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Graphical Abstract (for review)
• Operation of Ni-based SOFC with simulated syngas of varying H₂:CO ratio
• H₂:CO ratio selected to represent C₁ to C₄ reforming products
• Increasing CO concentration decreased cell power only when using low flow rates
• Decreased power at low flow attributed to carbon deposition on Ni catalyst
• Carbon balance showed losses >2% only for high CO concentration with low flow rates
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 H₂:CO ratios depending on the hydrocarbon used. This paper examines the effect of varying the H₂:CO ratio with respect to C₁ to C₄ 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 H₂: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.

Keywords: solid oxide fuel cell, syngas, carbon monoxide
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 1996, Singhal 2000, Ahmed 2002, Weber 2002, Gorte 2003, Goodenough 2007, Huang 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 H2: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 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 2003, Lin 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 2000, Gunji 2004, Alzate-Restrepo 2010). To avoid carbon deposition, constructing anodes from alternative materials, such as replacing nickel with bi-layers (Atkinson 2004, Zheng 2008) or altering anode geometry (Zhu 2006), has been heavily researched to address disadvantages associated with their use such as poor electrochemical catalyst activity, low conductivity or complicated fabrication (Boder 2006, Chen 2011).

Huang has investigated the operation of alternative anodes fuelled with syngas. The investigation using LSCF (La$_{0.8}$Si$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$) 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 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 2011). This was supported by Sasaki et al who identified that increasing the mole fraction of hydrogen produces a higher output voltage (Sasaki 2002). Similarly Wang observed decreases in cell performance when operating on high carbon monoxide concentration (>90%) (Wang 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 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 2010). Matsuzaki and Yasuda 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 (Matsuzaki 2000).

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.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &\rightarrow 3\text{H}_2 + \text{CO} & 3:1 & (1) \\
\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} &\rightarrow 5\text{H}_2 + 2\text{CO} & 5:2 & (2) \\
\text{C}_3\text{H}_8 + 3\text{H}_2\text{O} &\rightarrow 7\text{H}_2 + 3\text{CO} & 7:3 & (3) \\
\text{C}_4\text{H}_{10} + 4\text{H}_2\text{O} &\rightarrow 9\text{H}_2 + 4\text{CO} & 9:4 & (4) 
\end{align*}
\]
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.

\[
\begin{align*}
C_3H_6O + 2H_2O & \rightarrow 5H_2 + 3CO \quad 5:3 \quad (5) \\
C_2H_4O + 2H_2O & \rightarrow 4H_2 + 3CO \quad 4:3 \quad (6)
\end{align*}
\]

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

\[
\begin{align*}
CH_4 + CO_2 & \rightarrow 2H_2 + 2CO \quad 1:1 \quad (7) \\
C_2H_6 + 2CO_2 & \rightarrow 3H_2 + 4CO \quad 3:4 \quad (8) \\
C_2H_2 + 3CO_2 & \rightarrow 4H_2 + 6CO \quad 2:3 \quad (9) \\
C_4H_{10} + 4CO_2 & \rightarrow 5H_2 + 6CO \quad 5:8 \quad (10) \\
C_3H_8O + 2CO_2 & \rightarrow 3H_2 + 5CO \quad 3:5 \quad (11) \\
C_2H_4O + 2CO_2 & \rightarrow 2H_2 + 5CO \quad 2:5 \quad (12)
\end{align*}
\]

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.

**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 28cm² 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 Figure 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 hours 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 to create a complete seal with the glass. To ensure the cell had completely sealed, 40% helium in nitrogen was passed through the anode and nitrogen though the cathode with both the flow rate and gas concentrations of the outlets measured. There were no losses of nitrogen through the cathode, with only a difference of less than 0.5% (deemed to be within error), small losses of helium in the anode (<4% deemed to be caused by diffusion at elevated temperatures) and no crossover of gases, indicating that there was no significant leaks.
Results and Discussion

Initial reactions were completed utilising total anode flow rates of 300 cm\textsuperscript{3}.min\textsuperscript{-1} and syngas concentrations of 50% in nitrogen. As can be seen from Figure 2 there are no significant differences between syngas samples containing high hydrogen concentrations and those containing high carbon monoxide concentrations. Previous work by Huang investigated the effect of carbon monoxide concentration, identifying that over La\textsubscript{0.58}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} anode increasing carbon monoxide concentration resulted in higher cell power (Huang 2009), while an anode of La\textsubscript{0.7}Ag\textsubscript{0.3}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} (Huang 2011) produced larger cell power and fuel reactivity with higher hydrogen concentrations.

