IMPROVEMENT IN ANODIC ACTIVITY OF Ni BY Fe ADDITION FOR INTERMEDIATE TEMPERATURE SOFC USING LaGaO₃ ELECTROLYTE

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ABSTRACT
Effects of various additives to Ni anode on SOFC using La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃ based oxide electrolyte were investigated in this study for increasing the surface activity. Among the examined additives, it was found that the addition of small amount of Fe is highly effective for increasing the anodic activity. When 5 wt% Fe was added to Ni anode, the anodic overpotential was as small as 34 mV at 873 K, 0.1 A/cm², which is almost half of pure Ni anode. Since the estimated activation energy for anodic reaction decreased, addition of Fe to Ni seems to be effective for increasing the activity of Ni for anodic reaction. XRD measurement after power generation measurement suggests that added Fe formed alloy with Ni. Addition of third element to Ni-Fe bimetallic anode was also studied and it was found that addition of small amount of Pt is effective for further increasing the activity of Ni anode. Consequently, this study reveals that Ni-Fe-Pt is highly active for anodic reaction of SOFCs at decreased temperatures.

INTRODUCTION
Development of intermediate temperature solid oxide fuel cells is an important subject, since the variety of materials, which are usable for the cell fabrication, becomes wider and quick start-up can be achieved. Therefore, intensive studies have been performed for the development of intermediate temperature SOFCs (1). In our previous study, it was found that high power density can be achieved by using a new fast oxide ion conductor, LaGaO₃ doped with Sr and Mg, and application of Sm₀.₅Sr₀.₅CoO₃ for cathode (2). It is generally known that cathode overpotential becomes significant with decreasing operating temperature due to large activation energy. However, overpotential of Sm₀.₅Sr₀.₅CoO₃ cathode was small at decreased temperatures (2). Although the main internal resistance of the present cell is electrical resistance, which can be assigned to that of electrolyte, anodic overpotential also became significant with decreasing temperatures. Therefore, in order to improve the power density at decreased temperatures, improvement of anodic performance is also an important subject. Up to now, there are many studies on...
Ni based anode and it is reported that cermet consisting of Ni and Y$_2$O$_3$ stabilized ZrO$_2$ could expand the reaction area and it is widely used for anode (3-4). However, anodic performance of the present Ni-YSZ cermet is not high enough for the SOFC operating at intermediate temperatures. Although reports on bimetallic anode for SOFC are limited so far, it is well known that the catalytic activity greatly changes by addition of small amount of additives, and metal additives for anode have also been investigated (5,6). In this study, we investigated the effects of additives to anodic Ni metal on the power generating property of the cell using LaGaO$_3$ based oxide for electrolyte for increasing the power density at intermediate temperatures.

**EXPERIMENTAL**

Preparation of Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC) cathode and LaGaO$_3$ based oxide electrolyte was performed by using the conventional solid state mixing method (2,4). For the preparation of LaGaO$_3$ based oxide, commercial oxides of La$_2$O$_3$, Ga$_2$O$_3$, MgO, CoO and also the commercial SrCO$_3$ were mixed in a ball mill mixer. The composition, La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM), was always used in this study. The obtained powder mixture was precalcined at 1473 K for 3 h and sintered at 1773K. XRD measurement demonstrated that no significant peaks from the secondary phases were present in the obtained electrolyte. The thickness of the electrolyte was always set to 0.5 mm by grinding with a diamond wheel.

Nickel anode added with small amount of metal was prepared by impregnation of metal nitrate on NiO. Unless otherwise noted, the amount of additive was fixed at 10 wt% against Ni. After evaporation to dryness, the powder was precalcined at 1273 K for 6 h. NiO added with small amount of metal and Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ was painted on each face of the LSGM disk with n-butyric acetate solvent for anode and cathode, respectively, at diameter of 5 mm. The prepared single cell was calcined at 1273 K for 0.5 h before measurement of power generating property. Platinum electrode was used for reference electrode and put on the cathode side. Pt meshes were covered on the surface of anode and cathode, respectively, as current collectors. Pt lead wire was used to connect the electrodes to electrochemical equipments. 100 ml/min H$_2$ saturated with humidity at room temperature was used as fuel, and 100 ml/min pure oxygen was used as oxidant.

Power generating property of the cell was measured with four-probe method and ca. 3 vol% humidified H$_2$ was used for fuel (100 ml/min), and O$_2$ was fed to the cathode side. The overpotentials of anode and cathode were estimated by using the complex impedance (Solartron 1260) and the current interruption methods. The constant current was generated by using a current pulse generator (Hokuto HC111) and the potential response was measured with a Memory Hicorder (Hioki 8835).

