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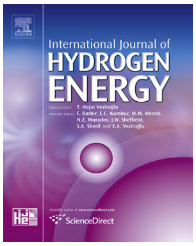

Experimental study of SOFC system heat-up without safety gases

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ABSTRACT

Premixed safety gas is conventionally used to keep the anode of a solid oxide fuel cell (SOFC) under reducing conditions during heat-up. This article presents the results of an experimental study to heat up a SOFC system and stack without the said premixed safety gases, i.e. by utilizing a natural gas pre-reformer and anode off-gas recycling (AOGR). Firstly, ex-situ experiments were conducted to investigate the operability of a pre-reformer during system heat-up. It was found that any oxygen fed to the reformer hinders the reforming reactions at low temperatures. Secondly, based on the ex-situ findings, series of heat-up cycles were conducted with a complete 10 kW system using AOGR and a planar SOFC stack. In these experiments it was found that the system heat-up is possible with fuel gas and steam only, without the need for premixed reducing safety gases. Use of the fuel gas instead of a premixed safety gas did not result in a significant performance loss in the SOFC stack. Therefore, such a heat-up strategy was developed for SOFC systems that reduces the need of premixed safety gas storage space and thus decreases the system cost.

1. Introduction

Solid oxide fuel cells (SOFCs) enable energy production from different hydrocarbon fuels with high efficiency. SOFCs require high operating temperatures, e.g. 700–800 °C for anode supported cell types. Thus the fuel cell stack and other system components have to be heated up to operating temperature before the electricity production can begin. Lengthy heat-up times of several hours may be required to maintain the temperature gradient and the thermal stresses in the stack at acceptable level [1].

The nickel in the SOFC anode substrate has to remain at reduced state at elevated temperatures. This is accomplished by supplying sufficient amount of fuel or other reducing gas to the stack. If the reducing gas supply is discontinued, then the nickel in the anode substrate will start to re-oxidize, which will first deteriorate the cell performance and eventually destroy the SOFC by cracking the cell [2]. First signs of the oxidation of the nickel cermet anode have been measured as low as 290 °C [3], and it has been shown that the oxidation of the anode substrate proceeds more rapidly as the temperature increases [4]. Permanent damage to the cell may occur in a matter of minutes if there is forced oxygen supply to the anode [5]. Indeed, without the forced oxygen supply and by minimizing the time under oxidizing conditions at elevated temperatures, the redox tolerance of the stack can increase significantly [6]. Ideally, the re-oxidation could be avoided, if no oxygen is transported to anode. However, the anode supported SOFC stack is not a hermetically sealed device, and some air will eventually leak from the cathode side of the stack via the electrolyte or stack seals [7]. Additionally, ambient air can leak to the anode through other fuel system

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Table 1 – Test gas mixtures used for determining the light-off temperature.

Run		1	2	3	4	5	6	7
Gas flow/NLPM	Natural gas	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	H_2O	10	10	10	10	10	10	10
	N_2	10	10	10	10	10	10	10
	H_2	–	–	0.2	0.05	0.1	0.15	0.4
	Air	–	0.5	0.5	0.5	0.5	0.5	0.5
H_2/O_2			0	2	0.5	1	1.5	4

components (e.g. reformer or heat exchanger) or through connecting piping from the air system. Therefore, it is necessary to feed reducing gas to the stack during the heat-up cycle to displace the oxygen in the fuel system and to protect the stack from re-oxidation. Furthermore, it may be necessary to sustain the flow of reducing gas for several hours during the system heat-up and cool-down, while the stack temperature is still high enough for significant re-oxidation and cell damage.

SOFC system concepts based on the anode off-gas recirculation (AOGR) achieve higher efficiencies and potentially simpler design when compared to systems without AOGR [8]. Therefore, they are considered technically advantageous, and there are studies where the AOGR has been successfully used in SOFC systems [9–11]. However, for a planar stack with cross-over leakage (air is leaking to fuel side and vice versa), utilization of AOGR complicates the heat-up procedure since there is a forced supply of oxygen to the fuel system due to the leakages. Furthermore, prior to starting the SOFC system electricity production, all fuel system components have to be heated up above the dew point before the recirculation of the anode off-gas with high steam content can be initiated. Otherwise, water could condensate to the system components (e.g. reformer catalysts and recirculation blowers), which would have detrimental effects on their operation.

The most straightforward way to provide a reducing gas supply is to utilize gas containers of premixed safety gas e.g. hydrogen–nitrogen mixtures. Indeed, due to its simplicity, this approach has been adopted by the majority of research laboratories that conduct research on solid oxide fuel cells or stacks. For example, the 10 kW demo unit at VTT [9] would consume ca. 5 bottles (50 L, 200 bars) of premixed safety gas with 4 vol-% of hydrogen during a heat-up cycle. In commercial products however, this approach is not desirable, due to large amount of gases needed for heat-up cycles spanning several hours. The gas containers require additional space, and increase the cost of both installation and servicing of the system. Thus it would be beneficial if the reducing gas could be generated with the existing Balance-of-Plant equipment which is fundamental for system operation. The most obvious solution would be to utilize the fuel supply (e.g. natural gas), the pre-reformer and the start-up steam generator to produce hydrogen-containing natural gas reformate.

In this article, the heat-up of a SOFC system and stack without using the premixed safety gases is investigated experimentally. Firstly, ex-situ experiments are conducted in a stand-alone reformer test bench. The experiments were done to realize the restrictions of reforming at low temperature in a system with AOGR and air leakage (i.e. forced oxygen supply to the fuel system). Secondly, series of heat-up cycles were done with a complete 10 kW SOFC system using AOGR and a planar SOFC stack. The results of the ex-situ experiments were applied to devise a safe heat-up procedure that would not damage the stack and removes the need for premixed safety gas. The performance of the stack was investigated after each heat-up to evaluate possible damage to the stack due to these heat-up procedures. There are several studies where the heat-up of a SOFC has been investigated by modelling [1,12–18], but to the authors' knowledge, no experimental work with a complete planar SOFC system utilizing AOGR has been published previously.

2. Experimental

2.1. *Ex-situ reformer experiments*

The ex-situ experiments were conducted in a separate reformer test bench described in detail in Ref. [19]. The aim of the experiment was to assess the activity of the catalyst at low temperature in steam reforming (Eq. (1)) using different inlet gas mixtures. This information is highly relevant to conduct the heat-up experiment on the SOFC system. The light-off temperature was determined by the reformer inlet gas temperature at which the reformer starts to convert methane to hydrogen according to Eq. (1).

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (1)$$

The reformer included a commercial precious metal monolithic catalyst (Süd-Chemie). The gas composition at the reformer outlet was monitored continuously with an online gas analysis equipment (IR-based for CH_4, thermal conductivity for H_2 and paramagnetic for O_2, Sick Maihak S700 series). Due to different channels cross-sensitivity, the analyser results should be used to evaluate trends and not as quantitative measurements. The temperature of the inlet gas was ramped up from 200…250–550 °C with a rate of ca. 2 °C min^{-1}. The gas hourly space velocity (GHSV i.e. gas volume flow at NTP divided by catalyst volume) used was ca. 32,000 h^{-1}. The different inlet gas mixtures investigated (Table 1) are relevant to SOFC system operated on natural gas including an anode-off gas recycling (AOGR) loop during first stages of the heat-up, where the fuel and steam supply have just been initiated. At that time, the temperature of both the pre-reformer and the stack are low and little or no reforming activity is expected to occur. Without reforming reactions, the gas