

Power-generating property of direct CH₄ fueled SOFC using LaGaO₃ electrolyte

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Abstract A composite anode of NiFe–MgO (2.5 wt.%)–La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) (10 wt.%) for solid oxide fuel cells using directly CH₄ as fuel was studied. Compared with previously reported NiFe–LSGM (10 wt.%) cermet anode, the NiFe–MgO–LSGM anode exhibited superior power generation performance, stability under CH₄ atmosphere at 973 K, and high tolerance against the carbon deposition. These improvements by the additives are explained by the increase in basic property of anode material. The anode activity of NiFe–MgO–LSGM cermet for CH₄ fuel is still lower than that for H₂ one. However, comparing with that of NiFe–LSGM cermet, anodic overpotential slightly decreased by the addition of MgO, suggesting the improved surface activity.

Keywords SOFC · Direct hydrocarbon · Ni–Fe anode · LSGM electrolyte

Introduction

Solid oxide fuel cell (SOFC) can directly utilize various hydrocarbons as fuel without an external reforming reaction, and this is a great advantage of SOFCs, i.e., simple fuel process, compared with other fuel cell system. Therefore, the

power generation system with low cost as well as compact system can be constructed in the case of SOFC [1, 2]. At present, nickel has been widely used as an anode material because of its high activity to the H₂ electrochemical oxidation and low cost. However, when hydrocarbon is directly used as fuel, coke deposition is formed at the surface and pores of the Ni-based anode, leading to deactivation of anode performance [3, 4]. At present, one of the most important subjects for SOFC development is high reliability, therefore, high tolerance against coke deposition is strongly requested for the internal reforming type SOFC.

In our previous study on direct CH₄ type SOFC, it was found that NiFe–La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) (10 wt.%) cermet anode exhibited high performance, and the formation of coke was much prevented on this cermet anode comparing with that of pure Ni at 1,073 K. However, unfortunately, the cell became unstable when the operation temperature was down to 973 K, and the coke deposition became significant. Because the improvement of NiFe–LSGM in CH₄ might be achieved by increase in the basic property of anode material [5–7], further increase in basic property of anode catalyst may be effective for preventing coke formation at low temperature range.

In this study, NiFe–MgO (2.5 wt.%)–LSGM (10 wt.%) composite anode for direct CH₄ SOFC was investigated firstly. Since MgO is a kind of low conductivity material, addition of MgO into Ni–Fe bimetallic system may decrease the conductivity and also surface activity of anode. Therefore, the comparison of the activity in H₂ and CH₄ electrochemical oxidation was also discussed.

Experimental

LSGM electrolyte was used for the electrolyte in this study. LSGM powders were prepared by using a conventional

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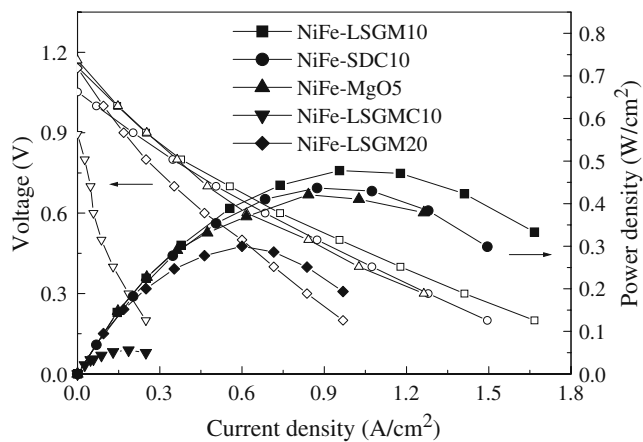


Fig. 1 Effects of mixing oxide in NiFe base cermet anode on power generation property of the cell using LSGM electrolyte at 1,073 K. *LSGM10* means $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ mixed with NiFe at 10 wt.%, and *SDC* is $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_2$. *LSGMC10* is 10 wt.% $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_3$

solid-state reaction with commercial reagents of La_2O_3 (99.99%), SrCO_3 (99.99%), MgO (99.99%), and Ga_2O_3 (99.99%). The powders at a stoichiometric ratio were mixed by using Al_2O_3 mortar and pestle for 0.5 h. The mixture was pre-calcined at 1,273 K for 6 h and isostatically pressed into a disk shape. The obtained disk was sintered at 1,773 K for 6 h in air. The sintered disk was polished to keep 0.5 mm in thickness.

