Direct Operation of Methane Fueled Solid Oxide Fuel Cells with Ni Cermet Anode via Sn modification

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ABSTRACT: Traditional solid oxide fuel cells (SOFCs) with Ni cermet anode are not stable operating in CH₄ due to carbon deposition. Here we report excellent long-term stability of the cell with Ni/SDC anode is achieved in 3% H₂O humidified CH₄ in a temperature range of 700~800°C by addition of 1wt%Sn to the porous anode. The addition of a small amount of Sn does not compromise the electrochemical performance of the cell in humidified H₂. For the 1%Sn-Ni/SDC anode, the peak power density of the cell reaches 0.28Wcm⁻² in 3% H₂O humidified CH₄ and the current density decreases only by 30% after the cell is operated under a constant voltage of 0.8V

in humidified CH₄ for 230 hours at 700°C. The Ni and Sn mappings of the tested cell indicate that Sn is enriched on the anode surface and Sn-Ni intermetallics form. It is found that a critical process is essential to oxidize the impregnated SnCl₂ into SnO₂ at a temperature higher than 800°C, hence metallic Sn can be obtained and consequently it further forms highly catalytic activity Sn-Ni intermetallics in H₂. These results demonstrate that the addition of 1wt%Sn can significantly enhance the coking tolerance of the Ni/SDC anode.

Keywords: solid oxide fuel cells, Ni cermet anode, Sn modification, direct oxidation of methane

1. Introduction

There has been considerable interest in the direct operation of solid oxide fuel cells (SOFCs) with hydrocarbon fuels [1-11]. Unlike an internal reforming, directly electrochemical oxidation of hydrocarbon in SOFCs do not need to introduce a substantial amount of H₂O, CO₂ or O₂, which greatly simplifies the system and reduces the cost [12-13]. The most commonly used nickel/yttria-stabilized zirconia (Ni/YSZ) anodes have showed excellent performance in H₂ fuel; however, there is serious carbon deposition when hydrocarbon fuels are used [1,2].

In recent years, great efforts have been devoted to develop alternative anodes to alleviate carbon deposition issue encountered in Ni-based cermet anode [3-10]. However, the long-term stability and catalytic activity of the proposed alternative anode materials so far are still not satisfactory yet when hydrocarbon fuels are used. Lee *et al.* have reported that the addition of 1wt%Sn to the traditional Ni/YSZ anode could decrease carbon deposition. They observed that a higher amount of Sn existed on the surface of anode [14]. Hyun *et al.* also demonstrated that Sn could increase the activation energy of methane pyrolysis and thus the carbon deposition rate is reduced [15]. However, their preparation method was relatively complex. Furthermore, Hill *et al.* [16] also found that the addition of Sn did not improve the carbon tolerance of the traditional Ni cermet anode when the SnCl₂ infiltrating NiO-YSZ composite anode was calcined at a lower temperature of 500°C. Inspired by the above promising results and the idea of liquid tin/antimony anode for direct carbon SOFCs [17-19], herein, we prepared Sn-modified Ni/SDC cermet anode for SOFCs with methane fuel. The

feasibility of the Sn-Ni/SDC as an anode material for methane-fueled SOFCs was investigated with a $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM, $\sim 250\mu\text{m}$ thick) electrolyte-supported configuration with a composite cathode consisting of $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{CoO}_{3-\delta}$ and SDC (30wt%). The phase, distribution and morphology of Sn was revealed by high angle annular dark field scanning transmission electron microscopy (HAADF STEM).

