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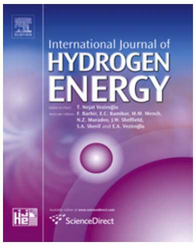

Iron incorporated Ni–ZrO_2 catalysts for electric power generation from methane

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A B S T R A C T

On the purpose to perform as functional layer of SOFCs operating on methane fuel, NiFe–ZrO_2 alloy catalysts have been synthesized and investigated for methane partial oxidation reactions. Ni_4Fe_1–ZrO_2 shows catalytic activity comparable to that of Ni–ZrO_2 and superior to other Fe-containing catalysts. In addition, O_2-TPO analysis indicates iron is also prone to coke formation; as a result, most of NiFe–ZrO_2 catalysts do not show improved coking resistance than Ni–ZrO_2. Anyway, Ni_4Fe_1–ZrO_2 (Ni:Fe = 4:1 by weight) prepared by glycine-nitrate process shows somewhat less carbon deposition than the others. However, Raman spectroscopy demonstrates that the addition of Fe does reduce the graphitization degree of the deposited carbon, suggesting the easier elimination of carbon once it is deposited over the catalyst. Ni_4Fe_1–ZrO_2 has an excellent long-term stability for partial oxidation of methane reaction at 850 °C. A solid oxide fuel cell with conventional nickel cermet anode and Ni_4Fe_1–ZrO_2 functional layer is operated on CH_4–O_2 gas mixture to yield a peak power density of 1038 mW cm^{-2} at 850 °C, which is comparable to that of hydrogen fuel. In summary, the Ni_4Fe_1–ZrO_2 catalyst is potential catalyst as functional layer for solid-oxide fuel cells operating on methane fuel.

1. Introduction

Renewable energy in combination with highly efficient energy conversion technology may be an ideal way for future clean power generation. As the main component of biogas, methane can be treated as a renewable energy. In addition, methane is much cleaner than oil and coal, due to its much higher hydrogen content. Due to the large stress in global oil shortage and huge pressure in environmental pollution from the burning of fossil fuel, there is increasing interest in efficient utilization of methane. As highly efficient energy conversion devices with low emissions, fuel cells are one of the most promising energy conversion devices [1,2]. High temperature solid oxide fuel cells (SOFCs) with all solid components offer the highest fuel efficiency among the various types of fuel cells [3–7]. Methane fuel in combination with SOFC technology is thus highly attractive, and it actually has received many attention during the past decade [8–12].

Despite the big advantage, direct operation of SOFCs on methane fuel, however, still suffer from several important challenges, including low electro-oxidation rate of methane over conventional nickel cermet anode and serious coke

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formation over anode due to the high catalytic activity for methane cracking of nickel. Thus, methane is typically externally pre-reformed to hydrogen before introducing into SOFCs [13–15], which, however, not only consumes a lot of energy due to the endothermic nature for the steam reforming reaction but also increases the complexity of the reactor system, making it less economically attractive. Thereby, various strategies have been adopted to allow the SOFCs directly operate on methane fuel with high power output and minimized coke formation, either by exploiting new electrode materials or modifying/improving the existing Ni-based cermets [16–20]. Nowadays, a relative new ideal is the modification of conventional nickel cermet anode with a thin functional layer which shows high catalytic activity for methane partial oxidation/reforming and also possesses good resistance toward coke formation [21–24]. This technique is highly attractive for its simplicity and effectiveness in improving the cell performance.

For practical application, it is always preferable to have a catalyst with high performance while low price. From this consideration, the modification of nickel-based catalyst is intrinsically more promising than the development of precious metal catalysts. Previously, by modifying Ni–Al_2O_3 with lanthanide or/and alkaline earth metal oxides, the coking resistance of the catalysts is improved obviously, while the catalytic activity can be comparable to noble metal catalysts [25].

