



Ammonia-mediated suppression of coke formation in direct-methane solid oxide fuel cells with nickel-based anodes



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HIGHLIGHTS

- The addition of NH₃ could decrease the coke formation rates of Ni–YSZ anode.
- The addition of NH₃ could also decrease the coke formation rates of Ni–Al₂O₃.
- The addition of NH₃ could increase the power output of the fuel cells.
- The addition of NH₃ could improve the operational stability of the fuel cells.
- No NO_x was detected in the exhaust gas.

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ABSTRACT

In this study, we report a novel approach for suppressing coke formation in direct-methane solid oxide fuel cells (SOFCs) with a conventional nickel cermet anode by simply adding ammonia to the fuel gas. Because ammonia preferentially occupies the acidic sites of the anode catalyst materials, a significant decrease in the coke formation rate is realized by introducing ammonia into the methane gas. In addition, hydrogen, a decomposition product of ammonia, also acts as an additional fuel for the SOFCs, resulting in high cell performance. At 700 °C, the coke formation rate over the Ni–YSZ anode is suppressed by 71% after the addition of 33.3% NH₃ into CH₄. Suppressed coke formation is also observed for other Ni catalysts such as Ni/Al₂O₃, a common catalyst for methane reforming that has been successfully used as the anode catalyst layer for SOFCs operating on methane, which suggests that introducing NH₃ as an additive gas is a general method for suppressing the coke formation. The addition of ammonia can also effectively improve the power output and operational stability and offers a novel means for developing new coke-resistant SOFCs operating on widely available hydrocarbons for clean power generation to realize a sustainable future.

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1. Introduction

SOFCs have several outstanding properties, in addition to being fabricated from relatively inexpensive materials, they show low sensitivity to impurities in the fuel gas, very high energy efficiency and fuel flexibility [1–5]. Direct-methane SOFCs have been the subject of much research during the past decade because natural

gas, which consists of mainly methane, is an abundant and widely accessible fuel and methane is also the main component of biogas, a renewable energy resource [6–9]. Unfortunately, the state-of-the-art nickel-based cermet anodes suffer from serious coke formation during operation when methane fuel is used because nickel is a good catalyst for the methane cracking reaction. Recently, tremendous efforts have been focused on the development of copper-based or perovskite-based anode materials with improved coking resistance [10,11]. However, due to the relatively low catalytic activity of these materials for methane conversion, they are not currently commercially viable.

Suppressing coke formation by introducing another gas into the fuel gas, such as steam, CO₂, O₂ and H₂, has been explored

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previously [12–14]. However, the main purpose of the additive gas is to increase the coking resistance thermodynamically. For example, Chen et al. [12] have demonstrated that the carbon deposition on a Ni–YSZ anode of an SOFC was greatly suppressed after the addition of 10% H₂O into the methane fuel gas. Pillai et al. [13] also have demonstrated that the addition of CO₂ or air to methane can improve the SOFC stability by suppressing coke formation over the Ni-based anode. Recently, the addition of hydrogen into methane fuel gas was also demonstrated to inhibit coke formation [14]. To completely prevent the coke formation thermodynamically, however, a large amount of such additive gas is required, which could decrease the cell voltage and increase the possibility of anode oxidation. Furthermore, the presence of air or oxygen could also increase the risk of explosions.

In addition to the thermodynamics, the kinetics also played an important role in the coke formation and it might be more effective to suppress the coke formation by altering the kinetics. It was well known that the coke formation behavior of a Ni-based catalyst is strongly dependent on its surface structure and acidity [15] and catalysts with many acidic sites on the surface are prone to coke formation. Basic additives or promoters that favor water adsorption and OH surface mobility can lower the coke formation rate by neutralizing the acidity of the support [16,17]. Horiuchi et al. have studied the effect of basic metal oxides on the catalytic activity and carbon deposition properties of Ni/Al₂O₃ catalysts for CO₂ reforming of methane [18]. They found that basic metal oxides affected both the catalytic activity and coke formation rate. It was suggested that the Ni/Al₂O₃ catalyst adsorbed mostly CO₂ when a basic metal oxide was present, which could limit the CH₄ decomposition reaction rate whereas the catalyst without a basic metal oxide adsorbed mostly CH₄. It was also found that an increase in the basicity of the catalyst can enhance the coke resistance because basic oxides can promote the reaction between steam/CO₂ and solid carbon [19].

Whisker carbon is one of the most destructive forms of carbon formed in methane steam reforming over Ni-based catalysts. This type of carbon was formed by the decomposition of hydrocarbons or CO on one side of the nickel particle and the subsequent nucleation of graphitized carbon on the other side of the nickel particle [20]. The process apparently began with the formation of nickel carbide [21], which has been suggested to be the essential intermediate in the coke formation process [22]. The formation of metal carbides might lead to the development of the layered carbon intermediates that grow into filamentous carbons. These initial carbonaceous materials might be further dissolved and diffuse into the nickel particles; this process was considered to be essential for the growth of carbon whiskers [21].

