Effect of inlet fuel type on the degradation of Ni/YSZ anode of solid oxide fuel cell by carbon deposition

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Abstract

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According to the high operating temperature of Solid Oxide Fuel Cell (SOFC) (700-1100ºC), it is known that some hydrocarbon fuels can be directly used as inlet fuel instead of hydrogen by feeding straight to the anode. This operation is called a direct internal reforming SOFC (DIR-SOFC). However, the major difficulty of this operation is the possible degradation of anode by the carbon deposition, as the carbon species are easily formed. In the present work, the effect of inlet fuel (i.e. H2, synthesis gas (H2+CO), CH4, CH2+H2O, CH3OH+H2O, and C2H5OH+H2O) on the degradation of nickel cermet (Ni/YSZ), which is the most common anode material of SOFC, was studied.

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It was found from the work that hydrogen and synthesis gas (CO+H₂) are proper to be used as direct inlet fuels for DIR-SOFC with Ni/YSZ anode, since the carbon formation on Ni/YSZ occurred in the small quantity. The mixture of methane and steam (CH₄+H₂O) can also be used as the inlet feed, but the H₂O/CH₄ ratio plays an important role. In contrast, pure methane (CH₄), methanol with steam (CH₃OH+H₂O) and ethanol with steam (C₂H₅OH+H₂O) are not suitable for using as direct inlet fuel for DIR-SOFC with Ni/YSZ anode even the higher H₂O/CH₃OH and H₂O/C₂H₅OH ratios were applied.

Key words : carbon formation, hydrogen, SOFC

Combustion process has been used to produce energy for a long time. Although it is a well-developed and cost effective process, the main disadvantage is the unwanted by-products such as NOₓ or COₓ, which could lead to the greenhouse effect. Fuel cell is an electrochemical energy conversion unit that converts chemical energy to electrical energy and heat with greater energy efficiency and lower pollutant emission than combustion process (George, 2002). Several types of fuel cells have been developed for different purposes including mobile, stationary, and portable applications. Fuel cell can be divided into two main groups according to operating temperature. The first group is low temperature fuel cell which is used for mobile application, nowadays;
proton exchange membrane fuel cell (PEMFC) is used to power the vehicles. This type of fuel cell is also used for portable application such as replacing the rechargeable battery, or powering the cellular phone and notebook (George, 2002). The second group is high temperature fuel cell such as molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) which are expected to apply in power applications i.e. for power plant (300 MWe) or as combined heat and power generation (George, 2002; Lundberg, 2001). SOFC is also being investigated whether it can be used as an auxiliary power unit (APU) in mobile applications and as a portable system (George, 2002).

SOFC consists of three main parts which are cathode electrode (air electrode), solid electrolyte, and anode electrode (fuel electrode) (Yamamoto, 2000). Within the electrolyte, the oxygen ions (O\(^2-\)) which are produced from the reduction of air at the cathode are transported and reacted with the fuel (H\(_2\)) at the anode and electrons from anode electrode flow pass external load to cathode electrode. The products from the chemical reaction are H\(_2\)O or CO\(_2\), heat and electricity (direct current, dc.). Hydrogen is generally used as the fuel since it has high electrochemical activity; moreover, carbon monoxide (CO) can also be used as the fuel together with hydrogen. As SOFC is normally operated at high temperature, it is known that some hydrocarbon fuels can be fed directly at the anode side of SOFC instead of hydrogen. This operation is called a direct internal reforming SOFC (DIR-SOFC) (Aguiar et al., 2002; George, 2002). According to this operation, simultaneously, the hydrocarbon fuels are reformed producing H\(_2\) and CO, which are electrochemically consumed and generating electricity.

