Direct-DME SOFC for Intermediate Operation Temperature Using Proton Conductor as the Electrolyte

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We have developed intermediate-temperature solid oxide fuel cell (SOFC) with a proton conducting oxide $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCY20) as the electrolyte for direct utilization of dimethylether (DME) fuel. We tried to improve the cell performance of the SOFC by using Fe, Fe-Ni and Fe-Pd/MnO₂ as a catalyst for the anode. Fe showed high catalytic activity for DME, furthermore attending Ni or Pd/MnO₂ catalysts to Fe remarkably improved the cell performance.

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 0.03Scm^{-1} ionic conductivity (10) at 600°C and transference number of proton was almost one (11). On the other hand, 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-temperatures (12) and finally it is possible for DME to use the existing infrastructure for propane gas (13) (14). Besides, because of high cetane number and environmentally-friendly, DME is regarded as promising resource for future low emission society (15). In this study, we developed the direct-DME fuel cell operated at intermediate-temperature using BCY20 as a solid electrolyte (thickness 500 μm). Especially, we focused development of anodic catalysts. The Fe, Fe-Ni and Fe-Pd/MnO₂ anode were developed.

Experimental

$\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCY20) powder was pressed in a pellet ($\Phi=20\text{mm}$). This pellet was sintered at 1600°C for 12h in air. The sintered pellet was polished to 0.5mm in thick, and was used as the solid electrolyte. As a cathode, Pt paste (TR-7905, Tanaka precious

metals) was applied to one side of the pellet ($\Phi=8\text{mm}$), and calcined at 930°C for 1h in air. Three kinds of anode materials Fe, Ni-BCY20, and Fe-Ni were respectively used. 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 TMS-1, NiO powder (Aldrich), and BCY20 powder. Fe_2O_3 -NiO paste was prepared from TMS-1, Fe_2O_3 powder (Aldrich), and NiO powder (Aldrich). These anodic pastes were applied to the other side of the BCY20 pellet ($\Phi=8\text{mm}$), and calcined at 800°C for 1h (Fe_2O_3), at 1300°C for 1.5h (NiO-BCY20), and at 900°C for 2h (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 . V - I characteristics were measured by using a galvanostat (NPGFZ-251-B, Nikko Keisoku) at 600°C .

Results and discussion

Fe, Pt and Ni-BaCe_{0.8}Y_{0.2}O_{3- δ} catalysts were used as the anodic materials of an intermediate temperature SOFC for direct utilization of DME gas fuel. The cell was operated at 600°C . The maximum power density of the cell with the Fe anodic catalyst was 36.4 mWcm^{-2} at 70 mAcm^{-2} , while the maximum power density of the cell with a Ni-BCY20 and the Pt anode were 5.5 mWcm^{-2} at 10 mAcm^{-2} and 8.4 mWcm^{-2} at 20 mAcm^{-2} , respectively (Fig. 1).

Fig. 1 Cell performance test with DME gas fuel at 600°C .
Anode; $\bigcirc$ $\bullet$: Fe, $\triangle$ $\blacktriangle$: Pt, $\square$ $\blacksquare$: Ni-BCY20

We considered anodic reactions of DME fuel with gas chromatograph (Fig. 2). This result suggested Fe catalyst decomposes DME to H_2 , CO and CH_4 at 600°C . And it was found that H_2 and CO could be used as the fuels in this SOFC, however most of CH_4 was not used. So, it is necessary to accelerate utilization of CH_4 as fuel and to improve the cell performance and utilization efficiency of DME fuel.

Fig. 2 Composition of outlet gas from the cell using Fe anode with DME gas fuel at 600°C.

▼: DME conversion, Formation rate ● : H₂, ▲ : CH₄, ■ : CO, ◆ : CO₂.

Fig. 3 Cell performance test with DME gas fuel at 600°C.

Anode; ×: Fe ○, ●: Fe9-Ni1 □, ■: Fe8-Ni2

◇, ◆: Fe7-Ni3 △, ▲: Fe5-Ni5 — : Ni-BCY20.

Perry Murray et al.(16) reported a high catalytic activity of Ni, which is also inexpensive material as well as Fe, for CH₄ decomposition in a direct-methane fuel cell. So, the addition of Ni to Fe anode was investigated. Figure 3 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 the cell was 46.4 mWcm⁻² at 80 mAcm⁻². The maximum power density was improved about 27% compare with the Fe anode. The Fe9-Ni1 anode showed remarkable improvement of cell performance compared with the Fe anode. The reason Fe-Ni anode showed superior performance is assumed that Ni in the anode promoted steam reforming of CH₄ produced from DME and amount of H₂ and CO which can use as fuel were increased.

On the other hand, we had found that the Pd/MnO₂ catalyst decomposed CH₄ at an intermediate-temperature. The Pd/MnO₂ catalyst had morphology that nano-Pd particles were dispersed on a manganese oxide with meso-scaled pores. Therefore, we attempted Pd/MnO₂ catalyst to anode material for intermediate-temperature SOFC. The cell was operated at 600°C. Maximum power density of the cell using Pt-Pd/MnO₂ anode (Pd/MnO₂ content of 16.6 wt.%) was 21 mWcm⁻² at 50 mWcm⁻², while the cells using Pt and Pd/MnO₂ as anode materials exhibited maximum power densities of 9 and 10 mWcm⁻² at 20 mWcm⁻², respectively (Fig. 4).

Fig.4 Cell performance test with DME gas fuel at 600°C.

Anode; ○, ●: Pt, □, ■: Pt-Pd/MnO₂ (Pd/MnO₂ 16.6 wt.% in anode), △, ▲: Pt-MnO₂ (MnO₂ 25.0 wt.% in anode), ◇, ◆: Pt-Pd (PdO 4.1 wt.% in anode), ▽, ▼: Pd/MnO₂.

It was found that Pd/MnO₂ showed higher activity for anode catalyst of SOFC. So, the addition of Pd/MnO₂ to Fe anode was also investigated. As the result, the Fe-Pd/MnO₂ (7-3 weight ratio) anode showed 58.8mWcm⁻² maximum power density with DME at 600°C. The maximum power density was improved about 62% compare with the Fe anode (Fig. 5).

Fig. 5 Cell performance test with DME gas fuel at 600°C.

Anode; ○●: Fe:Ni=9:1(molar ratio), △▲: 7:3, ◇◆: 5:5, □■:Pd/MnO₂, X: Fe

It was concluded that Fe showed high catalytic activity for DME, furthermore attending Ni or Pd/MnO₂ catalysts to Fe remarkably improved the cell performance.

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