**RESULTS AND DISCUSSION**

Table 1 summarizes the effects of small additives to Ni anode on the power generating property at 1073 K. It is seen that small additives to NiO anode have a great influence on the maximum power density, while the open circuit potential is almost independent of
anode. In the case of Mn or Ag addition, the maximum power density decreased greatly. Detailed analysis of the internal resistance of the cell suggests that the decreased power density is due to the enlarged IR loss at anode side and anodic overpotential. Therefore, surface activity of Ni anode may decrease by addition of Mn or Ag and also it is expected that surface of Ni may be covered with these additives resulting in decreased electrical conductivity. In contrast, the maximum power density increased by using Fe, Au, Pd, or Co added Ni for anode. Therefore, addition of Au, Fe or Co is effective for increasing the power density. From the detailed analysis of internal resistance as shown in Table 1, positive effects of Au, Fe or Co addition can be explained by the decreased IR loss at anode side and anodic overpotential.

Table 2 also shows the effects of additives to Ni anode at 873 K. Comparing with the results at 1073 K, effects of additives are different at 873 K. At 1073 K, overpotential of Au added Ni is the smallest, however, at 873 K, this Ni-Au bimetallic anode is not small but slightly larger than that of pure Ni. This difference could be explained by different activation energy. As shown in Table 2, not only at 1073 K but also at 873 K, the positive effects of Fe addition to Ni anode were observed. At 873 K, it is seen that the anodic overpotential of Ni became much larger, ca. 80 mV at 0.1A/cm² when pure Ni was used. However, by addition of Fe, anodic overpotential was less than 50 mV at 0.1A/cm², which is almost half of Ni. Therefore, it is seen that the addition of Fe to Ni anode is highly effective for increasing the anodic activity of Ni. In the following, anodic performance of Fe added Ni bimetallic anode was further studied.

Figure 1 shows the Arrhenius plots of current at anodic overpotential of 30 mV. From slope of this Arrhenius plots, one can estimate the apparent activation energy for anodic reaction. It is clear that the apparent activation energy for anodic reaction was strongly affected by additives. When Mn or Ag was added, the estimated activation energy for anodic reaction increased. Therefore, the activity of reaction site in Ni anode may decrease by addition of Ag or Mn. In contrast, addition of Fe greatly suppressed the apparent activation energy of Ni anode and so, the activity of reaction site on Ni seems to be improved by addition of Fe. As a result, anodic overpotential could be sustained to a smaller value by addition of Fe.

Figure 2 shows the anodic overpotential of Ni added with various metal or metal oxides at 873 K. In accordance with the results in Tables 1 and 2, anodic overpotential was strongly dependent on the additives and it was seen that Fe added Ni anode always exhibited the smallest overpotential at all current densities. On this anode, the overpotential was smaller than 100 mV up to a current density of 0.5A/cm². Therefore, not only at small current density but also at high current density, Fe added Ni anode is highly active for electrochemical oxidation of H₂ and it is expected as the active anode for intermediate temperature SOFCs.

The maximum power density, potential drop by IR loss at anode side and anodic overpotential at 0.1 A/cm² at 1073 K are shown in Fig. 3 as a function of Fe amount. It is seen that anodic overpotential decreased with increasing Fe amount and attained the smallest value at 5 mol% Fe added. Since pure Fe electrode exhibits extremely large overpotential, improvement in anodic performance by addition of small amount of Fe is quite interesting phenomena. On the other hand, IR loss at anode side also decreased with increasing Fe and the smallest IR loss was also obtained at 5 wt% Fe. Since the observed
electrical resistance at anode side is much larger than that estimated by ionic conductivity of \(\text{LaGaO}_3\) based electrolyte, it is suspected that reaction of NiO anode and \(\text{LaGaO}_3\) based oxide forms a highly resistive layer between electrolyte and anode. In accordance with decreased internal resistance and overpotential, the maximum power density of the cell increased and the largest value of 670 mW/cm\(^2\) was achieved when 5 wt\% Fe was added. Therefore, it is seen that the optimum amount for Fe addition exists around 5 wt\%.

Figure 4 shows the power generating characteristics of the cell using 95Ni5Fe for anode. Almost the theoretical open circuit potential was obtained at temperatures above 873 K and so the activity of Ni-Fe anode is high at decreased temperatures. On the other hand, the maximum power density was much improved by using 95Ni5Fe anode and at 873 K, the maximum power density was achieved at a value of ca. 180 mW/cm\(^2\) which is almost three times larger than that of the cell using Ni anode. Therefore, it is clear that the application of Ni-Fe for anode is highly effective for increasing the power density of the cell using \(\text{LaGaO}_3\) based oxide for electrolyte.

