivity values of LaNiO$_3$ either obtained in this study using the dense sample or reported in the literature.
While the temperature dependences (or the slopes) of the present and the reported data are consistent, significant discrepancies are seen in the electrical conductivity values. The present data and those obtained from a single-crystal \( \text{LaNi}_{1-x} \text{Fe}_x \text{O}_3 \) are almost one order of magnitude higher than the other literature values. In general, the apparent electrical conductivity of a pressed/sintered material is heavily dependent on its relative density. The apparent electrical conductivity varies from the inherent value of the material to almost an order of magnitude lower values as its relative density changes from 100% to 50%. The \( \text{LaNiO}_3 \) samples used in the cited studies in Figure 3 except the single crystal were only pressed or sintered at around 1000 °C or lower due to the poor thermal stability of \( \text{LaNiO}_3 \) under an ordinary partial pressure of oxygen (1 bar \( \text{O}_2 \) or less).

Based on previous studies \cite{12,49,51,52,53,54} and our recent study on the \( \text{LaNiO}_3 \) system \cite{46}, it is thought to be difficult to obtain fully dense samples (relative density over 95%) under such conditions. Therefore, the literature values of the electrical conductivity of \( \text{LaNiO}_3 \) are likely to be much underestimated due to the lower relative densities. It is worth mentioning that this large discrepancy cannot be attributed to the difference in the atmosphere where the electrical conductivity measurements were carried out, as the variation of the electrical conductivity of \( \text{LaNiO}_3 \) is less than 12% in the range of \( 10^3 \) to 1 bar at 800 °C (see Figure S1).

The composition dependence of the electrical conductivity of \( \text{LaNi}_{1-x} \text{Fe}_x \text{O}_3 \) is proved to be monotonic. Figure 4(a)(b) shows the iron content dependence of the electrical conductivity of \( \text{LaNi}_{1-x} \text{Fe}_x \text{O}_3 \) at room temperature and 800 °C in 0.2 bar \( \text{O}_2 \). The electrical conductivity values at \( x = 0.4 \) obtained in this study agree reasonably with literature values. At \( x = 0.4 \), the electrical conductivity increases with decreasing \( x \) (increasing Ni content), reaching 1.0 \times 10^4 S cm\(^{-1}\) and 2.5 \times 10^5 S cm\(^{-1}\) at 800 °C, respectively, while the literature data do not show a clear trend. This discrepancy can be due to…
the underestimation of the conductivity of Ni-rich samples in the previous studies due to the lower relative densities as discussed in the previous paragraphs or the existence of secondary phases. 

The increasing trend of the electrical conductivity with Ni content could be attributed to the previously proposed picture that the metal-insulator transition is driven by disorder effects arising from the substitution for Ni in metallic LaNiO3 with Fe. However, further experimental and theoretical studies using appropriately synthesized samples are desirable to elucidate the nature of M-I transition in this system. Referring also to literature data on Ni-poor compositions, we can see that the electrical conductivity of LaNi1−xFe3O3 increases monotonically with decreasing x in the whole composition range.

In Figure 5 (a), the electrical conductivity of LaNi1−xFe3O3 is compared with that of simple perovskite or perovskite-related (layered-perovskite) oxides based on 3d transition metals Cr, Mn, Fe, Co, Ni, and/or Cu. These oxides are stable in air and at high temperatures (~500-800 °C), and have potential applications as the cathodes and interconnects of SOFCs. The electrical conductivity of LaNiO3 (LaNi1−xFe3O3 with x = 0) is found to be the highest among the above oxides including popular cathode materials such as La0.5Sr0.5CoO3 (LSCF), Ba0.5Sr0.5CoO2 (BSF), La0.5Sr0.5MnO3 (LSM), and La0.5Sr0.5CoO3 (LSC). More broadly, Figure 5 (b) compares the electrical conductivities of LaNi1−xFe3O3 and other representative electrically conducting oxides out of the above category, based on 3d, 4d, or 5d transition metals. ReO3 exhibits 1-2 orders of magnitude higher conductivity than that of LaNiO3. Also, RuO2 with rutile structure, TiO2 (x = 1/2) with NaCl structure, Ti2O3 with corundum structure, and Na2WO3, La1.2Sr1.8VO3, SrMoO2, and SrRuO3 with perovskite structure exhibit equal or higher conductivity than LaNiO3. However, many of them (ReO3, NaCl-type TiO2, Ti2O3, Na2WO3, La1.2Sr1.8VO3, and SrRuO3) are unstable in high-temperature air and the rest of them (SrRuO3 and RuO2) are based on precious metal, both can be drawbacks for practical use. Therefore LaNiO3 is now considered as the precious-metal-free oxide with the highest electrical conductivity in high-temperature air.

Conclusions

In conclusion, the electrical conductivity of Ni-rich LaNi1−xFe3O3 (0 ≤ x ≤ 0.4) is found to monotonically increase with decreasing x (increasing Ni content) at both room temperature and 800 °C by use of the fully dense single-phase polycrystalline samples prepared by the post-sintering oxidation process. The confirmed trend suggests that LaNi1−xFe3O3 with smaller x (higher Ni content) might be more suitable for the cathodes of SOFCs than the widely-studied composition LaNi0.5Fe0.5O3 (x = 0.4). It should be noted, however, that a higher conductivity does not necessarily lead to a better electrode performance. Therefore, it is desirable to investigate the electrochemical properties of Ni-rich LaNi1−xFe3O3 (0 ≤ x ≤ 0.4). One concern with Ni-rich LaNi1−xFe3O3 is the thermal instability during operation at high temperatures, but it may be less problematic for the applications in low-temperature SOFCs, which are under active development. In addition, Ni-rich LaNi1−xFe3O3 can be more readily applicable as oxygen electrodes in solid oxide electrolyzer cells (SOECs) because the electrodes are operated in highly oxidative conditions, where LaNi1−xFe3O3 is more stable. 

Conflicts of interest

There are no conflicts to declare.

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Notes and references

5 Fe may partially occupy the Ni-sites in LaNi2O3 and NiO. 

6 Based on XRD patterns (Figure 1), the amount of secondary phases (NiO and an unknown phase) is estimated to be ~1 wt% or less. Therefore the secondary phases would not constitute a long-range conduction network and the high electrical conductivity observed in this study can be attributed to the main phase, LaNi1−xFe3O3. Also, the fact that the conductivity value of the LaNiO3 polycrystal obtained in this study are almost identical to that of a single crystal at room temperature (Figure 3(a))

55) suggests that the influence of secondary phases is not significant.

56 In LaNi1−xFe3O3 (0 ≤ x ≤ 0.4) solid solutions, electronic conduction should dominate over ionic conduction. Although they contain oxygen vacancies and can conduct oxide ions, the oxide ion conductivity at 800 °C is assumed to be less than 1 S/cm as in the case of other best oxide-ion-conducting perovskite oxides (LSC, LSM, etc.)

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