One approach for controlling coke formation is based on the idea of preventing carbide formation. It was reasoned that inhibiting carbide formation on the surface could slow down coke formation because the dissolution and precipitation of carbon could most likely only occur via carbide formation. It was found that basic oxides could prevent the carbide formation. For instance, Bouarab et al. [23] have found that an MgO promoter in a SiO₂-supported catalyst acted as the specific medium for ensuring a constant feed of surface oxygen to immediately oxidize surface carbide formed from methane cracking into carbon monoxide. However, it was also found that the addition of basic oxides such as K and Ca oxides could decrease the catalytic activity of Ni-based catalysts for methane conversion [24,25].

Here, for the first time, we report a unique and facile way to suppress coke formation on direct-methane SOFCs with a Ni-based anode by simply using ammonia as an additional fuel gas. The basic ammonia could occupy acidic sites on the Ni-based anode, thus effectively reducing the coke formation kinetically. In addition, the

decomposition of ammonia also provides additional hydrogen for the fuel cell. Ammonia is already available worldwide, and its use as a potential hydrogen carrier for energy applications has been proposed. As a basic gas, ammonia can occupy the acidic sites of the anode; in fact, it has been widely used as a probe molecule to detect the surface acidity of catalysts [26,27]. Because the acidic sites would be preferentially occupied by NH₃ when it was introduced into the methane fuel gas, the methane cracking reaction can be effectively inhibited, and the coke formation over the nickel catalyst is expected to be suppressed.

2. Experimental

2.1. Powder synthesis

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF), Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC) and Sm_{0.2}Ce_{0.8}O₂ (SDC) powders were synthesized using an EDTA-citrate complexing sol-gel process. The appropriate metal nitrates were dissolved in water, and a combination of EDTA and citric acid served as the complexing agents. After stirring and heating, a clear gel was obtained, which was held at 240 °C for several hours and further calcined under static air at 950 °C (BSCF), 900 °C (SSC) and 800 °C (SDC) for 5 h to obtain the desired pure-phase oxides. The Ni/Al₂O₃ catalyst, composed of 15 wt.% nickel and 85 wt.% Al₂O₃, and the Li and La co-promoted Ni/Al₂O₃ catalyst, composed of 15 wt.% nickel, 1 wt.% Li₂O, 5 wt.% La₂O₃ and 79 wt.% Al₂O₃, were synthesized by a glycine nitrite process (GNP). Stoichiometric amounts of various metal nitrates were dissolved in deionized water to form a solution, and glycine was then added at a molar ratio of glycine to total metal cations of 2. The solution was heated on a hot plate under stirring to evaporate the water until a gel precursor was obtained. This gel precursor was then transferred to a preheated electric oven at 240 °C to initialize auto-combustion. The primary powder obtained was further calcined at 850 °C for 5 h in static air to yield the desired catalyst.

2.2. Fuel cell fabrication

The fuel cell is fabricated as follows. The anode substrates were prepared by a tape casting process. The slurry for the tape casting process was prepared by two-step ball milling. The anode substrates for the single cells were drilled from the NiO + YSZ tape with a diameter of 16 mm. The disks were then sintered at an elevated

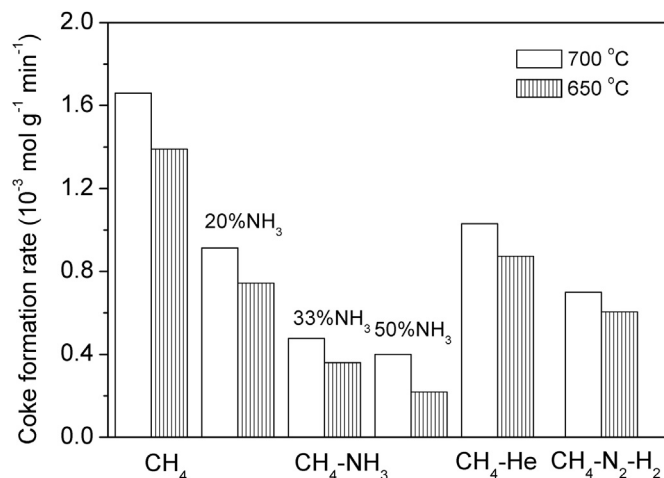


Fig. 1. Coke formation rates on the Ni-YSZ anode after treatment in CH₄-containing atmospheres for 30 min at 700 and 650 °C.

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