Performance of $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x$ ($\text{M} = \text{Fe}$ and Co) alloy-based cermet anodes for intermediate-temperature solid oxide fuel cells fueled with syngas

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The performance of Ni-based trimetallic alloy cermet anodes, $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x$ ($\text{M} = \text{Fe}$ and Co ; $x = 0.1, 0.2$, and 0.3)/ $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), was investigated for intermediate-temperature ($500\text{--}700^\circ\text{C}$) solid oxide fuel cells (IT-SOFCs), using humidified (3% H_2O) model syngas with a molar ratio of $\text{H}_2/\text{CO} = 3/2$ as the fuel. Though doping Fe or Co 10 mol % into the $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ anode led the cell performance to the increase, the cell performance decreased as Fe or Co content increased further. On the one hand, doping Fe or Co into the $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ anode further effectively inhibited carbon deposition owing to CO on the anode. Our results suggest that the $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC}$ and $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}/\text{SDC}$ anodes are more promising materials than $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ anode for syngas fuel in IT-SOFCs.

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1. Introduction

Biogas is mainly composed of CH_4 and CO_2 and is saturated with water vapor.^{1)–3)} The application of biogas as a fuel for solid oxide fuel cells (SOFCs) has attracted much attention in terms of environmental protection.^{4)–6)} We are developing intermediate-temperature ($500\text{--}700^\circ\text{C}$) SOFCs (IT-SOFCs) fueled with syngas derived from biogas in an external process.⁷⁾ Biogas is transformed to the syngas by CH_4 dry reforming with CO_2 (1) and CH_4 steam reforming with H_2O (2), as shown below.

In the process of developing IT-SOFCs fueled with syngas, inhibiting carbon deposition on the anode is important because it lowers the power generation performance. Coking from CO in the syngas is due to the reverse water gas reaction (3) and disproportionation reaction (4).

Carbon deposition reactions become dominant below 700°C .⁸⁾ We recently investigated the electrochemical performance of $\text{Ni}_{1-x}\text{Cu}_x/\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) cermet anodes in IT-SOFCs at 600 and 700°C using a model syngas fuel humidified (3% H_2O) with a molar ratio of $\text{H}_2/\text{CO} = 3/2$. In this previous study, we found that the $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ cermet anode remarkably suppresses carbon deposition and its electrochemical performance is comparable to that of the Ni/SDC cermet anode.⁹⁾ Still, it is necessary to develop improved anode materials that can further inhibit carbon deposition and show high electrochemical performances for practical applications.

Based on the studies of the Ni-based alloy anode catalysts for H_2 ^{10)–12)} or CH_4 ^{13),14)} fueled SOFCs, here, we added Fe, Co and Zn as a third component to the $\text{Ni}_{0.8}\text{Cu}_{0.2}$ alloy, replacing some Ni with these transition metals to examine its electrochemical performance for practical applications. Our results suggest that adding a small amount of Fe or Co can improve the inhibition of carbon deposition. We also report the power generation performance of IT-SOFCs with $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ or $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Co}_x/\text{SDC}$ cermet anodes using model syngas fuel with $\text{H}_2/\text{CO} = 3/2$ at 700 and 600°C .

2. Experimental procedures

Precursors of $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x$ ($\text{M} = \text{Fe}$ and Co ; $x = 0.0, 0.1, 0.2$, and 0.3) alloys, $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x\text{O}$, were prepared by a solid-state reaction, using NiO (99.97%, Japan Pure Chemical, Japan), CuO (99.99%, Kanto Chemical, Japan), Fe_2O_3 (99.99%, Japan Pure Chemical, Japan), and Co_3O_4 (99.99%, Kanto Chemical, Japan) as starting materials. NiO, CuO and Fe_2O_3 (or Co_2O_3) in desired molar ratios were mixed and ground in ethanol for 24 h using a ball mill, and then calcined at 900°C for 12 h in air. Mixture of the calcined $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x\text{O}$ and SDC (AGC Seimi Chemical, Japan) powders in a mass ratio of $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x\text{O}/\text{SDC} = 70/30$ for cermet anode was ground in ethanol for 24 h using a ball mill and then dried at 50°C overnight.

