Improved solid oxide fuel cell anodes for the direct utilization of methane using Sn-doped Ni/YSZ catalysts

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1. Introduction

High-performance anode catalysts are critical to enable the practical application of solid oxide fuel cells (SOFCs). Ni/YSZ is currently the dominant SOFC anode catalyst when H2 is used as the fuel [1]. H2, produced by reforming hydrocarbons, is a popular fuel because it is a clean energy source. However, storage and transport of H2 become major obstacles to its use. Therefore, the direct use of hydrocarbons is preferred until H2 is produced by an environmentally friendly process (e.g., water splitting) and until safe storage and transport methods are developed [2,3]. However, severe deactivation of Ni/YSZ anodes occurs when hydrocarbon fuels are used, due to carbonization of the hydrocarbon on the surface of Ni catalysts [4]. The accumulated coke causes the cell to expand significantly, destroying its integrated structure and resulting in marked reductions in its activity and long-term stability.

Various studies have sought to suppress deactivation. One proposal in this regard is to place an additional layer that enables internal reforming of hydrocarbons on the anode surface. Hydrocarbons turn to H2 inside the cell by reforming reaction, and the internal reforming of hydrocarbons on the anode surface. Hydrocarbons turn to H2 inside the cell by reforming reaction, and the internal reforming of hydrocarbons on the anode surface. Hydrocarbons turn to H2 inside the cell by reforming reaction, and the internal reforming of hydrocarbons on the anode surface. Hydrocarbons turn to H2 inside the cell by reforming reaction, and the internal reforming of hydrocarbons on the anode surface.

Another method involves developing new ceramic anode materials. Goedenough et al. produced a ceramic anode based on double perovskites (e.g., Sr$_x$Mn$_{1-x}$MoO$_6$) [6]. Their ceramic anode was operated stably for 16 h at 800 °C with 97% of methane (3% H2O) as fuels. Since Murray and Barnett reported that ceria can be used as an anode catalyst enabling the direct oxidation of methane in 1999 [7], various efforts have been tried to improve power density and stability of SOFC for hydrocarbon fuels by using ceria-based materials. Gorte et al. developed a composite anode of Cu and samaria-doped ceria, and demonstrated that the anode can extract electrons from various hydrocarbons without severe deactivation of the catalyst [8,9]. The single cell was operated stably under alternating flows of various kinds of hydrocarbon fuels (butane, toluene, methane, ethane, etc.) at 700 °C. However, it is more complicated to manufacture the above cells than to produce a Ni/YSZ single cell, which is equivalent to that obtained using a Ni/YSZ cell (0.40 W/cm$^2$). Stability tests reveal that the stability of the Sn-doped Ni/YSZ cell is an order of magnitude higher than that of the Ni/YSZ cell. The Sn-doped Ni/YSZ cell operates for 49.0 h, whereas the Ni/YSZ cell stops after 2.3 h. The Ni/YSZ fuel cell is destroyed by cell expansion caused by the rapid accumulation of graphitic coke. In contrast, much less graphitic carbon is deposited on Sn-doped Ni/YSZ, leading to improved stability.

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that a fuel cell using Sn-doped Ni/YSZ as the catalyst can achieve the same power density as a fuel cell using Ni/YSZ and that it is more stable than Ni/YSZ fuel cells when methane is used directly as the fuel at 800 °C. This minimal modification of Ni/YSZ significantly improves the stability of the fuel cell.