For NiFe cermet anode, NiFe (Ni/Fe=9:1 weight ratio) oxide composite powders were firstly prepared by a conventional wet process method: Fe_3O_4 was loaded on NiO by using $\text{Fe}(\text{NO}_3)_3$ solution, and then after evaporation of $\text{Fe}(\text{NO}_3)_3$ solution, the resulting powders were calcined at 673 K for 2 h followed by calcination at 1,073 K for 6 h in air. Preparation of NiFe–LSGM cermet anode and NiFe–MgO–LSGM composite anode were performed by mixing the obtained NiO– Fe_3O_4 with LSGM powders (ca. 20 vol.%) or with MgO powders (ca.10 vol.%) and LSGM powders, by using a planetary ball mill mixer. The mixing ratio of the cermet is 9:1 in weight (8:2 in volume) unless otherwise mentioned. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ used for cathode was prepared using the conventional solid-state

reaction method [5–7]. The prepared anode and cathode powders were symmetrically slurry-coated on the each side of LSGM disk and then calcined at 1,373 and 1,223 K for 1 h in air, respectively. Pt reference electrode was prepared on the side of the cathode by using Pt paste.

Electrochemical characterization was performed after heating the cell to measure the temperature in air and changing the atmosphere to fuel. Electrical power generation characteristics of the cell were measured with the four-probe method using humidified H_2 (100 cm^3/min , with 3 vol.% H_2O) or CH_4 (100 cm^3/min , with 3 vol.% H_2O or dry) as fuel and oxygen (100 cm^3/min) as oxidizing agent. Potential drop by *IR* loss and electrode overpotential was separately measured by using a current interruption method. The polarization resistance, R_p , was measured by impedance spectroscopy (Solartron 1260 and Electrochemical interface 1270) by using Pt reference electrode put close to the cathode.

Results and discussion

Figure 1 shows the power generation property of the cell using NiFe cermets anode of various oxides at 1,073 K. Although humidified CH_4 was used for fuel, all cells showed the open circuit potential of ca. 1.13 V in CH_4 . It can be seen that the power density was strongly dependent on the oxide combined with NiFe for anode. The maximum power density of the cell increased in the following order for the oxides mixed with NiFe: $\text{LSGM} > \text{SDC} > \text{MgO} > \text{LSGMC}$. In addition, it was found that the cell using NiFe–MgO cermet anode also exhibited a reasonably high power density ($\sim 0.4 \text{ W}/\text{cm}^2$) in CH_4 atmosphere. It is well known that basic oxides such as MgO are effective as a supporting oxide for preventing coke deposition in steam reforming reaction of CH_4 [7–10]. Therefore, high performance and coke tolerance of NiFe–based oxide composite anode may come from its basic property. Since MgO is a low conductivity material, which is much lower than that of LSGM, the better performance of NiFe–LSGM anode should be assigned to its higher conductivity. On the other

Table 1 Comparison of NiFe–MgO (2.5%)–LSGM (10%) and NiFe–LSGM (10%) on power-generating property in CH_4

Temperature	NiFe–MgO (2.5%)–LSGM		NiFe–LSGM	
	OCV (V)	MPD (W/cm^2)	OCV (V)	MPD (W/cm^2)
1,073 K	1.13	0.28	1.12	0.51
973 K	1.11	0.14	0.99	$\sim 0.07^a$
873 K	1.07	$\sim 0.06^a$	/	/

^a When temperature decreased to these marked points, cell voltage became unstable. Therefore, an estimated MPD value at ~ 0.5 V in initial stage is just showed here

hand, the cell using NiFe–LSGMC anode shows the lowest power density in spite of similar conductivity of LSGMC with that of LSGM. At present, the reason why LSGMC cermet shows the poor activity is not clear. However, considering the decreased OCV and large IR loss, decomposition of LSGMC into La_2O_3 and Co or Ga base oxides seems to occur. Reaction of Ni with LSGMC cermet is also expected. However, at present, details for decreased power density are now under-performed, and this will be reported in the future.

Furthermore, the NiFe–LSGM anode could not be used at 973 K; in this case, large amount of coke was deposited on anode, and the anodic overpotential became large. Since MgO exhibited a superior property to prevent the carbon deposition, co-mixing MgO and LSGM with NiFe bimetal catalyst might be effective for further improving cell performance at lower temperature range (<973 K).