Electrolyte-supported single test-cells were fabricated with the SDC powder, the prepared $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x\text{O}/\text{SDC}$ powder and commercial $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF; Hosokawa Powder Technology Research Institute, Japan) cathode powder, according to the previous paper.⁹⁾ The SDC electrolyte pellet uniaxially pressed at 10 MPa and sintered at 1400°C for 10 h was approximately $490\text{ }\mu\text{m}$ thick. An anode paste of the prepared powder and polyethylene glycol (Hampton Research, USA) was screen-printed on the SDC electrolyte pellet followed by heating at 1000°C for 2 h. A cathode paste of LSCF powder and polyethylene glycol was also screen-printed onto the opposite side of

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the anode-coated SDC electrolyte pellet followed by heating at 1000°C for 2 h. The electrode areas were estimated to be 28.3 mm². The test-cell, which a Pt reference electrode was attached to, was set in a device for measurements of cell performance followed by heating in situ at 700°C under H₂ atmosphere to reduce $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x\text{O}$ to trimetallic $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x$ alloy for forming cermet anode. Commercial soft-glass rings were used for gas seal. The cell performances were measured at 700 and 600°C using humidified (3% H₂O) model syngas and dry air fed as fuel and oxidant, respectively, at a controlled gas flow rate of 50 cm³/min. Considering the composition of reformed model biogas,¹⁵⁾ the model syngas composition was maintained at H₂/CO = 3/2 because both reactions (1) and (2) occur in biogas reforming at once.

Pt mesh current collectors were availed for both electrodes. Current-voltage curves and electrochemical impedance spectra were measured using an electrochemical analyzer (BioLogic, single-channel potentiostat SP-150, France). The current-interruption method was separately employed to estimate ohmic and overpotential losses in the test-cell in the similar way to the previous paper.⁹⁾ The time dependence of cell performance was examined under a load of 0.1 A/cm² using humidified syngas at 700°C for 24 h.

The anode materials were characterized using powder X-ray diffraction (XRD; Rigaku RINT2100/PC, Japan) with monochromated CuK α radiation and scanning electron microscopy (SEM; Jeol JSM-6380, Japan). The chemical composition and distribution images of $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{M}_x$ alloy particles in the anodes were examined using energy-dispersive X-ray spectroscopy (EDS; Jeol EX-54175JMU, Japan) attached to SEM. The amounts of carbon deposited on the anodes after the 24 h electrochemical tests were also estimated by semi-quantitative analysis using SEM-EDS.

3. Results and discussion

3.1 $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ cermet anode

XRD patterns of the prepared anode materials are shown in Fig. 1. The XRD peaks at $2\theta \approx 44.4$ and 51.6° due to the $\text{Ni}_{0.8}\text{Cu}_{0.2}$ alloy shifted to lower angles as Fe content increased, suggesting the formation of a $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x$ alloy, because the atomic radius of Fe is larger than that of Ni.¹⁶⁾ The other XRD peaks were due to SDC. Therefore, the $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ anodes were confirmed to be a mixture of $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x$ and SDC.

The power density curves of the test-cells with $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ anodes at 700 and 600°C are shown in Fig. 2. The maximum power density of the test-cell with $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$

Fig. 1. X-ray diffraction patterns of the $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ anodes after reduction treatment at 700°C.

anode was about 148 mW/cm² at 700°C. This value is 126% of the previously reported maximum power density for a $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ anode test-cell.⁹⁾ The difference is attributable to the decrease in the ohmic loss of the electrolyte pellet because the present electrolyte pellet is thinner than the previous one that was about 660 μm thick. At 700°C, there was no significant difference between power densities of the test-cells with $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ and $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC}$ anodes, but the power densities decreased as Fe content increased further. In other words, the order of the maximum power densities at 700°C was $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC} \approx \text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC} > \text{Ni}_{0.6}\text{Cu}_{0.2}\text{Fe}_{0.2}/\text{SDC} \approx \text{Ni}_{0.5}\text{Cu}_{0.2}\text{Fe}_{0.3}/\text{SDC}$. The differences among the cell performances were explored by the current-interruption technique, i.e., by splitting the resistance into ohmic loss and overpotential loss. The overpotential losses for the test-cells slightly increased at $x = 0.2$ and 0.3 , while no remarkable differences in the ohmic losses were observed. The increase in the overpotential loss, namely the decrease in triple-phase boundaries, resulted in a decrease in the power density.

The power densities at 600°C showed a similar trend to those observed at 700°C, but their values were about 40% of those at 700°C. The order of the maximum power densities at 600°C was $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC} \approx \text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC} > \text{Ni}_{0.6}\text{Cu}_{0.2}\text{Fe}_{0.2}/\text{SDC} \gg \text{Ni}_{0.5}\text{Cu}_{0.2}\text{Fe}_{0.3}/\text{SDC}$. The current-interruption method revealed that the notable increase in the overpotential loss at $x = 0.3$ caused a decrease in the power density.

Figure 3 shows the time dependence of voltages of the test-cells with $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ anodes under a 0.1 A/cm² load at 700°C. The voltage of the test-cell with $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ anode decreased slightly for 24 h. On the other hand, the voltages of the test-cell with Fe-doped anodes were relatively stable. The order of the cell voltages after 24 h was $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC} \approx \text{Ni}_{0.5}\text{Cu}_{0.2}\text{Fe}_{0.3}/\text{SDC} > \text{Ni}_{0.6}\text{Cu}_{0.2}\text{Fe}_{0.2}/\text{SDC} > \text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$. These results indicate that the cell performance with $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC}$ anode hardly changed during electrochemical tests and can last 24 h.

