



# Electrochemical characteristics and carbon tolerance of solid oxide fuel cells with direct internal dry reforming of methane



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## HIGHLIGHTS

- Effect of CO<sub>2</sub> on the performance of CH<sub>4</sub>-fueled SOFCs was investigated.
- Distribution of relaxation time for SOFCs operated under hydrocarbon was proposed.
- Enhancement of performance was achieved by adding appropriate N<sub>2</sub> to fuel gas.

## ARTICLE INFO

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## ABSTRACT

Direct internal dry reforming is a promising way for solid oxide fuel cells (SOFCs) to directly use hydrocarbon fuels, since biogas already contains carbon dioxide and methane, which are both greenhouse gas contributing to global warming. In this paper, detailed experimental investigation and thermodynamic calculation were carried out to investigate the influence of CO<sub>2</sub> addition on fuel cell's electrochemical characteristics and stability using CO<sub>2</sub> to CH<sub>4</sub> ratio ranging from 0 to 3. The maximum power densities were obtained at CO<sub>2</sub> to CH<sub>4</sub> ratios of 1.5 and 1.7 for fuel gas mixture with and without N<sub>2</sub> carrier gas, respectively. These two values are very close to thermodynamic calculation results about non-carbon limit. An analysis of distribution of relaxation time (DRT) for SOFC operated under dry reforming gas mixtures was first proposed in this study. The results show that the addition of CO<sub>2</sub> can significantly reduce both the anode activation polarization and the fuel gas diffusion resistance at low CO<sub>2</sub> to CH<sub>4</sub> ratio, while the influence became weaker at higher CO<sub>2</sub> to CH<sub>4</sub> ratio. An additional peak, with a larger relaxation time of 10<sup>-1</sup> ~ 10<sup>1</sup> s, was observed with dry reforming gas mixtures. This process, related to dry reforming reaction and water-gas shift reaction, was also influenced by the addition of CO<sub>2</sub>. Besides, we observed an improvement of fuel cell performance by adding appropriate N<sub>2</sub> carrier gas to fuel gas, which may provide a new way to enhance the performance and durability of biogas-fueled SOFC.

## 1. Introduction

Solid oxide fuel cell (SOFC) is a kind of clean and environmental friendly power generation device, which directly converts the chemical energy of fuel to electric energy [1]. With the advantages such as high efficiency, low pollutant emission, good fuel flexibility and long-term stability, SOFC can play an important role in now transitional phase from an energy structure based on fossil fuels to one capable of exploiting renewable fuels on a large scale. In all types of fuel cells, SOFC has the highest operating temperature (generally higher than 600 °C), thus has the potential to directly use natural gas, coal gas and other hydrocarbon fuels [2,3].

However, a significant problem with the direct utilization of

hydrocarbon fuels for SOFC is the carbon deposition on anodes by side reactions [4,5]. When SOFC is operated under hydrocarbon fuels, undesirable carbon deposition occurs on the anode side due to the disproportionation of carbon monoxide and the cracking of hydrocarbon fuels, especially on state-of-the-art Ni-YSZ (Yttria-Stabilized Zirconia) cermet anode because of its good catalytic performance for C–H bond breaking. The deposited carbon can block the porous anode and increase the diffusion resistance of fuel gas, thus results in the reduction of cell performance and stability.

Since Ni-based catalysts have been widely used in the chemical process such as oil reforming and coal gasification, carbon formed on Ni surface has been studied in depth. Carbon deposition on Ni-YSZ anodes is mainly due to the adsorption and catalytic cracking of the

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hydrocarbon fuel molecules on the surface of Ni particles. The adsorbed hydrocarbon molecules could form carbon nanofibers or soot by heterogeneous reaction and homogeneous reaction, respectively [6,7]. The dehydrogenation process of hydrocarbon molecules, like  $\text{CH}_4$  molecules, gives rise to incomplete dehydrogenation intermediates  $\text{CH}_x$ , which may form soot through polymerization and recombination reactions [8,9]. Alternatively, the  $\text{CH}_x$  intermediates may dissolve into the Ni particles, followed by precipitation of carbon atoms as carbon nanofibers at outer surface [10,11]. The dissolution and precipitation process leads to the volume expansion of Ni particles and the separation between Ni particles and YSZ substrates, resulting in the increase of internal stress in anodes and even the rupture of anodes [12].

