In-situ studies of gas phase composition and anode surface temperature through a model DIR-SOFC steam–methane reformer at 973.15 K

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ABSTRACT

A comparative study into the effects of total volume flow rate, methane 'residency time', methane volume flow rate, and steam-to-carbon ratio on the steam–methane reforming process was performed in a model Direct Internal Reforming SOFC (DIR-SOFC) reformer operating in steady state at a nominal temperature of 973 K. The spatial distributions of major gas species (CH_4, H_2O, CO, CO_2, and H_2) over the reformer surface were measured *in-situ* using Vibrational Raman Spectroscopy. Surface temperature measurements were recorded using IR thermometry. The effects of varying the intake mole fractions of methane and water were considered. The results of this work have demonstrated a strong positive correlation between the intake mole fraction of methane and the rate of the steam–methane reformation reaction. A weak negative correlation between the intake mole fraction of water and the rate of the reformation reaction was also shown.

1. Introduction

The potential benefits of Solid Oxide Fuel Cells (SOFC's) over other fuel cell types with regard to fuel flexibility are well established [1]. High operating temperatures—typically, in the range of 875–1275 K—combined with the exothermic nature of the SOFC's electrochemical reaction result in the generation of high-quality thermal energy that can be used for the reformation of a variety of hydrocarbon fuels. Although reformation may be arranged to occur in a external reformer, the Direct Internal Reforming SOFC (DIR-SOFC) arrangement—whereby the heat from the electrochemical reaction is used to reform hydrocarbon fuels directly in the anode—is highly attractive due to its potentially greater efficiency and reduced physical complexity [1–3]. There are however a number of practical difficulties associated with direct internal reforming. In contrast to the electrochemical reactions, hydrocarbon reforming reactions are typically endothermic. Simultaneously optimizing the reforming and electrochemical reactions in the anode is a particular challenge [4]. Since the kinetics of the reforming reactions are fast, the endothermic reactions tend to occur in the entrance region of the fuel cell leading to substantial local cooling [5]. This may introduce significant thermal stresses into the anode that can lead to premature mechanical failure [6–8]. Given the dual requirements of optimising the operation of the SOFC while simultaneously ensuring its mechanical reliability, obtaining a detailed knowledge of the chemical processes occurring at the anode of a DIR-SOFC must
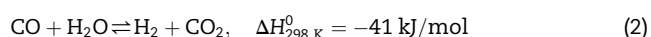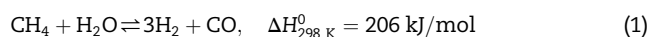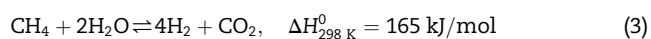
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be considered essential to the development of the technology. Ideally, this knowledge will include information in both the temporal and the spatial domains.

In previous works [9,10], the authors detailed the development of a novel experimental apparatus and measurement system for the study of gas phase composition and distribution in SOFC applications. In Saunders and Davy [10], the system was demonstrated on a model DIR-SOFC reformer fuelled with methane. A sample set of results was presented in the context of a 'proof-of-concept' investigation into the apparatus and measurement system. The major findings of this proof-of-concept study were that the authors' experimental set-up was capable of providing high precision measurements of major gas species from within the operating reformer under steady-state operating conditions. It was also concluded that results from the model reformer, an electrochemically non-operating half-cell device, would not be fully representative of real-world DIR-SOFC operation due to details of the design. In particular, it was noted that the absence of the SOFC electrochemical reactions—which result in the internal production of water vapour in a fully operating cell—required the feed gases to the model reformer to be highly humidified. In the authors' experimental set-up the reformer is supplied with a substantial quantity of humidified nitrogen. The reforming reaction and methane conversion rates are decreased accordingly [11]. As a result, the very rapid and almost complete consumption of methane typically predicted to occur within a short distance from the cell entrance for DIR-SOFC's, e.g. [3,6,12], is not seen in the authors' results. The model reformer was also noted to be imperfectly sealed as some evidence of air ingress into the channel was observed in the results. Note that the issue of leakage, including a detailed argument for air ingress, is discussed in [9,13]. These issues notwithstanding, the authors concluded that the apparatus was suitable for comparative studies into reformer performance subject to variations in operating condition or hardware without further modification [10].

