Interactions of Ni/YSZ Anodes with Coal Gas Contaminants

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Goal: Establish Maximum Acceptable Coal Gas Contaminant Concentrations

Part of a coordinated study involving:

- Randy Gemmen, Kirk Gerdes, NETL
- Gopala Krishnan, SRI International
- Stephen Sofie, MSU
- Jason Trembly, RTI
- PNNL team
Approach

- Thermodynamic assessment of coal gas contaminant - Ni phase equilibria
- Button cell testing of Ni interactions with coal gas contaminants. Parameters addressed included contaminant concentration, temperature, reaction time, fuel utilization, and current density
- Post-test analyses to determine the composition and extent of nickel modification
- Coupon tests in flow-through and flow-by arrangements to determine penetration rate and nature of contaminant/Ni interactions – companion to button cell tests
Phosphorus and arsenic interact strongly with Ni and are nearly completely captured by the anode.

One degradation mode involves loss of electronic percolation due to nickel phosphide and nickel arsenide formation, grain growth, and inducement of micro-fractures within the anode support.

Electrochemical degradation may be very low if an electrical pathway to the active interface is maintained (“shadowing effect” for strongly interacting contaminants).

Nickel conversion to the active interface by P and As results in significant degradation.

Selenium poisoning occurs quickly, similar to but slower than sulfur, and reaches steady state performance.
**Phosphorus and Arsenic: Very Strong Interactions with Nickel**

- **Ni$_5$P$_2$** stable
- **Ni$_3$P** stable
- **Ni-P solid solution** stable, 0.32 at% at 870°C

- **Ni$_5$As$_2$** stable
- **Ni-As solid solution** stable, 4.5 at% at 897°C
Schematic of Button Cell Test Stands

Eight button cells installed per box furnace, with individual gas flow controls

- Ni/YSZ anode-supported cells
- Electrolyte supported cells with 30 μm Ni/YSZ anode (from Fuel Cell Materials, NexTech)
Glass Coated Contact

- Glass seal
- Ni mesh
- Screen-printed Ni grid
- Glass coated Pt wire

Single Point Contact

- Fuel Gas
- Ni wire
- Ni mesh
- Glass seal

Current Contact Method Important in Degradation Studies

Pt and Ni wire instability affected some earlier results
Anode after Exposure to 5 ppm of PH$_3$ in Coal Gas for 790 hours at 700°C
Glass Coated Contacts: Minimal Effect of PH₃ or AsH₃ on Cell Performance

Contaminants Started at 25.4 Hours

Voltage Loss (V)

Time (Hours)

i=0.25A/cm² at 800°C
Low Degradation Rates at Different Fuel Utilizations* at 700°C with 1 ppm of AsH₃

* Fuel utilizations were adjusted by adding oxygen to the coal gas mix
Single Point Contact Tests with PH$_3$: Electrical Percolation Losses More Visible

![Graph showing cell voltage (V) over time (Hours) for different contaminant concentrations at T = 750°C. The graph depicts the voltage drop over time for baseline, 2 ppm, 1 ppm, 5 ppm, and 10 ppm contaminant levels, with a power bump and adjusted el. contacts indicated.]
Single Point Contact: Impedance Spectra of Anode-Supported Cell at 750°C in Coal Gas with 5 ppm of PH₃

- Ohmic and electrodic resistances double after 1000 hours of exposure
- New process appears at around 50-100 Hz
Single Point Contact: Ohmic Losses Increase More Rapidly with Exposure than Electrodic Losses

![Graph showing resistance increase in 1000 hours for PH₃ Pressure (ppm) at 750°C](image)

- **Ohmic Losses** increase more rapidly with exposure than **Electrodic Losses**.

