RUSS COLLEGE of Engineering and Technology

Adapting Planar Solid Oxide Fuel Cells for Distributed Power Generation Project PDP 40

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Objectives

Program Objectives

- Quantify impacts of synthesis gas composition on performance of a commercial planar solid oxide fuel cell system (cell and stack)
  - H_2S content
  - CO/H_2 ratio and energy content of gas
  - Particulate
  - Metal content
- Demonstrate long term operation of pSOFCs using actual sold fuel-derived synthesis gas

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Overview

Timeline

- Project start 10/2/2003
- Project end date 10/1/2008
- Percent complete 80%

Budget

- Total project funding
  - DOE share $3,903,000
  - Contractor share $1,023,000
- Funding received in FY06: $0
- Funding for FY07 $0

Barriers

- DOE Technical Barriers for Distributed Generation
  - Improved CO tolerance
  - Develop CHP fuel cell systems
  - Verify integrated stationary fuel cell systems
  - Mitigate technical barriers to stationary fuel cells
- DOE Technical Targets for 2010
  - 40,000 hours durability
  - $1000/kWe

Partners

- SOFCo-EFS (Fuel Cells)
- Case Western Reserve University
- University of Cincinnati
- State of Ohio's Air Quality Development Authority
- BAARD (Power Generation)
- Enercon (Gasification/Steam Reforming)

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Stack Testing – Effect of H_2S

Methodology

•Galvanostatic operation (0.21±0.01Amps/cm^2) at 850°C utilizing simulated O_2 blown Pittsburgh No.8 coal syn gas

•PSOFC Area Specific Resistance (ASR) measured by completing V-I scans; ASR histories plotted and studied

• Voltage (power) performance over time monitored and studied

• Material analyses on the anodes (before and post tests): scanning electron microscopy (SEM), x-ray diffraction (XRD), and X-Ray Photoelectron Spectroscopy (XPS); to determine if any structural or composition changes had taken place.

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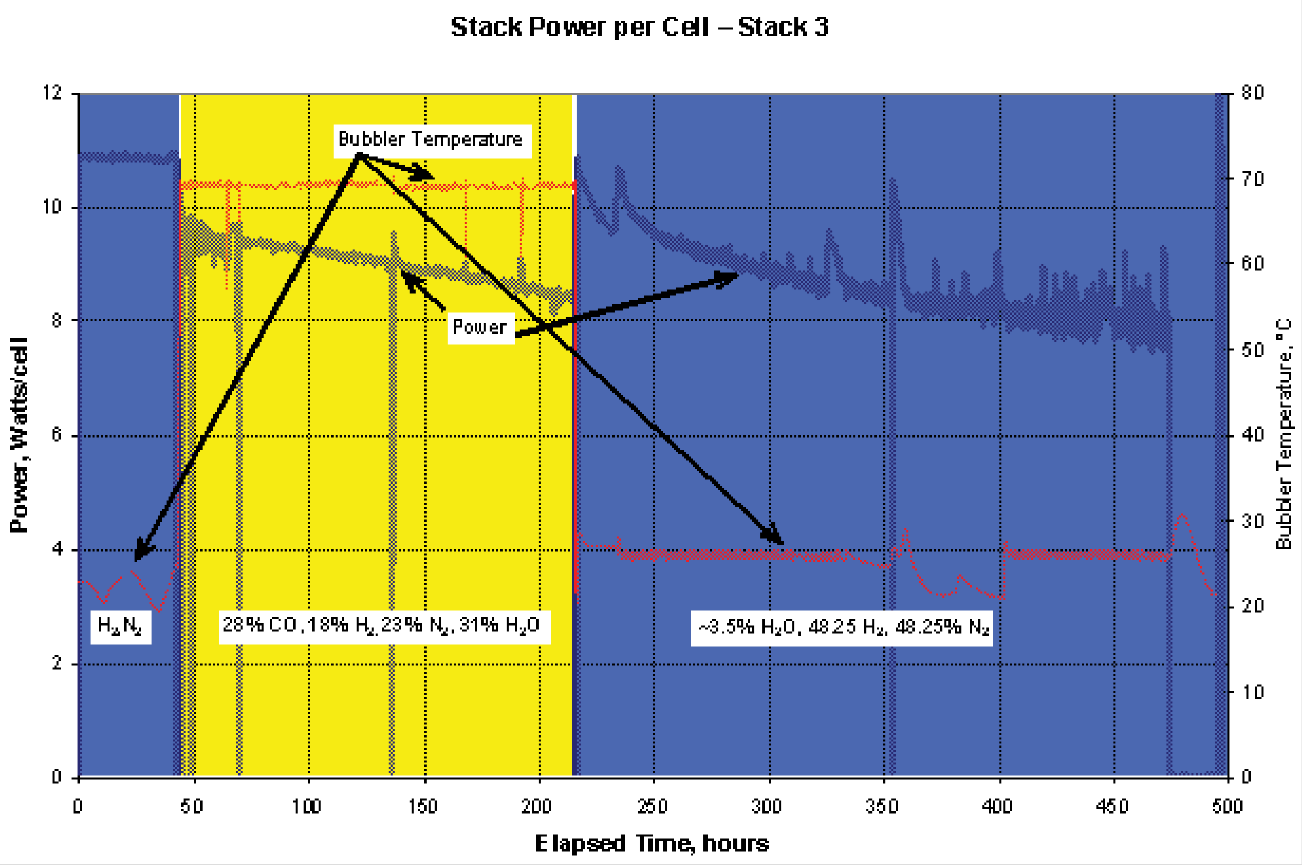
Stack Testing – Effect of H_2S

Results



Power and bubbler temperature traces for a two-cell stack, running with syngas for about 170 hours. The bubbler temperature was raised to 70 °C to ensure high water content (30-31% in the mixture), for 170 hours to match CO injection

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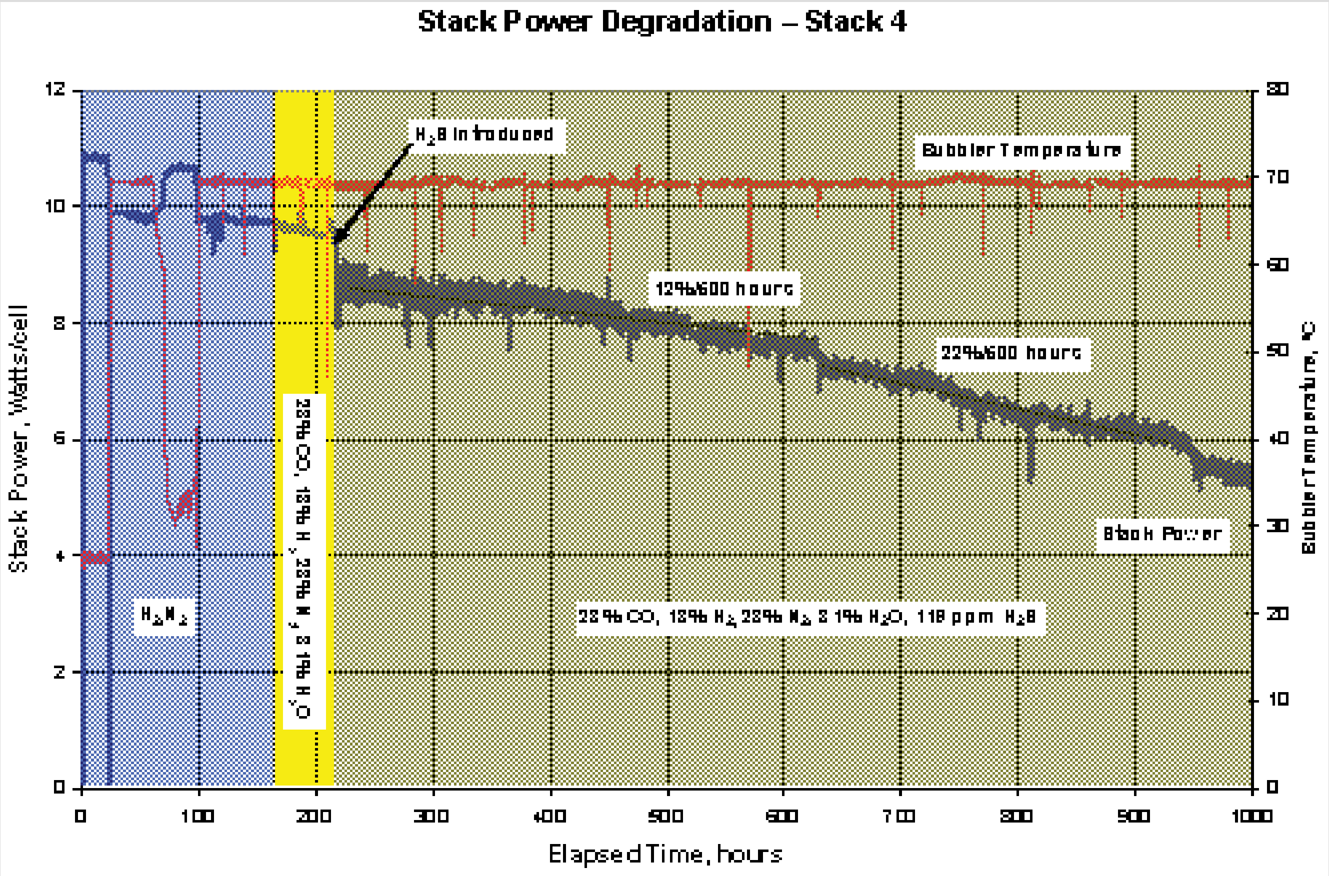
Stack Testing – Effect of H_2S