Fig. 2. Power density versus current density at (a) 700°C and (b) 600°C for the $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ anodes.

Fig. 3. Time dependences of cell voltages for the $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ anodes under 0.1 A/cm² load at 700°C.

Fig. 4. Amounts of carbon deposited on the Ni_{0.8-x}Cu_{0.2}Fe_x/SDC anodes during the 24 h electrochemical test.

Fig. 5. Scanning electron micrographs of cross-sectional views of the Ni_{0.7}Cu_{0.2}Fe_{0.1}/SDC anodes (a) before and (b) after the electrochemical test for 24 h.

Carbon deposition is mainly generated by reactions (3) and (4) when syngas fuel is used. **Figure 4** shows the amounts of carbon deposited on the anodes during the 24 h electrochemical test, estimated by SEM-EDS. The amount of carbon deposited on the present Ni_{0.8}Cu_{0.2}/SDC anode was smaller than the previously reported value; it decreased from 13.6 to 7.6 mass %. This reduced carbon deposition can be attributed to the improvement of the power density owing to decrease in the ohmic loss. Doping Fe into the Ni_{0.8}Cu_{0.2}/SDC anode further inhibited carbon deposition and the amount of deposited carbon decreased to about 4 mass %. The effect of doping Fe to Ni/GDC cermet anodes on carbon deposition have been elucidated as follows: Fe addition (i) restrains C–C bond formation and/or reduces the thermodynamic driving force for carbon nucleation¹³⁾ and (ii) promotes the formation of disordered amorphous carbon which can be easily removed as CO by the water gas reaction, i.e., the reverse of reaction (3).^{14),17)}

XRD patterns revealed that the structures of anode materials were maintained after the 24 h electrochemical tests. **Figure 5** shows SEM micrographs of the test-cell with the Ni_{0.7}Cu_{0.2}Fe_{0.1}/SDC anode before and after the 24 h electrochemical test. As seen in the images, the Ni_{0.7}Cu_{0.2}Fe_{0.1}/SDC anode was in close contact with the electrolyte. A comparison of the SEM micrographs before and after the 24 h electrochemical test demonstrates that the sinterability did not change significantly. Moreover, a comparison of the analytical results by SEM-EDS showed that the chemical composition and particle distribution of the Ni_{0.7}Cu_{0.2}Fe_{0.1} alloy in the anode hardly changed, suggesting minimal change in overpotential loss and that the test-cell output was maintained, as shown in Fig. 3. Overall, we found that the Ni_{0.7}Cu_{0.2}Fe_{0.1}/SDC anode was the best Ni_{0.8-x}Cu_{0.2}Fe_x/SDC anode for syngas fuel with H₂/CO = 3/2.

3.2 Ni_{0.8-x}Cu_{0.2}Co_x/SDC anode

XRD patterns of the prepared anode materials are shown in **Fig. 6**. The Ni_{0.8}Cu_{0.2} alloy peaks at $2\theta \approx 44.4$ and 51.6° slightly shifted to lower angles as the Co content increased. This suggests

Fig. 6. X-ray diffraction patterns of the Ni_{0.8-x}Cu_{0.2}Co_x/SDC anodes after reduction treatment at 700°C.

Fig. 7. Power density versus current density at (a) 700°C and (b) 600°C for the Ni_{0.8-x}Cu_{0.2}Co_x/SDC anodes.

that Co was also occluded in the Ni_{0.8}Cu_{0.2} alloy like Fe, forming the Ni_{0.8-x}Cu_{0.2}Co_x alloy because the atomic radius of Co is slightly larger than that of Ni.¹⁶⁾ The other XRD peaks were due to SDC. Therefore, the Ni_{0.8-x}Cu_{0.2}Co_x/SDC anodes were confirmed to be a mixture of Ni_{0.8-x}Cu_{0.2}Co_x and SDC.

