Effects of Phosphorus and Arsenic on SOFC Anodes

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Outline

- Introduction / Summary of Previous Work
- Objectives / Experimental Approach
- Experimental Results
- Summary
- Future Work
- Acknowledgements
Introduction

- Coals contain a wide variety of impurities.
- Different impurities lead to different types of interactions with SOFC anode.
- Anode performance degradation due to coal gas impurities is affected by various factors, such as concentration of contaminants, temperature, operation time, cell voltage, and fuel utilization.
- Previous studies at PNNL focused on effects of P, As, Sb, S, Se, Cl at ppm levels
- Current studies are focused effects of sub-ppm levels of P and/or As on anode chemistry/microstructure
Anode–Phosphorus Interactions: Conclusions from Previous Work

- Strong interaction between Ni and P-containing contaminants in coal gas (PH$_3$, PO$_2$, etc.)
  - Nickel phosphide solid phases: Ni$_3$P, Ni$_5$P$_2$, Ni$_{12}$P$_5$, Ni$_2$P, etc.
  - Sharp boundary observed between reacted and un-reacted parts of the anode

- Degradation Mechanisms
  - Increased Ohmic resistance due to
    - Loss of electrical connectivity in the anode support due to phosphide formation (Ni depletion)
    - Micro-crack formation due to particle coalescence
  - Poisoning due to transport of phosphorus to the active interface (increased electrodic polarization)
    - P adsorbs on surface of Ni grains in unreacted anode (observed by XPS, ToF-SIMS)

- Effect of Contaminant Level
  - For [PH$_3$] = 1-10 ppm, both ohmic and electrodic losses in tested cells increased substantially during 1000 hours of testing
Anode–Phosphorus Interaction

SEM Analysis of anode-supported button cells after exposure

- Sharp boundary between reacted and unreacted anode
- WDS confirmed P is associated only with nickel, not zirconia.
Anode–Arsenic Interactions: Conclusions from Previous Work

- Strong interaction between Ni and As-containing contaminants in coal gas (AsH$_3$, As$_2$, etc.)
  - Nickel arsenide solid phases: Ni$_5$As$_2$, Ni$_{11}$As$_8$, etc.
  - Sharp boundary observed between reacted and un-reacted parts of the anode

- Degradation Mechanisms
  - Loss of electrical connectivity in the anode support due to arsenide formation: Ni depletion (increased Ohmic resistance)
    - Abrupt failure after long-term operation upon loss of electrical percolation
  - Unlike case for P, poisoning effects due to adsorption of As at active anode interface were not observed

- For [AsH$_3$] = 1 – 10 ppm, substantial degradation of performance observed in 1000 hours or less
Anode–Arsenic Interaction

SEM Cross-Section Image (800°C, 500 hours)

- AsH₃ Concentration ↑ ~ Depth of Reaction ↑, Agglomeration ↑

Conversion of Nickel to Nickel Arsenide (Ni₅As₂, Ni₁₁As₈)

- 700°C, 50 Hours
- Red: Ni, Dark Yellow: Ni-As Solid Solution, Green: YSZ, Blue: Ni₅As₂, Magenta: Ni₁₁As₈
Phosphide/Arsenide Formation

Ni Phosphide / Ni Arsenide formation expected to occur even at sub-ppb contaminant levels:
Effect of contaminant level on conversion rate

- Expect lower rate of reaction as contaminant level decreases due to lower contaminant delivery rate

- Calculated rates of Ni conversion
  
  Assumptions:
  
  - 50/50 vol% Ni/YSZ anode w/ 40% porosity; 500 microns thick
  
  - 65% fuel utilization, 0.8 A/cm² current density
  
  - Complete capture of contaminant by anode (worst-case scenario)
  
  - Dominant phase formed:
    
    - P: Ni₃P
    - As: Ni₅As₂

- Graph showing the relationship between years and percentage of Ni conversion for different contaminant levels (10 ppb AsH₃, 10 ppb PH₃, 1 ppm AsH₃, 1 ppm PH₃)
Objective/Approach

Objective: Study effects of sub-ppm levels of P, As on Ni/YSZ anode chemistry and microstructure

- Coal gasification cleanup may reduce P, As levels to the level of ~10 ppb.

Previous studies verified substantial reaction phase formation at ppm levels. Do the nature and extent of anode/contaminant interactions change as contaminant concentration decreases below 1 ppm?

Approach:

- Perform “flow-by” reaction tests over a range of contaminant levels (between 10 ppb and 1 ppm)
- Adjust test time to deliver equivalent total dosage for all tests (concentration x time = constant)
- Use surface and cross-section electron microscope analyses of tested samples to assess relationships between contaminant type, contaminant level, dosing time, and secondary phase formation
“Flow-by” anode contaminant tests

- Flow rate: 200 sccm, corresponding to ~65% fuel utilization at 0.8 A/cm²
- Gas composition: Simulated coal gas (55% H₂; 45% CO₂)
- Contaminant: AsH₃ and/or PH₃
- Temperature: 700, 800°C
Experimental parameters

- Perform tests over a range of contaminant levels (between 10 ppb and 1 ppm)
  - Equivalent total dosage of contaminant
    (dosing rate x time = Constant)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time (h)</th>
<th>Total Moles Supplied</th>
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<td>1.00 ppm</td>
<td>50</td>
<td>$2.68 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.50 ppm</td>
<td>100</td>
<td>$2.68 \times 10^{-5}$</td>
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<tr>
<td>0.10 ppm (100 ppb)</td>
<td>500</td>
<td>$2.68 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.05 ppm (50 ppb)</td>
<td>1000</td>
<td>$2.68 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.01 ppm (10 ppb)</td>
<td>5000</td>
<td>$2.68 \times 10^{-5}$</td>
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Experimental Results
50 h, 1 ppm AsH$_3$ in simulated coal gas, 800°C