Results



Power and bubbler temperature history for the test of a two-cell stack (Stack 4), with syngas and H_2S. CO was introduced after 165 hours; H_2S was added after 219 hours

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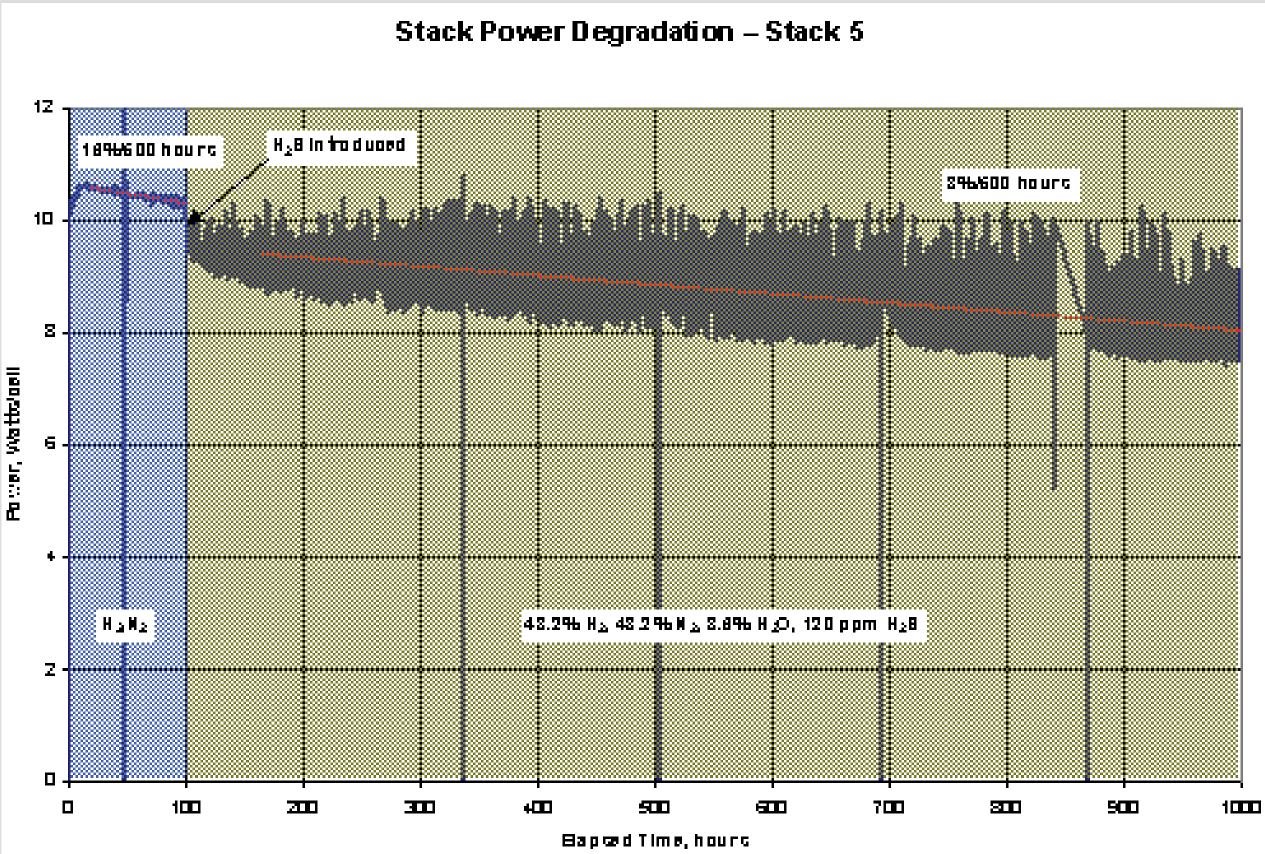
Stack Testing – Effect of H_2S

Results



Power trace for a test of a two-cell stack (Stack 5) with only H_2/N_2 and H_2S. After 100 hours, H_2S was introduced (119-120 ppm) and was kept constant until the conclusion of the test at 1000 hours.

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Stack Testing – Effect of H_2S

Conclusions

- Effects of coal syngas, with and without H_2S, were studied on the performance of short-stack pSOFC
- Results indicate that the separate effects of water content, CO, and H_2S can have significant deleterious effects on the long-term stack performance.
- The introduction of 119-120 ppm of H_2S caused an immediate power decay of approximately 10%. Tests with syngas and H_2S had an average final power decay rate per 500 hours of 23%, almost double that for tests with only H_2 and H_2S (12%).
- Material analysis suggest that the presence of GDC improved the sulfur tolerance of the individual cells, but other components of the stack system require more analysis.

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Effect of Trace Contaminant Species

Background

- Analysis was done to find what species in biomass and coal syngas would potentially affect performance of SOFCs
- Modeling was done to identify the possible species
- Experimental work was then done to quantify the effect

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Effect of Trace Contaminant Species

- Trace Species in CSG
  - Trace elements contained in syngas are classified into three groups base upon their volatility [1].
    - *Class I*: Least volatile, will remain in the ash.
    - *Class II*: More volatile, partition between condensed and gas phases.
    - *Class III*: Volatile, show little to no tendency to condense.
  - Previous reports have shown the presence of As, P, Sb, Cd, Be, Cr, Hg, K, Se, Na, V, Pb, Zn.

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Effect of Trace Contaminant Species

Thermodynamic Evaluation

- Thermodynamics were used to determine the condensation behavior of trace species contained in syngas
  - Gaseous species are assumed to travel to SOFC module
  - Solid species are assumed to have a 100% removal efficiency
  - System temperatures and pressures were varied from 200-500°C and 1-15atm.
- Thermodynamic analyses of the anode was also completed based upon warm gas cleanup results
  - Study evaluated anode composition (Ni, ZrO_2, and Y_2O_3)
  - Study completed over SOFC operational temperatures 700-900°C and anticipated pressures 1-15atm

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Effect of Trace Contaminant Species

Thermodynamic Evaluation

Trace Species Contained in Coal Syngas [1,7-11].

Component	Concentration (ppmv)	Volatility Class
AsH_3	**0.6**	**II**
HCl	**1**	**III**
PH_3	**1.91**	**II**
Sb	**0.07**	**II**
Cd	**0.011**	**II**
Be	**0.025**	**II**
Cr	**6**	**II**
Hg	**0.025**	**II**
K	**512**	**I**
Se	**0.15**	**II**
Na	**320**	**I**
V	**0.025**	**II**
Pb	**0.26**	**II**
Zn	**9**	**II**

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Effect of Trace Contaminant Species

Thermodynamic Evaluation

Trace Species Behavior [10].

