Enhanced stability of Ni–Fe/GDC solid oxide fuel cell anodes for dry methane fuel

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The addition of Fe into Ni/GDC (Gadolinium-Doped Ceria) anodes significantly improved the long-term stability of SOFC. While a Ni/GDC anode failed to operate after 12 h at a current density of 0.2 A cm⁻² and 650 °C with dry methane flow, the cell performance of a Ni₀.₉Fe₀.₁/GDC anode showed no degradation over 50 h. The outlet gas of SOFC was analyzed by mass spectrometry, and the results revealed that methane was oxidized more completely on a Ni–Fe/GDC anode compared to a Ni/GDC anode. The change in catalytic properties due to the addition of Fe caused methane fuel oxidized more completely, which enhanced the long-term stability of the cell.

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1. Introduction

Solid oxide fuel cells (SOFC) have been actively investigated due to their high energy efficiency and potential operation with various hydrogen and hydrocarbons fuels [1,2]. Hydrogen is currently produced from hydrocarbons by steam-reforming reaction; thus, the direct use of hydrocarbons in SOFCs would reduce overall energy costs and increase the efficiency of the cell [3,4]. Operating temperatures greater than 800 °C cause significant problems such as electrode sintering and interfacial diffusion between the electrode and the electrolyte. Moreover, high operating temperatures limit the types of materials that can be used in the cell and decrease the mechanical strength due to creep and expansion [5]. Due to the aforementioned limitations, an intermediate temperature range is more desired in SOFC. While yttrium-stabilized zirconia (YSZ) is often used in high temperature SOFCs, YSZ does not display sufficient ionic conductivity at intermediate temperatures. New electrolytes with high ionic conductivity at intermediate temperatures have been actively investigated [6–8]. Ceria-based materials showed significantly higher ionic conductivity than YSZ and enhanced direct oxidation of hydrocarbons due to rapid lattice oxygen mobility [9,10].

Anodic materials also require electron conductors that can collect electrons generated during the oxidation of hydrocarbon fuels. Nickel is the most popular electron conductor because it possesses high catalytic activity and is stable under the harsh conditions typically encountered during the cell fabrication process. However, severe coking occurs when hydrocarbons are treated on a nickel surface at high temperature. To avoid this problem, other metals such as copper have been investigated as an electron conductor. However, copper is not stable above 1100 °C (m.p. = 1083 °C), although higher temperatures are required to fabricate a high quality SOFC single cell.

Carbon deposition on the nickel surface is caused by pyrolysis reaction or the Boudouard reaction (2CO (g) → C (s) + CO₂ (g)) [4,11]. Pyrolysis occurs above 700 °C, while the thermodynamic equilibrium of the Boudouard reaction is shifted to the right at lower temperatures [12]. At operating temperatures below 700 °C, carbon deposition occurs mainly due to Boudouard reaction. Therefore, Boudouard reaction should be avoided below 700 °C to minimize the carbon deposition, which causes the degradation of cell performance.

In this study, the cell performance and long-term stability of SOFCs with Ni–Fe bimetallic catalysts were evaluated at 650 °C under a flow of dry methane. The addition of 10% Fe to the anode catalyst increased the power density of the cell, and no degradation in cell performance was observed. The catalytic properties of Ni/GDC anodes were improved in the presence of Fe causing methane fuel oxidized more completely, leading to enhanced cell stability.

2. Experimental section

NiO–Fe₂O₃/GDC catalysts were prepared using a solid-state reaction method. 55 wt.% of Fe₂O₃ (Aldrich, 99%) and NiO (J.T Baker), 36 wt.% of GDC (Gd₀.₁Ce₀.₉O₂, Rhodia), and 9 wt.% of starch (Aldrich) were mixed by ball-milling in ethanol. The ratio of Fe to Ni was changed from 0 wt.% to 50 wt.% The mixture was dried at 100 °C for 24 h and pressed at 100 MPa into a disc with a diameter of 36 mm and a thickness of 1.2 mm. The pellets were sintered at 1200 °C for 3 h in air. GDC (Gd₀.₁Ce₀.₉O₂, Rhodia) slurry was then applied onto the
anode via dip-coating, and the electrode was sintered at 1350 °C for 5 h to yield a dense GDC electrolyte layer. The cathode paste was prepared using La0.6Sr0.4Co0.2Fe0.8O3 (LSCF, Praxair, 50 wt.%) and GDC (Gd0.1Ce0.9O2, 50 wt.%). The cathode layer was screen-printed on the anode-supported electrolyte with a thickness of 20–30 µm. The pellet was sintered at 1000 °C for 3 h. The single cell was reduced under H2 flow with a flow rate of 50 cm3 min⁻¹ at 850 °C prior to cell operation. The gas flow rate was measured by a mass flow controller at atmospheric pressure and room temperature. The catalytic activity of Ni0.5Fe0.5/GDC anodes was sintered at 1000 °C for 3 h. The single cell was reduced under H2 flow with a flow rate of 50 cm3 min⁻¹ at 850 °C prior to cell operation. The catalytic activity of Ni–Fe/GDC anode was further examined by temperature-programmed reduction (TPR; Belcat-M) and X-ray diffraction (XRD; Rigaku, Rint 2700). TPR was measured with a ramping rate of 10 °C min⁻¹ and a gas feed rate of 45 cm3 min⁻¹ (10% CH4/He for CH4-TPR and 5% CO/He for CO-TPR). The anodes after the cell operation were observed by scanning electron microscopy (SEM; Jeol 6500F).