2. Experimental

Single cells were fabricated by a $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM, >99% dense) electrolyte-supported technique. LSGM electrolyte was prepared by uniaxially pressing a well-milled mixture of LSGM (PRAXAIR Inc) powder and 1wt% polyvinyl butyral (PVB), and then sintered at 1450°C for 10 hours [20]. A thin buffer layer of $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_{2-\delta}$ (LDC) between the anode and the electrolyte was used to prevent cation migration between NiO and LSGM [21]. The NiO- $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (SDC) composite anode (weight ratio of NiO:SDC is 65:35) and $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{CoO}_3$ (SCCO)-SDC composite cathode (weight ratio of SCCO and SDC is 70:30) were both prepared by a screen-printing method and heated at 1200°C for 2 hours and 1050°C for 2 hours, respectively. NiO and SDC powders were synthesized by a glycine-nitrate combustion process [22]. SCCO powder was prepared by a sol-gel method [23]. Tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) solution of ethyl alcohol was introduced into the anode by an impregnating method. The Sn loading was about 1wt % with respect to the Ni content in the catalyst. Ag paste was used as a current collector on the anode side while Pt

paste was used as a current collector on the cathode side. Before testing, the anode catalyst was calcined at 850°C in air for 1 hour to fully oxidize the SnCl₂ to SnO₂.

Since the literature reported that the addition of Sn did not enhance the carbon tolerance of the traditional Ni cermet anode when the SnCl₂ infiltrating NiO-YSZ anode was calcined at a lower temperature of 500°C [16]. To examine the existing phase and morphology of Sn for the anodes calcined at lower temperatures, another two cells were calcined at 800°C and 750°C in air respectively before reducing at 700°C in 3% H₂O humidified H₂ for 2 hours. These three cells are hereafter referred to as Cell-850, Cell-800 and Cell-750, respectively.

The open circuit voltage (OCV) curves and current density-voltage curves were measured with an IM6 electrochemical workstation (ZAHNER, Germany) at the operating temperature range of 700°C to 800°C. The cathode side was exposed to air and the anode side was exposed to 3%H₂O humidified hydrogen or CH₄ at a flow rate of 100 mLmin⁻¹. Impedance spectra were measured at the open-circuit voltage (OCV) in a frequency range of 50mHz to 100kHz with an amplitude of 5mV. The cell structure was analyzed by scanning electron microscope (SEM, Hitachi-S4800). The existing state and the distribution of Sn were analyzed by elemental mapping and the selected area electron diffraction (SAED) with JEM 2200FS. The accelerating voltage is 200kV.

3. Results and Discussion

Fig. 1a shows the cross-sectional SEM image of the 1wt%Sn-Ni/SDC single cell.

The cell consists of a SnCl_2 solution of ethyl alcohol infiltrating NiO-SDC composite anode, a LDC buffer layer, a LSGM electrolyte and a SCCO-SDC composite cathode. The thicknesses of the anode and cathode are about $35\mu\text{m}$, and the thickness of the electrolyte is about $250\mu\text{m}$. It can be seen that the four layers are well bonded. The SEM images of the porous anode and cathode are shown in Fig. 1b and Fig. 1c, respectively.

Fig. 2 shows the cell voltages and power densities as a function of current density for cells with 1wt%Sn-Ni/SDC and pristine Ni/SDC as anodes respectively at different temperatures in 3% H_2O humidified H_2 . As shown in Fig. 2a, the peak power density of the cell with 1wt%Sn-Ni/SDC anode reaches 1.16Wcm^{-2} at 800°C , 0.77Wcm^{-2} at 750°C and 0.58Wcm^{-2} at 700°C in humidified H_2 . These values are close to those of the cells with the pristine Ni/SDC anode, i.e., 1.20Wcm^{-2} at 800°C , 0.83Wcm^{-2} at 750°C and 0.59Wcm^{-2} at 700°C , as shown in Fig. 2b. The durability of both cells were tested in humidified H_2 at 0.8V for 100h at 700°C (Fig. 2c). The cell with 1wt%Sn-Ni/SDC anode has a similar performance to that of the cell with the pristine Ni/SDC cell. These results indicate that the addition of a small amount of Sn does not compromise the cell performance with humidified H_2 as the fuel at the temperatures studied. The peak power densities of the cell with 1wt%Sn-Ni/SDC anode reach 0.64 , 0.39 and 0.28Wcm^{-2} at 800 , 750 and 700°C , respectively, in humidified CH_4 , as shown in Fig. 3. It indicates that the cell with 1wt%Sn-Ni/SDC shows excellent performance operating in humidified CH_4 . Fig. 4 shows the OCV change as a function of time for the cell with 1wt%Sn-Ni/SDC anode and the pristine

Ni/SDC anode when the fuel was switched from humidified H₂ to CH₄ at 700°C. It can be seen that the OCV of the cell with 1wt%Sn-Ni/SDC anode keep stable in two hours while the OCV of the cell without Sn modification drops dramatically. This result unequivocally indicates that the addition of 1wt%Sn to the Ni cermet anode can enhance the coking tolerance.

