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The effect of synthesis gas composition on the performance of Ni-based solid oxide fuel cells

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ABSTRACT

An increased interest in using hydrocarbons in solid oxide fuel cells for the production of power has led to research into operation on synthesis (syn) gas, a mixture of hydrogen and carbon monoxide. Hydrocarbons are typically reformed, either internally or in an external reformer prior to the fuel cell, producing syngas with various H_2:CO ratios depending on the hydrocarbon used. This paper examines the effect of varying the H_2:CO ratio with respect to C_1 to C_4 steam reforming reactions and additionally a mixture containing a higher ratio of carbon monoxide. It was found that there was no significant relationship between cell performance and H_2:CO ratio when a high feed rate was employed. For low flow rates, however, the high carbon monoxide concentration resulted in a significant decrease in cell performance. It was determined that this was caused by reversible carbon deposition as opposed to a decrease in carbon monoxide reactivity.

1. Introduction

Research into sustainable energy has dramatically intensified with increasing public awareness of the effects associated with traditional energy generation; to this end, solid oxide fuel cells have become the subject of intense research. Solid oxide fuel cells operate at high temperatures to produce electricity from chemical reactions in a highly efficient manner. Fuel cells utilise a solid electrolyte which at typical operating conditions are able to conduct ions through the lattice but do not conduct electricity.

Hydrogen is considered as the most basic fuel for use in solid oxide fuel cells, however currently the inability to practically generate and store hydrogen for use is considered to be a significant technological impediment. The high operating temperature presents an opportunity for a wide variety of fuels, with short chain hydrocarbons such as methane and ethane considered as the most viable fuel for use in solid oxide fuel cells due to the ease of supply and relative abundance. The use of hydrocarbons has been investigated (Zheng et al., 1996; Singhal, 2000; Ahmed et al., 2002; Weber et al., 2002; Gorte and Vohs, 2003; Goodenough and Huang, 2007; Huang et al., 2011) with many groups researching both direct oxidation and external reforming. If the hydrocarbon is either internally or externally reformed it will form a mixture of hydrogen and carbon monoxide (syngas) with various ratios depending on the hydrocarbon used. While the effects of modifying the H_2:CO ratio has been investigated in the past, the results have shown conflicting effects and have not been performed using commercially available cell configurations.

The use of carbon based fuels can add an additional complication in the form of carbon deposition and deactivation

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of the anode. It has been proposed that this can be prevented by operating the fuel cell at lower temperatures or by utilising higher current densities (Liu and Barnett, 2003; Lin et al., 2005). A high steam:carbon ratio can also be used but this can dilute the fuel and cause large temperature gradients within the cell (Vernoux et al., 2000; Gunji et al., 2004; Alzate-Restrepo and Hill, 2010). To avoid carbon deposition, constructing anodes from alternative materials, such as replacing nickel with bi-layers (Atkinson et al., 2004; Zheng et al., 2008) or altering anode geometry (Zhu et al., 2006), has been heavily researched to address disadvantages associated with their use such as poor electrochemical catalyst activity, low conductivity or complicated fabrication (Boder and Dittmeyer, 2006; Chen et al., 2011).

Huang has investigated the operation of alternative anodes fuelled with syngas. The investigation using LSCF ($La_{0.58}Si_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) gadolinia-doped-ceria (GDC) identified that the power density increases with increasing carbon monoxide concentration. It was also noted that hydrogen reactivity increases, with carbon monoxide reactivity decreasing, with increasing LSCF content, with the maximum power density at its highest when using Ni-added LSCF–GDC, suggesting that nickel based anodes would be the most suitable option for use of carbon-based fuels (Huang et al., 2009).

The same group investigated $La_{0.7}Ag_{0.3}Co_{0.2}Fe_{0.8}O_3$ as an anode material with syngas fuel. In this instance syngas activity increased with increasing hydrogen content (Huang and Chen, 2011). This was supported by Sasaki et al. who identified that increasing the mole fraction of hydrogen produces a higher output voltage (Sasaki et al., 2002). Similarly Wang observed decreases in cell performance when operating on high carbon monoxide concentration (>90%) (Wang et al., 2011).