Component	Behavior
As	Gas/Solid
P	Gas/Solid
Sb	Gas
Cd	Gas/Solid
Be	**Solid**
Cr	**Solid**
Hg	Gas
K	**Solid**
Se	Gas/Solid
Na	**Solid**
V	**Solid**
Pb	Gas/Solid
Zn	**Solid**

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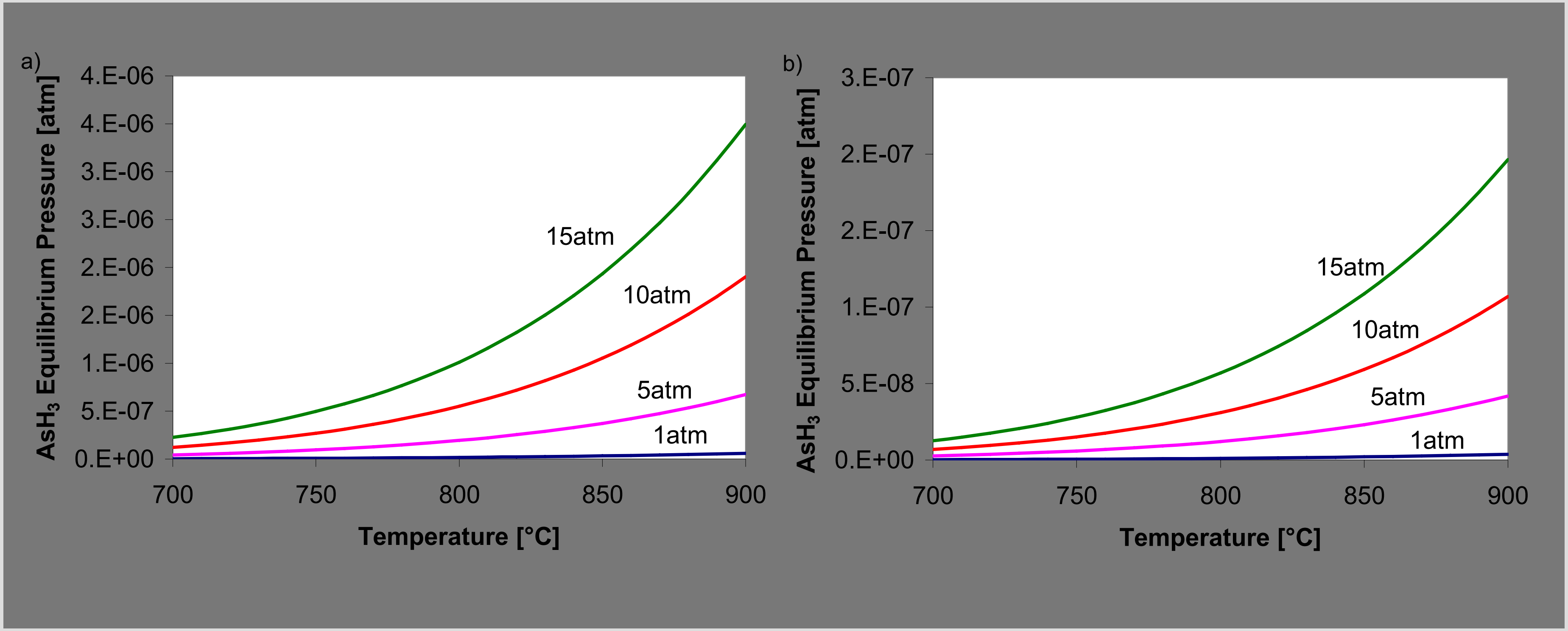
Effect of Trace Contaminant Species

As/Anode Interactions

$$AsH_3(g) + Ni(s) \rightarrow NiAs(s) + 1.5H_2(g)$$



Equilibrium Pressures of AsH_3 at SOFC Operation Conditions at the Inlet (a) and Outlet (b) [10].

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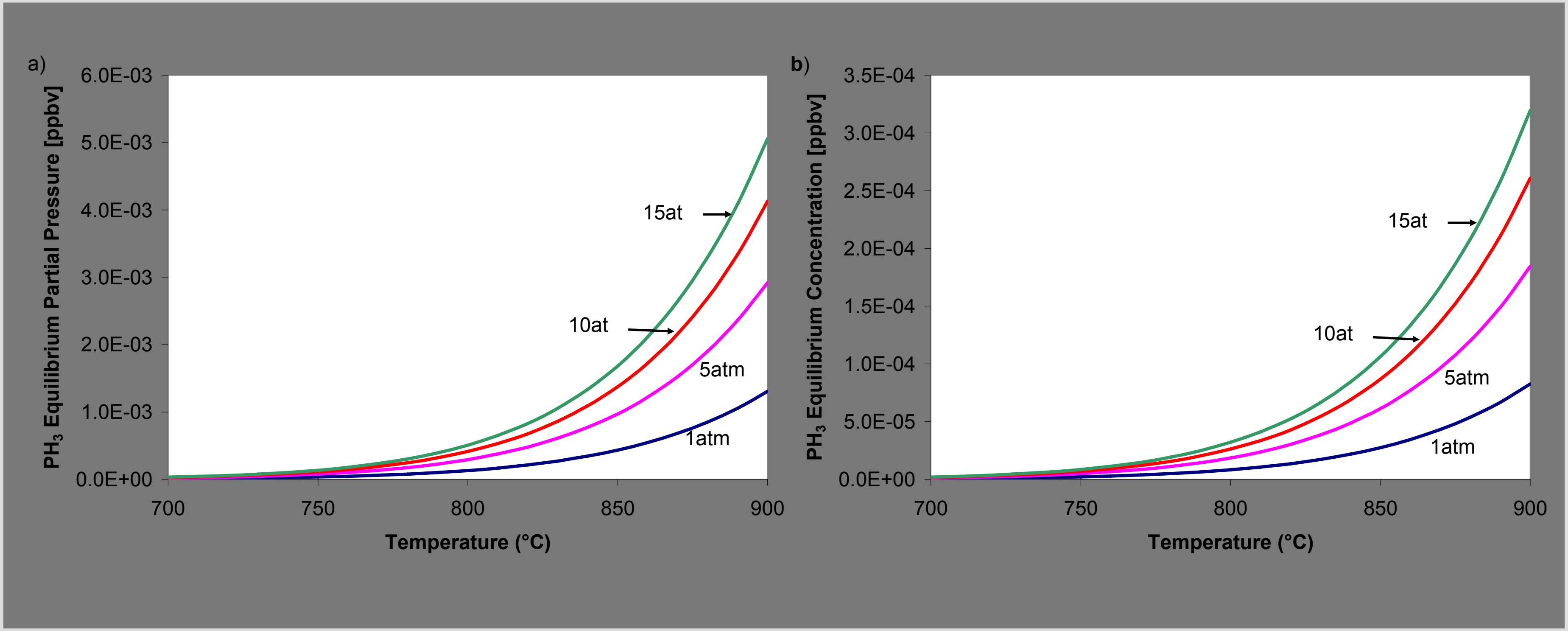
Effect of Trace Contaminant Species

P/Anode Interactions

$$2PH_3(g) + 5Ni(s) \rightarrow Ni_5P_2(s) + 3H_2(g)$$



Equilibrium Pressures of PH_3 Associated with Equation 9 Over SOFC Operation Conditions at the Inlet (a) and Outlet (b) [10].

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Effect of Trace Contaminant Species

Trace Metal Oxidation

$$Pb(g) + 0.5O_2(g) \rightarrow PbO(s)$$
$$Cd(g) + 0.5O_2(g) \rightarrow CdO(s)$$
$$Hg(g) + 0.5O_2(g) \rightarrow HgO(g)$$
$$Ni(s) + 0.5O_2(g) \rightarrow NiO(g)$$

O_2 Equilibrium Partial Pressures [10]

T(ºC)	pO_2(syngas)	pO_2(Pb)	pO_2(Cd)	pO_2(Hg)	pO_2(Ni)
700	**1.60E-17**	**9.80E-15**	**8.50E-07**	**7.50E+15**	**5.42E-17**
800	**6.40E-15**	**1.00E-10**	**3.50E-03**	**1.90E+17**	**1.20E-14**
900	**9.80E-13**	**2.20E-07**	**3.40E+00**	**2.70E+18**	**1.04E-12**

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Effect of Trace Contaminant Species

Chlorine in Syngas

- Found as sodium and potassium chlorides in 0.01% to 0.5% in weight.
- Nearly all the chlorine in coal is converted to HCl in the reducing environment of coal gasification.
- HCl concentrations as high as 500 ppm have been measured in raw syngas [1].
- Up to one-third of chlorides in coal syngas may remain after water scrubbing [2].