Cell performance of the anode-supported single cells was evaluated at 650 °C with dry methane (60 cm3 min⁻¹) on the anode side and air (200 cm3 min⁻¹) on the cathode side. Cell testing equipment was depicted elsewhere [13]. All the anodes were evaluated with the same testing procedure. I–V curve was measured first, then electrochemical impedance was measured. The long-term stability was tested by operating the cell at the constant current density of 0.2 A cm⁻² afterwards. The current collector was Pt mesh (Alfa) on the cathode side and Au felt on the anode side. I–V characterization and durability were measured with the Solartron 1260 frequency analyzer and the Solartron 1287 interface. The output gas was analyzed with mass spectrometer (Hiden QIC-20, UK) at the anode side.

3. Results and discussion

3.1. Ni–Fe/GDC single cell performance and stability

Fig. 1 shows the power density and long-term stability of SOFC single cells based on Ni0.9Fe0.1/GDC anode catalysts operated at 650 °C with dry methane. The maximum power density was 0.30, 0.34, 0.27, and 0.21 Wcm⁻² for Ni/GDC, Ni0.9Fe0.1/GDC, Ni0.5Fe0.5/GDC, and Ni0.5Fe0.5/GDC, respectively. Ni0.9Fe0.1/GDC anode provided the highest power density. As shown in Fig. 2, impedance tests revealed that the addition of 10% Fe minimized electrode resistance, while the addition of 30% or 50% Fe increased the electrode resistance of the anode. Previously, it was reported that electrode resistance decreased upon the addition of Fe [14,15]. The improved power density of Ni0.9Fe0.1/GDC likely resulted from reduced electrode resistance.

On the other hand, long-term stability tests in Fig. 1(b) indicated that the addition of Fe significantly improved the cell stability, regardless of the amount of Fe added to the anode catalyst. While Ni/GDC anode stopped operating in 12 h, Ni–Fe/GDC anodes operated stably for 50 h. In particular, the cell performance of Ni0.9Fe0.1/GDC anode showed no degradation. The voltage of Ni0.9Fe0.3/GDC or Ni0.9Fe0.5/GDC anodes decreased slightly in the early stage of operation, but these anodes operated for 50 h without shutdown. Fig. 3 shows the SEM images of Ni/GDC anode and Ni0.9Fe0.1/GDC anode after the long-term stability tests. Many wire-type carbon depositions were observed on Ni/GDC, while no carbon was observed on Ni0.9Fe0.1/GDC. The rapid deposition of carbon cokes seems to cause the shutdown of the Ni/GDC cell.

3.2. Catalytic properties of Ni–Fe/GDC

XRD data revealed that Ni and Fe did not exist as separate phases, and Ni–Fe alloy were observed in all Ni0.9Fe0.1−x/GDC catalysts. Temperature-programmed reductions (TPR) were performed to evaluate the catalytic properties of Ni0.9Fe0.1−x/GDC anode catalysts. The CH4-TPR results in Fig. 4(a) showed that methane started to decompose at 620 °C, 661 °C and 670 °C on Ni0.9Fe0.1/GDC, Ni0.9Fe0.3/GDC and Ni0.9Fe0.5/GDC catalysts, respectively. On the other hand, methane started to decompose at temperature greater than 700 °C on Ni/GDC catalyst. Pure Fe did not cause methane decomposition. Methane decomposition on the surface of Ni occurred at lower temperatures in the presence of Fe.

In hydrocarbons oxidation on Ni surface, carbon accumulates due to pyrolysis or the Boudouard reaction [4,11]. Hydrocarbon pyrolysis rarely occurs below 700 °C; thus, at intermediate temperatures, carbon deposition is caused by the Boudouard reaction. As the amount of CO formed within the cell increases, the Boudouard reaction also increases, and carbon accumulates on the catalyst. Under these conditions, carbon deposition increase as the oxidation of CO increases. To evaluate the activity of Ni–Fe/GDC catalysts in CO...
oxidation, CO-TPR was performed. As shown in Fig. 4(b), the results indicated that CO oxidation on the surface of Ni–Fe/GDC catalysts was greater than on Ni/GDC catalysts; thus, the amount of carbon deposition by the Boudouard reaction was significantly lower on Ni–Fe/GDC catalysts. The concentration of Fe did not have an effect on the extent of CO oxidation. A single cell supplied continuously with oxygen would reveal larger differences between Ni/GDC and Ni–Fe/GDC catalysts.

