LaNi$_{1-x}$Fe$_x$O$_3$ CATHODE MATERIAL FOR SOFC OPERATING AT A REDUCED TEMPERATURE

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ABSTRACT

We prepared LaNi$_{1-x}$Fe$_x$O$_3$ (LNF) samples and investigated their characteristics as solid oxide fuel cell (SOFC) cathode materials. We found that the LaNi$_{1-x}$Fe$_x$O$_3$ satisfies the important requirements for a cathode, if x in this system is around 0.4. LaNi$_{0.6}$Fe$_{0.4}$O$_3$ has its highest electronic conductivity of 580 S/cm at 800°C. This value is more than three times higher than that of La$_{0.8}$Sr$_{0.2}$O$_{1.9}$ (80 S/cm). The average thermal expansion coefficient of LaNi$_{0.6}$Fe$_{0.4}$O$_3$ from 30°C to 1000°C was relatively low (11.4 x 10$^{-6}$/K) and closer to the 0.92ZrO$_2$-0.08Y$_2$O$_3$ (YSZ) value (10.0 x 10$^{-6}$/K) than La$_{0.8}$Sr$_{0.2}$MnO$_3$ (12.0 x 10$^{-6}$/K). We prepared a single cell with a cathode made of this new material, 0.8ZrO$_2$-0.2Sc$_2$O$_3$-0.01Al$_2$O$_3$ electrolyte and a Ni-YSZ anode. We measured the activation overvoltage of the cathode with different compositions at 800°C by the current interruption method. We found that the activation overvoltage of the cathode reached minimum when the x in LaNi$_{1-x}$Fe$_x$O$_3$ was 0.4. This cell generated 0.72 W/cm$^2$ at 1.6 A/cm$^2$ at 800°C.

INTRODUCTION

Solid oxide fuel cells (SOFC) operating at about 1000°C have been frequently studied (1,2). However, such high temperature operation causes material problems including electrode sintering and interfacial diffusion between electrolytes and electrode (1). One possible way to overcome this problem is to reduce the SOFC operating temperature (1,3). To achieve this, efforts have been made to reduce the ohmic loss of electrolytes by fabricating a thin layer of YSZ or finding new materials with high ionic conductivity (1-7). Moreover, the ohmic loss and overvoltage in the cathode and anode are factors which also reduce the power generation efficiency of SOFCs (1). The electronic conductivity in the cathode is particularly important for cathode supported type cells, because their electronic current path is very long (1,2).

Perovskite type oxides (ABO$_3$) containing Co ions in their B sites are known to have much higher conductivities than those of the most commonly used cathode material La$_{1-x}$Sr$_x$MnO$_3$ (LSM) (8,9). However, the thermal expansion coefficients of these materials are much larger (22.0 x 10$^{-6}$/K) than that of La$_{0.8}$Sr$_{0.2}$MnO$_3$ (12.0 x 10$^{-6}$/K) (1). Some studies have been undertaken to surmount this thermal expansion problem by substituting some of the Co ions with Mn or Fe ions (10-14). These studies show that the thermal expansion of La(Sr)CoO$_3$ can not be reduced to the value of its counterparts (La(Sr)MnO$_3$, La(Sr)FeO$_3$) without losing high electronic conductivity.
LaNiO$_3$ and La$_3$NiO$_4$ are perovskite type and K$_2$NiF$_4$ type oxides, respectively. It is known that LaNiO$_3$ has a very high electronic conductivity at room temperature (15,16). However this material is unstable above 850°C and decomposes to La$_2$NiO$_4$ and NiO, whose conductivities are insufficiently high (17). This instability prevents this material from being used as a cathode material in SOFCs. M. Hrovat et al. showed that LaNiO$_3$ can be stabilized even at high temperature, if some of the Ni is substituted by Co ions (18). We found that LaNi$_{1-x}$Fe$_x$O$_3$ has both a high electronic conductivity and a thermal expansion coefficient which is close to that of the zirconia electrolyte (19). Therefore, we thoroughly investigated the composition dependence of the characteristics in the LaNi$_{1-x}$Fe$_x$O$_3$ ($x = 0.0 - 1.0$) system. We also prepared a single cell with a cathode made of this new material and investigated the composition dependence of the cathode performance at 800°C.