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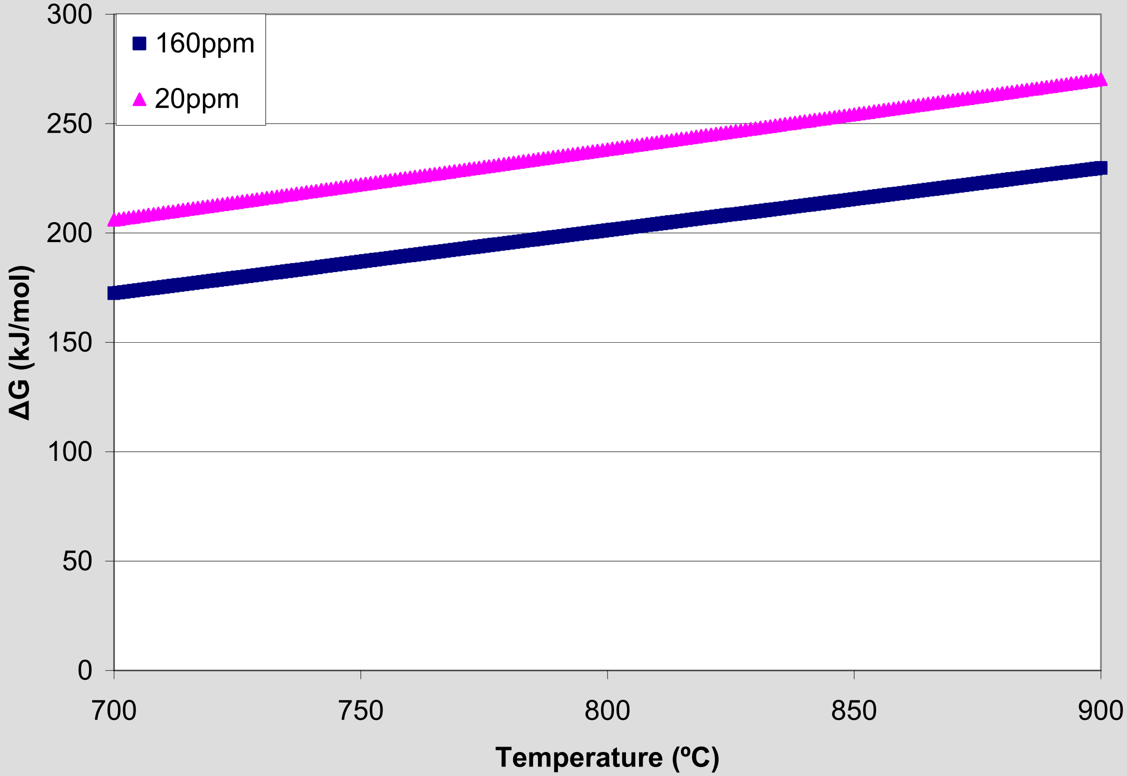
Effect of Trace Contaminant Species

Chlorine in Syngas

$$Ni(s) + 2HCl(g) \rightarrow NiCl_2(s) + H_2(g)$$



Gibb's Free Energy of Reaction over SOFC Operating Temperature Range, 0.29atm H_2, 20ppm and 160ppm HCl.

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Experimental

Test Stands

- Furnace units capable of 1000°C
- Solartron EIS unit
- Built in data acquisition using National Instrument’s Labview
- Alicat mass flow controllers (eight units) meter gas delivery
- Integrated safety system on stands and in containment room

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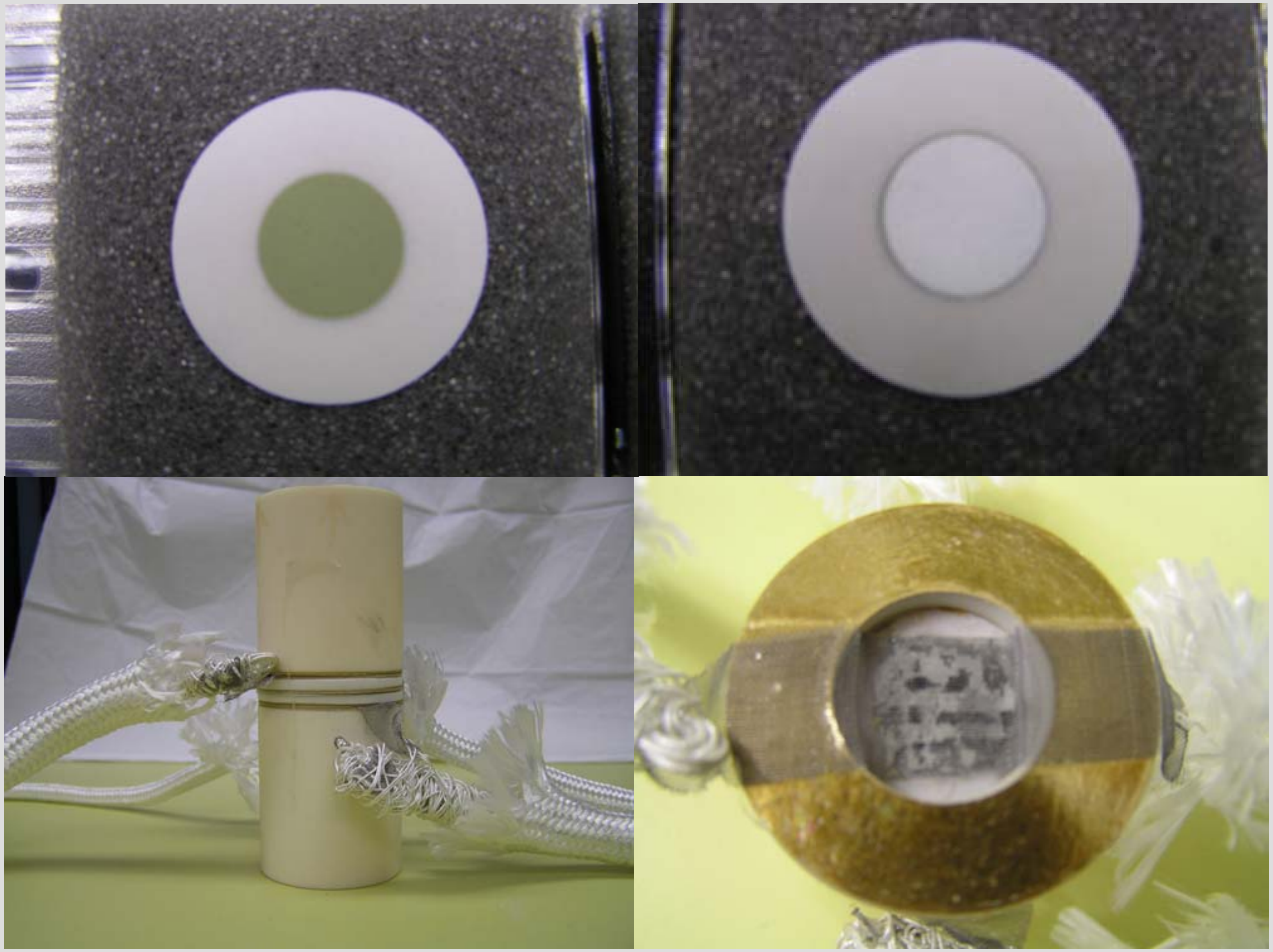
Experimental

Button Cells



Screen Printed Top Layer and Button Cell Setup

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Effect of Trace Contaminant Species

Effect of HCl on SOFCs

Performance Degradation Rates Over 100hrs

Temperature (°C)	HCl Concentration (ppm)		
	0	20	160
800	0.5	17.4	26.1
900	1.2	13.3	51.8