In order to analyze the state of added Fe in Ni anode, XRD measurement was performed after power generating measurement. Figure 5 shows the XRD patterns of the anode at different Fe amounts. XRD patterns consisted of Ni and \(\text{LaGaO}_3\) electrolyte. Although the amount of Fe was small, diffraction peaks from Fe or Fe oxide were not recognized. In addition, diffraction angle of Ni main peaks were shifted to a lower angle. Considering the larger ionic size of Fe than that of Ni, it is reasonable to assume that the added iron forms alloy with Ni and under working conditions, Ni-Fe bimetallic alloy stably worked as anode.

In order to further improve the anodic performance, effects of additives to Ni-Fe bimetallic anode were further studied. Table 3 shows the power generating property and internal resistance of the cell using metal added Ni-Fe bimetallic anode at 1073 K. Obviously, not only power density but also anodic overpotential decreased by addition of second additive to Ni-Fe anode. However, among the examined second additives, it is seen that the anodic overpotential decreased by addition of Pt or Ce. In particular, addition of Pt is the most effective for increasing the power density of the cell. The maximum power density of the cell was 0.96 W/cm\(^2\) at 1073 K, which is almost two times...
larger than that of the cell using Ni anode. Increase in power density can be explained by decreased anodic overpotential. Therefore, this study reveals that Ni-Fe-Pt alloy anode is highly active for intermediate temperature SOFCs.

Figure 8 shows a comparison of power density of the cells with Ni, Ni-Fe, and Ni-Fe-Pt alloy anodes. It is seen that the power density increases in the following order; Ni-Fe-Pt>Ni-Fe>Ni. In particular, increase in power density at high temperatures is significant. Consequently, this study reveals that the bimetallic Ni-Fe alloy exhibits high activity for anodic reaction in SOFC and is suitable as anode for intermediate temperature SOFCs.

CONCLUSIONS

Studies on bimetallic anodes for SOFCs have been limited up to now; however, it was found that a Ni-Fe bimetallic alloy is highly active for anodic reaction and so the anodic overpotential can be small decreased temperatures. Considering the decreased apparent activation energy of anode, the decreased overpotential of Ni-Fe bimetallic alloy may result from increased oxidation activity of active site. Since it is reported that mixed oxide ion conductor with Ni is effective for expanding the reaction area, it is expected that anodic overpotential could be further decreased by a combination of oxide ion conductor. Application of Ni-Fe alloy for cermet anode is now under investigation.

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### Table 1: Effect of metal added to Ni anode on overpotential and power generating characteristics

| Temperature (K) | Open-circuit Voltage/V | Maximum Power Density/Wcm⁻² | Overpotential/mV¹) | \( \eta_{An}²) | \( \eta_{Ca}³) |
|-----------------|------------------------|-----------------------------|-------------------|----------------|----------------|
| 1073K           |                        |                             |                   |                |                |
| Ni              | 1.14                   | 0.522                       | 32.6              | 12.4           | 28.7           | 10.9           |
| 90Ni-10Au       | 1.12                   | 0.605                       | 72.5              | 2.5            | 17.5           | 3.1            |
| 90Ni-10Fe       | 1.12                   | 0.570                       | 33.1              | 18.8           | 26.3           | 13.7           |
| 90Ni-10Co       | 1.13                   | 0.532                       | 42.5              | 11.3           | 30.6           | 10.2           |
| 90Ni-10Pd       | 1.12                   | 0.514                       | 67.5              | 11.3           | 26.9           | 1.88           |
| 90Ni-10Pt       | 1.13                   | 0.457                       | 33.1              | 12.1           | 38.8           | 8.8            |
| 90Ni-10Ir       | 1.12                   | 0.398                       | 56.3              | 10.3           | 68.7           | 10.1           |
| 90Ni-10Rh       | 1.13                   | 0.370                       | 101.2             | 6.9            | 30.6           | 1.87           |
| 90Ni-10Re       | 1.13                   | 0.311                       | 86.8              | 11.3           | 73.8           | 11.3           |
| 90Ni-10Ag       | 1.13                   | 0.252                       | 80.0              | 12.5           | 57.5           | 11.9           |
| 90Ni-10Mn       | 1.13                   | 0.209                       | 48.8              | 16.3           | 73.8           | 11.3           |
| 90Ni-10Ga       | 1.12                   | 0.198                       | 136.9             | 21.9           | 48.6           | 14.8           |
| 90Ni-10Cu       | 1.12                   | 0.117                       | 294.4             | 3.8            | 30.6           | 3.75           |