**EXPERIMENTAL**

**Sample Preparation**

The samples were prepared by a solid state reaction. La$_2$O$_3$ (99.99%), NiO (99.9%), Fe$_2$O$_3$ (99.9%) powders were used for the LNF samples. First they were mixed and then calcined in air at 1100°C for 8 hours. Then they were ground and calcined in air at 1200°C for 24 hours, and ground again. For well-sintered samples, we prepared very fine powders as follows; the calcined powders were milled in plastic pots with zirconia balls and C$_2$H$_5$OH for 48 hours, and then dried. These powders were pressed into pellets at a pressure of 1 ton/cm$^2$. The pellets were sintered in air at 1250°C or 1400°C for 24 hours. After the sintering, some of these samples were annealed in air at 1000°C for 48 hours.

**Measurements of Material Properties**

We used an X-ray diffractometer to analyze the crystal structures of the sintered samples. The sample surfaces were polished before the measurements. The sintered pellets were cut into rods, about 0.18 cm x 0.24 cm x 2.2 cm, with a diamond cutter. Four Pt leads were attached to the samples to allow us to measure conductivity by the dc four terminal method. The electrical conductivity was measured from 100°C to 1000°C in air at a heating and cooling rate of 2°C/min. The thermal expansion coefficients for the rod-like samples were measured in air from room temperature to 1000°C at a heating rate of 2°C/min with a dilatometer.

**Single Cell Measurements**

The geometry of the cell we used is shown in Fig.1. We used Ni-YSZ, LNF or LSM, and porous Pt for the anode, cathode and reference electrode, respectively. First, NiO-YSZ powder with PVA was painted on a 0.2 mm-thick SASZ (0.89ZrO$_2$-0.10Sc$_2$O$_3$-0.01Al$_2$O$_3$) plate and fired at 1400°C for 12 hours, then LNF powder with ethylene glycol and Pt paste were painted on the plate and fired at 800°C in air for 24 hours. The LNF powder had a mean diameter of 1.5 μm. Pt mesh was used as the current collector. The area of the cathode and anode was about 0.283 cm$^2$ (6 mm diameter).

Figure 1 shows the structure of the fuel cell. Oxygen gas (99.9% purity) was supplied to the cathode compartment and reference electrode at flow rates of 150 cc/min and 500 cc/min, respectively. Hydrogen gas was supplied to the anode compartment at a flow rate of 300 cc/min. To estimate the electrode resistance and activation overvoltage at the cathode/electrolyte interface, we conducted current interruption measurements at 800°C. We supplied DC current to the cells with a current source and interrupted the current with a mercury contact relay. We traced the voltage change between the cathode and reference...
electrode using a digital oscilloscope which had a 12 bit resolution and a 20 MHz sampling rate. Then the signal data were transferred to a computer and analyzed. Before starting the measurements, the DC current was held at its maximum value until the cell reached a steady state (about 12 hours). After one interruption measurement, we reduced the current to the next value and held it for 30 minutes before the next interruption. In this way, the current density was decreased from the maximum value to 0 mA. This procedure enabled us to measure the cell in a steady state for each current density.