For the SOFC materials, Y\(_2\)O\(_3\)-ZrO\(_2\) (YSZ) is widely used as SOFC electrolyte due to its good chemical and mechanical stability (Badwal et al., 2000; Singhal, 2000; Wincewicz et al., 2005), while Ni/YSZ is the most common type of anode material due to its cost effective and well fitting with most of the anode design requirements. The nickel content is usually 40 to 60% in order to match the thermal expansion of YSZ (Wincewicz et al., 2005). However, Ni/YSZ is difficult to run on dry methane and higher hydrocarbons because of the formation of carbon fibers above 700ºC (Costa-Nunes et al., 2005) which can obstruct gas access, and degrade anode performance by blocking the catalyst active sites. When the hydrocarbon fuels are required to use as direct fuel feed to SOFC, there must be sufficient steam for a water gas reaction. In the present work, the effect of inlet fuel (i.e. H\(_2\), synthesis gas (H\(_2\)+CO), CH\(_4\), CH\(_4\)+H\(_2\)O, CH\(_3\)OH+H\(_2\)O, and C\(_2\)H\(_5\)OH+H\(_2\)O) on the degradation of Ni/YSZ was studied in order to optimize the suitable conditions for DIR-SOFC operation.

**Experimental**

1. **Ni/YSZ preparation**

Ni/YSZ was prepared by mixing NiO (42.86 vol. %) with YSZ (57.14 vol. %) at room temperature. This solution was mixed by ball milling for 18 hours, and calcined in air at 800ºC for 6 hours and then reduced with 10% H\(_2\)/He at 700ºC for 6 hours before used.

2. **Experimental setup**

The schematic diagram of testing system was shown in Figure 1. The testing system can be divided into three main groups: gas or liquid handling and control unit, furnace and temperature control unit, and measurement unit. In the first group, there were gas handling and gas control units for supplying gaseous fuels (hydrogen (H\(_2\)), carbon monoxide (CO) and methane (CH\(_4\))). For liquid fuels such as methanol with steam (CH\(_3\)OH +H\(_2\)O) and ethanol with steam (C\(_2\)H\(_5\)OH+H\(_2\)O), the syringe pump was used to inject them into the system and the evaporator unit was used to change the liquid to vapor or steam. When liquid fuels were used, helium (He) was added to the system and mixed until a total flow rate of 100 ml.min\(^{-1}\) was attained before introducing them to the system. The second group was a high temperature furnace which was controlled by temperature controller. The temperature inside the furnace was detected by a thermocouple, K-type. For each
experiment, the 100 mg of Ni/YSZ was packed in a reactor and put into the furnace. The last group was the measurement device; an online Mass Spectrometer (MS) was used to investigate the outlet gas from the experiment.

3. Temperature programmed techniques (TP)

In the present work, temperature programmed techniques (TP) were applied to investigate the amount of carbon formation on Ni/YSZ surface. Firstly, temperature programmed adsorption (TPA) was used to make the carbon adsorption on Ni/YSZ. Then, the carbon formation on Ni/YSZ was investigated by temperature programmed oxidation (TPO). Before testing, the Ni/YSZ was reduced with 10% H2/He at 700°C for 6 hours. The experiment was started from purging helium (He) to the system until the signals from MS were stable, and then processing of the TPA started by feeding 5% of methane (CH4) in helium (He) to produce the carbon adsorption on the surface of Ni/YSZ, called temperature programmed methane adsorption (TPMA). The total gas flow rate of 100 ml.min⁻¹ was fed to the reactor and the temperature in the reactor was heated up from 100°C to 900°C at the rate of 20°C.min⁻¹. After finishing the heating, the system was cooled down to room temperature under helium flow. When TPMA experiment was finished the carbon formation on the Ni/YSZ was investigated by using the TPO process. 10% of oxygen in helium with the total flow rate 100 ml.min⁻¹ was introduced to the system.

Subsequently, the influence of temperature on the amount of carbon formation was investigated by changing the TPMA temperature from 900°C to 925, 950, 975 and 1000°C respectively. In addition, the effect of inlet fuel types on the amount of carbon formation was studied by introducing pure hydrogen (H2), synthesis gas (CO + H2 with the ratio of 1:3), methane + steam (with the ratio of 1:3), methanol + steam (with the ratio of 1:3), and ethanol + steam (with the ratio of 1:3).