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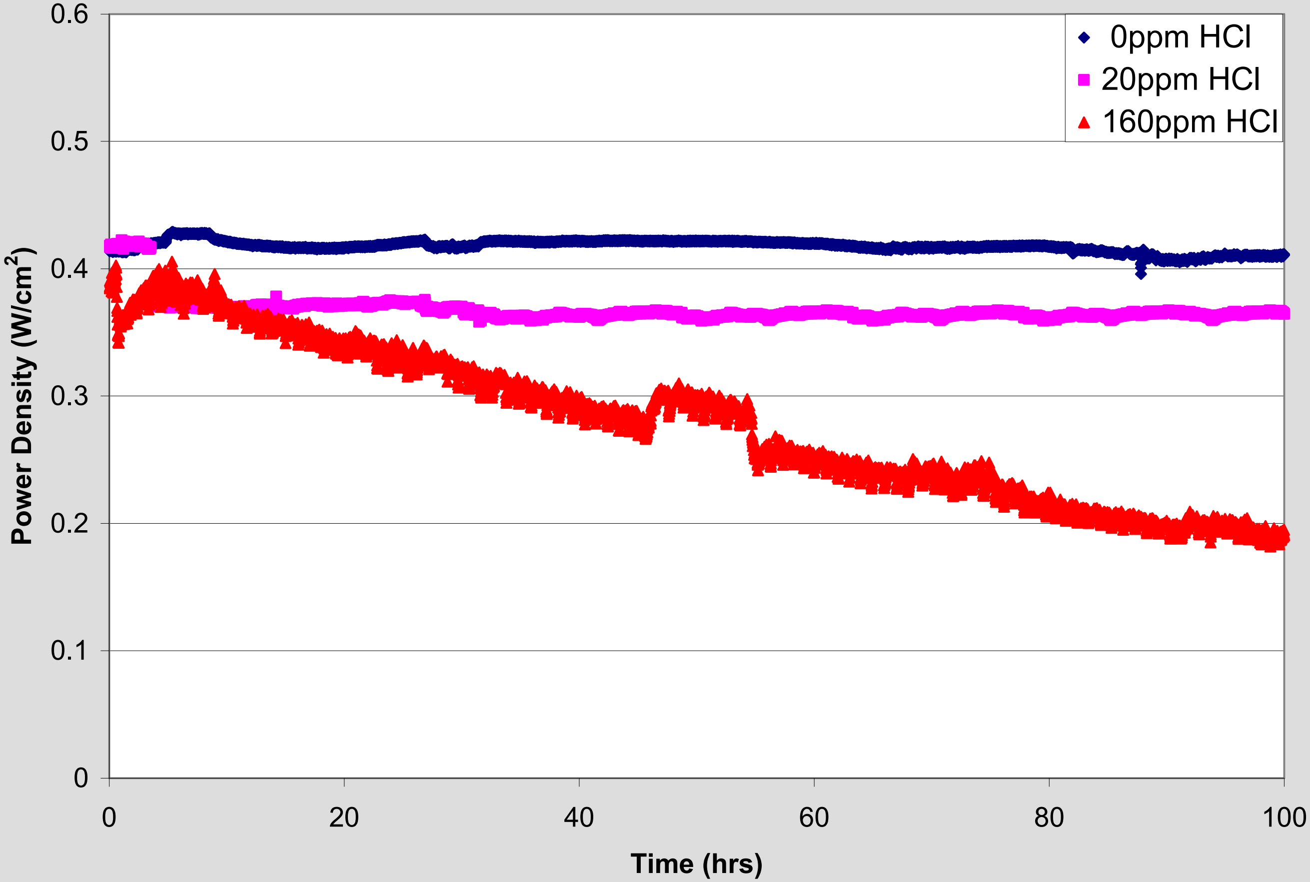
Effect of Trace Contaminant Species

Results: 20ppm and 160ppm HCl



SOFC Power Density Operating at 900°C and 0.7V Over Time with HCl Concentrations of 0ppm, 20ppm, and 160ppm [11].

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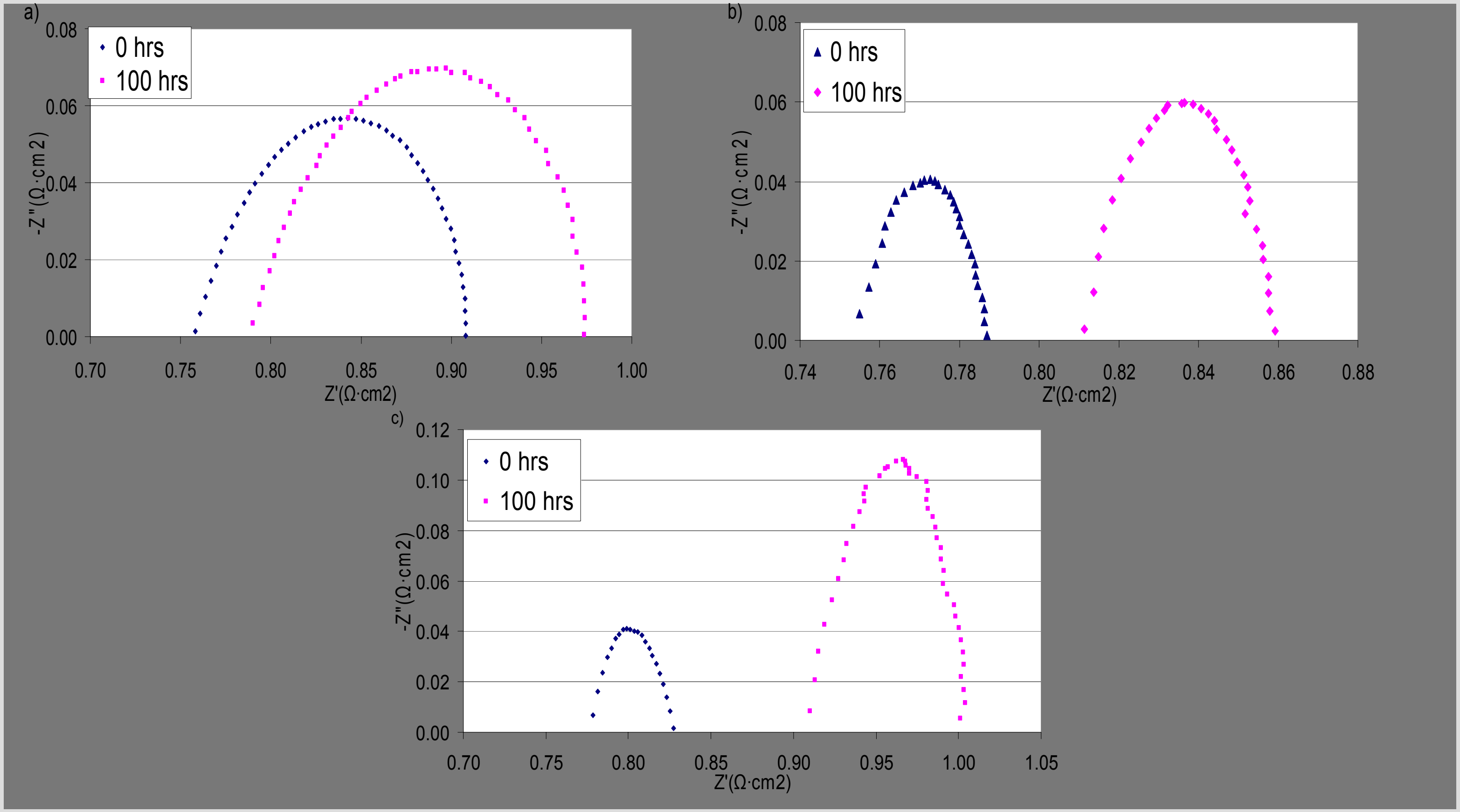
Effect of Trace Contaminant Species

Results: 20ppm and 160ppm HCl



EIS Data for SOFC Operating at 800°C and 0.7V Over Time with HCl Concentrations of 0ppm, 20ppm, and 160ppm [11].

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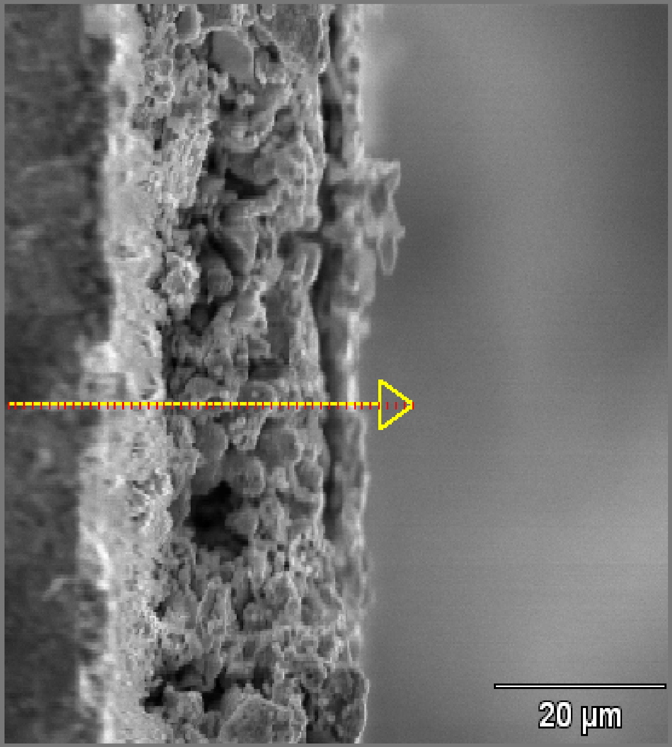
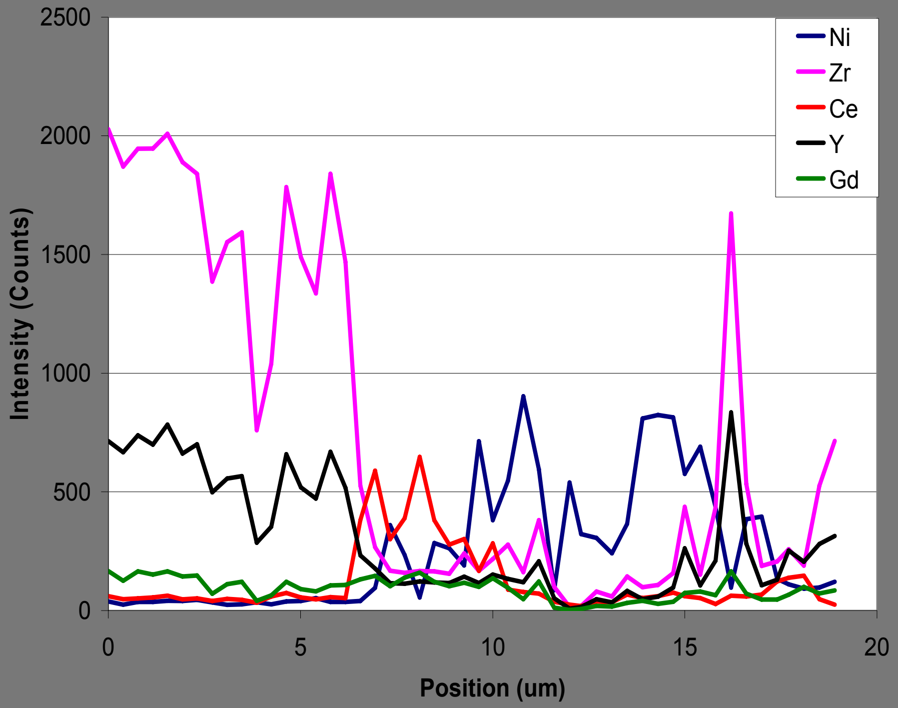
Effect of Trace Contaminant Species