RESULTS AND DISCUSSION

Crystal Structure of LaNi$_{1-x}$Fe$_x$O$_3$

We used an X-ray diffractometer to analyze the crystal structures of the sintered samples. When $x$ in LaNi$_{1-x}$Fe$_x$O$_3$ was greater than 0.5, the crystal structures were in the orthorhombic phase, which is the same as that of LaFeO$_3$. When $x$ was 0.4, the structure was in the rhombohedral phase, which is the same as that of LaNiO$_3$. When $x$ was between 0.4 and 0.2, the crystal structure was basically in the rhombohedral phase, but also contained the orthorhombic (La$_4$Ni$_3$O$_{10}$) phase. When $x$ was smaller than 0.2, the samples were a mixture of the orthorhombic and tetragonal phases. The existence of the tetragonal phase indicated that the rhombohedral phase had decomposed into the tetragonal phase (K$_2$NiF$_4$ structure) during the sintering process at 1250°C. This means that material with this composition is not stable at this temperature. The perovskite structure became more stable as $x$ became larger in LaNi$_{1-x}$Fe$_x$O$_3$. This means that the substitution of Fe for Ni increased the thermodynamic stability of this material. The crystal structures and lattice constants of LaNi$_{1-x}$Fe$_x$O$_3$ ($x =$ 0.2-1.0) are listed in Table 1. They were calculated with 20 for peaks in the X-ray diffraction patterns. We used (312), (214), (223), (042) peaks for the rhombohedral phase and (204), (260), (440) peaks for the orthorhombic phase. The lattice constants decreased with decreases in $x$ in the LaNi$_{1-x}$Fe$_x$O$_3$ system, because the Fe ion radius is larger than that of Ni.

Temperature Dependence of Electronic Conductivity

The temperature dependence of electronic conductivity for LaNi$_{1-x}$Fe$_x$O$_3$ ($x =$ 0.0 - 0.9) is shown in Fig. 2. Here, ln($\sigma$) is plotted against 1000/ T. The electronic conductivity of perovskite oxides such as La$_{0.9}$Sr$_{0.1}$MnO$_3$ and La$_{0.9}$Sr$_{0.1}$CrO$_3$ has a semiconductor like temperature dependence (1,20,21). This dependence can be described as follows;

$$\sigma = C_o \exp[-E_a / k_B T] \tag{1}$$

where $\sigma$, $C_o$, $T$, $E_a$, $k_B$ indicate electronic conductivity, a constant, absolute temperature, activation energy and the Boltzmann constant, respectively. When $x$ is between 0.6 and 0.9 the plots are almost on straight lines and can be described by equation (1). The slope of the line decreases with decreases in $x$. This corresponds to the activation energy decrease in the equation. When $x$ is 0.5 or below, the conductivity is almost independent of temperature. At high temperature, the conductivity decreases with temperature, which is typical for metallic conductors such as LaNiO$_3$ (15).

Composition Dependence of Electronic Conductivity

We prepared LaNi$_{1-x}$Fe$_x$O$_3$ ($x =$ 0.36, 0.38, 0.40, 0.42, 0.44) samples to investigate the composition dependence of the conductivity near $x =$ 0.4. We used powders milled after the
solid state reaction process. Pellets made from the powders were sintered at 1400°C for 24 hours then annealed at 1000°C for 48 hours. The density of the pellets was 97% of the theoretical density. Figure 3 shows the temperature dependence of the conductivities for these well-sintered samples. They had a similar temperature dependence. At 800°C, the conductivity of the x = 0.4 sample was 580 S/cm, which was higher than that of other samples. When x in LaNi_{1-x}Fe_xO_3 was decreased from 0.4, the drop in the conductivity was twice as large as that when x was increased from 0.4. The reduction of x in LaNi_{1-x}Fe_xO_3 caused a decrease in the d value (lattice constants) and an increase in the symmetry of the crystal structure. These changes are advantageous in terms of electron conduction. By contrast, the x reduction reduced the thermodynamic stability at high temperature. This can cause some decomposition to La_4(Ni-Fe)_3O_{10} or La_{8}(Ni-Fe)_2O_3, which may reduce the conductivity. The composition dependence of the electronic conductivity in Fig. 3 is the result of these effects opposing each other.

**Composition Dependence of the Thermal Expansion Coefficient**

The thermal expansion coefficients of LaNi_{1-x}Fe_xO_3 are plotted against x in Fig. 4. They are average values between room temperature (30°C) and 800°C or 1000°C. The value changes with x almost sigmoidally between the end members. The thermal expansion coefficient did not change greatly with changes in composition, while the electronic conductivity changed greatly with the B site substitution. The value for the LaNi_{0.6}Fe_{0.4}O_3 sample, which has the highest conductivity at 800°C, was 11.4 x 10^{-6} K^{-1} between room temperature and 1000°C. This is closer to the YSZ value of 10.0 x 10^{-6} K^{-1} than LSM (12.0 x 10^{-6} K^{-1}). The thermal expansion coefficient decreased with the increase in x from 0.4 to 0.5, while the electronic conductivity did not drop steeply. Therefore, the optimum composition for the cathode material is probably between x = 0.4 and 0.5.