3.3. Mass spectrometry analysis

A single cell was operated at 650 °C with a current load of 0.2 A cm\(^{-2}\), and the reaction products were analyzed by connecting the gas output line to a mass spectrometer. As shown in Fig. 5(a), the product distribution of a Ni/GDC anode was slightly variable at early stages of operation. After 10 h, 41.1% H\(_2\), 19.6% CO, 8.1% CO\(_2\) and 22.3% H\(_2\)O were obtained. High concentrations of H\(_2\) and CO revealed that the incomplete oxidation of methane (CH\(_4\) + O\(^{2-}\) → CO + 2H\(_2\) + 2e\(^{-}\)) occurred more than the complete oxidation of methane (CH\(_4\) + 4O\(^{2-}\) → CO\(_2\) + 2H\(_2\)O + 8e\(^{-}\)). CO produced on Ni/GDC catalysts was converted to carbon by the Boudouard reaction and the carbon was deposited on the surface of the catalyst, resulting in poor cell performance. The ratio of C to H in the outlet stream was 0.88:4, which is less than the expected ratio (1:4). The concentration of carbon in the outlet gas was less than the concentration of the inlet gas, indicating that carbon deposition occurred inside the single cell. On the other hand, the product distribution of Ni\(_{0.9}\)Fe\(_{0.1}/\)GDC catalysts remained stable for 10 h, as shown in Fig. 5(b). The outlet stream contained 33.2% H\(_2\), 11.2% CO, 19.5% CO\(_2\), and 27.8% H\(_2\)O after 10 h of reaction. The ratio of C to H in the outlet stream was 1:4, indicating that carbon deposition did not occur inside the cell. The concentration of H\(_2\)O and CO\(_2\) was significantly higher in Ni\(_{0.9}\)Fe\(_{0.1}/\)GDC cell, indicating that complete methane oxidation was superior on Ni\(_{0.9}\)Fe\(_{0.1}/\)GDC catalyst. The product distribution was 37.5% H\(_2\), 10.8% CO, 17.5% CO\(_2\), and 25.9% H\(_2\)O for Ni\(_{0.7}\)Fe\(_{0.3}/\)GDC catalysts, and 36.8% H\(_2\), 11.9% CO, 17.4% CO\(_2\), and 25.7% H\(_2\)O for Ni\(_{0.5}\)Fe\(_{0.5}/\)GDC catalysts after 10 h of reaction. Ni\(_{0.7}\)Fe\(_{0.3}/\)GDC and Ni\(_{0.5}\)Fe\(_{0.5}/\)GDC catalysts also produced more H\(_2\)O and CO\(_2\), compared to Ni/GDC catalyst. As shown in CH\(_4\)-TPR and CO-TPR, methane decomposes at lower temperature and CO is oxidized more on Ni–Fe/GDC catalysts. These improved catalytic properties of Ni–Fe/GDC anode enhanced long-term stability of the single cell significantly.

4. Conclusions

The power density and long-term stability of Ni–Fe/GDC anodes were evaluated in the oxidation of dry methane. Ni\(_{0.9}\)Fe\(_{0.1}/\)GDC produced a maximum power density of 0.34 W cm\(^{-2}\) at 650 °C, while Ni/GDC, Ni\(_{0.7}\)Fe\(_{0.3}/\)GDC and Ni\(_{0.5}\)Fe\(_{0.5}/\)GDC provided a power density of 0.30, 0.27 and 0.21 W cm\(^{-2}\), respectively. The cell performance of Ni–Fe/GDC anodes was stable for 50 h, while Ni/GDC anode was limited to 12 h of operation, indicating that Ni–Fe/GDC catalysts displayed higher long-term stability. The addition of Fe on Ni/GDC anode induces the methane fuel decomposed more easily and oxidized more completely, enhancing long-term stability significantly.

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Fig. 4. (a) CH₄-TPR and (b) CO-TPR for Ni/GDC or Ni–Fe/GDC anode catalysts. The catalyst powders were reduced under H₂ before TPR measurements.

Fig. 5. Outlet gas analysis measured with mass spectrometer for the single cells supported by (a) Ni/GDC and (b) Ni₀.₉Fe₀.₁/GDC anode. Applied load of current density was 0.2 A cm⁻², dry methane was used as a fuel, and the operation temperature was 650 °C.

References