The power density curves of the test-cells with the Ni_{0.8-x}Cu_{0.2}Co_x/SDC anodes at 700 and 600°C are shown in **Fig. 7**. At 700°C, the power density of the Ni_{0.7}Cu_{0.2}Co_{0.1}/SDC anode test-cell was superior to that of the Ni_{0.8}Cu_{0.2}/SDC anode test-cell, but the power density decreased as the Co content increased further. The order of the maximum power densities at 700°C was Ni_{0.7}Cu_{0.2}Co_{0.1}/SDC > Ni_{0.8}Cu_{0.2}/SDC ≈ Ni_{0.6}Cu_{0.2}Co_{0.2}/SDC > Ni_{0.5}Cu_{0.2}Co_{0.3}/SDC. The current-interruption method revealed that there were no remarkable differences in the ohmic and overpotential losses of the test-cells with different anodes except for the Ni_{0.5}Cu_{0.2}Co_{0.3}/SDC anode. The power densities at 600°C decreased to about 40% of those at 700°C. The order of the maximum power densities at 600°C was Ni_{0.7}Cu_{0.2}Co_{0.1}/SDC > Ni_{0.6}Cu_{0.2}Co_{0.2}/SDC > Ni_{0.8}Cu_{0.2}/SDC > Ni_{0.5}Cu_{0.2}Co_{0.3}/SDC.

Figure 8 shows the time dependence of voltages of the test-cells under a 0.1 A/cm² load at 700°C. The voltages of the test-cell with the Co-doped anodes were relatively stable for 24 h. The order of the cell voltages after 24 h was Ni_{0.7}Cu_{0.2}Co_{0.1}/SDC > Ni_{0.6}Cu_{0.2}Co_{0.2}/SDC > Ni_{0.5}Cu_{0.2}Co_{0.3}/SDC > Ni_{0.8}Cu_{0.2}/SDC. These indicate that the cell performance of the Ni_{0.7}Cu_{0.2}Co_{0.1}/SDC anode test-cell hardly changed during the 24 h electrochemical test.

Figure 9 shows the amounts of carbon deposited on the anodes, estimated using SEM-EDS, during the 24 h electrochemical test. Doping Co into the Ni_{0.8}Cu_{0.2}/SDC anode also inhibited carbon deposition, and the amount of deposited carbon decreased to about 4 mass %. The role of Co in the Ni_{0.8-x}Cu_{0.2}Co_x/SDC cermet anode is probably similar to that of Fe in the

Fig. 8. Time dependences of cell voltages for the $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Co}_x/\text{SDC}$ anodes under 0.1 A/cm^2 load at 700°C .

Fig. 9. Amounts of carbon deposited on the $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Co}_x/\text{SDC}$ anodes during the 24 h electrochemical test.

Fig. 10. Scanning electron micrographs of cross-sectional views of the $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}/\text{SDC}$ anodes (a) before and (b) after the electrochemical test for 24 h.

$\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Fe}_x/\text{SDC}$ cermet anode. XRD patterns revealed that the structures of anode materials were maintained after the 24 h electrochemical test. **Figure 10** shows SEM micrographs of the $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}/\text{SDC}$ anode test-cell before and after the 24 h electrochemical test. The images show that the $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}/\text{SDC}$ anode was in close contact with the electrolyte. A comparison of the SEM micrographs observed before and after the 24 h electrochemical test demonstrates that the sinterability hardly changed. In addition, the analytical results of SEM-EDS revealed that the chemical composition and particle distribution of the $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}$ alloy in the anode hardly changed, suggesting minimal change in the overpotential loss and that the test-cell output was maintained, as shown in Fig. 8. Based on the overall results, the $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}/\text{SDC}$ anode was found to be the best $\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Co}_x/\text{SDC}$ anode for syngas fuel with $\text{H}_2/\text{CO} = 3/2$.

4. Conclusion

The effect of Fe or Co addition to $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ cermet anode on the performance of fuel test-cells was examined using humidified (3% H_2O) syngas fuel with $\text{H}_2/\text{CO} = 3/2$ at 700 and 600°C . Doping Fe or Co 0.1 mol% into the $\text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ anode brought the increase in the cell performance, and effectively restrained carbon deposition owing to CO on the anode, exhibiting the reduced amounts of deposited carbon. As the Fe and Co contents increased further, the cell performance decreased due to the increase in the overpotential loss in the anode. In the electrochemical test for 24 h, the test-cells revealed the cell performance in the order of $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC} \approx \text{Ni}_{0.5}\text{Cu}_{0.2}\text{Fe}_{0.3}/\text{SDC} > \text{Ni}_{0.6}\text{Cu}_{0.2}\text{Fe}_{0.2}/\text{SDC} > \text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ for the Fe-doped anodes and $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}/\text{SDC} > \text{Ni}_{0.6}\text{Cu}_{0.2}\text{Co}_{0.2}/\text{SDC} > \text{Ni}_{0.5}\text{Cu}_{0.2}\text{Co}_{0.3}/\text{SDC} > \text{Ni}_{0.8}\text{Cu}_{0.2}/\text{SDC}$ for the Co-doped anodes. This study suggests that the $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.1}/\text{SDC}$ and $\text{Ni}_{0.7}\text{Cu}_{0.2}\text{Co}_{0.1}/\text{SDC}$ cermet anodes are promising candidates for practical applications.

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