The amount of carbon formations on the surface of catalysts was determined by measuring the CO and CO2 yields from the TPO results (using Microcal Origin Software) assuming a
value of 0.026 nm$^2$ for the area occupied by a carbon atom in a surface monolayer of the basal plane in graphite. The calibrations of CO and CO$_2$ productions were performed by injecting a known amount of these calibration gases from a loop, in an injection valve in the bypass line. The response factors were obtained by dividing the number of moles for each component over the respective areas under the peaks.

**Results**

1. **Carbon adsorption on Ni/YSZ surface by TPMA**

   The experiment was started by reducing Ni/YSZ with 10% H$_2$/He at 700ºC for 6 hours and purging helium (He) to the system until the signals from MS were stable, and then the temperature programmed methane adsorption (TPMA) process started. The total gas of flow rate 100 ml.min$^{-1}$ was fed to the reactor and the temperature in the reactor was heated up from 100ºC to 900ºC at the rate of 20ºC.min$^{-1}$. After 80 min, the system was cooled down to room temperature under helium flow. Figure 2 showed the signal of CH$_4$ and H$_2$ from MS, the carbon adsorption occurred at temperature above 600ºC. Hydrogen (H$_2$) was produced from the cracking of methane (CH$_4$). In the mean time, the carbon was adsorbed on Ni/YSZ surface.

2. **Investigation of the amount of carbon formation by TPO**

   When TPMA process was finished, the carbon formation on the Ni/YSZ surface was investigated by using TPO process. 10% of oxygen in helium with the total flow rate 100 ml.min$^{-1}$ was introduced to the system. Figure 3 shows the signal of O$_2$, CO and CO$_2$ from MS, the carbon deformation occurred at temperature above 600ºC. Carbon on the surface of Ni/YSZ was reacted with inlet O$_2$ and desorpted to carbon monoxide (CO) and carbon dioxide (CO$_2$). As shown in Figure 3, O$_2$ decreased when CO and CO$_2$ were increased. The amount of carbon formation was calculated from the amount of CO and CO$_2$.

3. **Effect of temperature on the amount of carbon formation**

   The experiment was started by reducing Ni/YSZ with 10% H$_2$/He at 700ºC for 6 hours. The system was purged by helium (He) until the signals from MS were stable. Before the TPMA process was started, the temperature in the reactor was heated up from 100ºC to 900ºC at the rate of 20ºC. min$^{-1}$. After the temperature was stable, the 5% of methane (CH$_4$) in helium (He) was fed into the reactor. After reaching 900ºC, the operating temperature was changed from 900 to 925, 950, 975 and 1000ºC respectively. Figure 4 shows the signal of CH$_4$ from MS, the carbon adsorption on

![Figure 2. Temperature programmed methane adsorption (TPMA) on Ni/YSZ](image-url)
the Ni/YSZ surface could be investigated from the amount of CH₄. The amount of carbon adsorption increased with increasing operating temperature. After running all TPMA processes, the carbon formation was investigated by the TPO process. The increase of methane adsorption with increasing temperature is mainly due to the promotion of endothermic methane cracking reaction (CH₄ → C + H₂) by increasing the operating temperature.