Results: 20ppm and 160ppm HCl





SEM Image of SOFC Cross Section and EDS Linescan. [11].

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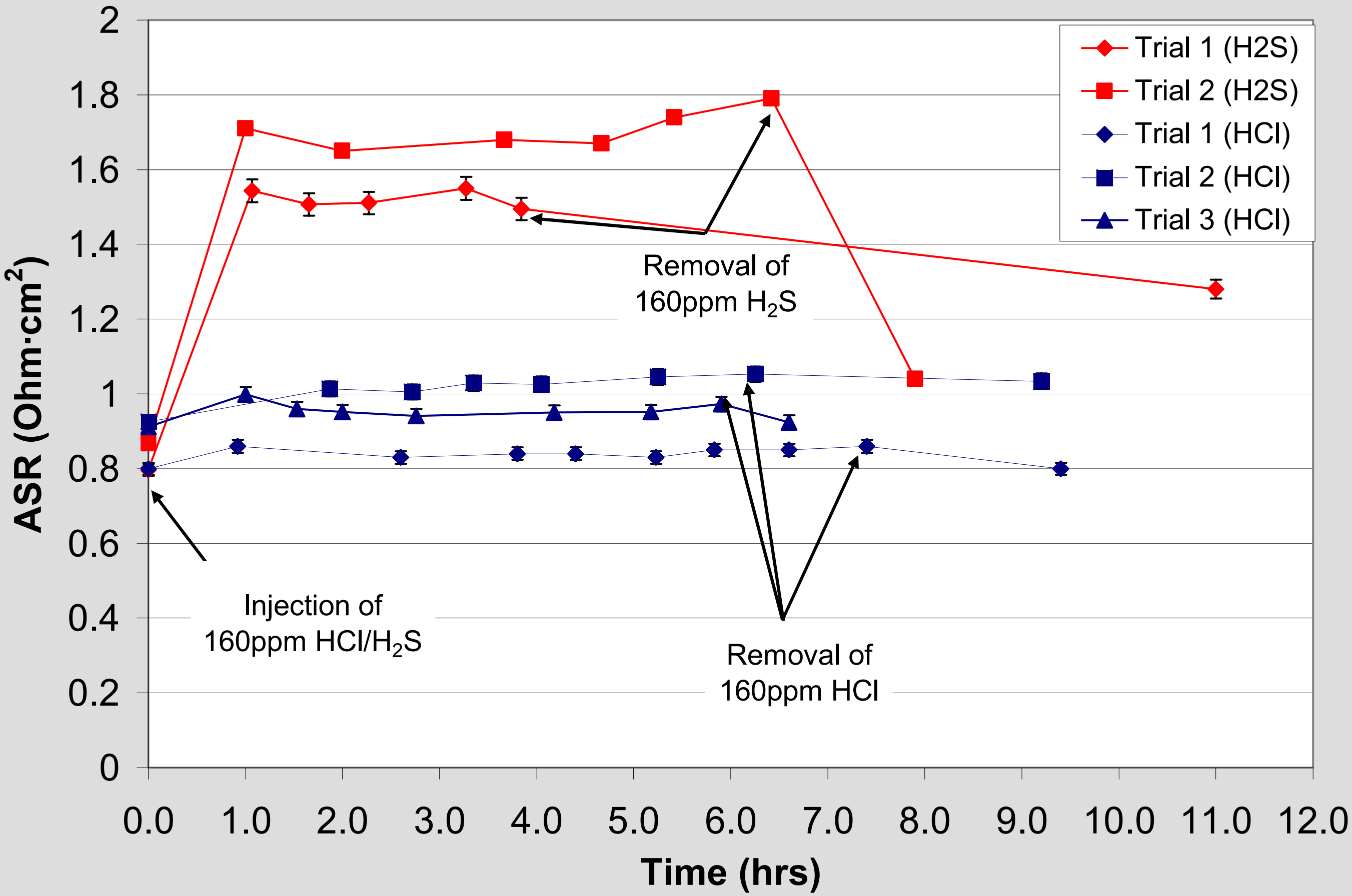
Effect of Trace Contaminant Species

Results: H_2S and HCl Comparison



ASR measurement results for PSOFC utilizing CSG with 160ppm HCl and H_2S [11].

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Effect of Trace Contaminant Species

Conclusions

- HCl concentrations of 20ppm and 160ppm cause SOFC performance losses.
- The performance losses are reversible.
- It is believed that physical adsorption of Cl onto Ni reaction sites is the cause of performance loss.
- Reduction of HCl to levels below 1ppm will not cause any SOFC performance losses.

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Effect of Trace Contaminant Species

AsH_3

- Found in concentrations from 0.5-2090 ppmw [14-16].
- Nearly all the As is converted to AsH_3 in the reducing environment of gasification
- Form may change over hot/warm gas cleanup contiditons.
- AsH_3 concentrations as high as 0.6 ppm have been measured in syngas derived from coal [17].
- As has shown to cause poisoning of steam shift catalyst
- Thermodynamics show that 0.15-0.6 ppmv AsH_3 may react with Ni to form secondary nickel arsenide phases.

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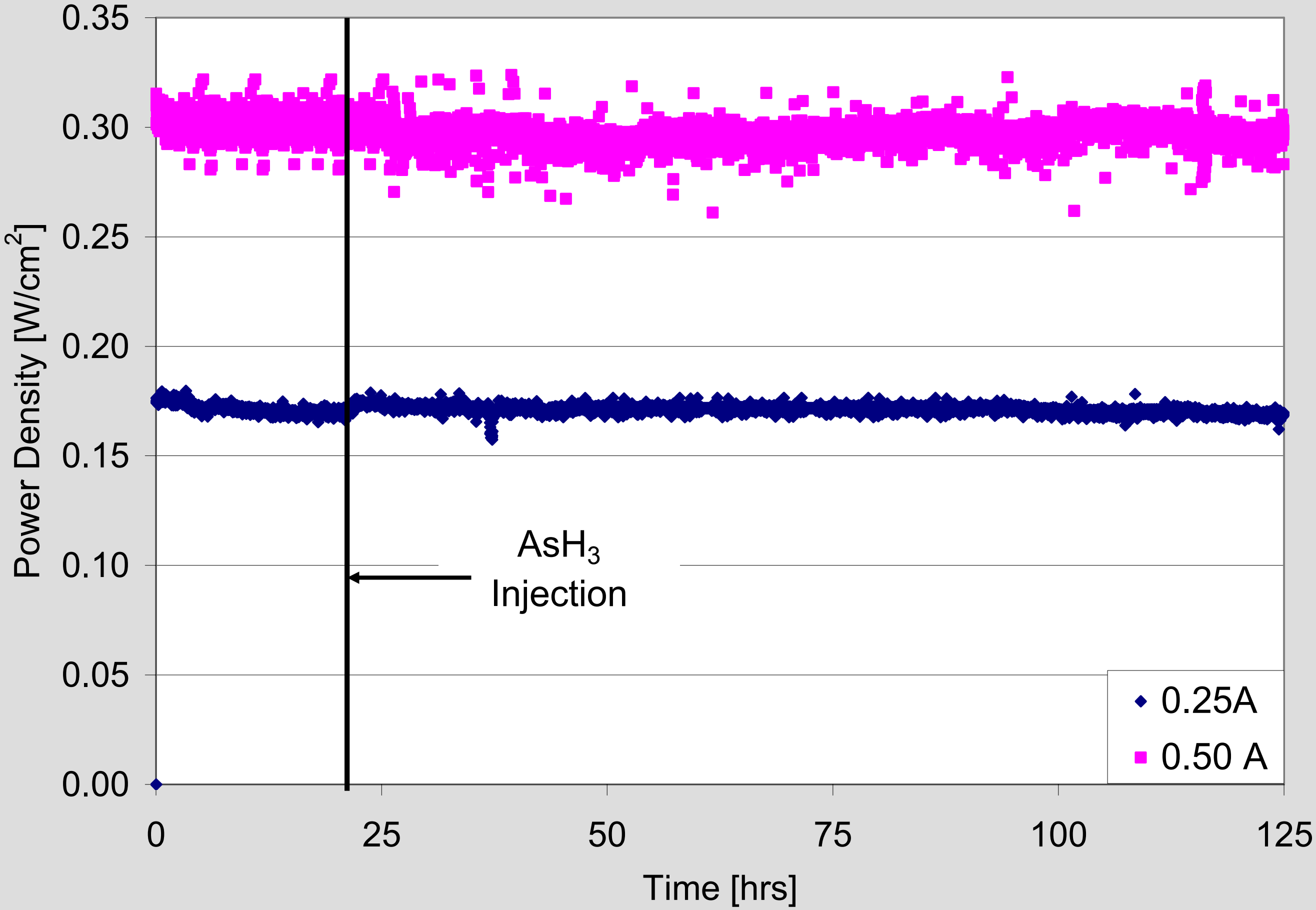
Effect of Trace Contaminant Species