In order to prevent the adverse effects of carbon, researchers have put forward various methods, among which the most promising and simple one is adding  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2$  or other oxidizing gases to reform the hydrocarbon fuel internally, or the so-called direct internal reforming (DIR) [13,14]. Sasaki et al. [15] constructed C–H–O ternary diagrams to describe the carbon deposition region and the non-carbon region through thermodynamic equilibrium for various fuels. According to the calculation, common hydrocarbon fuels such as methane, methanol, ethanol and olefins are all in the carbon deposition region when temperature is higher than  $600^\circ\text{C}$ . However, adding  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  or  $\text{O}_2$  can move the fuel gas mixtures to the outside of the carbon deposition region, thus eliminates the possibility of carbon deposition thermodynamically. Moreover, the direct heat exchange between the endothermic reforming reactions and the exothermic electrochemical reactions is one of the main advantages of DIR configuration, along with its potential to simplify the system structure and to increase the system efficiency by anode off-gas recycle [16].

$\text{CO}_2$  reforming (known as dry reforming) is an interesting option for DIR-SOFCs, for  $\text{CH}_4$  and  $\text{CO}_2$  are both greenhouse gas contributing to global warming. The source of  $\text{CO}_2$  can be carbon capture and storage devices from power plant, or directly from the anode tail gas of SOFC stacks. Moreover, since biogas already contains  $\text{CH}_4$  and  $\text{CO}_2$ , SOFCs with direct internal dry reforming are seemed to be an economic and competitive way to efficiently use biogas in the near future [17,18]. Therefore, more and more researchers are involved in the study of biogas-fueled SOFCs in the last few years.

Effect of some operating parameters, such as temperature, current density, fuel utilization and  $\text{CO}_2$  to  $\text{CH}_4$  ratio, on fuel cell's performance and stability has been studied in some previous works. Goula et al. [19,20] tested conventional SOFC with Ni-YSZ cermet anodes on direct feed of different simulated biogas (equal, poor and rich biogas). No carbon was visibly observed on the anode after the cells were operated stably at the points of peak power density (PPD) for more than 200 h in each feed at  $875^\circ\text{C}$ . Shiratori et al. operated electrolyte-supported [21,22] and anode-supported [23,24] SOFC with Ni-based anodes on simulated biogas (a fuel mixture of  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{CO}_2$ ) and real biogas at  $800$ – $1000^\circ\text{C}$ . They found that the electrochemical oxidation of  $\text{CH}_4$  could occur at high  $\text{CH}_4$  to  $\text{CO}_2$  ratios whereas at low  $\text{CH}_4$  to  $\text{CO}_2$  ratios the  $\text{O}^{2-}$  transported from cathodes totally reacted with  $\text{H}_2$  and/or  $\text{CO}$ . Besides, the fuel cells operated under real biogas showed voltage fluctuation with severe carbon deposition occurred during long term stability test, which was mainly caused by the sulfur component of real biogas. Sumi et al. [25] examined the durability for Ni-based anodes in comparison with steam and  $\text{CO}_2$  DIR of  $\text{CH}_4$  at  $850^\circ\text{C}$  and  $1000^\circ\text{C}$ . More carbon was observed at  $1000^\circ\text{C}$  because the  $\text{CH}_4$  cracking reaction was facilitated at higher temperature. Accordantly, the fuel cell operated at  $850^\circ\text{C}$  was more stable than that at  $1000^\circ\text{C}$ , with the voltage degradation rates of  $0.5\text{ mV/h}$  and  $8.3\text{ mV/h}$ , respectively. Lanzini et al. [26] tested a single planar fuel cell with 3 variable  $\text{CO}_2$  to  $\text{CH}_4$  ratios (2, 1.5 and 1) for more than 350 h. Their results showed that the degradation rate increased with increasing  $\text{CO}_2$  to  $\text{CH}_4$  ratios, which means an excess of  $\text{CO}_2$  may not help reduce fuel cell degradation. They also found that the  $\text{CO}_2$  to  $\text{CH}_4$  ratio in the range 1.5–2 are beneficial to the conversion of methane and help to obtain the highest  $\text{H}_2$  and  $\text{CO}$

concentration in the products [27].