Table 1 shows the power density of NiFe–MgO (2.5 wt.%)–LSGM (10 wt.%) (denoted as NiFe–MgO–LSGM in the following section) and NiFe–LSGM (10 wt.%) from 1,073 to 873 K. As shown in this table, OCV of NiFe–MgO–LSGM showed almost 1.1 V at all temperature range, whereas that of NiFe–LSGM decreased to 0.99 V even at 973 K. As for power density property, at 973 K, MPD of NiFe–MgO–LSGM anode cell still showed about 0.14 W/cm^2 , whereas NiFe–LSGM anode cell was only $\sim 0.07 \text{ W/cm}^2$, even though the power density of NiFe–LSGM ($\sim 0.5 \text{ W/cm}^2$) is much larger than that of NiFe–MgO–LSGM ($\sim 0.3 \text{ W/cm}^2$) at 1,073 K.

Figure 2 shows the impedance plots of NiFe–MgO–LSGM and NiFe–LSGM anode in CH_4 at 973 K. Both the anodic IR loss and anodic overpotential of NiFe–LSGM were larger than those of NiFe–MgO–LSGM at 973 K. This large anodic semicircle of NiFe–LSGM was attributed to

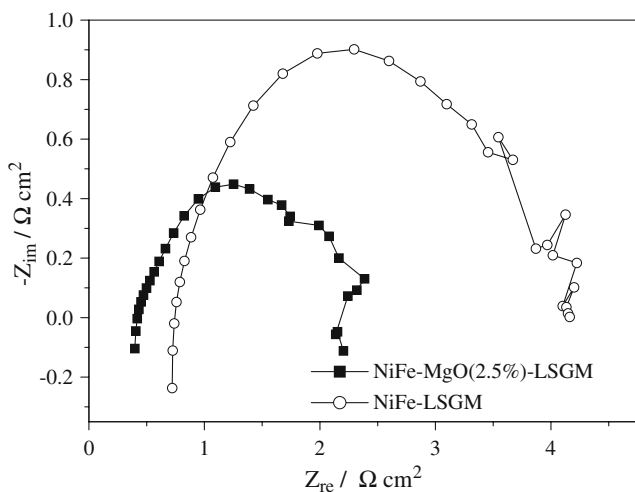


Fig. 2 Comparison of NiFe–MgO–LSGM and NiFe–LSGM on anodic impedance in CH_4 at 973 K

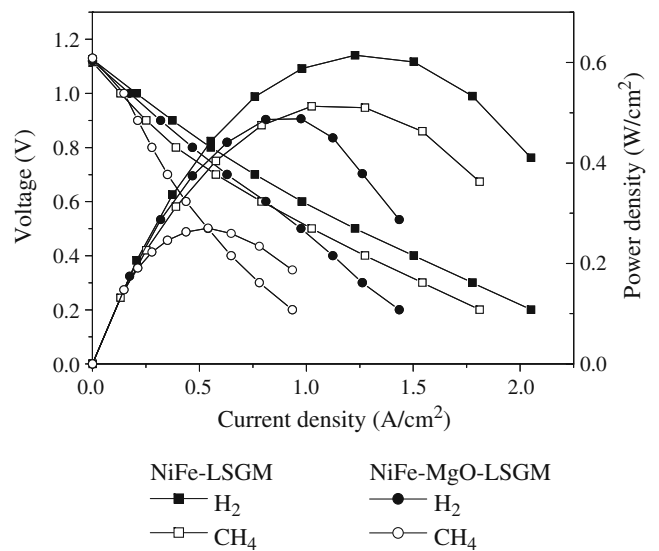


Fig. 3 Power-generating property of NiFe–LSGM and NiFe–MgO (2.5%)–LSGM anode in H_2 and CH_4 atmosphere at 1,073 K

the coke deposition; thus, it can be concluded that MgO additive decreased the coke deposition. These results indicate that co-mixing MgO and LSGM with NiFe may have more positive effects for preventing the coke deposition at temperature lower than 1,073 K, and MgO is an effective material for preventing coke from depositing on anode metal, even though it may decrease the activity of anode due to its low conductivity and low surface activity (Table 1, column 1,073 K). Since NiFe–LSGM cermets exhibited a maximum power density of about 0.5 W/cm^2 at 1,073 K, NiFe–MgO–LSGM may have a potential for further improving the power-generating property. The ratio