4. Effect of inlet fuel on the amount of carbon formation

At temperature 900°C, the carbon formation was investigated by changing the various types of fuel (CH₄, H₂, CO+H₂ (ratio 1:3), CH₃+H₂O (ratio 1:3), CH₃OH+H₂O (ratio 1:3), C₂H₅OH+H₂O (ratio 1:3)). The TPO results for each fuel are shown in Figure 5. The relative amounts of carbon formation on the surface of Ni/YSZ when supplied different inlet fuel are shown in Figure 6. After 60 minutes exposure time, the amounts of carbon formation were constant and the system was in the steady state; they are shown in Table 1. For the synthesis gas (CO+H₂ (ratio 1:3)) and CH₃+H₂O (ratio 1:3), the amounts of carbon formation were 0.51 and 1.03 mmol/g, which were small when compared with H₂. In contrast, when CH₄, CH₃OH+H₂O (ratio 1:3), C₂H₅OH+H₂O (ratio 1:3) were used as fuel, the
amounts of carbon formation were 2.19, 3.19, and 4.31 mmol/g, which were larger when compared with H₂. The relative amount of carbon formation on the surface of Ni/YSZ when supplied various types of inlet fuel and varied temperature are shown in Figure 7. When the temperature was increased, the relative amount of carbon formation on Ni/YSZ increased in all the ranges of temperature from 900°C to 1000°C for all types of fuel. For synthesis gas (CO+H₂ (ratio 1:3)) and CH₃H₂O (ratio 1:3), the amount of carbon formation was small when compared with H₂ for all the ranges of temperature. But, in contrast, when CH₄, CH₃OH+H₂O (ratio 1:3) and C₂H₅OH+H₂O (ratio 1:3) were used as fuels, the amounts of carbon formation were larger.

5. Effect of inlet steam to hydrocarbon (CH₄, CH₃OH and C₂H₅OH) ratios

At temperature 900°C, the carbon formation was investigated by changing the ratio of steam to hydrocarbon fuel (CH₄+H₂O, CH₃OH+H₂O, C₂H₅OH+H₂O). When the ratio of steam to fuel (CH₄, CH₃OH and C₂H₅OH) was increased from 3:1 to 4:1 and 5:1 respectively, the amount of carbon formation were as shown in Table 2. For
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CH$_4$+H$_2$O, when the ratio of steam was increased from 3:1 to 5:1, the amount of carbon formation was significantly decreased 66.99%. But, for CH$_3$OH+H$_2$O and C$_2$H$_5$OH+H$_2$O, the amount of carbon formation was decreased only 14.73% and 4.64% respectively.

Table 1. Amounts of carbon formation on the surface of Ni/YSZ for different inlet fuel at 900ºC.

<table>
<thead>
<tr>
<th>Type of Inlet Fuel</th>
<th>Amount of carbon formation at 900ºC (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.0</td>
</tr>
<tr>
<td>CO + H$_2$</td>
<td>0.51</td>
</tr>
<tr>
<td>CH$_4$ + H$_2$O</td>
<td>1.03</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2.19</td>
</tr>
<tr>
<td>CH$_3$OH + H$_2$O</td>
<td>3.19</td>
</tr>
<tr>
<td>C$_2$H$_5$OH + H$_2$O</td>
<td>4.31</td>
</tr>
</tbody>
</table>

Table 2. Effect of the ratio of steam to hydrocarbon fuel (CH$_4$, CH$_3$OH and C$_2$H$_5$OH) on the amount of carbon formation at 900ºC.

<table>
<thead>
<tr>
<th>Type of Inlet Fuel</th>
<th>Amount of carbon formation at 900ºC (mmol/g)</th>
<th>Steam /hydrocarbon (HC) ratio</th>
<th>Steam /hydrocarbon (HC) ratio</th>
<th>Steam /hydrocarbon (HC) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3:1</td>
<td>4:1</td>
<td>5:1</td>
</tr>
<tr>
<td>CH$_4$ + H$_2$O</td>
<td>1.03</td>
<td>0.66</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH + H$_2$O</td>
<td>3.19</td>
<td>3.01</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5$OH + H$_2$O</td>
<td>4.31</td>
<td>4.25</td>
<td>4.11</td>
<td></td>
</tr>
</tbody>
</table>

Discussion

The formation of carbon on the surface of Ni/YSZ is the major difficulty for the DIR-SOFC operation. It is clear from the work that ethanol + steam cannot be used as the direct feed to the anode.
side of SOFC due to the observation of significant carbon formation. It was widely established that, at 300-500°C, ethanol cracks and converts to acetaldehyde, hydrogen, methane, and carbon monoxide via the dehydrogenation of ethanol and simultaneous fast decomposition of acetaldehyde (Eqs. 1 and 2).