The graph illustrates the resistance increase in 1000 hours at 750°C for different PH₃ Pressure (ppm) levels, showing a clear comparison between Ohmic and Electrodic losses.
Ohmic and electrodic resistances calculated from the impedance spectra obtained at 750°C at a bias current of 0.1A/cm² in coal gas with 1, 2, 5 and 10 ppm of PH₃. Single point contact test configuration.
Extensive Re-crystallization in the Upper Part of the Cell

800°C, 770 hours with 5 ppm PH₃
Anode Current Collector Surface after 357 Hour Test in Coal Gas with 2 ppm of PH$_3$, 1 ppm of AsH$_3$, and 1 ppm of H$_2$S at 800°C

Ni$_3$P - Ni$_5$As$_2$
No Ni-S (by SEM/EDS)

Ni mesh corroded to form Ni$_3$P and Ni$_5$P$_2$
Anode-Supported Cells after 990 Hour Test at 700°C with 1, 2, 5 and 10 ppm of PH$_3$ in Coal Gas

Ni$_3$P, Ni$_5$P$_2$, Ni$_2$P

Ni$_3$P/YSZ

Ni/YSZ

YSZ

YSZ is here

1 ppm

2 ppm

5 ppm

10 ppm

P penetration depth per hour (um/h)

1000/T (K$^{-1}$)

1

10

0.1
Active Interface of an Anode-Supported Cell after 1000 h Test at 700°C with 10 ppm of PH₃

Unreacted interface

Complete conversion of nickel to Ni-P showing extensive coarsening
Elemental Maps of Bulk Ni/YSZ after 1000 hour Test at 700°C with 5 ppm of PH$_3$
The same configuration for both cell types
Electrolyte Supported Cell
Voltage Losses in Coal Gas with PH$_3$ at 800°C

Contaminants Started at 0 Hours

- 0.2
- 0.4
- 0.6
- 0.8

Time (Hours)

Coal gas
0.5 ppm PH$_3$
1 ppm PH$_3$
2 ppm PH$_3$
5 ppm PH$_3$
10 ppm PH$_3$

Baseline
Electrolyte-Supported Cell Degradation Rate with Phosphorus

- Higher degradation rate at higher $\rho PH_3$
- No clear temperature dependence in this range
Ni/YSZ after 100 Hour Test in Coal Gas at 800°C (Ni – Red, YSZ – Green, Ni-P – Blue)

- No contaminants
- 0.5 ppm PH₃
- 1 ppm PH₃
- 2 ppm PH₃
- 5 ppm PH₃
- 10 ppm PH₃
Time Dependence for the YSZ Supported Cells after Exposure to 1 ppm of PH$_3$ at 800$^\circ$C (Ni-Red, Ni-P – Blue, YSZ – Green)

Moved towards higher order Ni-P phases with increased exposure
At highest exposures, observed mixture of Ni$_2$P and Ni$_5$P$_4$
Anode-Support Coupon Test in Flow Through Configuration Shows Ni Redistribution (no current collector)

Ni is red, Ni-P is magenta, YSZ is green
How Long Does It Take to Consume Nickel?

The graph shows the time to complete Ni conversion for both anode-supported (550 micron) and electrolyte-supported (10 micron) cells, assuming 0.5 watts at 0.7 volts.

- **Anode-supported (550 micron) cell**
- **Electrolyte-supported (10 micron) cell**

The y-axis represents the time to complete Ni conversion, while the x-axis represents the phosphine concentration in coal gas, ppm.
Much Higher Se Concentration Needed to Form Nickel Alteration Phase

The diagram shows the critical Se activity as a function of temperature (°C). The critical activity ranges from 1.0E-08 to 1.0E-02. The graph indicates that Ni3Se2 is stable above a certain temperature, NiSe is stable between specific temperature ranges, and Ni(ss) is stable within a lower temperature range. The temperature axis ranges from 300 to 900 °C.
Effect of 1 ppm of Hydrogen Sulfide or Hydrogen Selenide on Anode Supported SOFC at 800°C
Summary

- Phosphorus and arsenic interact strongly with Ni and are nearly completely captured by the anode.

- One degradation mode involves loss of electronic percolation due to nickel phosphide and nickel arsenide formation, grain growth, and inducement of micro-fractures within the anode support.

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