



A comprehensive evaluation of a Ni–Al₂O₃ catalyst as a functional layer of solid-oxide fuel cell anode

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ABSTRACT

An inexpensive 7 wt.% Ni–Al₂O₃ composite is synthesized by a glycine–nitrate process and systematically investigated as anode catalyst layer of solid-oxide fuel cells operating on methane fuel by examining its catalytic activity towards methane partial oxidation, steam and CO₂ reforming at 600–850 °C, cell performance, mechanical performance, and carbon deposition properties. Ni–Al₂O₃ shows comparable catalytic activities to Ru–CeO₂ for the above three reactions. The cell with a Ni–Al₂O₃ catalyst layer delivers maximum peak power densities of 494 and 532 mW cm^{−2} at 850 °C, operating on methane–H₂O and methane–CO₂ mixture gases, respectively, which are comparable to those operating on hydrogen. Ni–Al₂O₃ is found to have better mechanical performance than Ru–CeO₂. O₂–TPO demonstrates that Ni–Al₂O₃ does not inhibit the carbon formation under pure methane atmosphere, while the introduction of steam or CO₂ can effectively suppress coke formation. However, due to the low nickel content in the catalyst layer, the coke formation over the catalyst layer is actually not serious under real cell operation conditions. More importantly, Ni–Al₂O₃ effectively protects the anode layer by greatly suppressing carbon formation over the anode layer, especially near the anode–electrolyte interface. Ni–Al₂O₃ is highly promising as an anode functional layer for solid-oxide fuel cells.

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1. Introduction

Recently, there has been tremendous interest in fuel cells as electrical power generators because of their high energy-conversion efficiency, low emissions, and size flexibility, with capacities ranging from several milliwatts to the megawatts level [1–3]. Among the many types of fuel cells, solid-oxide fuel cells (SOFCs) have attracted particular attention because of their fuel flexibility [4,5]. Besides hydrogen, hydrocarbons, carbon monoxide, ammonia, alcohols, and solid carbon can all be used as potential fuels [6–12]. This feature is very attractive for near-future applications since the public infrastructure for hydrogen production, storage and transportation is still far from mature, while hydrocarbons are currently widely available. Actually, hydrogen is presently produced mainly by steam reforming of hydrocarbons.

When hydrocarbons are adopted as the fuels for SOFCs, they are typically first externally reformed to CO + H₂ before being introduced into the fuel cell reactor [13,14]. The external reforming process, however, not only reduces the overall energy-conversion efficiency, but also produces additional greenhouse gases. Because of this, direct hydrocarbon-fueled SOFCs have been gaining more

and more attention recently [15–18]. As the simplest hydrocarbon, methane is the main component in the huge reserves of natural gas and coal-bed gas, and also the renewable resource of biogas. In principle, the simplest way to operate an SOFC on methane fuel is direct electro-catalytic oxidation of methane over the anode. However, the state-of-the-art sintered nickel–cermet anode catalyzes the CH₄ decomposition reaction that easily causes coke formation over the nickel catalyst surface and consequently, fast deterioration of the cell performance [19,20]. The development of novel anode materials with high coking-resistant capabilities has been extensively explored. Among them, CeO₂–Cu cermet anodes and perovskite-type La_{1–x}Sr_xCr_{1–y}Mn_yO₃ oxide anodes have shown high resistance towards coke formation [21–24]. However, such anodes always show poor electrochemical activity for methane oxidation and consequently, poor cell performance was obtained [21–24]. Development of new anode materials with high electro-catalytic activity for methane oxidation but not for the methane cracking reaction is the key to realizing direct-methane SOFCs.

An alternative way to operate on methane fuel is to integrate the catalytic conversion of methane to syngas reaction (i.e., partial oxidation, steam reforming or CO₂ reforming) with SOFCs internally [25–29]. Since CO and H₂ have much higher electrochemical activity than methane, such an operating mode can effectively improve the cell performance when using methane fuel. Furthermore, it can also effectively suppress carbon deposition over the

