Effect of Coal Contaminants on SOFC System Performance and Service Life

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OBJECTIVE

- Determine the sensitivity on the performance of SOFC to trace level contaminants present in a coal-derived gas stream in the temperature range 750° to 900°C.
- Assess short-term risk and long-term cumulative effect of the trace-level contaminants.
- Assess the life-time expectancy of SOFC systems fueled with coal-derived gas streams.
Coal and SOFC

- Coal is an abundant fuel in the U.S.
- Integrated coal gasification-fuel cell system ⇒ Efficient and potentially low cost generation of electricity from domestic sources.
- Contaminants in the coal-derived gas can degrade the performance of SOFC.
Trace Elements in Coal-Derived Gas

- Coal contains nearly 80 elements!
- In the gas stream leaving a coal gasifier, many of these elements are present at various levels in the gas stream.
- Components of a coal-derived gas:
  - Major: $\text{H}_2$, CO, $\text{CO}_2$, $\text{H}_2\text{O}$ (% level)
  - Minor: $\text{H}_2\text{S}$, $\text{NH}_3$, $\text{HCl}$ (10 to 10,000 ppm)
  - Trace: As, P, Hg, Cd, Zn, Sb, Pb, Bi, Na, K, Fe, and Ni (<1 to 10 ppm)
  - Fine ash particulates (fume) – contains several condensed trace element species
Technical Approach

- Literature review.
- Thermodynamic calculations.
- Determine the performance of small SOFC samples to simulated coal gas containing trace element vapor.
  - Individual contaminants;
  - Synergistic effect of multiple contaminants;
  - Effect of coal ash fumes.
- Assess the SOFC degradation and recommend tolerance limits.
Coal-Derived Gas Stream Processing

800° - 1100°C

Coal Gasifier

400° to 800°C

Ash Removal
Coarse
Fine

25° to 300°C

Contaminant Removal
Cold Gas Cleanup
Warm Gas Cleanup

750° to 1000°C

Heat Recovery
GT, ST

SOFC

CO₂ Capture

Air

Vent

Air/O₂

Coal

Steam
Nature of the Trace Element Vapor Species  
(Equilibrium Thermodynamic Estimate)

<table>
<thead>
<tr>
<th>Element</th>
<th>&gt;1000°C</th>
<th>400° to 800°C</th>
<th>100° to 400°C</th>
<th>&lt;100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>AsO, As₂</td>
<td>AsO, As₄</td>
<td>As₂,</td>
<td>AsH₃,</td>
</tr>
<tr>
<td>Be</td>
<td>Be(OH)₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Hg</td>
<td>Hg</td>
<td>Hg</td>
<td>Hg, HgCl₂</td>
<td>Hg, HgCl₂</td>
</tr>
<tr>
<td>B</td>
<td>HBO</td>
<td>HBO</td>
<td>HBO</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>VO₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Se</td>
<td>H₂Se, Se, SeO</td>
<td>H₂Se</td>
<td>H₂Se</td>
<td>H₂Se</td>
</tr>
<tr>
<td>Ni</td>
<td>NiCl, NiCl₂</td>
<td>Condensed Species</td>
<td>Ni(CO)₄</td>
<td>Ni(CO)₄</td>
</tr>
<tr>
<td>Co</td>
<td>CoCl₂, CoCl</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Sb</td>
<td>SbO, Sb₂</td>
<td>SbO, Sb₂</td>
<td>Sb₄</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Cd</td>
<td>Cd</td>
<td>Cd</td>
<td>CdCl₂</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb, PbCl₂</td>
<td>PbS, Pb, PbCl₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn</td>
<td>Zn, ZnCl₂</td>
<td>Condensed Species</td>
<td>Condensed Species</td>
</tr>
</tbody>
</table>
The concentrations of many trace contaminants in coal-derived gas stream are not known accurately.