2. Experimental

2.1. Single cell fabrication

An Sn-doped Ni/YSZ SOFC anode catalyst was prepared by impregnating NiO powder (J.T. Baker) with SnCl2·2H2O (Aldrich) by the incipient wetness technique. One weight-percent of Sn (with respect to Ni) was doped. We mixed 17.5 wt.% coarse YSZ powder (FTY 13.0-101H, Unitec Ceramics), 17.5 wt.% fine YSZ powder (TZ-8Y, Tosoh), and 65 wt.% NiO (or Sn-doped NiO) by ball milling in ethanol for 24 h. The catalyst was filtered and dried at 60 °C. The NiO/YSZ or Sn-doped NiO/YSZ anode catalyst (90 wt.%) and carbon black forming agent (Raven 430, Columbian Chemical, 10 wt.%) were mixed by ball milling in ethanol for 24 h and pressed at 100 MPa into a disc (24.36 mm in diameter and 1.2 mm thick). The pellets were sintered at 1200 °C for 3 h in air. A YSZ (TZ-8YS, Tosoh) slurry was then applied to the anode by dip coating and sintered at 1400 °C for 3 h to yield a thin, dense YSZ electrolyte layer [11]. The cathode paste was prepared using La0.8Sr0.2MnO3 (LSM; Praxair, 50 wt.%) and YSZ (TZ-8YS, Tosoh, 50 wt.%). The cathode layer was screen-printed on the anode-supported electrolyte with an active area of 1.5 cm² and a thickness of 20–30 μm. The pellet was sintered at 1150 °C for 3 h. The cell was reduced with hydrogen for 3-h prior to running the cell. The cell was examined by SEM (JEOL 6500F) and EDX (JEOL 2100).

2.2. Cell testing

The performance of anode-supported single cells was evaluated at 800 °C with humidified hydrogen (200 cm³/min, 3% H₂O) or wet methane (100 cm³/min, 3% H₂O) on the anode side and air (300 cm³/min) on the cathode side. The employed cell-testing equipment is described elsewhere [12]. The current collector was a Pt mesh (Alfa) on the cathode side and an Au felt on the anode side. I–V characterization and durability were measured using a Solartron 1260 frequency analyzer and a Solartron 1287 interface. The carbon deposited on the anode was further examined by temperature-programmed oxidation (TPO; Telcat-M) and X-ray diffration (XRD; Rigaku, Rint 2700). TPO was measured with a ramping rate of 5 °C/min and a gas feed rate of 30 ml/min (20% O₂ and 80% He). The Sn content was measured by elemental analysis using an inductively coupled plasma (ICP; IRIS Intrepid II, Thermo Elemental).

3. Results and discussion

Sn-doped Ni/YSZ was used as the anode catalyst to fabricate a single SOFC. Fig 1a shows a cross-sectional SEM image of the single cell. The anode is porous, allowing the fuel gas to permeate it, but the anode itself is well-connected, as shown in Fig. 1b. An EDX spectrum was obtained to determine the distribution of Sn on the anode. Fig 1c shows the Ni distribution on the anode surface and Fig. 1d shows the Sn distribution at the same site. Sn is uniformly distributed with Ni on the anode surface. Although 1 wt.% of Sn (with respect to Ni) was used in preparing the catalyst, EDX spectroscopy reveals that 23.5 wt.% of Sn (with respect to Ni) is present on the surface. Therefore, Sn is preferentially distributed on the surface.

A single SOFC was also prepared using Ni/YSZ as the anode catalyst, and its performance was compared with that of the SOFC with an Sn-doped Ni/YSZ anode catalyst. When H₂ (humidified with 3% H₂O) was used as the fuel, the power densities of the Ni–YSZ and Sn-doped Ni/YSZ cells were 0.48 and 0.47 W/cm², respectively. When wet methane (humidified with 3% H₂O) was used as the fuel, the power densities of the Ni–YSZ and Sn-doped Ni/YSZ cells were 0.40 and 0.39 W/cm², respectively (Fig. 2a

Fig. 1. SEM images of (a) a cross-sectional area of an anode-supported Sn-doped Ni/YSZ single cell, and (b) expanded view of anode side. EDX images of the anode for (c) Ni and (d) Sn. The scale bar in EDX images is 100 nm.
and c). Thus, the Sn-doped Ni/YSZ cell exhibited an equivalent power density to the Ni/YSZ cell. The presence of a small amount of Sn has little effect on the activity of the anode catalyst.

The long-term stability of the single cells was tested using wet methane as the fuel (Fig. 2b and d). A current density of 0.2 A/cm² was applied. For the Ni/YSZ cell, the power density fell off and the cell eventually stopped after 2.3 h, whereas the Sn-doped Ni/YSZ cell operated for 49.0 h. The stability of the Sn-doped Ni/YSZ cell was an order of magnitude higher than that of the Ni/YSZ cell.

The characteristics of the carbon deposited on the anode surface were examined by comparing the Ni/YSZ cell after the cell stopped (i.e., after 2.3 h of operation) with the Sn-doped Ni/YSZ cell after

Fig. 2. I–V curves and stability tests measured at 800 °C for Ni/YSZ (a and b) and Sn-doped Ni/YSZ (c and d). Applied load of current density was 0.2 A/cm² and wet methane was used as fuels for (b) and (d).