Alloying the nickel catalyst with other metal(s) is another way exploited for increasing the activity and coking resistance of fuel cell anodes [26–29]. Huang et al. have reported a Fe–Ni/ScSZ (scandia stabilized zirconia) anode material for SOFC operating on ethanol and they found that carbon deposition was greatly restrained as compared to the conventional Ni–ScSZ cermet anode [28]. Kan et al. have also demonstrated that the addition of a proper amount of Fe to Ni-GDC (Gadolinia-doped ceria) anodes could inhibit coke formation and the stability of the cell was enhanced operating on methane fuel [29]. However, some discrepancies about the iron alloying effect on the coking resistance of nickel-based anodes were appeared in literature. For examples, Lu et al. reported that the anodic overpotential increased by introducing 5 wt. % Fe into nickel anode [27] while Ishihara et al. just gave the opposite conclusion [30]. It suggests more researches are still needed to interpret such discrepancy. Different from the anode, the anode functional layer just performs as a catalyst for chemical onversion of methane to hydrogen. The anode requires a high activity for fuel electro-oxidation, so nickel cermets have turned out still to be the most electrocactive anode materials. Thus, the alloy catalyst may be more suitable as the material for functional layer than the anode. Suprisingly, up to now, no reports about the application of supported alloy catalyst as functional layer of SOFCs was appeared in literature.

Recently, zirconia has been used as either a promoter or a support for Ni-based catalysts in many reactions, such as partial oxidation, steam and dry reforming of methane [31–33]. Zirconia has some beneficial characteristics, for example, it has weak acidic sites and basic sites, good redox capability and high thermal stability. Recently, Lercher et al. have demonstrated that ZrO_2 was essential for Pt and Ni catalysts to minimize carbon deposition under the methane CO_2-reforming conditions [34]. It was also reported that, for the supported Ni catalysts, ZrO_2 was proved to be a highly active and stable support for methane reforming reactions [35]. In addition, ZrO_2 is also a component of SOFCs; thus, the reaction between the ZrO_2-based catalyst layer with the SOFC components can be avoided. A well-dispersed nickel catalyst on ZrO_2 seems to be a viable alternative to the noble metal-based catalyst, especially for fuel cell applications.

In this study, bimetallic NiFe–ZrO_2 catalysts were developed and investigated for methane partial oxidation. The effect of Ni-to-Fe weight ratios on the catalytic performance and carbon deposition properties of NiFe–ZrO_2 were systematically investigated. Finally, the potential NiFe–ZrO_2 catalyst was applied as an anode functional layer of a SOFC, and the performance of the cell operating on methane-oxygen was studied.

2. Experimental

2.1. Synthesis and fabrication

The total amount of active metals in the catalysts was kept at 15 wt.%, while weight ratios of Ni to Fe (x:y) of 1:0, 4:1, 2:1, 1:1, 1:2, 1:4, and 0:1 were tried in this study, for convenience, the corresponding catalysts were named as Ni_xFe_y–ZrO_2. All catalyst powders were synthesized via a glycine-nitrate process (GNP) [36]. The primary powders were further calcined at 850 °C in static air for 5 h to obtain the desired catalysts. After cooling down to room temperature, the powder was pressed into disk-shaped pellets and then crushed into small grains with the desired particle size for the catalytic activity and carbon deposition tests.

An anode-supported thin-film electrolyte fuel cell configuration was adopted in this study. The unreduced anode was composed of NiO and $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (YSZ) at the weight ratio of 60:40, YSZ was applied as the electrolyte and $La_{0.8}Sr_{0.2}MnO_3$ (LSM) as the cathode. LSM was synthesized using a standard EDTA-citrate sol–gel process with metal nitrates (analytical reagents) as the raw materials [37]. The NiO and YSZ powders were commercial products (Chengdu Shudu Nano-science Co., Ltd. for NiO and Tosoh for YSZ).

To fabricate the fuel cells, disk-shaped anode substrates were first prepared by a tape-casting technique, and the detailed information of the fabrication of the three-layer single cell was reported in our previous work [36]. To prepare the catalyst layer, a slurry of the catalyst powder was first prepared, which was then screen-painted onto the outer surface of the anode layer and sintered at 850 °C in air for 1 h.

2.2. Catalytic evaluation

Catalytic activity of the various Ni_xFe_y–ZrO_2 catalysts was tested in a flow-through type fixed-bed quartz-tube reactor with an inner diameter of 8 mm. Typically, 0.2 g catalyst particles in the size range of 0.42–0.63 mm, diluted with 0.4 g of SiO_2 sand, was packed into the reactor to achieve a catalyst bed height of 1.0 cm. A K-type thermocouple was inserted into the center of the catalyst bed to detect the reaction temperatures. The gases, which flowed at the rates of CH_4, O_2, He