Development of Ni-Fe Based Cermet Anode for Direct CH₄ Fueled Intermediate Temperature SOFC Using LaGaO₃ Electrolyte

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Cermet anode of NiFe(9:1)-La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) was studied for direct CH₄ fueled SOFC operating at intermediate temperature. In case of NiFe bimetal anode, power density of the cell decreased drastically in CH₄. On the other hand, mixing Sm doped CeO₂, MgO, or LSGM is effective for improving the long-term stability. The cell with NiFe-LSGM anode exhibited much stable power density under CH₄ feeding condition. At 1073K, the maximum power density of the cell using NiFe-LSGM anode is achieved a value of 0.48 W/cm², and after 15 hours operation, degradation in the power density is slightly observed. However, stability in the power density is much improved. Deposition of coke is also hardly detected by Raman spectroscopy, and so it was found that NiFe-LSGM10 shows a high tolerance against the coke deposition.

Key Words : NiFe-LaGaO₃ Cermet, Direct CH₄ Fuel, Carbon Deposition

1 Introduction

Solid oxide fuel cells (SOFCs) are attracting much attention as a power generator with high conversion efficiency from chemical to electrical energy. In addition, SOFCs can utilize various hydrocarbons for fuel without an external reforming reaction, which means a simple fuel process is enough for the system as a power generator and so, low cost as well as a compact system could be achieved in case of SOFC.¹⁻²⁾ At present, one of the most important subjects for SOFC development is a high reliability and a tolerance to the coke deposition is strongly requested for the internal reforming type SOFC. Nickel has been widely used as an anode material since the early stage of SOFC development. However, when hydrocarbon is used directly for fuel, Ni-based anode easily forms coke resulting in deactivation.³⁻⁴⁾ Since the coke deposition becomes the most significant around 873K, development of the Ni based anode with the high tolerance to coke deposition is particularly important for the direct hydrocarbon fueled SOFC.

Some Ni-free materials such as Cu-ceria cermets and LaCr(Mn)O₃-based oxides anode are reported by several groups recently for direct CH₄ fueled SOFC.⁵⁻⁸⁾ However, activity of these materials is still not sufficiently high. In our previous study,⁹⁻¹⁰⁾ NiFe bimetal exhibits the smaller anodic overpotential than that of pure Ni, and the power generation property and stability are further improved by mixing NiFe bimetal with La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) because of expanding the three-phase boundary. However, performance of NiFe-LSGM cermet anode for CH₄ oxidation is still not thoroughly investigated. In this study, NiFe-based anode mixed with various oxides was studied as the direct CH₄ fueled SOFC using La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ electrolyte, and the coke deposition performance on NiFe and NiFe-LSGM cermet anode was further studied.

2 Experimental

La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) electrolyte was always used for the electrolyte in this study and LSGM is prepared by using a conventional solid-state reaction method. Precursor powder at a stoichiometric ratio was mixed by using Al₂O₃ mortar and pestle for 0.5 h. The mixture was precalcined at 1273K for 6 h followed by pressing isostatically into a disk. The obtained disk was sintered at 1773K for 6 h in air. The sintered disk was polished to keep 0.5 mm in thickness.

NiFe91 (Ni:Fe = 9:1 wt%) bimetal was prepared by a conventional wet method.⁹⁻¹⁰⁾ Preparation of NiFe-LSGM cermet anode was prepared by mixing thus obtained NiO-Fe₃O₄ oxide with LSGM power with a planetary ball mixer. The composition of cermet is 9:1 in weight ratio otherwise noted, and the cermet anode is generally denoted as NiFe-oxide10 (For example, NiFe-SDC10), which means 10 weight % oxide mixed with NiFe.

Planer type single cell using LSGM electrolyte is prepared by using NiFe91 based cermets as anode and Sm_{0.5}Sr_{0.5}CoO₃ (SSC55) as cathode. Details of the preparation method of the cell were reported previously.⁹⁻¹⁰⁾ Pt reference electrode was prepared on the side of the cathode by using Pt paste. Electrical power generation characteristics of the cell were measured with the four-probe method using humidified CH₄ (100 cc/min, with 3 vol% H₂O) as fuel and oxygen (100 cc/min) as oxidizing agent. Deposited carbon on anode was investigated by a Raman spectrometer (Horiba type LabRAM HR-800).

3 Results and Discussion

Figure 1 shows the power generation property of the cell using NiFe cermet anode, which uses various oxides, at 1073 K. Although humidified CH₄ was used for fuel, all cells showed the open circuit potential of ca. 1.14 V. The power density is strongly dependent on the oxide com-

Fig. 1 Effects of mixing oxide in NiFe base cermet anode on power generation property of the cell using LSGM electrolyte at 1073 K.

Table 1 Effects of oxide used for NiFe base cermet anode on the initial power generation property and internal resistance of the cell using LSGM electrolyte.