In accordance with the above, the current work presents results from a comparative study into the effects of feed gas flow rate, composition, and humidification level on the performance of a model DIR-SOFC methane–steam reformer operating at a nominal temperature of 973 K as indicated by the internal distribution of major gas species (CH_4, H_2O, CO, CO_2, and H_2) above the anode. The chemical reactions under consideration in this study are then; the steam/methane reforming reaction (1)—which results in the production of carbon monoxide and hydrogen, and the water–gas shift reaction (2)—in which carbon monoxide is reacted with steam to produce carbon dioxide and hydrogen.

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO, \quad \Delta H^0_{298\ K} = 206\ kJ/mol \quad (1)$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2, \quad \Delta H^0_{298\ K} = -41\ kJ/mol \quad (2)$$

The overall steam–methane reforming reaction (3) is then:

$$CH_4 + 2H_2O \rightleftharpoons 4H_2 + CO_2, \quad \Delta H^0_{298\ K} = 165\ kJ/mol \quad (3)$$

As noted by Dicks [14], hydrogen production through reaction Eq. (1) is thermodynamically favoured by high temperatures and low pressures. Dicks further states that, "over an

active catalyst, the products of steam reforming are dictated by the thermodynamic equilibria set up between Eq. (1) and Eq. (2)".

2.   Experimental setup

Fig. 1 shows the basic experimental set-up used in this study. A 100 mm × 50 mm DIR-SOFC anode sample was positioned within a stainless steel channel so as to leave an approximately 6 mm high flow passage over the full width and length of the anode surface. Sapphire windows in the front wall and roof of the channel provided unobstructed optical access normal to the anode surface and a full-height and full-width view along flow passage. The anode, which was provided by Versa Power Systems (Alberta, Canada), was a 1 mm thick porous yttria stabilized zirconia (YSZ) cermet with a nickel catalyst (57 Wt.% NiO). The porosity of anode was approximately 37% in the fully reduced condition. The channel was positioned within a purpose-built oven consisting of two semi-circular radiant heating elements contained within a well-insulated stainless steel enclosure. Two recessed sapphire viewing windows in the oven walls provided direct optical access to the channel and anode surface. Full details of the channel assembly and oven are given in Saunders and Davy [9], Saunders [13], and Saunders and Davy [10].

The reformer was supplied with gas mixtures via the arrangement shown schematically in Fig. 2. The individual flow rates of hydrogen, methane, and nitrogen were controlled by calibrated, back-pressure compensated rotameters. The hydrogen and nitrogen supplies were Research Grade, 99.999% pure. The methane supply was classified as Ultra High Purity 99.97% pure. The methane supply was also assayed to confirm the absence of sulphur. As can be seen from Fig. 2, the arrangement of the supply lines was such that the metered gases could be humidified prior to entering the reformer by means of a custom-built bubbler humidifier. As the volume flow rate through the humidifier was limited to 1.0 SLPM of dry gases, an additional dry nitrogen supply was used downstream of the humidifier to increase the total volume flow through the reformer beyond 1.0 SLPM where necessary. Table 1 details the matrix of test conditions examined, where $\dot{V}_{total}$ is the total volume flow rate over the anode surface, SCR is the steam-to-carbon ratio (H_2O/CH_4), and n_{CH_4}, n_{N_2} and n_{H_2O} are, respectively, the metered inlet mole fractions of methane, nitrogen and water vapour.

The reformer was operated in steady-state at a temperature of 973.15 K and the spatial distribution of major species flowing over the anode surface was interrogated using Vibrational Raman Spectroscopy (VRS). The development, calibration, and performance of the authors' Raman measurement system, shown schematically in Fig. 1, is detailed in previous publications [9,10,13]. For the reported work the laser was pulsed at a frequency of 10 Hz. The pulse energy was 169 mJ per pulse. The beam was polarised, and focussed to form an interrogation region approximately 0.8 mm in width, 6 mm in height and 1.5 mm thick, above the anode surface. Raman measurements were taken at 7 discrete locations along the longitudinal centreline of the anode sample designated as the 0, 10, 20, 30, 50, 70 and 87 mm positions, where