The expected levels depend on:

- Type of coal
- Coal gasifier
- Gas stream cleanup technology.
## Estimate of Trace Level Contaminant Levels in Coal-Derived Gas

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Concentration (ppmv) at the Kingsport Facility</th>
<th>UND-EERC Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (AsH₃)</td>
<td>0.15 to 0.58</td>
<td>0.2</td>
</tr>
<tr>
<td>Thiophene</td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>CH₃F</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>Fe(CO)₅</td>
<td>0.05 to 5.6</td>
<td></td>
</tr>
<tr>
<td>Ni(CO)₅</td>
<td>0.001 to 0.025</td>
<td></td>
</tr>
<tr>
<td>CH₃SCN</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>PH₃</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Antimony</td>
<td>0.025</td>
<td>0.07</td>
</tr>
<tr>
<td>Cadmium</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.025</td>
<td>6.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.025</td>
<td>0.002</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt;0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>Vanadium</td>
<td>&lt;0.025</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td></td>
<td>0.26</td>
</tr>
<tr>
<td>Zinc</td>
<td>9.0</td>
<td></td>
</tr>
</tbody>
</table>
Effect of Coal Contaminants on SOFC Anode Performance

- Affect the ability of Ni crystallites to promote electrochemical reactions
  - Sulfur atoms on the surface poison Ni to dissociate H₂ molecules or adsorb CO
- Affect the ability of YSZ to transport oxygen ions
  - Formation of other phases such as zirconium silicate
- Affect the electrical conductivity
  - Formation of alloys or bulk phases such as sulfides
Known Effect of Contaminants

- Published literature indicate the effect of H₂S, NH₃, and HCl on SOFC performance.

- Tolerance limits for SOFC:
  - H₂S and HCl: Few ppm; NH₃: 5,000 ppm

- Catalyst literature on Ni-based catalysts indicate:
  - H₂S reduces the steam reforming activity;
  - As (1 ppm) affect the steam reforming activity;
  - Cl reduces H₂ and CO adsorption on Ni;
  - P inhibits H₂ uptake by Ni;
  - Bi reduces CO chemisorption;
  - Addition of Zn to Ni prevent agglomeration of Ni/alumina catalysts.
  - Most of the catalyst studies were performed at temperatures lower than the SOFC operation.
Experimental Determination of the Effect of Trace Elements on SOFC Performance

- We are concentrating on contaminants other than H₂S.
- We are exposing SOFC samples at 750° to 850°C to simulated coal-derived gas containing various contaminants (10 to 50 ppm).
- Scoping experiments to determine the effect of following contaminants on SOFC performance:
  - HCl, CH₃Cl
  - Zn, P
  - As
Experimental Setup

InDec B.V. Cells; 1 in Dia; 4-6μm electrolyte;

5 to 10 μm Ni-YSZ anode; 520 to 600 μm anode support; 30 to 40 μm LSM-YSZ cathode;

Peak power: 0.15 W/cm² at 700°C; 0.35 W/cm² at 800°C <10% degradation over 2000 h

Gas Composition: 30.0% CO, 30.6% H₂, 11.8% CO₂, 27.6% H₂O
Performance of SOFC in Clean Gas
(800°C, ~0.7V and 0.2A/cm²)

- Cell Power Density (mW/cm²) in H₂
- Cell Power Density (mW/cm²) in simulated coal-derived gas mixture

Note: The power density was 182 mW/cm² during 0 to 300h.
Performance of SOFC with 38 ppm HCl Vapor at 750° and 800°C (~0.7V and 0.2A/cm²)

Power Density (mW/cm²) at 750°C

Power Density (mW/cm²) at 800°C
Performance of SOFC with 40 ppm CH$_3$Cl Vapor at 800 and 850°C (~0.7V and 0.2A/cm$^2$)
Nature of Zn Vapor Species under SOFC Anode Conditions (10 ppm feed)