¹) Value at current density of 0.1 Acm⁻²
²) \( \eta_{An}, \eta_{Ca} \) means IR drop at anode and cathode sides, respectively
³) \( \eta_{An}, \eta_{Ca} \) means overpotential at anode and cathode sides, respectively

### Table 2: Effect of metal added to Ni anode on overpotential and power generating characteristics

| Temperature (K) | Open-circuit Voltage/V | Maximum Power Density/Wcm⁻² | Overpotential/mV¹) | \( \eta_{An}²) | \( \eta_{Ca}³) |
|-----------------|------------------------|-----------------------------|-------------------|----------------|----------------|
| 873K            |                        |                             |                   |                |                |
| Ni              | 1.16                   | 0.082                       | 153.8             | 75.0           | 61.3           | 12.5           |
| 90Ni-10Fe       | 1.16                   | 0.110                       | 112.5             | 55.6           | 43.8           | 33.8           |
| 90Ni-10Co       | 1.15                   | 0.089                       | 135.0             | 31.0           | 85.0           | 25.3           |
| 90Ni-10Pd       | 1.15                   | 0.045                       | 405.9             | 72.0           | 58.7           | 29.0           |
| 90Ni-10Pt       | 1.16                   | 0.069                       | 163.8             | 37.5           | 58.1           | 25.6           |
| 90Ni-10Au       | 1.15                   | 0.073                       | 411.3             | 13.8           | 88.1           | 9.38           |
| 90Ni-10Ir       | 1.15                   | 0.073                       | 184.4             | 41.0           | 168.8          | 28.0           |
| 90Ni-10Rh       | 1.16                   | 0.038                       | 552.5             | 26.9           | 78.8           | 7.5            |
| 90Ni-10Re       | 1.17                   | 0.062                       | 355.6             | 39.2           | 147.5          | 13.4           |
| 90Ni-10Ag       | 1.16                   | 0.045                       | 240.6             | 40.0           | 125.0          | 19.4           |
| 90Ni-10Mn       | 1.16                   | 0.034                       | 142.7             | 48.8           | 89.8           | 23.8           |
| 90Ni-10Cu       | 1.16                   | 0.016                       | 600               | 52.6           | 200<           | 28.6           |

¹) Value at current density of 0.1 Acm⁻²
²) \( \eta_{An}, \eta_{Ca} \) means IR drop at anode and cathode sides, respectively
³) \( \eta_{An}, \eta_{Ca} \) means overpotential at anode and cathode sides, respectively
Figure 1. Arrhenius plots of current density at anodic overpotential of 30 mV on various Ni based anodes.

Figure 2. Anodic overpotential of various Ni based anodes as a function of current density at 873 K.
Figure 3. Maximum power density, potential drop by IR loss at anode side and anodic overpotential at 0.1 A/cm$^2$ at 1073 K as a function of Fe amount.

Figure 4. Temperature dependence of power generating characteristics of the cell using 95Ni5Fe for anode.
Figure 5. XRD patterns of the anode at different Fe amounts.

Figure 6. SEM observation results of Ni and Ni-Fe anodes after power generation measurement.

Table 3. Effect of metal added to Ni-Fe anode on overpotential and power generation characteristics.

| Metal         | Open-circuit Voltage/V | Maximum power density/Wcm² | Overpotential/mV |
|---------------|------------------------|-----------------------------|-----------------|
|               | IRₐᵃ, IRₖᵃ           | ηₐᵃ, ηₖᵃ                  |                 |
| Ni-Fe-Pt      | 1.13                   | 0.960                       | 25.6, 10.0, 10.0, 8.1 |
| Ni-Fe-Ce      | 1.12                   | 0.785                       | 38.1, 11.3, 9.4, 6.3 |
| Ni-Pt-Pd      | 1.10                   | 0.604                       | 29.4, 11.3, 21.3, 5.1 |
| Ni-Fe-La      | 1.14                   | 0.576                       | 61.9, 15.0, 11.9, 6.3 |
| Ni-Pt-Co      | 1.12                   | 0.400                       | 95.6, 15.0, 31.9, 5.0 |
| 95N i-5Fe     | 1.11                   | 0.675                       | 31.9, 13.8, 12.5, 6.2 |

1) Value at current density of 0.1 Acm²
2) IRₐᵃ, IRₖᵃ means IR drop at anode and cathode sides, respectively
3) ηₐᵃ, ηₖᵃ means overpotential at anode and cathode sides, respectively
Figure 7. Impedance spectra of Ni and Ni-5 wt% Fe anodes at 1073 K.

Figure 8. Temperature dependence of open circuit potential and maximum power density of the cell using various anodes.