- Region 1 (inlet)
- Region 2
- Region 3
50 h, 1 ppm AsH$_3$ in simulated coal gas, 800ºC

- Region 4
- Region 5
50 h, 1 ppm AsH$_3$ in simulated coal gas, 800ºC: EDS Analysis

Purple is Ni$_5$As$_2$ phase
EBSD Analysis confirmed surface (points 1-4) and bulk reaction phase (point 8) to be Ni$_5$As$_2$

Points 6, 7 are YSZ
Note eutectics at 897 and 804°C
### 50 h, 1 ppm AsH₃ in simulated coal gas, 800°C: EDS area concentration profiles

![Image of EDS area concentration profiles]

**Profile height = 10µm**

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Ni</th>
<th>As</th>
<th>Y</th>
<th>Zr</th>
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<td>As Profile(18)</td>
<td>37.56</td>
<td>43.02</td>
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<td>18.65</td>
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</table>

All results in atomic%
1000 h, 0.05 ppm AsH$_3$ in simulated coal gas, 800ºC

- Region 1 (inlet)
- Region 2
- Region 3
1000 h, 0.05 ppm AsH$_3$ in simulated coal gas, 800ºC

All results in atomic%

Points 2,3,5,6,7 are Ni$_5$As$_2$

Ni (red); Zr (green); As (blue)
1000 h, 0.05 ppm AsH$_3$ in simulated coal gas, 800$^\circ$C

Yellow orange is Ni$_5$As$_2$, orange-red is Ni with varying levels of As, blue purple is YSZ
1000 h, 0.05 ppm AsH₃ in simulated coal gas, 800°C

As is detectable down to ~150 µm below the surface.

Average values of both depth profiles.
All results in atomic%

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Ni</th>
<th>As</th>
<th>Y</th>
<th>Zr</th>
<th>O</th>
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<td>17.955</td>
<td>40.635</td>
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</table>
500 h, 0.1 ppm AsH$_3$ in simulated coal gas, 800ºC

- Region 1 (inlet)
- Region 2
- Region 3
500 h, 0.1 ppm AsH$_3$ in simulated coal gas, 800ºC

Green is Ni$_5$As$_2$, Orange is Ni with levels of As below that of Ni$_5$As$_2$, purple is YSZ.
500 h, 0.1 ppm AsH₃ in simulated coal gas, 800°C

As is detectable down to ~140 µm below the surface.
Concentration profiles from EDS analyses: Absolute concentration (at%)  

- Extensive arsenide formation zone at 1 ppm; negligible As doping of Ni below arsenide zone; Ni depletion in reaction zone resulted from extensive formation of arsenide above surface of anode  
- Narrower arsenide formation zone at 50 or 100 ppb, but extensive region of As-doped Ni below the arsenide zone
Depth Profile: As / (Ni + As)

Solubility of As in Ni

Ni₅As₂
Length of primary reaction zone as \( f(\text{concentration/time}) \)

<table>
<thead>
<tr>
<th>Test #</th>
<th>Concentration</th>
<th>Time (h)</th>
<th>Approx. Length of “Arsenide zone”</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00 ppm</td>
<td>50</td>
<td>5 mm</td>
</tr>
<tr>
<td>2</td>
<td>0.50 ppm</td>
<td>100</td>
<td>TBD</td>
</tr>
<tr>
<td>3</td>
<td>0.10 ppm (100 ppb)</td>
<td>500</td>
<td>2 mm</td>
</tr>
<tr>
<td>4</td>
<td>0.05 ppm (50 ppb)</td>
<td>1000</td>
<td>2 mm</td>
</tr>
<tr>
<td>5</td>
<td>0.01 ppm (10 ppb)</td>
<td>5000</td>
<td>TBD</td>
</tr>
</tbody>
</table>
Summary

Strong interactions occur between Ni-based anodes and P and/or As contaminants in fuel

These interactions result in formation of secondary phases
- Nickel phosphide solid phases: e.g., \( \text{Ni}_3\text{P} \), \( \text{Ni}_5\text{P}_2 \)
- Nickel arsenide solid phases: e.g., \( \text{Ni}_5\text{As}_2 \), \( \text{Ni}_{11}\text{As}_8 \)

Arsenide formation (\( \text{Ni}_5\text{As}_2 \)) was confirmed with As concentrations as low as 50 ppb (in simulated coal gas)
- Consistent with thermodynamic calculations, which indicate arsenide formation at much lower concentrations (< 1 ppb at 800ºC)
- Arsenide formation zone occurred in anode surface region near fuel inlet
- Sharp boundaries were observed between arsenide formation zone and “unreacted” anode below that region
- However, for [As] = 50 or 100 ppb, substantial As doping of Ni was observed underneath the arsenide formation region

Implications for SOFC stacks:
- Interaction zone between anode and arsenic will be concentrated near the fuel gas inlet of the cells, but will, of course, lengthen over time
- For coal gas fuels cleaned to ppb levels, secondary phase formation is expected, but the low rate of contaminant delivery may significantly reduce degradation rates, and also simplify upstream mitigation
Future Work

► Complete analysis of results of equivalent dosage tests (As, P, As+P between 10 ppb and 1 ppm) at 700 and 800°
  ■ Correlate dosing level and time with extent and nature of interactions between anode and contaminant(s)

► Perform variable time reaction tests at a constant contaminant level to evaluate development of reaction zone geometry and composition
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- PNNL: Clyde Chamberlin and Alan Schemer-Kohrn