Development of the Fe-Ni Anodic Catalyst for Solid Oxide Fuel Cell Operated at Intermediate-temperature Direct Utilizing of Dimethylether Fuel

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The Fe, Ni-BCY20 and Fe-Ni catalysts were used as the materials for anode of an intermediate-temperature Solid Oxide Fuel Cell (SOFC) for direct utilization of dimethylether(DME) gas fuel. A proton conducting oxide $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ was employed as the electrolyte(thickness 500 μm) and a Pt was applied as the cathode. The cell was operated at 600 °C. The maximum power density of the cell with the Fe9-Ni1 anode that has 9/1 molar ratio of Fe to Ni was 46.4 mW cm^{-2} at 80 mA cm^{-2} . The Fe9-Ni1 anode showed remarkable improvement of cell performance in comparison with the Fe anode that we reported before.

Key Words : SOFC, Dimethylether (DME), Proton Conducting Oxide, Anode

1 Introduction

Solid Oxide Fuel Cell (SOFC) has higher power generation efficiency and more fuel flexibility than other fuel cells and is developed for practical use.¹⁾

However, existing SOFC were operated at about 1000 °C. High operating temperatures precludes the use of inexpensive metal components as interconnects. It also produces thermal stresses and solid-phase reactions.^{2,3)} Furthermore, using hydrogen as fuel is impractical in terms of storage and handling.^{4,5)}

Recently, many researchers make an effort to operate SOFC at intermediate-temperatures (600 °C – 800 °C) and to accomplish direct utilization of hydrocarbon fuel at the same time.⁶⁻⁹⁾ In order to enable fuel cells to operate at intermediate-temperatures, it is necessary to develop the electrolyte that has high ionic conductivity at these temperatures. Iwahara, *et al.* reported that $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCY20) showed about $3 \cdot 10^{-2}$ S cm^{-1} ionic conductivity¹⁰⁾ at 600 °C and transference number of proton was almost one.¹¹⁾ That is the reason why we regarded BCY20 as suitable electrolyte for intermediate SOFC.

Dimethylether (DME) is one of the candidates for fuel of the intermediate SOFC. First, DME gas becomes easily liquid with high pressure, second it is easily oxidized at intermediate-temperatures¹⁸⁾ and finally it is possible for DME to use the existing infrastructure for propane gas.^{16,17)} Besides, because of high cetane number and environmentally-friendly, DME is regarded as promising resource for future low emission society.¹⁹⁾

We have developed the direct-DME fuel cell operated at intermediate-temperature using BCY20 as a solid electrolyte. It was found that Fe, which is inexpensive material, showed excellent performance as a catalyst.²³⁾ Fe catalyst decomposes DME to H_2 , CO and CH_4 at 600 °C. H_2 and CO could be used as the fuels in this SOFC, however most of CH_4 was not used. Perry Murray *et al.*²⁰⁾

reported a high catalytic activity of Ni, which is also inexpensive material as well as Fe, for CH_4 decomposition in a direct-methane fuel cell.

In this study, the addition of Ni to Fe anode was investigated to improve the cell performance of the SOFC for direct utilization of DME at 600 °C.

2 Experimental

$\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCY20)²¹⁾ powder was pressed in a pellet with 20 mm in dia. This pellet was sintered at 1600 °C for 12 h in air. The sintered pellet was polished to 0.5 mm in thick, and was used as the solid electrolyte. As a cathode, Pt paste (TR-7905, Tanaka precious metals) was applied with 8 mm in dia. to one side of the pellet and was calcined at 930 °C for 1 h in air. Three kinds of anode materials were prepared: Fe, Ni-BCY20 and Fe-Ni. Fe_2O_3 paste was prepared by mixing Fe_2O_3 powder (Aldrich) with a binder (TMS-1, Tanaka precious metals). NiO-BCY20 paste was prepared from NiO powder (Aldrich), BCY20 powder and TMS-1. Fe_2O_3 -NiO paste was prepared from Fe_2O_3 powder (Aldrich), NiO powder (Aldrich) and TMS-1. These pastes were applied with 8 mm in dia. to the other side of the BCY20 pellet and were calcined at 800 °C for 1 h (Fe_2O_3), at 1300 °C for 1.5 h (NiO-BCY20) or at 900 °C for 2 h (Fe_2O_3 -NiO) in air. Before the electrochemical measurements, these oxides were reduced to Fe, Ni-BCY20 and Fe-Ni in H_2 gas at 600 °C. In Fe-Ni anodes, four samples were prepared with the molar ratio of Fe to Ni was 9/1, 8/2, 7/3 and 5/5. The electrodes were denoted as Fe9-Ni1, Fe8-Ni2, Fe7-Ni3, and Fe5-Ni5, respectively. Single cell consisted of the BCY20 electrolyte with the anode and the cathode. DME gas or CH_4 gas was bubbling into water under the flow rate of 50 ml min^{-1} at 35 °C, and then they were supplied to the anode side. Dry air was supplied to the cathode side with the flow rate of 100 ml min^{-1} . *V-I* characteristics

of each cell were measured by using a galvanostat (NPGFZ-251-B, Nikko Keisoku) at 600 °C.

3 Result and Discussion

In a previous study,²³⁾ we reported that Fe anode showed higher performance than Ni-BCY20 anode; with the Ni-BCY20 anode, the open circuit voltage (OCV) was 0.87 V and the maximum power density was 5.5 mW cm⁻². On the other hand, with the Fe anode, the OCV was 0.97 V and the maximum power density was 36.4 mW cm⁻² using DME as fuel at 600 °C. As a result of examination for figuring out the reaction mechanism of DME in the cell with a Fe anode at 600 °C, we found that DME decomposed to H₂, CO and CH₄ on the Fe anode. However, CH₄ did not have anodic reaction on Fe while H₂ and CO did. It means that CH₄ that produced from DME was not used as fuel for the cell with Fe anode. It is necessary to use CH₄ as fuel for bringing out the potential capability of DME, then, we started finding suitable catalyst for CH₄. Perry Murray et al.²⁰⁾ reported a high catalytic activity of Ni for CH₄ decomposition in a direct-methane fuel cell. Therefore, the addition of Ni to Fe anode was investigated to improve the cell performance in this study.