**Cell Current Dependence of the Cathode Overvoltage**

The cathode activation overvoltage separated from the ohmic drop by current interruption is plotted against the current density on a log scale in Fig. 5. The composition of the cathode is LaNi_{0.6}Fe_{0.4}O_3. When the current density is high enough, the dependence of current density, i, on activation overvoltage, η, can be described by Tafel's equation as follows;

\[ i = i_0 \exp \left( \frac{\alpha n F}{RT} \eta \right) \]

Where \( i_0 \) is the exchange current density and \( \alpha \) is the charge transfer coefficient. R, F, T, and n indicate the gas constant, Faraday constant, temperature and number of electrons transferred in the reaction, respectively (23, 24). n is 4 for ordinary reaction in cathode of SOFCs. The Tafel’s plots for La_{0.8}Sr_{0.2}MnO_3 whose mean particle size is 1.0 μm are also shown in Fig. 5. The activation overvoltage of LNF was much lower than that of LSM. This shows the LNF has very high catalytic activity. The plots for both LSM and LNF are on lines except in the low current density region. This means that both activation overvoltages can be described by Tafel’s equation. While for LSM was almost 0.5, \( \alpha \) for LNF was estimated to be about 0.97. Since the \( \alpha \) value must be between 0 and 1.0, the value for LNF is very high. This is probably due to the very high charge transfer reaction in the cathode. In such a reaction, the rate can be influenced by material transport process such as a diffusion of oxygen ions from the expanded three phase boundary (TPB) into electrolyte. The tendency of the electronic conductivity and the sintering temperature suggest that the non-stoichiometry of the oxygen or oxygen vacancies in this material is increased in the reduced atmosphere. At a higher activation overvoltage, the oxygen partial pressure was locally reduced. This may increase the oxygen vacancies in this material and expand the TPB (23, 24). This also increases the slope of Tafel’s plot.

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Composition Dependence of the Cathode Overvoltage

We measured the overvoltage at 800°C for cathodes whose composition was LaNi$_{1-x}$Fe$_x$O$_3$ ($x = 0.0-0.8$). The overvoltage at 1.06 A/cm$^2$ is plotted against the composition in Fig.6. The overvoltage for a cathode without Fe was more than 0.11 V. This value decreased sharply with increases in the Fe concentration and we obtained the lowest value for LaNi$_{0.6}$Fe$_{0.4}$O$_3$. With further increases in the Fe concentration, the overvoltage gradually increased. The composition for the lowest overvoltage coincided with the composition for the highest electronic conductivity. This suggests that the electronic conductivity affects the cathode performance. Only the particles near the zirconia electrolyte contribute to form the TPB for oxygen reduction. Some of these particles are thought to be weakly connected to the electronic current path or completely isolated. These particles do not contribute to the reaction, because high grain boundary resistance prevents the electric current from reaching those particles. When the electronic conductivity is high, the grain boundary resistance for such weakly connected particles becomes low enough for the current to reach them. Then they can contribute to the reaction. Another interpretation of the result in Fig.6 is that LNF is probably a mixed conductor and the oxygen ionic conductivity influences the effective TPB area. Therefore the overvoltage and the oxygen ionic conductivity may have the same composition dependence. The ionic conductivity decreases with increases in the Fe concentration because such increases cause the unit cell structure to deform from rhombohedral to orthorhombic. The sharp increase in overvoltage between $x=0.0$ and 0.4 can be attributed to the appearance of the second phase whose ionic conductivity is very low.