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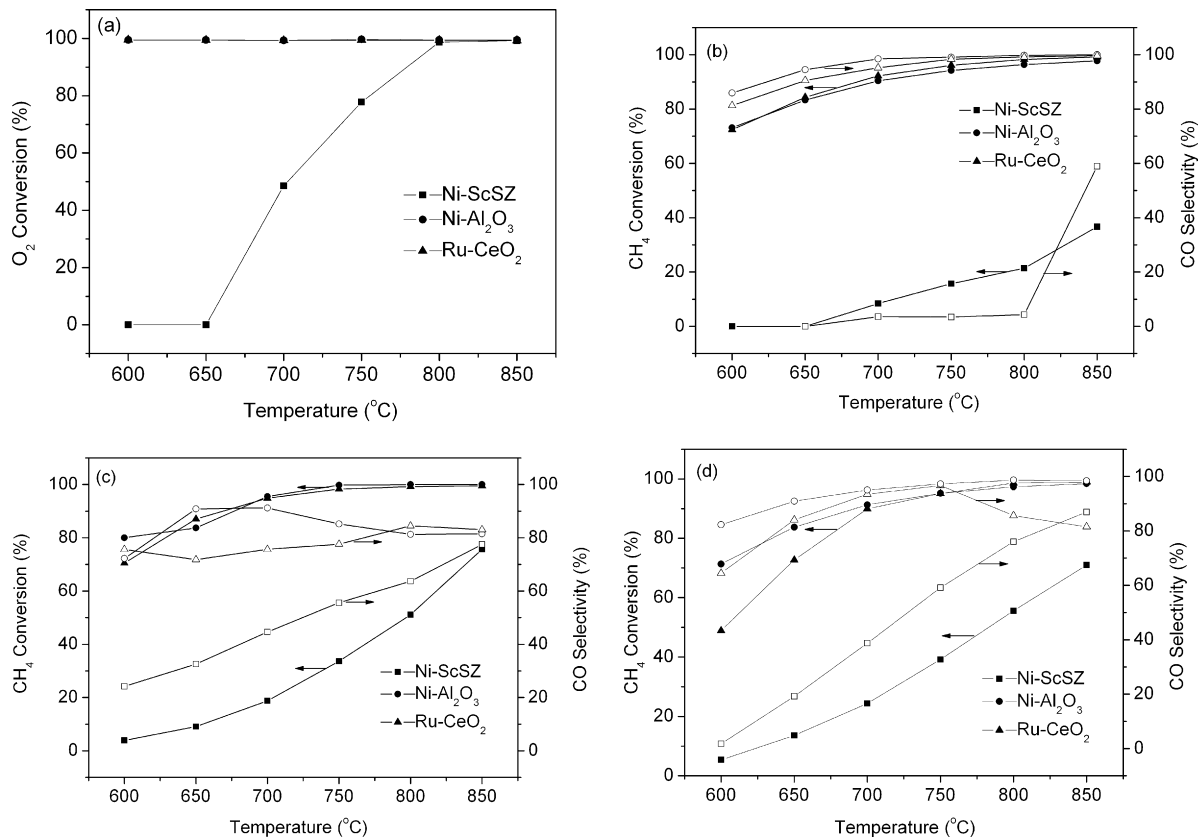


Fig. 1. Catalytic activity of Ni–Al₂O₃, Ru–CeO₂ and Ni–ScSZ catalysts for (a and b) partial oxidation (CH₄:O₂ = 2:1), (c) steam reforming (CH₄:H₂O = 1:1) and (d) CO₂ reforming (CH₄:CO₂ = 1:1).

anode surface. However, the traditional Ni-cermet anodes usually show poor catalytic activity towards the above reactions, especially at reduced temperatures. Very recently, the deposition of a highly active catalyst layer over the anode surface was found to be an effective way of increasing the cell performance when operating on hydrocarbon fuels [30–33]. It not only increases the cell power output, but also obviously suppresses the coke formation over the anode surface. In particular, Ru–CeO₂ has been found to be an efficient catalyst for operating on methane, propane and butane fuels, in both single-chamber and dual-chamber cell configurations [30,32–36]. However, the high price of Ru–CeO₂ is the main obstacle towards its large-scale application. The development of cheap and highly active materials for the functional layer is then critical.

In our previous communication, we demonstrated that an inexpensive Ni–Al₂O₃ catalyst also had very high catalytic activity towards methane partial oxidation, methane steam reforming and methane CO₂ reforming reactions at 750–850 °C [31]. The cell with the Ni–Al₂O₃ catalyst layer showed significant improvement in cell performance, operating on both pure methane and methane–oxygen mixtures of gases. Furthermore, the cell performance deterioration rate was also greatly reduced even when operating on pure methane fuel.

In this paper, we present a comprehensive investigation of Ni–Al₂O₃ as the catalyst layer of SOFC anode operating on methane–oxygen, methane–H₂O, and methane–CO₂ gas mixtures. The following characterizations were investigated: catalytic activity for syngas production from methane–oxygen, methane–CO₂ and methane–H₂O mixture gases, cell performance, mechanical performance of the catalyst layer under repeated thermal and redox cycling, and coke deposition properties. A comparative study with Ru–CeO₂ catalyst was also conducted.

2. Experimental

2.1. Catalyst powder synthesis and cell fabrication

Both 7 wt.% Ni–Al₂O₃ and 7 wt.% Ru–CeO₂ powders, investigated as the materials for the catalyst layer, were synthesized by a glycine nitrite process (GNP) [37]. Taking the synthesis of Ni–Al₂O₃ as an example, stoichiometric amounts of nickel nitrate and alumina nitrate were first dissolved in de-ionized water, glycine was then added at a molar ratio of 2.0 between the glycine and total metallic cations. The water in the solution was then evaporated by heating over a hot plate under stirring to create a liquid precursor, which was then moved to an electrical oven at 240 °C to induce auto-combustion. The primary powder was further calcined at 850 °C for 5 h in static air.

The fuel cell materials, including the cathode La_{0.8}Sr_{0.2}MnO₃ (LSM) and the electrolyte (Sc₂O₃)_{0.1}(ZrO₂)_{0.9} (ScSZ), were prepared by an EDTA–citrate complexing process [38,39]. The fuel cell adopted in this study was a 60 wt.% NiO + 40 wt.% ScSZ anode-supported thin-film ScSZ electrolyte fuel cell (~20 μm), fabricated by a dual dry-pressing/sintering process [39]. Ni–ScSZ anode powder was first pressed into a substrate disk using a stainless steel die under a pressure of 120 MPa. ScSZ powder was distributed over the anode surface homogeneously and followed by a second press under a pressure of 240 MPa to form the green dual layer cell, which was then sintered at 1500 °C for 5 h to densify the electrolyte layer. The sintered cells had a diameter of ~13 mm and a thickness of ~0.3 mm.

2.2. Catalytic evaluation

The catalytic activity of the catalysts and anode material was studied in a flow-through type fixed-bed quartz-tube reactor with

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