![Figure 2. Cell performance with 50% syngas diluted in nitrogen with a total anode flow rate of 300 cm\textsuperscript{3}.min\textsuperscript{-1}. Syngas H\textsubscript{2}:CO ratios of 3:1 (○), 5:2 (□), 7:3 (△), 9:4 (◊) and 2:5 (X) with voltage and power densities represented by shaded and hollow symbols respectively.](image)

The maximum power and current densities were found to decrease slightly as the carbon monoxide concentration in the syngas increased, with the exception of the 2:5 ratio exhibiting an increase compared to the lower hydrogen concentrations, namely 7:3 and 9:4, as exhibited in Table 1.
Table 1. Maximum cell power measurements for cell operating with 50% syngas diluted in nitrogen and an anode flow rate of 300 cm$^3$.min$^{-1}$.

<table>
<thead>
<tr>
<th>H$_2$:CO</th>
<th>Maximum Power Density [mW.cm$^{-2}$]</th>
<th>Maximum Current Density [mA.cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>97.06</td>
<td>159.95</td>
</tr>
<tr>
<td>5:2</td>
<td>96.16</td>
<td>158.51</td>
</tr>
<tr>
<td>7:3</td>
<td>92.64</td>
<td>154.95</td>
</tr>
<tr>
<td>9:4</td>
<td>90.74</td>
<td>150.61</td>
</tr>
<tr>
<td>2:5</td>
<td>94.23</td>
<td>158.06</td>
</tr>
</tbody>
</table>

The experiment was repeated maintaining a flow rate of 300 cm$^3$.min$^{-1}$ but with a syngas concentration of 35% in nitrogen. Figure 3 and Table 2 show that there was similarly no significant difference in voltage or power density with varying syngas ratios.

![Figure 3](image_url)

Figure 3. Cell performance with 35% syngas diluted in nitrogen with a total anode flow rate of 300 cm$^3$.min$^{-1}$. Syngas H$_2$:CO ratios of 3:1 (○), 5:2 (□), 7:3 (△), 9:4 (◇) and 2:5 (X) with voltage and power densities represented by shaded and hollow symbols respectively.
Table 2. Maximum cell power measurements for cell operating with 35% syngas diluted in nitrogen and an anode flow rate of 300 cm$^3$.min$^{-1}$.

<table>
<thead>
<tr>
<th>H$_2$:CO</th>
<th>Maximum Power Density [mW.cm$^{-2}$]</th>
<th>Maximum Current Density [mA.cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>89.89</td>
<td>150.41</td>
</tr>
<tr>
<td>5:2</td>
<td>93.56</td>
<td>156.29</td>
</tr>
<tr>
<td>7:3</td>
<td>88.76</td>
<td>147.67</td>
</tr>
<tr>
<td>9:4</td>
<td>91.35</td>
<td>152.29</td>
</tr>
<tr>
<td>2:5</td>
<td>87.33</td>
<td>145.58</td>
</tr>
</tbody>
</table>

Although previous investigations on lanthanum oxide showed a clear relationship between carbon monoxide concentration and cell performance, the use of the nickel anode on a commercial fuel cell indicated no significant differences, particularly on the smaller range of ratios which represent products from C$_1$ to C$_4$ hydrocarbon reforming. Nickel is currently the most common choice for commercial fuel cells due to its high catalytic activity. It is predicted that the higher carbon monoxide reactivity compared to previous work is due to the activity of the anode material, with nickel in particular being known as a catalyst favoured for use with carbon based reactants (Weber 2002, Hirata 2012). This indicates the predicted cell power decrease from decreasing hydrogen concentration does not occur as the carbon monoxide reactivity increases to maintain cell performance.
Figure 4. Cell performance with 35% syngas diluted in nitrogen with a total anode flow rate of 100 cm$^3$.min$^{-1}$. Syngas H$_2$:CO ratios of 3:1 (○), 5:2 (□), 7:3 (△), 9:4 (○) and 2:5 (X) with voltage and power densities represented by shaded and hollow symbols respectively.

Table 3. Maximum cell power measurements for cell operating with 35% syngas diluted in nitrogen and an anode flow rate of 100 cm$^3$.min$^{-1}$.