Performance Test of a Single Cell with a LaNi$_{1-x}$Fe$_x$O$_3$ Cathode

The result of a performance test on the single cell at 800°C is shown in Fig.7. The cell voltage and cell power density are plotted against the cell current density. The open circuit voltage was 1.13 V, and this value was expected from Nernst’s equation. A maximum power density 0.72 W/cm$^2$ was achieved at 1.6 A/cm$^2$. The very low overvoltage at the cathode and the high ionic conductivity in the SASZ electrolyte contributed to high performance of this cell. This excellent performance demonstrates that this new material is suitable for the cathode of an SOFC. The main power generation loss is caused at the anode in this cell. Therefore, the anode overvoltage must be reduced to the same level as that of the cathode to improve SOFCs operating at around 800°C.

CONCLUSIONS

When $x$ in LaNi$_{1-x}$Fe$_x$O$_3$ was greater than 0.4, the samples were in the orthorhombic phase, which is the same as that of LaFeO$_3$. When $x$ was around 0.4, the samples were in the rhombohedral phase, which is the same as that of LaNiO$_3$. When $x$ was 0.3 or smaller, the samples were a mixture of the rhombohedral phase and other phases. When $x$ in LaNi$_{1-x}$Fe$_x$O$_3$ was 0.4, this system had its highest electronic conductivity of 580 S/cm, at 800°C. This value is more than three times higher than that of La$_{0.8}$Sr$_{0.2}$MnO$_3$. The average thermal expansion coefficient of LaNi$_{0.6}$Fe$_{0.4}$O$_3$ from 30°C to 1000°C, was relatively low (11.4x 10$^{-6}$/K). It is closer to the 0.9ZrO$_2$-0.08Y$_2$O$_3$ (YSZ) value (10.0 x 10$^{-6}$/K) than La$_{0.8}$Sr$_{0.2}$MnO$_3$.

The activation overvoltage of the cathode reached minimum when the $x$ in LaNi$_{1-x}$Fe$_x$O$_3$ was 0.4. The cell whose cathode composition was LaNi$_{0.6}$Fe$_{0.4}$O$_3$ generated 0.72 W/cm$^2$ at 1.6 A/cm$^2$ at 800°C.
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REFERENCES

1. N.Q.Minh, J. Am. Ceram. Soc., 76, (3), 563 (1993).
2. S.C.Singhal, in Proceedings of the 3rd Int. Symp. on SOFC, Vol.93-4, p.665(1993).
3. K.Krist, J. D. Wright, in ibid., p.782 (1993).
4. T.Ishii, T.Iwata and Y.Tajima, in ibid., p.59 (1993).
5. T.Ishii, Solid State Ionics, 78, 333 (1995).
6. R.Chiba, F.Yoshimura, J.Yamaki, T.Ishii, T.Yonezawa and K.Endou, Solid State Ionics 104, 259 (1997).
7. R.Chiba, F.Yoshimura and J.Yamaki, Proc. of Mat. Res. Symp., 496, 185 (1998).
8. J.Mizusaki, J.Tabuchi, T.Matsuura, S. Yamauchi and K.Fueki, J. Electrochem. Soc., 136, (7), 2082 (1989).
9. O.Yamamoto, Y.Takeda, R.Kanno and M.Noda, Solid State Ionics, 22, 241 (1987).
10. P.Shuk, V.Charton and V.Samochnival, Materials Science Forum, 76, 161 (1991).
11. R.Chiba and T.Ishii, in Proc. of 4th Int. Symp. on SOFC, Vol.95-1, p.482 (1995).
12. R.Koc and H.U.Anderson, Journal of Materials Science, 27, 5477 (1992).
13. J.H.Kuo and H.U.Anderson, J. Solid State Chem., 87, 55 (1990).
14. E.Ivers-Tiffee, W.Wersomg, M.Shießl and H.Greiner, Ber. Bunsenges. Phys. Chem., 94, 978 (1990).
15. H.W.King, K.M.Castelliz, G.J.Murphy and A.S.Rizkalla, J. Canadian Ceram. Soc., 55, 10 (1986).
16. K.P.Rajeev and A.K.Raychaudhuri, Phys. Rev., 46, No.3, 1309 (1992).
17. J.Drennan, C.P.Travares and B.C.H.Steele, Mater. Res. Bull, 17, 621 (1982).
18. M.Hrovat, N.Katsarakis, K.Reichmann, S.Bernik, D.Kuscer and J.Holc, Solid State Ionics, 83, 99 (1996).
19. R.Chiba, F.Yoshimura and Y.Sakurai, Extended Abstracts of the 23rd Symposium on Solid State Ionics in Japan, 2A06, p.91 (1997).
20. R.Koc and H.U.Anderson, J. Materials Science, 27, 5477 (1992).
21. Vasanthacharya N.Y., Raychaudhuri A.K., Ganguly P. and Rao C.N.R, J. Magn. Mater. 81, (1-2), 133 (1989).
22. H. Falcon, A.E. Goeta, G. Punte and R.E. Carbonio, J. Solid State Chem., 133, 379 (1997).
23. D. Y. Wang, A. S. Nowick, J. Electrochem. Soc., 126, (7), 1166 (1979).
24. T. Kawada, N. Sakai, H. Yokokawa M. Dokiya, M. Mori, T. Iwata, J. Electrochem. Soc., 137, (10), 3042 (1990).
25. B.Gharbage, T.Pagnier, A.Hammou, Solid State Ionics, 72, 248 (1994).
Table 1. Crystal structure and lattice constants of LaNi$_{1-x}$Fe$_x$O$_3$ ($x = 0.2 - 1.0$).