Fig. 3. SEM images of the anode over (a and b) Ni/YSZ after the cell stopped in 2.7 h and (c and d) Sn-doped Ni/YSZ after the cell operated for 30 h at 800 °C.
the cell had been operating for 30 h. Fig 3 shows SEM images of the anodes after the cell test. Large pores and wire-like carbon coke are visible on the Ni/YSZ anode. The accumulation of carbon is generally severe at high temperatures such as 800 °C, commonly causing the cell pellet to expand, inducing cracking of the cell [4]. Cell expansion was also observed in our case, and the cell became fragile after the cell test. The large amount of coke destroyed the integrated structure of the anode, causing cell operation to stop. In contrast, the Sn-doped Ni/YSZ anode retained its integrated structure even after 30 h of operation, as shown in the SEM image in Fig. 3c; no carbon wires were observed in this case.

The TPO results shown in Fig. 4a demonstrate the difference between the two anodes more clearly. Twice the amount of carbon was deposited on the Ni/YSZ anode than on the Sn-doped Ni/YSZ anode. Considering the difference in operating times (2.3 vs. 30 h), much less carbon accumulated on the Sn-doped Ni/YSZ anode than on the Ni/YSZ anode. In addition, the characteristics of the deposited carbon appear to be different in the two cases. Whereas the carbon on the Sn-doped Ni/YSZ anode was oxidized at a relatively low temperature (peak at 407 °C), the majority of the carbon on the Ni/YSZ anode was removed at a much higher temperature of 500–650 °C (peak at 582 °C). Carbon that is removed at a higher temperature is more strongly bound to the catalyst surface. The XRD data in Fig. 4b reveal a graphitic carbon peak at 27° for the Ni/YSZ anode, whereas no carbon peak was observed for the Sn-doped Ni/YSZ anode. The carbon on the Sn-doped Ni/YSZ anode did not exhibit any crystallinity according to the XRD data; thus, it appears to exist as amorphous carbon. The TPO results for Ni/YSZ show another small peak at 388 °C, also indicating the existence of a higher degree of graphitic carbon. This result is consistent with the XRD results, which reveal a weaker peak in the Sn-doped Ni/YSZ anode, indicating a higher degree of graphitization.

Sn stability was examined by measuring the Sn content using ICP. The Sn/Ni atomic ratio was 0.75% before the cell was operated, 0.61% after the cell had been operated for 30 h, and 0.40% after the cell stopped after 49 h. In the case of the Sn-doped Ni/YSZ cell, the degradation in cell stability was possibly caused by decreasing Sn. Preliminary tests revealed that Sn stability can be greatly improved when the cell is operated at 650 °C. A SOFC able to run at an intermediate-temperature range (400–700 °C) has been actively investigated, as there are fewer restrictions on the cell component materials at these temperatures [13]. Sn-doped Ni/YSZ may be particularly effective in an intermediate-temperature SOFC system. We are currently investigating ways to further improve the cell stability.

4. Conclusions

An anode-supported single cell was fabricated using Sn-doped Ni/YSZ as the anode catalyst with a YSZ electrolyte and a LSM-YSZ cathode catalyst. The cell had power densities of 0.47 W/cm² for humidified H2 (3% H2O) and 0.39 W/cm² for wet methane (3% H2O) at 800 °C, equivalent to the power densities of a Ni/YSZ cell (0.48 and 0.40 W/cm², respectively). A cell stability test revealed that the cell with a Ni–YSZ anode stopped operating after 2.3 h, whereas the cell with an Sn-doped Ni/YSZ anode operated for 49.0 h. The rapid accumulation of coke led to the destruction of the cell with the Ni/YSZ anode, whereas much less carbon was deposited on the Sn-doped Ni/YSZ anode, resulting in improved stability of the fuel cell. The characteristics of the deposited carbon differed between the cells: graphitic carbon was deposited on Ni/YSZ, whereas amorphous carbon was deposited on Sn-doped Ni/YSZ. The transformation of amorphous carbon to graphite appears to be hindered on Sn-doped Ni/YSZ.

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References