

Effect of anode-additive PrBaInO₄ and its derivative products on the electrochemical performance of solid oxide fuel cells.

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Introduction

Solid oxide fuel cells (SOFCs) can directly use hydrocarbons as fuel because the operating temperature is generally 600°C to 1000°C. Hydrocarbons have many advantages such as low cost and low storage pressure. Moreover, dry hydrocarbon-fueled operation leads to high open-circuit voltage. However, performance of SOFCs is decreased due to solid carbon deposited on the anode when dry hydrocarbon is the fuel. Our research group has focused on adding a proton conductor as co-catalyst to improve both the power density and the electrode endurance against deposited carbon. A previous study suggested that both power density in H₂ and dry CH₄ and the electrode endurance against carbon deposition in dry CH₄ were improved by adding a proton conductor, such as BZY (BaZr_{0.95}Y_{0.05}O_{3-α}), SZY (SrZr_{0.95}Y_{0.05}O_{3-α}), SCYb (SrCe_{0.95}Yb_{0.05}O_{3-α}), to the anode electrode⁽¹⁾⁻⁽³⁾. To stabilize the additive on the electrode, previous studies have added either a Ce-type proton conductor such as SCYb to Ni/GDC anodes⁽¹⁾, or a Zr-type proton conductor such as BZY or SZY to Ni/YSZ anodes.⁽²⁾⁽³⁾ However, the addition effect might be further enhanced by using a proton conductor that differs from Zr- or Ce-types. In our laboratory, Li et al. developed a novel proton conductor, PrBaInO₄ (PBI), which has K₂NiF₄ structure, and successfully used it in SOFCs with H₂ as fuel⁽⁴⁾. Because PBI is not a Zr- or Ce-type proton conductor, it can be expected to function as an anode co-catalyst.

In this study, we used PBI as an additive and first evaluated the chemical stability of the anode, such as reactivity with electrode material and fuel. Because synthesizing PBI from nitrate precursor solution could not be successful, we also evaluated our developed particle addition method. We then studied the effect of adding PBI derivative products to the anode, such as reaction products with GDC and decomposition products. Finally, we evaluated the anode reaction mechanism by comparing measured electrochemical characteristics (anode potential, power density, and *I-V* characteristics) of SOFCs that have Ni/GDC anodes with and without PBI as an additive.

Experimental

Chemical stability test of PBI and GDC was conducted, and then identified via XRD pattern. In the SOFC studied here, the electrolyte was a YSZ disk (8 mol% Y₂O₃ - 92 mol% ZrO₂, 0.25 mm thickness and 20 mm diameter), the Ni cermet anode was a Ni/Gd_{0.1}Ce_{0.9}O_{1.95} (Ni/GDC) anode, and the oxide cathode was a LSM (La_{0.8}Sr_{0.2}MnO_{3-α})/ScSZ (10 mol% Sc₂O₃ - 1 mol% CeO₂ - 89 mol% ZrO₂) cathode. PBI was added via our developed particle addition method as follows. First, PBI powder was finely ground into particles using a planetary ball mill with a 1-mm-diameter Zr ball, and then added to an ethanol solution. Then, this particle solution was injected into the anode electrode of a cell. Finally, the cell sample was sintered at 1000°C for 2 h. Electrochemical measurements of Current-voltage (*I-V*) characteristics were carried out for the cell samples at 700°C to 900°C using either 1% humidified H₂ or dry CH₄ as fuel at a feed rate of 200 ml min⁻¹. The anode potential was then measured using the current interruption method.

Results and Discussion

From the chemical stability test, derivative products such as PrInO₃ were identified by XRD pattern. This suggests that over 1100°C, PBI powder reacted with GDC powder and then produced derivative products such as PrInO₃. PBI was added to the Ni/GDC anode by particle addition method, because synthesizing PBI by nitrate precursor solution could not be successful. However, though PBI particle on the Ni/GDC anode was stable below 900°C in air, in fact, it was broken down into derivative products such as PrInO₃ after sintering at 1000°C because its grain size was minute so that its reactivity against GDC was enhanced. Therefore, That cell was defined as Ni/GDC-DP (Derivative Products).

Figure 1 shows an SEM image (1a) and EDX image (1b) of the cross-section of the Ni/GDC-DP anode, clearly showing that in this particle addition method, the PBI powder was mostly found near the surface.

Figure 2 shows the anode potential (2a) and the *I-V* characteristics and power density (2b) for Ni/GDC and Ni/GDC-DP in 3% humidified H₂ and dry CH₄ at 900 °C. Figure (2a) indicates that maximum power density for Ni/GDC in 1% humidified H₂ was lower than that for Ni/GDC-DP (i.e. 329 mW/cm² and 419 mW/cm², respectively). Although the anode potential is similar for both anodes (i.e., -0.838 V and -0.842 V, respectively, at 0.66 A/cm²), this lower value is due to the increasing ohmic loss caused by the addition of PBI derivative products, which have low electron conductivity, at the surface of the anode electrode. Maximum power density for Ni/GDC-DP in dry CH₄ was higher than that for Ni/GDC (i.e. 282 mW/cm² and 257 mW/cm², respectively), mainly because the anode potential of Ni/GDC-DP is lower than that of Ni/GDC (i.e., -0.766 V and -0.644 V, respectively, at 0.66 A/cm²).

In conclusion, PBI can be successfully added to Ni/GDC anodes by using our particle addition method, in which PBI particles exist mainly in the surface of the anode. Although maximum power density of Ni/GDC-DP in 1% humidified H₂ is lower than that of Ni/GDC, in the case of dry CH₄, Ni/GDC-DP was higher (from 257 mW to 282 mW), mainly due to a decrease in anode overvoltage. Therefore, the addition of PBI derivative products such as PrInO₃ might enhance the anode reaction in dry CH₄.

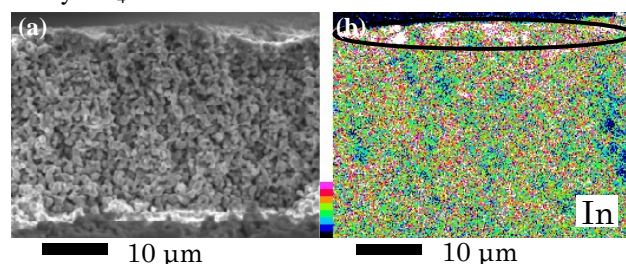


Fig. 1 (a) SEM and (b) EDX image of the cross-section of Ni/GDC-DP

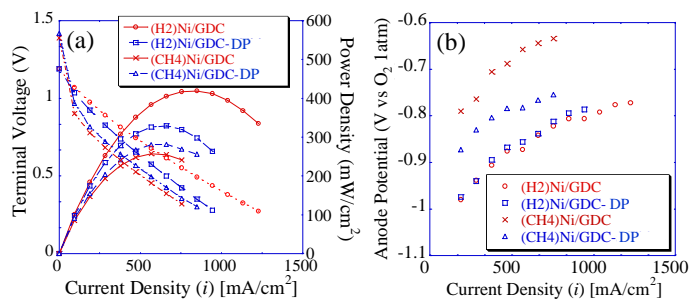


Fig. 2 (a) Anode potential and (b) *I-V* characteristics and power density for Ni/GDC and Ni/GDC-DP anode in 1% humidified H₂ and dry CH₄ at 900 °C.

References

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