| x   | crystal structure          | lattice constant (Å) |
|-----|----------------------------|----------------------|
|     |                            | a        | b              | c              |
| 1.0 | orthorhombic               | 5.5656   | 7.8548         | 5.5555         |
| 0.9 | orthorhombic               | 5.5539   | 7.8569         | 5.5523         |
| 0.8 | orthorhombic               | 5.5505   | 7.8312         | 5.5364         |
| 0.7 | orthorhombic               | 5.5436   | 7.8091         | 5.5258         |
| 0.6 | orthorhombic               | 5.5311   | 7.7862         | 5.5094         |
| 0.5 | orthorhombic               | 5.5243   | 7.7601         | 5.4949         |
| 0.4 | rhombohedral (+ orthorhombic) | 5.5118   | 6.6375         |                |
| 0.3 | rhombohedral (+ orthorhombic) | 5.5079   | 6.6281         |                |
| 0.2 | rhombohedral (+ orthorhombic) | 5.5019   | 6.6297         |                |

We used (312), (214), (223), (042) peaks for the rhombohedral phase (hexagonal) and (204), (260), (440) peaks for the orthorhombic phase to estimate the lattice constants.

Fig. 1. Cell geometry and fuel cell configuration.
Fig. 2. Temperature dependence of electronic conductivity of LaNi$_{1-x}$Fe$_x$O$_3$ ($x = 0.0-0.9$).

Fig. 3. Temperature dependence of electronic conductivity of well-sintered samples with compositions near LaNi$_{0.6}$Fe$_{0.4}$O$_3$; LaNi$_{1-x}$Fe$_x$O$_3$ ($x = 0.36-0.44$).
Fig. 4. Composition dependence of thermal expansion coefficients of LaNi$_{1-x}$Fe$_x$O$_3$ (x = 0.0 - 1.0).

Fig. 5. Tafel’s plots for LaNi$_{0.6}$Fe$_{0.4}$O$_3$ and La$_{0.8}$Sr$_{0.2}$MnO$_3$ cathodes at 800°C. The overvoltage was measured by the current interruption method.
Fig. 6. Composition dependence of LaNi$_{1-x}$Fe$_x$O$_3$ cathodes overvoltage measured at 1.06 A/cm$^2$ at 800°C.

Fig. 7. Cell voltage and cell power density vs. cell current density at 800°C. The cell has a LaNi$_{0.6}$Fe$_{0.4}$O$_3$ cathode, a 0.2 mm thick SASZ electrolyte and a Ni-YSZ anode. (electrode areas : 0.283 cm$^2$)