Fuel processing of H₂/CO₂ mixtures from biohydrogen production processes in solid oxide cell devices

Christian J. Laycock, Kleitos Panagi, James R. Reed and Alan J. Guwy
Sustainable Environment Research Centre, University of South Wales, UK

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Presentation Contents

• Electrochemical characterisation of a commercially available button SOFC running on H$_2$/CO$_2$ mixtures simulating gases from biohydrogen production processes

• Characterisation of fuel processing using quadrupole mass spectrometry

• Characterisation of fuel variability on cell performance and fuel processing

• Comparison of cell performance in fuel cell mode and electrolysis mode
Biohydrogen

- Biohydrogen production processes include dark fermentation, photofermentation, biophotolysis and bioelectrochemical techniques

✓ Biohydrogen does not contain methane and SOFC efficiencies are better with hydrogen

✓ Better SOFC resistance to carbon deposition and sulfur poisoning

✓ Versatility: electrochemical reduction of CO\textsubscript{2} potentially yields synthesis gas (H\textsubscript{2} + CO)

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**Composition of biohydrogen\textsuperscript{1}**

<table>
<thead>
<tr>
<th>Component</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>40-50 vol%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>50-55 vol%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3-8 vol%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1-4 vol%</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>&lt; 0.001 vol%</td>
</tr>
<tr>
<td>Methane</td>
<td>&lt; 0.01 vol%</td>
</tr>
<tr>
<td>Sulfur-containing compounds</td>
<td>&lt; 200 ppm</td>
</tr>
<tr>
<td>Other impurities</td>
<td>&lt; 2 vol%</td>
</tr>
</tbody>
</table>

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\textsuperscript{1}Leone et al. J.Power Sources 195 (2010) 239-248.
OCP Measurements

RWGS Reaction: $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$   $\Delta H = +75 \text{ kJ mol}^{-1}$

Fuel Cell Mode – 50/50 vol% $\text{H}_2$/CO$_2$

**Hydrogen Conversion:**
$\text{H}_2 + \text{O}^2- \rightleftharpoons \text{H}_2\text{O} + 2\text{e}^-$

**CO Conversion:**
$\text{CO} + \text{O}^2- \rightleftharpoons \text{CO}_2 + 2\text{e}^-$
(very slow when $\text{H}_2 >> \text{CO}$)$^{4-5}$

I-V Curve Measurements

Activation losses constant across all gas mixtures

Concentration losses present at < 40 vol% H₂
Cell performance and power output not significantly affected by fuel variability within the range 40-60 vol% $\text{H}_2$, particularly at high operating voltages.
Fuel Cell Mode Impedance

Low frequency arc width increases when \( \text{H}_2 < 40 \text{ vol\%} \): increased diffusion losses\(^6\) over this range.

High frequency arc width constant: no electrochemical\(^6\) \( \text{CO} \) conversion.


<table>
<thead>
<tr>
<th>( \text{H}_2/\text{CO}_2 ) vol%</th>
<th>High Frequency Arc Width / ( \Omega \text{ cm}^2 )</th>
<th>Low Frequency Arc Width / ( \Omega \text{ cm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80:20</td>
<td>0.5179</td>
<td>0.1316</td>
</tr>
<tr>
<td>60:40</td>
<td>0.5248</td>
<td>0.1245</td>
</tr>
<tr>
<td>50:50</td>
<td>0.5217</td>
<td>0.1214</td>
</tr>
<tr>
<td>40:60</td>
<td>0.5269</td>
<td>0.1240</td>
</tr>
<tr>
<td>20:80</td>
<td>0.5276</td>
<td>0.1530</td>
</tr>
<tr>
<td>10:90</td>
<td>0.5121</td>
<td>0.2255</td>
</tr>
</tbody>
</table>
CO Production

Equilibrium of RWGS reaction (and therefore CO production) varies as the fuel composition is changed.

Therefore, if CO conversion were electrochemical, the activation overpotentials would also change with fuel composition.

![Graph showing corrected signal intensity vs time for different fuel compositions: Pure H₂, 75:25 H₂/CO₂, 60:40 H₂/CO₂, 50:50 H₂/CO₂, 40:60 H₂/CO₂, 25:75 H₂/CO₂. The graph includes labels for OCP and Fuel Cell Mode (0.7 V).]
CO Conversion in Fuel Cell Mode

Hydrogen Conversion:
\[ \text{H}_2 + \text{O}^2- \rightleftharpoons \text{H}_2\text{O} + 2\text{e}^- \]

Electrochemical \( \text{H}_2 \) oxidation shifts RWGS reaction:
\[ \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \]
**Electrolysis Mode – 50/50 vol% H₂/CO₂**

**Reverse Water-Gas Shift:**
\[ \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \]

**Hydrogen Production:**
\[ \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + \text{O}^{2-} \]

**CO Production**\(^{7,8}\):
\[ \text{CO}_2 + 2e^- \rightleftharpoons \text{CO} + \text{O}^{2-} \]

or
\[ \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \]

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I-V Curve Measurements

Activation losses increase as the CO₂ content is decreased.

No concentration losses observed.
I-V Curve Measurements

Cell performance and power input not significantly affected by fuel variability within the range 40-60 vol% $H_2$
Electrolysis Mode Impedance

Low frequency arc width increases when CO₂ < 40 vol%: increased diffusion losses\(^6\) over this composition range

High frequency arc width increases with decreasing CO₂ content: H₂O and CO₂ are electrochemically\(^6\) reduced to produce H₂ and CO respectively

CO Production

CO production decreases when $\text{CO}_2 > 60 \text{ vol}\%$, indicating production is enhanced by the RWGS reaction.
Electrolysis Mode – 50/50 vol% H₂/CO₂

Reverse Water-Gas Shift:
\[ \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \]

Hydrogen Production:
\[ \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + \text{O}_2^- \]

CO Production:
\[ \text{CO}_2 + 2e^- \rightleftharpoons \text{CO} + \text{O}_2^- \]

and
\[ \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO} \]
Conclusions

• SOFCs can utilise H₂/CO₂ mixtures in fuel cell mode to yield electrical power and heat, or electrolysis mode to yield synthesis gas mixtures (H₂/CO)

• Performance and fuel processing are sensitive to fuel composition and variability, but are not significantly affected provided the H₂/CO₂ composition stays within 40-60 vol% H₂

• In fuel cell mode, power production is predominantly through electrochemical H₂ oxidation, whilst CO is converted in the WGS reaction and makes negligible contribution to power production

• In electrolysis mode, CO production is through a mixture of the RWGS reaction and electrochemical CO₂ reduction, while H₂ is regenerated via electrochemical H₂O reduction
Acknowledgements

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