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2 \quad (1)
\]

\[
\text{C}_2\text{H}_4\text{O} \rightarrow \text{CH}_4 + \text{CO} \quad (2)
\]

At SOFC temperature, the methane steam reforming and water-gas shift reactions (Eqs. 3 and 4) then take place. Ethylene is also formed by the dehydration of ethanol (Eq. 5) whereas the production of ethane is from ethylene hydrogenation (Eq. 6).

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (3)
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4)
\]

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (5)
\]

\[
\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 \quad (6)
\]

The formations of ethylene and ethane are the major difficulties for the reforming of ethanol at high temperature, as it has been widely established that ethane and ethylene act as very strong promoters of carbon formation. Eqs. 1-4 below present the most probable reactions that could lead to carbon deposition:

\[
\text{C}_n\text{H}_m \leftrightarrow m/2\text{H}_2 + n\text{C} \quad (7)
\]

\[
2\text{CO} \leftrightarrow \text{CO}_2 + \text{C} \quad (8)
\]

\[
\text{CO} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{C} \quad (9)
\]

\[
\text{CO}_2 + 2\text{H}_2 \leftrightarrow 2\text{H}_2\text{O} + \text{C} \quad (10)
\]

C is the carbonaceous deposits. At low temperature, Eqs. (9-10) are favorable, while Eqs. (7-8) are thermodynamically unfavored (Lwin et al., 2000). The decomposition of hydrocarbons (Eq. 7) and Boudouard reaction (Eq. 8) are the major pathways for carbon formation at such a high temperature as they show the largest change in Gibbs energy (Amor, 1999). According to the range of temperature in this study, carbon formation would be formed via the decomposition of hydrocarbons and Boudouard reactions. By increasing the inlet steam to hydrocarbon molar ratio, the degree of carbon formation decreases.

The equilibrium of water-gas shift reaction moves forward producing more CO₂ rather than CO and eventually avoids carbon deposition via the Boudouard reaction. However, a significant amount of carbon remains detected, particularly when high molecular weight hydrocarbons were used.

From the experiment, it is concluded that pure methane, methanol + steam, and ethanol + steam cannot be used as the direct feed to SOFC due to the significant observed carbon formation on Ni/YSZ anode. It should be noted that the ratio of CO/H₂ for synthesis gas (CO+H₂) and H₂O/CH₄ on the amount of carbon formation should be further investigated carefully in order to determine the most suitable ratio of CO to H₂ and H₂O to CH₄ which shows an acceptable amount of carbon deposition for DIR operation. In addition, the effects of fuel type and fuel inlet ratio on the degree of electrical generation from DIR-SOFC should also be tested in order to determine the level of electrical generation from DIR-SOFC fueled by hydrocarbons compared to that fueled by pure hydrogen.

Conclusion

Hydrogen and synthesis gas (CO+H₂) are good to use as direct inlet fuels for DIR-SOFC with Ni/YSZ anode, since the carbon formation on the surface of Ni/YSZ deposited was in small quantity. The mixture of methane and steam (CH₄ +H₂O) can also be used as the inlet feed, but the H₂O/CH₄ ratio plays an important role in carbon formation. For the mixture of methane and steam with the H₂O/CH₄ ratio 5:1, the amount of carbon formation was relatively low. In contrast, pure
methane (CH₄), methanol with steam (CH₃OH+H₂O) and ethanol with steam (C₂H₅OH+H₂O) are not suitable for using as a direct inlet fuel for DIR-SOFC with Ni/YSZ anode even if high ratios of H₂O/CH₃OH and H₂O/C₂H₅OH (5:1) are applied.

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References