Results: 1 ppm AsH_3



SOFC Power Density Operating at 800 °C and 0.25 and 0.50 Acm^{-2}
Over Time with AsH_3 concentration of 1 ppm.

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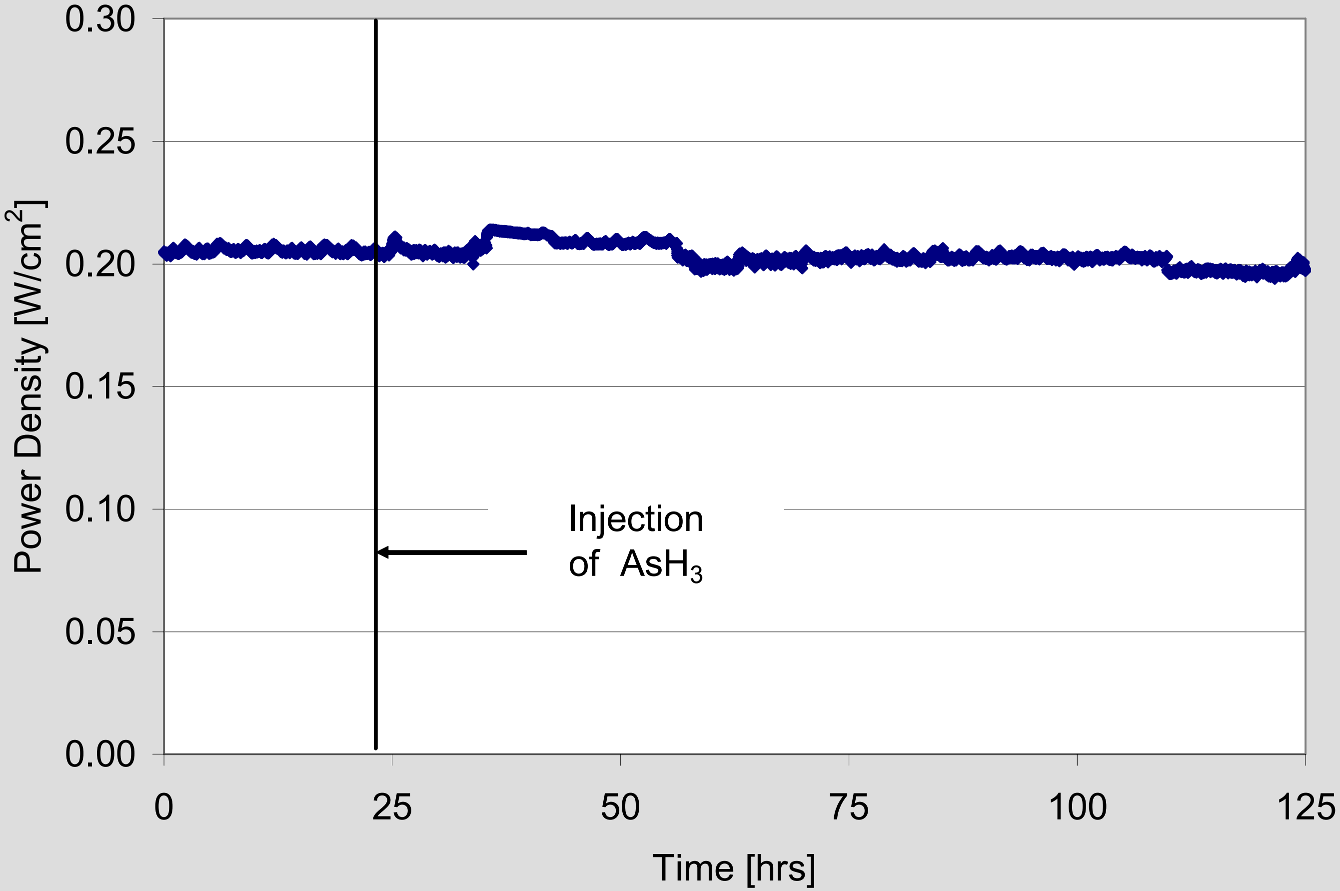
Effect of Trace Contaminant Species

Results: 2 ppm AsH_3



SOFC Power Density Operating at 800 °C and 0.25 Acm^{-2} Over Time with AsH_3 concentration of 2 ppm.

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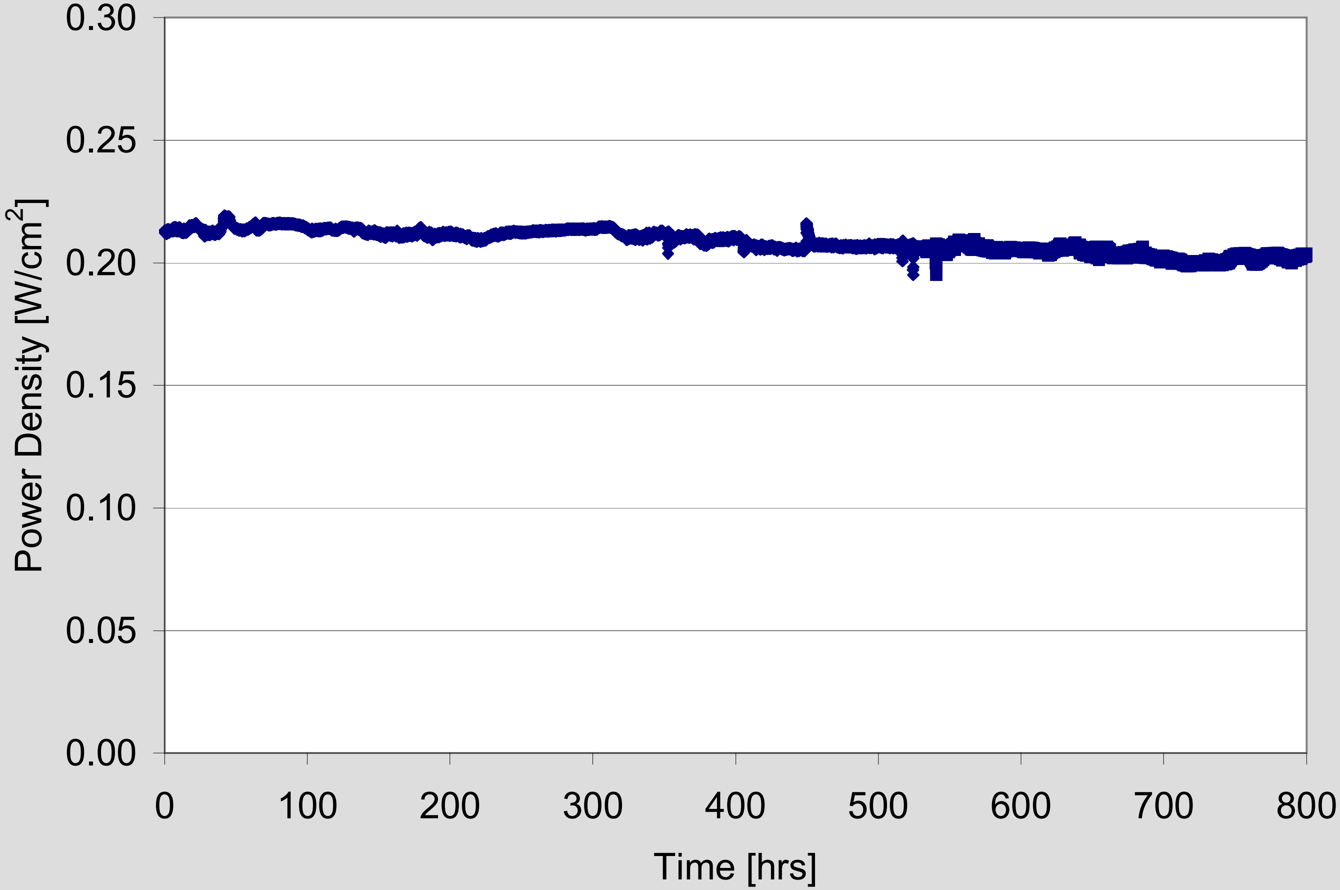
Effect of Trace Contaminant Species