<table>
<thead>
<tr>
<th>Gaseous Species</th>
<th>Partial pressures (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700°C</td>
</tr>
<tr>
<td>H₂(g)</td>
<td>0.38</td>
</tr>
<tr>
<td>CO(g)</td>
<td>0.23</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>0.19</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>0.20</td>
</tr>
<tr>
<td>Zn(g)</td>
<td>1.0E-05</td>
</tr>
<tr>
<td>ZnO(g)</td>
<td>7.7E-18</td>
</tr>
<tr>
<td>Zn(OH)₂(g)</td>
<td>7.3E-12</td>
</tr>
</tbody>
</table>
Performance of SOFC with 10 ppm Zn Vapor at 750°C (~0.7V and 0.2A/cm²)
Performance of SOFC with 10 ppm Zn Vapor at 800°C (~0.7V and 0.2A/cm²)
### Nature of P Vapor Species under SOFC Anode Conditions

<table>
<thead>
<tr>
<th>Gaseous Species</th>
<th>Partial pressures (atm)</th>
<th>727°C</th>
<th>777°C</th>
<th>827°C</th>
<th>877°C</th>
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</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.23</td>
<td>0.24</td>
<td>0.25</td>
<td>0.26</td>
<td></td>
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<tr>
<td>CO₂</td>
<td>0.19</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
<td></td>
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<tr>
<td>H₂</td>
<td>0.37</td>
<td>0.36</td>
<td>0.35</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.21</td>
<td>0.22</td>
<td>0.23</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>HPO</td>
<td>6.75E-08</td>
<td>9.33E-08</td>
<td>1.24E-07</td>
<td>1.61E-07</td>
<td></td>
</tr>
<tr>
<td>HPO₂</td>
<td>2.85E-05</td>
<td>2.83E-05</td>
<td>2.83E-05</td>
<td>2.82E-05</td>
<td></td>
</tr>
<tr>
<td>HPO₃</td>
<td>1.64E-07</td>
<td>1.82E-07</td>
<td>2.02E-07</td>
<td>2.23E-07</td>
<td></td>
</tr>
<tr>
<td>PH₃</td>
<td>1.00E-09</td>
<td>7.72E-10</td>
<td>5.96E-10</td>
<td>4.68E-10</td>
<td></td>
</tr>
</tbody>
</table>
Performance of SOFC with 10 ppm P$_2$O$_5$ Vapor at 750° and 800°C (~0.7V and 0.2A/cm$^2$)

![](image)

- Power Density (mW/cm$^2$) at 750° C
- Power Density (mW/cm$^2$) at 800° C
Performance of SOFC with 10 ppm As(g) Vapor at 750°C (~0.7V and 0.2A/cm²)
Performance of SOFC with 10 ppm As(g) Vapor at 750°C After 60 h

![Graph showing performance of SOFC with 10 ppm As(g) vapor at 750°C after 60 hours.](image)

- **Potential (mV)**
  - Initial
  - 60h Exposure

- **Power Density (mW/cm²)**
  - Initial
  - 60h Exposure

- **Current (mA/cm²)**

- **Cell 11 pg 14 750 H2 50 ccm air 9-5A**
Summary

- 100 h exposure tests in a simulated coal gas stream at 750° to 800°C show that:
  - HCl and CH$_3$Cl at 38 ppm level do not have a significant effect. At 850°C, CH$_3$Cl degrades the SOFC performance steadily.
  - Zn vapor at 10 ppm level leads to a slow decline in performance at 800°C.
  - P vapor (10 ppm) degrades the SOFC anode.
  - As vapor at 750°C affects the performance rapidly initially, but remains steady after 10 h.
Future Work

- Determination of the effect of Hg, Cd, Sb, and Bi.
- Characterize the anode degradation using bulk and surface analyses.
- Relative ranking of the effect of individual contaminants.
- Determination of the effect of coal ash fumes.
- Determination of synergistic effect of contaminants.
- Preliminary determination of the sensitivity of SOFC to contaminants.
- Long term experiments with selected contaminants in large area cells at different concentrations.
- Recommendation of tolerance limits.
PROJECT TEAM

- **SRI International**
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- **Research Triangle Institute**
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- **U.S. Department of Energy (NETL)**
  - Shawna Toth, Wayne Sardoval, Ayyakkannu Mannivannan

- Cooperative agreement: DE-FC26-05NT42627.