Long-term stability of the 1wt%Sn-Ni/SDC anode cell at 0.8V and 700°C in 3%H₂O humidified CH₄ is shown in Fig. 5. The decrease of current density is less than thirty percent after operating for 230 hours. However, for the Sn-free Ni/SDC anode cell, the current density of the cells quickly dropped below 0.1Acm⁻² when the fuel was switched from humidified H₂ to CH₄ (see Fig. 6). Therefore, we conclude that for the Cell-850 with addition of 1wt%Sn to the anode dramatically improves the Ni cermet anode stability in humidified CH₄.

To gain insights into the nature of the active component of anode for the CH₄ electro-oxidation reaction, HAADF STEM analysis was conducted on the anode after long-term stability testing. Fig. 7a shows the HAADF STEM image of the 1 wt%Sn-Ni/SDC anode after the long-term stability test. The inset shows the convergent nano-beam diffraction (CBED) pattern of the particle arrowed. It can be indexed as Ni₃Sn. The bright field (BF) STEM image and the corresponding elemental mapping are shown in Fig. 7b. Besides elemental mappings, we also picked up some nanoparticles for further energy dispersive spectrometry (EDS) analysis, as shown in Figs. 7d~f. For comparison, we also show the EDS spectrum collected on the overall mapping region when mapping was performing (Fig. 7g). Apparently, all

the analyzed particles are rich in Sn. This is consistent with the EDS mapping results. All the above results indicate that Sn enrichment happens by forming Sn-Ni intermetallics. Among them, Ni_3Sn is one of the highly active catalysts for hydrocarbon oxidation [24-26]. The formed Sn-Ni intermetallics nanoparticles block the active step sites of Ni and reduce the size of active Ni ensembles, which will mitigate the coke formation [27]. Moreover, the formation of hydroxyl groups from water activation is essential for the removal of deposited carbon from the anode surface [28]. In the presence of Sn-Ni intermetallics, the Ni cermet anode tends to absorb more water due to the oxophilic nature of Sn and the dissociation of H_2O happens more easily. Thus, the coking is suppressed significantly. Actually, Sn is one of oxophilic elements, which has been used to effectively reduce the serious CO poisoning at the anode of the Pt catalyst in direct methanol fuel cells (DMFCs) [29].

In order to examine whether the infiltrated SnCl_2 has to be oxidized to SnO_2 at above 800°C in air and subsequently forming highly active Sn-Ni intermetallics in H_2 , another two cells were calcined at 800°C and 750°C in air respectively before reducing at 700°C in 3% H_2O humidified H_2 for 2 hours. The durability of the cells operating at a constant voltage of 0.8V at 700°C in wet CH_4 is shown in Fig. 8. The Cell-800 shows much better durability than that of the Cell-750, which indicates that SnCl_2 can not be oxidized completely into SnO_2 in air at lower temperature. The HAADF STEM image of the anode of the Cell-750 was collected after the cell was cooled down to room temperature in dry N_2 , as shown in Fig. 9a. In this case, we found that Ni and Sn distributed homogeneously on the surface of the Ni cermet, no

obvious Sn enrichment was observed. We also conducted nano CBED on a similar area in the same sample. Fig. 9b shows the diffraction patterns. Indexation of the patterns A and B suggests that the corresponding particles are both metallic Ni. The zone axis of particle A is [011] while that for particle B is [-112]. Because the particle with pattern C is not at the edge of the sample and it is overlapped with other particles, we obtain a composite pattern. However, from the indicated indexation, we can conclude that the reflections belong to metallic Ni. All the CBED results provide extra evidence that there is no intermetallic phase formed between Ni and Sn for this sample. Therefore, it suggests that SnCl_2 can be oxidized more completely into SnO_2 in air for 1 hour only at a calcination temperature of above 800°C . Then it can be reduced to metallic Sn subsequently and form highly active Sn-Ni intermetallics in H_2 . Therefore, the appropriate procedures to be used for the anode preparation are as follows. Firstly, the SnCl_2 -infiltrated cell is calcined at 850°C in air for 1 hour to fully oxidize the SnCl_2 to SnO_2 , then the anode was reduced at 700°C in 3% H_2O humidified H_2 for 2 hours.