Results: Extended Testing



SOFC Power Density Operating at 800 °C and 0.25 Acm^{-2} Over Time with AsH_3 concentration of 0.1 ppm.

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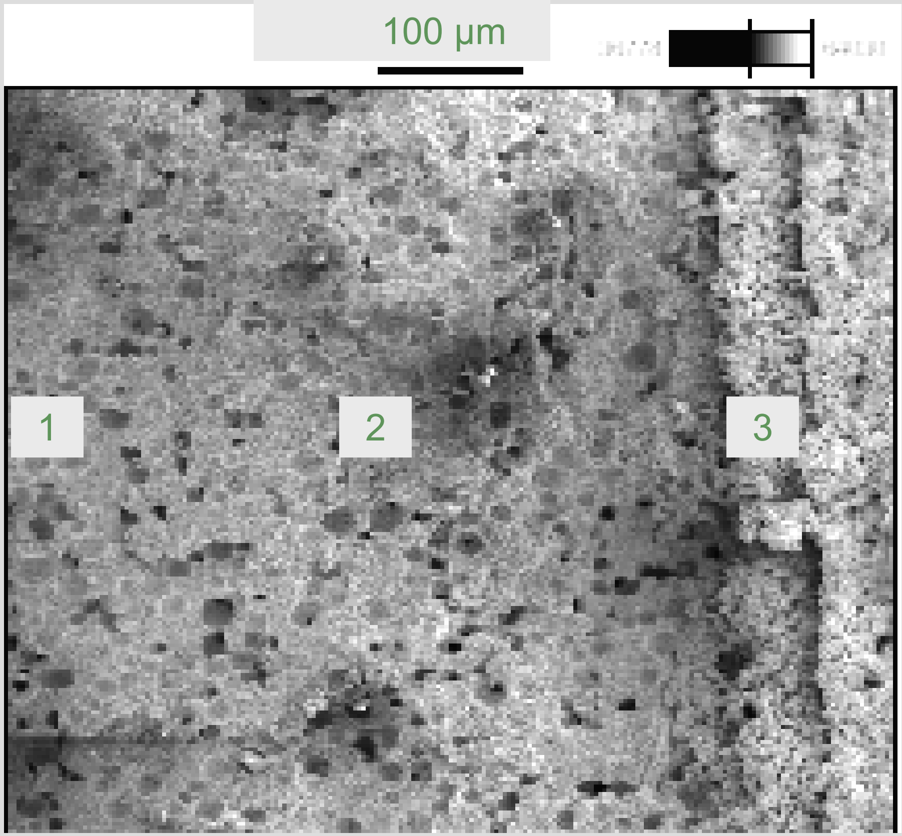
Effect of Trace Contaminant Species

Results: Post Trial Analyses (As)



Representative SOFC anode cross section at 200x.

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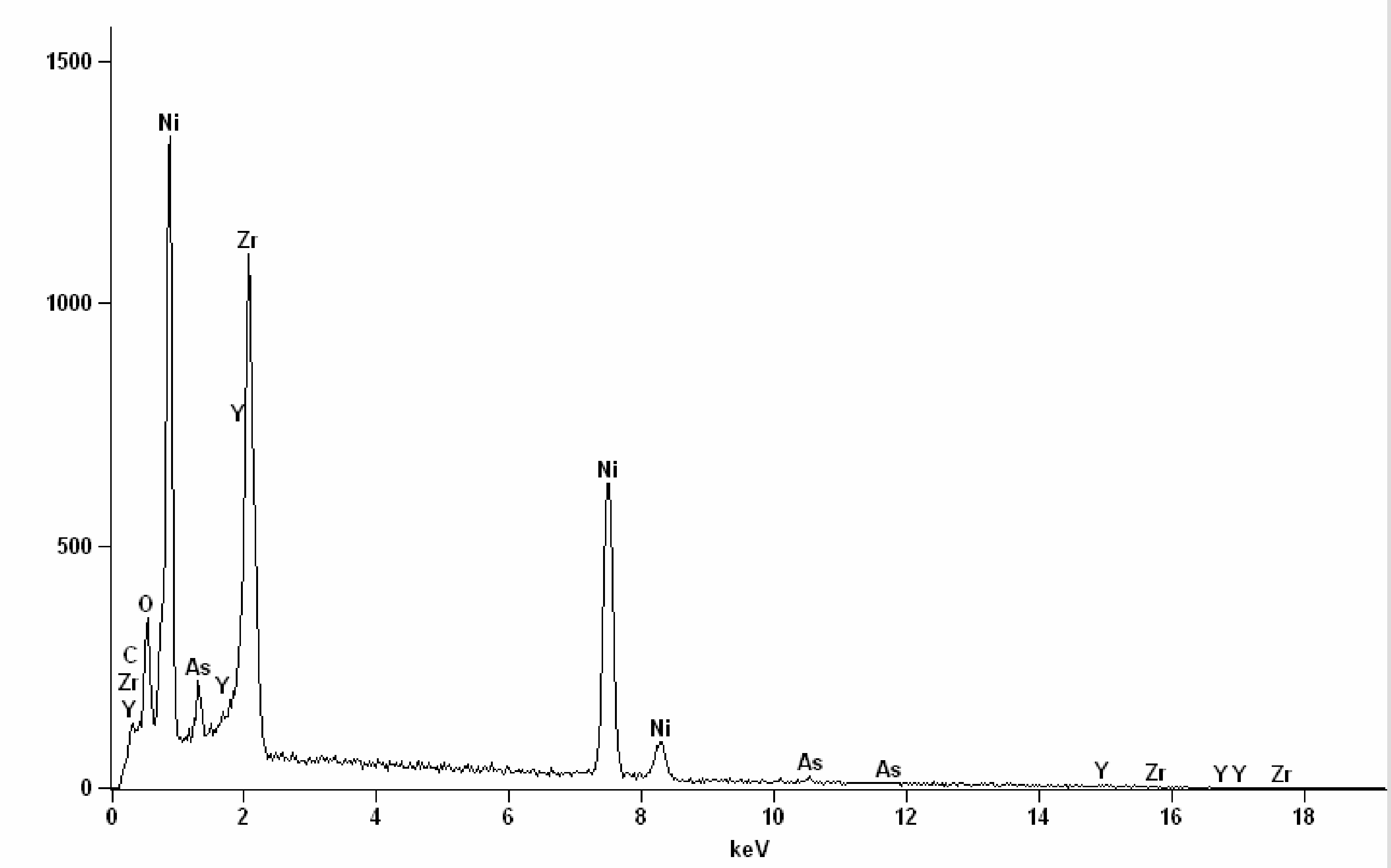
Effect of Trace Contaminant Species

Results: Post Trial Analyses



EDS spectrums from point shown in extended trial test with 0.1 ppm AsH_3.

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Effect of Trace Contaminant Species

AsH_3 Conclusions

- Results show that secondary nickel arsenide phase is able to form.
- 1 and 2 ppm AsH_3 causes little degradation initially.
- After 100 hrs of operation 1 and 2 ppm AsH_3 shows to cause some degradation.
- AsH_3 effect on SOFC not nearly as acute as other trace species such as HCl or H_2S.
- The kinetics associated with the formation of nickel arsenide are slow.
- The nickel arsenide phase that forms is not purely resistive.
- Longer term tests (> 1500 hrs) are recommended to better understand the formation of secondary nickel phase.

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Acknowledgments

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