<table>
<thead>
<tr>
<th>H$_2$:CO</th>
<th>Maximum Power Density [mW.cm$^{-2}$]</th>
<th>Maximum Current Density [mA.cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>68.40</td>
<td>114.75</td>
</tr>
<tr>
<td>5:2</td>
<td>70.75</td>
<td>117.16</td>
</tr>
<tr>
<td>7:3</td>
<td>69.04</td>
<td>114.43</td>
</tr>
<tr>
<td>9:4</td>
<td>68.47</td>
<td>113.39</td>
</tr>
<tr>
<td>2:5</td>
<td>59.90</td>
<td>99.95</td>
</tr>
</tbody>
</table>

When the flow rate was decreased to 100 cm$^3$.min$^{-1}$ as tested previously while maintaining the 35% syngas concentration a significant difference in cell output was observed for high carbon monoxide concentrations. As a difference in cell power was observed at this particular flow rate, additional experiments examining cell operation with pure hydrogen, pure carbon monoxide and syngas with a ratio of 1:3 were conducted to compare with the results already obtained.

Figure 5. Cell performance with 35% fuel diluted in nitrogen with a total anode flow rate of 100 cm$^3$.min$^{-1}$. Hydrogen (+), carbon monoxide (-) and syngas H$_2$:CO ratios of 3:1 (○), 2:5 (X) and 1:3 (*) with voltage and power densities represented by shaded and hollow symbols respectively.
Again, these measurements further highlighted the effect of high carbon monoxide concentrations at low flow rates, with both Figures 4 and 5 and Table 3 showing slightly lower values for operation on pure carbon monoxide and syngas ratios of 2:5 and 3:1. While these results agree with previous work where cell performance decreased as high carbon monoxide concentrations were used, it is suspected that this is not due to poor carbon monoxide activity as previously proposed (Huang 2009, Huang 2011) as the cell performance did not increase when the fuel was changed to pure hydrogen of the same concentration. Despite the decrease in cell power, a significant increase in reacted carbon monoxide (greater than 10% increase) indicates that it is likely the power decrease is caused by cell deactivation, possibly caused by CO disproportionation (Weber 2002, Hirata 2012).

\[2\text{CO} \rightarrow \text{CO}_2 + \text{C} \quad (13)\]

Completing a carbon balance on the cell, it was found that in the higher flow rate cases, greater than 98% of the carbon was accounted for in the carbon monoxide and carbon dioxide contained within the product stream, even in the case of high carbon monoxide concentration. However when a lower flow rate was examined, the experiments containing higher carbon monoxide concentrations showed significantly higher losses in carbon indicating the formation of solid carbon on the anode surface. The variation in carbon deposition can be seen in Figure 6.
Figure 6. Product concentration of carbonaceous species in outlet flow of solid oxide fuel cell operated on syn
gas diluted in nitrogen with a hydrogen to carbon monoxide ratio of 2:5. Carbon monoxide (○), carbon dioxide
(□) and carbon (△) with experiments examining 35% syn gas and total anode flow of 100 mL.min⁻¹, 35% syn
gas and total anode flow of 300 mL.min⁻¹ and 50% syn gas and total anode flow of 300 mL.min⁻¹ represented
by black shaded, grey shaded and hollow symbols respectively.

As nickel is considered an active catalyst for carbon synthesis (Gorte 2003) it is suspected that
decreasing the flow rate through the cell dramatically increases the residence time, resulting in
carbon deposition and subsequent cell deactivation (Miao 2010, Ye 2010). This theory is supported
by carbon balance calculations and time on stream measurements, which indicates a rapid but
reversible decrease in cell performance.

Conclusions
When considering operating a solid oxide fuel cell on a hydrocarbon fuel, the selection of that fuel
when considering cell power is not as important as previously thought. When operating the cell on a
syngas mixture there is little difference between the reformation products for C₁ to C₄ hydrocarbons,
indicating it is of greater importance to ensure complete reaction to produce a fuel stream
consisting of mainly hydrogen and carbon monoxide. When low flow rates were examined it was
found that low H₂:CO ratios (less than 1) produced lower cell power due to anode deactivation,
which implies prevention of carbon deposition when using fuels with high carbon monoxide is of
high importance to maintain cell performance.

References

Alzate-Restrepo, V., Hill, J. M. (2010). "Carbon deposition on Ni/YSZ anodes exposed to CO/H₂


reducing their activity for direct internal reforming of natural gas." Journal of Power Sources 155: 13
- 22.