Anode	OCV (V)	Power density (W/cm ²)		Initial potential drop (mV)*		
		start	15h	IR	η_{an}	η_{ca}
NiFe-LSGM10	1.145	0.48	0.46	63.3	54.5	5.5
NiFe-SDC10	1.120	0.43	0.31	61.5	74.6	6.2
NiFe-LSGMC10	1.070	0.06	0.00	—	—	—
NiFe-LSGM20	1.141	0.31	0.26	69	87.3	5.1
NiFe-MgO5%	1.144	0.42	0.40	71.4	72	8.7

*: potential drop at 100 mA/cm², η_{an} ; anodic overpotential, η_{ca} ; cathodic overpotential

bined with NiFe for anode. The maximum power density of the cell increased in the following order for oxide mixed with NiFe; LSGM > SDC > MgO > LSGMC. High activity of NiFe-LSGM or NiFe-SDC to anodic reaction is already reported in our previous paper for H₂. These cermet electrodes are also active for CH₄ fuel. In addition, it was found that the cell using NiFe combined with MgO of which electrical conductivity is low, also shows a reasonably high power density (> 300 mW/cm²). Therefore, if the amount is small, oxide with low electrical conductivity can also be used for the cermet anode. Since it is well known that basic oxides such as MgO are effective for preventing coke deposition in CH₄ as a supporting oxide, mixing MgO with NiFe for anode is expected for preventing coke deposition and this was discussed later.

Details of internal resistance of the cell using various NiFe cermet anodes are summarized in Table 1. IR loss and anodic overpotential are strongly dependent on the type of cermet. In case of MgO, slightly larger IR loss is observed comparing those of the examined cermet and this could be explained by a low conductivity of MgO. On the other hand, small anodic overpotential is observed on NiFe-LSGM cermet and so, NiFe-LSGM is the most active one among the examined cermet anode.

In case of the direct CH₄ fueled cell, deactivation of the anode by a coke deposition is another issue to overcome. Figure 2 shows a current density at 0.7 V, 1073K as a function of period after CH₄ feeding. Although the high initial power density is obtained on NiFe bimetal

anode, it decreased drastically with an operation time and after 1 h later, almost no electrical power is obtained. This drastic drop in power density could be explained by the coke deposition. In contrast, NiFe cermet anode shows the stable power density over examined 16 h. In case of NiFe-SDC anode, initial drop in power density is also observed and this may also be coke deposition. On the other hand, as expected, MgO mixing NiFe anode shows the stable power density over 16 h and combination of MgO with NiFe is effective for high stability in CH₄. Among the examined cermet anode, it is evident that NiFe-LSGM anode gives the highest power density as well as the long-term stability and this could be explained by the large three-phase boundary by high oxide ion conductivity of LSGM and also a basic property of LSGM. The maximum power density of the cell with NiFe-LSGM cermet anode is initially achieved a value of ca. 0.48 W/cm², and slightly decreases to about 0.46 W/cm² after 15 hours operation. In Table 1, power generation characteristic and internal resistance of the cell using NiFe-LSGM20 anode are also shown. Power density decreased by increasing LSGM content from 10 to 20 wt% and this could be assigned to the enlarged anodic overpotential. Therefore, anodic activity may be decreased by increasing content of LSGM of which surface activity to an electrochemical oxidation is poor and it seems that the optimum composition for NiFe-LSGM cermet seems to exist around 10 wt% of LSGM.

Figure 3 shows the complex impedance plots of NiFe

Fig. 2 Current density of the cell using various NiFe base cermet anode at 0.7 V, 1273 K as a function of period after CH_4 feeding.

Fig. 3 Complex impedance plots of NiFe and NiFe-LSGM10 anode in CH_4 at 1073 K.

and NiFe-LSGM10 anode in CH_4 at 1073 K. At initial period, diameter of impedance semicircle of NiFe is close to NiFe-LSGM. However, just after 30 min, the semicircle of NiFe becomes much larger by coke deposition. In particular, the impedance semicircle at a low frequency region was significantly enlarged. Therefore, it seems that a diffusion resistance becomes larger by the coke deposition because of the decreased porosity of anode.⁹⁻¹⁰ In contrast, change in the impedance semicircle is not significant after 15 h operation, albeit small increase at lower frequency is observed in case of NiFe-LSGM10. Therefore, mixing LSGM with NiFe is highly effective for preventing coke deposition in CH_4 fuel and also preventing the electrode powder aggregation.

Coke deposition was further studied by Raman spectroscopy. Figure 4 shows Raman spectra of NiFe and NiFe-LSGM10 anode after power generation measurement. The peaks appeared at 1585 and at 1330 cm^{-1} are assigned to graphite and disordered carbon, respectively.¹¹⁻¹² In case of NiFe, strong peaks are observed at 1585 and 1330 supporting the electrochemical measurement results of the significant coke deposition. On the other hand, Raman peaks assigned to carbon is hardly observed on NiFe-LSHM10. These data also confirmed that the coke deposition is strongly prevented

Fig. 4 Raman spectra of NiFe and NiFe-LSGM10 anode films after power generation measurement.

by mixing LSGM with NiFe bimetal. At present, detail mechanism of the suppression of coke formation by LSGM is not clear. It is anticipated that large number of three-phase boundary has some relationship for this. Further detail study is now under performed.

4 Conclusion

Although NiFe bimetal shows the high surface activity to CH_4 electrochemical oxidation, coke is easily formed on this anode resulting in the significant degradation of power density. Mixing LSGM is highly effective for preventing coke deposition under a CH_4 fuel condition and the stable power density is observed over 15 h operation. The optimum amount of LSGM mixed with NiFe seems to exist around 10 wt%. This study reveals that NiFe-LSGM cermet is useful for anode of intermediate temperature SOFC using CH_4 directly for fuel.

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