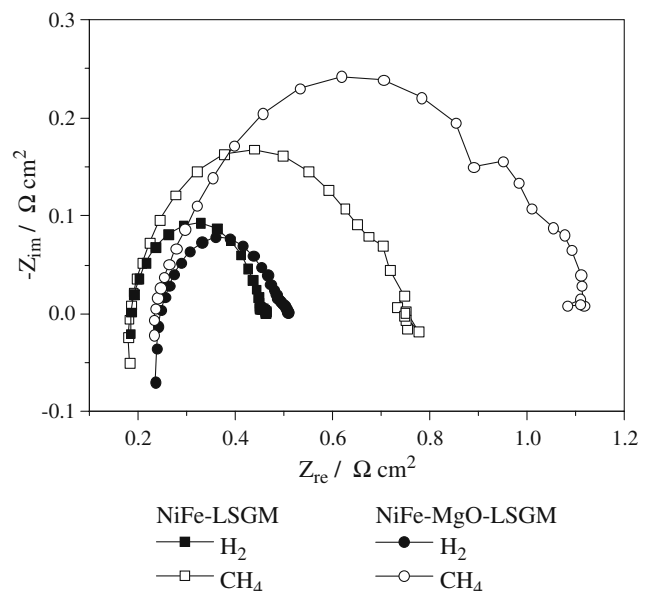


Fig. 4 Impedance plots of NiFe–LSGM and NiFe–MgO (2.5%)–LSGM anode in H_2 and CH_4 atmosphere at 1,073 K

of MgO and the preparation method for this composite anode should be further optimized, and this is now under investigation.

In order to investigate the reaction change in different fuel atmosphere and the effect of MgO additive on anode performance, in the following section, we discussed the difference in the cell performance between H₂ and CH₄ fuel using the same anode materials (NiFe–LSGM and NiFe–MgO–LSGM). As shown in Fig. 3, the hydrogen power densities are larger than those of methane performance in both NiFe–LSGM and NiFe–MgO–LSGM composite anode. Since the cell setup was totally the same among these cells, the reasonable explanation is only the difference in anode activity between H₂ and CH₄, that is, the anode activity in H₂ is better than that in CH₄ when using the same anode catalyst. However, as shown in Fig. 3, at 1,073 K, the performance of the cell using NiFe–MgO–LSGM anode is lower than that of NiFe–LSGM, suggesting that the anode activity of NiFe–MgO–LSGM composite is still insufficiently high and should be further optimized.

The impedance plots of NiFe–MgO–LSGM and NiFe–LSGM anode measured in H₂ or CH₄ atmosphere are shown in Fig. 4. Firstly, it is notable that, in either case of NiFe–LSGM anode cell and NiFe–MgO–LSGM anode one, the IR loss kept almost same value, and the anodic semicircle of CH₄ used cell was largely increased than that of H₂ used cell. The similarity in the IR losses may suggest that the contact between anode and electrolyte was not changed by fuel gas. The larger anodic semicircle of CH₄ is attributed to the decrease in anode surface reaction activity. This result agreed with the explanation of power density change in Fig. 3: the decrease in power density can be explained by decrease in anode activity in CH₄. The comparison of NiFe–LSGM and NiFe–MgO–LSGM is also shown in Fig. 4. It exhibits that IR loss of NiFe–MgO–LSGM cell, which is estimated by *X*-axis intercept of impedance arc at high frequency, is larger than those of the NiFe–LSGM. This means that the low conductivity of MgO may exist at the anode/electrolyte interface, so the effective contact area between anode and electrolyte may be decreased by addition of MgO, and so the IR loss increased. As for anodic overpotential, which is estimated by the size of semicircle, MgO additive is effective for improving the surface activity resulting in a slightly

decreased size of semicircles for overpotential. Therefore, the amount of MgO might be excess when 2.5 wt.% is used, so that the excess MgO will occupy the active anode surface and decrease the electrical conductivity. All these results suggest that the amount of MgO in NiFe bimetal system anode should be further optimized.

Conclusion

This study demonstrated that addition of MgO and LSGM to NiFe bimetallic anode is significantly effective for preventing coke deposition on anode at a temperature lower than 1,073 K under a CH₄ fuel condition. A stable output power density of around 0.14 W/cm² was obtained by using the NiFe–MgO–LSGM composite anode at 973 K. The comparison of the cell performances using hydrogen and methane fuel on both NiFe–LSGM and NiFe–MgO–LSGM anode suggested that the anode activity in H₂ is better than that in CH₄. MgO additive increases IR loss due to its low conductivity; however, it slightly decreased anode overpotential. Consequently, this study reveals that the further improved performance of anode for the cell using directly CH₄ for fuel is expected by optimizing the amount of added MgO.

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