Figure 1 shows the *V-I* characteristics measured using Fe and Ni-BCY20 anodes with supplying CH₄ gas to the anode side. The SOFC with the Fe anode indicated 0.25 V OCV and 0.14 mW cm⁻² maximum power density at 1.0 mA cm⁻². On the other hand, the SOFC with the Ni-BCY20 anode show 0.72 V OCV and the 0.38 mW cm⁻² maximum power density at 1.0 mA cm⁻². It was confirmed that the cell performance with the Ni-BCY20 anode was superior to the Fe anode using CH₄ as a direct fuel at 600 °C.

We especially call your attention to the fact that OCV using Ni-BCY20 anode was much higher than Fe anode. The higher OCV of Ni-BCY20 anode can be explained following mechanism.

When proton conducting oxides are used as electrolyte, electromotive force (EMF) is represented by the following Eq. 1, 2, 3 and 4²²⁾;

$$E = -\frac{2F}{\Delta G} \quad (1)$$

$$\Delta G = -RT \ln K \quad (2)$$

$$K = \frac{p(\text{H}_2\text{O})^2}{p(\text{O}_2) p(\text{H}_2)^2} \quad (3)$$

$$p(\text{H}_2) = p(\text{H}_2, \text{a}) \quad (4)$$

F is Faraday constant, *T* is temperature, *R* is constant, *p*(H₂O), *p*(O₂), and *p*(H₂) is partial pressure on three-phase-boundary (TPB) and *p*(H₂, a) is partial pressure of hydrogen adsorbed on the catalyst in TPB.

Proceedings of steam reforming of CH₄ shown in Eq. 5 increase the value of the partial pressure of H₂ *p*(H₂, a) in Eq. 4 and OCV, according these equations.

Therefore, the reason why Ni-BCY20 anode has higher

Fig. 1 Cell performance test with CH₄ gas.
Anode $\triangle, \blacktriangle$: Fe $\circ, \bullet$: Ni-BCY20.

Fig. 2 Cell performance test with DME gas fuel.
Anode $\times$: Fe $\circ, \bullet$: Fe9-Ni1 $\square, \blacksquare$: Fe8-Ni2 $\diamond, \blacklozenge$: Fe7-Ni3 $\triangle, \blacktriangle$: Fe5-Ni5 $-$: Ni-BCY20.

OCV is explained that the Ni-BCY20 anode accelerates the steam reforming reaction of CH₄ in Eq 5. It is the evidence that the catalytic activity of Ni-BCY20 for CH₄ with steam is higher than that of Fe anode.

From these facts, we found that Fe anode was more effective for DME decomposition to H₂, CO and CH₄ but Ni-BCY20 anode was more suitable for steam reforming of CH₄. Therefore, we investigated Fe-Ni bi-metal anode in order to improve catalytic activity for CH₄ with keeping high catalytic activity of Fe for DME. We try to develop the material that accomplishes higher catalytic activity for both DME and CH₄.

Figure 2 shows the *V-I* characteristics measured using various Fe-Ni anodes with supplying DME gas directly to the anode side. By using the Fe9-Ni1 anode, OCV of the cell was 0.98 V and the maximum power density of

Fig. 3 SEM images of the cross section of various Fe-Ni anodes.

the cell was 46.4 mW cm^{-2} at 80 mA cm^{-2} . The Fe9-Ni1 anode showed remarkable improvement of cell performance compared with the Fe anode. However, maximum power density was gradually decreased with increasing additive amount of Ni; 35.7 mW cm^{-2} (Fe8-Ni2), 20.8 mW cm^{-2} (Fe7-Ni3), 15.3 mW cm^{-2} (Fe5-Ni5).

The reason Fe-Ni anode showed superior performance is assumed that Ni in the anode promoted steam reforming of CH_4 produced from DME and amount of H_2 and CO which can use as fuel were increased.

Figure 3 shows that Fe9-Ni1 and Fe8-Ni2 anodes have good adhesion to the BCY20 electrolyte. However, detachment of anode from BCY20 was observed for Fe7-Ni3 and Fe5-Ni5 anodes. This result suggests that Ni hinders anode from sintering with BCY20 electrolyte, then excessive addition of Ni causes increasing of interface resistance. The decreasing of cell performances in Fe7-Ni3 and Fe5-Ni5 anodes is explained by these SEM images.

The reason of improving cell performance with Fe-Ni catalyst is following. First, Ni promotes steam reforming of CH_4 . Second, Fe prevents anode and the electrolyte from detaching because Fe has excellent sintering performance and it plays a role in holding Ni on the BCY20.

4 Conclusion

The Fe, Ni-BCY20 and Fe-Ni catalysts were investigated as the anodic materials of an intermediate-temperature SOFC for direct utilization of hydrocarbon fuel. BCY20 and Pt were used as the electrolyte and the cathode, respectively. The cell was operated at 600°C . Using CH_4 as a direct fuel, it was confirmed that the cell performance with the Ni-BCY20 anode was superior to the Fe anode. By impregnating with Ni catalyst to previous Fe anode, the cell performance was improved. And the Fe9-Ni1 anode showed 46.4 mW cm^{-2} maximum power density at 600°C .

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