4. Conclusion

In this study, we fabricated Sn modified Ni/SDC cermet anode cell by infiltrating SnCl_2 solution of ethyl alcohol into the porous Ni cermet anode. The addition of a small amount of Sn (1wt%) in the Cell-850 does not compromise the electrochemical performance in humidified H_2 . Stability tests reveal that the Cell-850 with 1wt%Sn-Ni/SDC anode is better than the cell with Sn-free Ni/SDC anode in humidified CH_4 at 700°C . The HAADF STEM image of the tested cell shows that the

incorporation of a small amount of Sn into the surface of Ni cermet facilitates the formation of highly active Sn-Ni intermetallics, and offers exceptional long-term stability without coking on operating with a humidified methane fuel. We also find that the infiltrated SnCl_2 has to be oxidized to SnO_2 at above 800°C in air for 1 hour for the purpose of being reduced to metallic Sn. Then the metallic Sn reacts with Ni to form highly active Sn-Ni intermetallics in H_2 .

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Figure Captions

Fig. 1. SEM images of the (a) cross-section of the cell, (b) anode surface and (c) cathode surface of the 1wt%Sn-NiO/SDC cell.

Fig. 2. Cell voltages and power densities as a function of current density for cells with (a) 1wt%Sn-Ni/SDC anode and (b) pristine Ni/SDC anode operating at different temperatures in 3% H₂O humidified H₂, (c) Long-term stability of both cells tested at 700°C in 3% H₂O humidified H₂ at 0.8V for 100h. Stationary air was used as oxidant in all cases.

Fig. 3. Cell voltages and current power densities as a function of current density for the cell with 1wt%Sn-Ni/SDC as anode at different temperatures in humidified CH₄.

Fig. 4. Open-circuit voltage (OCV) change as a function of time for the cell with 1wt%Sn-Ni/SDC anode and pristine Ni/SDC anode when the fuel was switched from humidified H₂ to CH₄ at 700°C.

Fig. 5. Long-term stability of the cell with 1wt%Sn-Ni/SDC as anode operating at a constant voltage of 0.8V at 700°C with 3% H₂O humidified CH₄ as fuel and stationary air as oxidant.

Fig. 6. Long-term stability of the cell with pure Ni/SDC as anode under a constant voltage

discharge at 0.8V and 700°C when the fuel was switched from humidified H₂ to CH₄; in the first two hours, the fuel was humidified H₂ and then it was switched to wet CH₄. The red arrow indicates the point where the fuel was switched from the humidified H₂ to CH₄.

Fig. 7. (a) HAADF STEM image, (b) the bright field (BF) STEM image and the corresponding element mappings, and (c) ADF image of the 1wt%Sn-Ni/SDC cell after the long-term stability test, (d~g) EDS of spots are indicated by arrows in Fig. c, (g) the EDS spectrum collected on overall mapping region when mapping was performing.

Fig. 8. The durability of the Cell-750 and Cell-800 operating at a constant voltage of 0.8V at 700°C with 3% H₂O humidified CH₄ as fuel and stationary air as oxidant.

Fig. 9. (a) The HAADF STEM image and the corresponding elemental mapping of the 1wt%Sn-Ni/SDC anode of Cell-750; (b) ADF image and CBED patterns of the indicated particles in the same cell sample.

Graphical Abstract

Excellent long-term stability of the cells with Ni/SDC anode is achieved in 3% H₂O humidified CH₄ in a temperature range of 700~800°C by addition of 1wt%Sn to the porous anode calcined at 850°C in air for 1 hour before reducing in wet H₂.