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# Methane internal reforming in solid oxide fuel cells with anode off-gas recirculation

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## ABSTRACT

In this study, methane steam and dry reforming have been investigated, from the perspective of methane conversion, hydrogen yield and the formation of solid carbon. Different ratios between methane, steam and carbon dioxide were used in order to simulate the methane internal reforming in a Solid Oxide Fuel Cell (SOFC) with anode off-gas recirculation. Thermodynamic equilibrium modelling was first employed to determine the concentrations of each gas in the equilibrium state. Crushed anode substrate material of a commercial SOFC half-cell was used as catalyst in the practical experiments. The modelling results showed that at 750 °C (1023 K), above 90% of methane conversion was found in all cases and carbon was formed when the oxygen to carbon (O/C) ratio was lower than 1.2. The experimental results showed that poor methane conversion rates (around 20%) were found within the steam reforming. The performance was highly affected by the total fuel flow rate and carbon formation could still be found in cases for the O/C ratio above 1.5.

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## Introduction

In solid oxide fuel cells (SOFCs), hydrocarbons can be directly reformed into hydrogen-rich gases inside the cell due to their high operating temperature [1]. Additionally, the energy required for the strongly endothermic reforming reactions can be derived from the heat generated inside the cell. Natural gas, for example, which mainly consists of methane, is a prime choice of fuel for SOFCs employed as residential Combined Heat and Power units (microCHP) due to the well established natural gas distribution infrastructure in households. SOFCs running on natural gas can be applied widely for both  $\mu$ CHP and Decentralised Generation (DG) in the drive to reducing

electricity transmission losses and increasing the efficiency of electricity supply.

Two methods are regularly used for converting methane into hydrogen-rich gases: steam methane reforming (SMR, Equation (1)) and dry methane reforming (DR, Equation (2)) [2].



However, solid carbon can be formed during the reforming process through methane cracking (MC, Equation (3)) and the

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Boudouard reaction (BD, Equation (4)). The carbon deposited will increasingly reduce the porosity in the anode and cover the nickel catalyst thus lowering the performance.



In order to overcome this problem, additional  $\text{H}_2\text{O}$  or  $\text{CO}_2$  needs to be added to the fuel, lowering the concentrations of  $\text{CH}_4$  or  $\text{CO}$  from the SMR or water gas shift reactions (WGS, Equation (5)). The formed solid carbon, though, can theoretically be removed by syngas formation (SF, Equation (6)).



Both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can be found in the SOFC anode exhaust as they are the products of  $\text{CO}$  and  $\text{H}_2$  oxidation. As a result, anode off-gas recirculation (AOGR) is an option to be applied in SOFC  $\mu\text{CHP}$  and DG systems, where the addition of purified water or carbon dioxide are undesired since they increase the system complexity and the requirements for maintenance. Moreover, the fuel cell system can further benefit from the exhaust gas recycling since the returned gas has a similar temperature as the cell, and thermal gradients can be prevented without or with reduced requirements on a pre-heater.

On the other hand, a more complex reaction system is formed due to the competition between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  for reacting with methane. Also, a lower system performance results from the lower fuel partial pressure due to the introduced non-fuel gases. As a result, a detailed inspection of the interaction among  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and,  $\text{CO}_2$  is required for a more in-depth investigation.

A study of methane dry reforming from the point of view of thermodynamics was carried out by Nikoo and Amin [3]. Al-Nakoua et al. [4] reported, that the combined methane steam and dry reforming had the ability to improve the catalyst stability, but the carbon formation and ratios among the reactants were less addressed. Kinetic modelling work was carried out by Maestri [5]. The conclusion that the water concentration could have a significant effect on the combined methane reforming was obtained by Soria et al. [6]; however, the carbon dioxide concentration was fixed in their experiments. A nickel-silica core@shell catalyst used for methane tri-reforming was reported by Majewski and Wood [7]. Research towards methane internal reforming with gold doped Ni/GDC was carried out by Niakolas et al. [8], which resulted in a higher tolerance to carbon formation; however, the amount of gold needs a further investigation. Goula et al. [9] investigated the methane internal reforming with a Ni based anode from the catalyst and electrocatalytic point of view. Their results suggest that a closed-circuit operating SOFC could operate stably for an extended period of time due to the carbon electro-oxidation reactions. A similar result was

obtained by Lin et al. [10], who suggests that the current density has a strong effect on carbon formation. This is particularly obvious when pure methane is used as fuel and the temperature is below  $700^\circ\text{C}$ . Oyama et al. [11] report that the methane dry reforming performs less efficient than steam reforming since the produced hydrogen can be consumed with carbon dioxide through the reversed WGS reaction. Additionally, a higher hydrogen yield can be obtained by steam reforming as the produced carbon monoxide (reacting with water) boosts the hydrogen yield. An investigation towards SOFC direct internal reforming of biogas was conducted by Lanzini and Leone [12]. The results suggested that a SOFC running on biogas without degradation is possible when the correct amount of oxidant is added, which is also agreed by Shiratori et al. [13]. The later ones suggested that the ratio of 1.5 between methane and carbon dioxide can enhance the electrochemical consumption of methane. A kinetic equation of hydrogen yield was derived and then verified by Fan et al. [14] when Ni-Co/MgO-ZrO<sub>2</sub> is used as the catalyst for the dry reforming of methane. Some dynamic modelling work relating to the control aspects were carried out by Görgün et al. [15], Varigonda and Kamat [16], and Pukrushpan et al. [17]. In these three papers, the chemical reactions were considered from a kinetic viewpoint and the heat management was also included. A controller could be designed based on these modelling results.

In this study, combined methane steam and dry reforming was investigated, from both thermodynamic equilibrium modelling and experiments. The aim of this work was to find the interactions among the reforming reactions, carbon formation, and the ratio among the reactants.

## Experiments

### Modelling

The National Aeronautics and Space Administration (NASA) Chemical Equilibrium with Applications (CEA) was employed to carry out the thermodynamic equilibrium calculations. In this software, the concentrations at equilibrium are obtained based on the minimised Gibbs free energy from a variety of initial conditions [18]. The reforming product compositions are not affected by the catalyst material and particle size used in the experiment. The reforming results can be calculated by the software from the given conditions including the reactants, temperature, pressure and expected products. The equilibrium results are expected to relate to the long-term operation of an SOFC system.

### Experimental study

#### Catalyst preparation and characterisation

A commercial anode-supported SOFC half cell that consisted of anode and electrolyte was used in this experiment as the catalyst to represent the SOFC internal reforming conditions. These SOFC half-cells were used due to their availability as standardised and commercial components with reproducible properties. They consisted of a  $400\ \mu\text{m}$  nickel-yttria-

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