O'Brien and Giorgi investigated operation of a bi-metallic Ni/Co anode over a wide range of carbon monoxide concentrations with hydrogen. As with other researchers, it was identified that for high CO ratios a lower exchange current density was measured. It was theorised that this was due to anode poisoning, as carbon monoxide adsorbed on the anode surface does not have thermodynamically favourable desorption, either electrochemically oxidising to carbon dioxide or undergoing disproportionation (O'Brien and Giorgi, 2012). Similarly, impedance spectroscopy was used to examine the effect of carbon monoxide concentration, where it was identified that increasing CO produced increased carbon deposition with the exception of the cell being operated on pure carbon monoxide, implying that the mechanism of carbon formation is via a hydrogen assisted CO dissociation route (Alzate-Restrepo and Hill, 2010). Matsuzaki and Yasuda (2000) also identified an increased polarisation resistance with increased carbon monoxide concentration, however the lower rate of chemical oxidation was attributed to a larger diffusion resistance of carbon monoxide compared to hydrogen.

This paper examines the effects of H_2:CO ratios in syngas on a commercially available scandia doped zirconia electrolyte utilising a nickel anode. Syngas ratios were selected based on the products of hydrocarbon steam reforming.

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad 3:1 \qquad (1)$$

$$C_2H_6 + 2H_2O \rightarrow 5H_2 + 2CO \qquad 5:2 \qquad (2)$$

$$C_3H_8 + 3H_2O \rightarrow 7H_2 + 2CO \qquad 7:3 \qquad (3)$$

$$C_2H_{10} + 4H_2O \rightarrow 9H_2 + 2CO \qquad 9:4 \qquad (4)$$

An increased production of biodiesel has led to an oversupply of glycerol, with significant research into potential uses for this abundant by-product. Acrolein and allyl alcohol are easily produced from glycerol and could potentially be used as a feed for solid oxide fuel cells, with the syngas produced having a higher carbon monoxide to hydrogen ratio.

$$C_3H_6O + 2H_2O \rightarrow 5H_2 + 3CO \qquad 5:3 \qquad (5)$$

$$C_3H_4O + 2H_2O \rightarrow 4H_2 + 3CO \qquad 4:3 \qquad (6)$$

Additionally, the hydrocarbons can be dry reformed in the presence of carbon dioxide, which would produce a ratio less than 1.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad 1:1 \qquad (7)$$

$$C_2H_6 + 2CO_2 \rightarrow 3H_2 + 4CO \qquad 3:4 \qquad (8)$$

$$C_3H_8 + 3CO_2 \rightarrow 4H_2 + 6CO \qquad 2:3 \qquad (9)$$

$$C_4H_{10} + 4CO_2 \rightarrow 5H_2 + 8CO \qquad 5:8 \qquad (10)$$

$$C_3H_6O + 2CO_2 \rightarrow 3H_2 + 5CO \qquad 3:5 \qquad (11)$$

$$C_3H_4O + 2CO_2 \rightarrow 2H_2 + 5CO \qquad 2:5 \qquad (12)$$

Owing to the significantly higher carbon monoxide concentration produced from dry reforming, the highest ratio produced from a complete reaction, 2:5, was also investigated.

2. Materials and methods

A planar solid oxide fuel cell was used (Fuel Cell Materials), consisting of a 150 μm thick scandia doped zirconia electrolyte made by tape casting, with screen printed 28 cm^2 electrodes of LSM/LSM–GDC cathode and Ni–YSZ/Ni–GDC anode. Nickel and platinum mesh were used as current collectors in the anode and cathode, respectively. Gas was supplied to the cell via a nickel manifold with the unit sealed using Kerafol glass seals and a compressive force of approximately 35 kPa; an exploded view of the set up can be seen in Fig. 1.

Synthesis gas (syngas consisting of hydrogen and carbon monoxide) of various ratios diluted in nitrogen was used as the fuel supplied to the anode at a constant flow, with the flow rate maintained using mass flow controllers (Aalborg Instrumentation) with total anode flows of 100 $cm^3\,min^{-1}$ and 300 $cm^3\,min^{-1}$ examined. Prior to the cell, this gas flowed through a humidifying unit, with the water concentration controlled via a recirculating bath (Huber UK). Oxygen was supplied to the cathode at a rate of 300 $cm^3\,min^{-1}$ of air via rotameter (Dwyer). The voltage and current produced by the cell was monitored using an in house built constant voltage dynamic load instrument. Current and voltage was captured using a digital data acquisition system (Datataker 505) with gas compositions measured using micro gas chromatography (Varian 490-GC).

The fuel cell was heated in a muffle furnace (Brother Furnace Company) up to 500 °C at a ramp rate of 1 °C min^{-1}. This temperature was maintained for 2 h to burn off the binding agent present on the glass seals before continuing heating at 1 °C min^{-1} up to 930 °C and cooling at the same rate to 850 °C