Some other studies were focused on the improvement of catalytic activity towards  $\text{CH}_4$  dry reforming reaction (reaction 3) and carbon tolerance of Ni-based anodes. Feng Wang et al. [28] modified conventional Ni-YSZ anodes with  $\text{Al}_2\text{O}_3$  and  $\text{SnO}_2$ . They found that incorporation of a suitable amount of  $\text{Al}_2\text{O}_3$  could improve both output performance and stability of fuel cell operated under simulated biogas, while modification with  $\text{SnO}_2$  reduced the performance. Nguyen et al. [29] studied the catalytic activities of three Ni-loaded paper-structured catalyst (PSC) with inorganic fiber network at  $750^\circ\text{C}$ , pure Ni-PSC, Ni-PSC with the dispersion of (Mg, Al)O, and Ni-PSC with the dispersion of (Ce, Zr)O. The Ni-PSC with the dispersion of (Ce, Zr)O was found to have the best catalytic activity for dry reforming of  $\text{CH}_4$ . Subsequently, their simulation results showed an enhancement of PPD up to 40% by using this PSC as an anode catalytic layer [30]. In addition to the composition of anode materials, the preparation process of anodes also has effects. Lanzini et al. [31] investigated the catalytic activity towards  $\text{CH}_4$  dry reforming of Ni-YSZ anodes sintered at different temperatures. They found that lower sintered temperature facilitates the  $\text{CH}_4$  conversion rate as a result of higher specific surface area. Except for Ni-based anodes, some other alternative anodes, such as Cu-based and Au-based [32] and some perovskites [33] have also been studied by researchers. Nevertheless, some drawbacks, such as poor activity towards electrochemical reaction and high cost, limit further application of these materials.

On the other hand, the strong endothermic dry reforming reaction could cause large internal stress within the fuel cell, especially in the entrance region. Therefore, reacting rate of reforming reaction should be properly controlled. Manoj Pillai et al. [34] adopted a PSZ (partially stabilized zirconia) barrier layer between the fuel compartment and the Ni-YSZ anode support to reduce the reacting rate of endothermic reforming reaction. Their combined experimental and simulation results showed that the barrier layer could greatly reduce the temperature difference between fuel cell and surroundings and the induced thermal–mechanical stresses. Similarly, by using a patterned gas-barrier mask made up of dense YSZ, Tran et al. [30] observed 20% decrease of the maximum thermal–mechanical stresses in their simulation results, with a sacrifice of 8% PPD.

When SOFCs are operated under DIR condition, the reforming reactions of  $\text{CH}_4$  occur simultaneously with the electrochemical oxidation reactions on the anode, along with some other reactions (see Table 1). The mixed reactions lead to a complex kinetics on the anode side, which is difficult to rationalize. Ge et al. [35] proposed the reaction steps of dry  $\text{CH}_4$  inside a SOFC anode, containing the electrochemical oxidation of cracked carbon, intermediates resulted from free radical reactions, and oxygenated compounds. However, the addition of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2$  or other oxidizing gases significantly complicates the reaction steps. Hecht et al. [36] proposed a non-electrochemical heterogeneous reaction mechanism for  $\text{CH}_4$  reforming on Ni-based porous catalysts, which consists of 42 reactions among 6 gas-phase species and 12 surface adsorbed species. However, it still remains unclear about the extent of electrochemical oxidation of  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$ , along with the detailed reaction and degradation mechanisms. Therefore, further experimental research is required to investigate the effect of the oxidizing gases addition and to get a more detailed understanding on the mechanism and interaction during degradation [37].

Although some previous studies have shown that SOFCs could work well on simulated/real biogas with several  $\text{CO}_2$  to  $\text{CH}_4$  ratios under relatively high temperature ( $800$ – $1000^\circ\text{C}$ ) and large current density, appropriate operating conditions are still to be determined. For excessive  $\text{CO}_2$  dilutes the fuel and causes reduction of the electromotive force of fuel cells, selection of suitable fuel gas composition is of vital importance. However, the complexity of reaction mechanism increases the difficulty of accurate numerical simulation, so it is important to investigate the effects of fuel gas composition on the electrochemical characteristics and performance of DIR-SOFCs through experimental

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