RUSS COLLEGE of Engineering and Technology

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

Dave Bayless, Jason Trembly, Greg Kremer, Ben Stuart, and Andres Marquez

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

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)

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

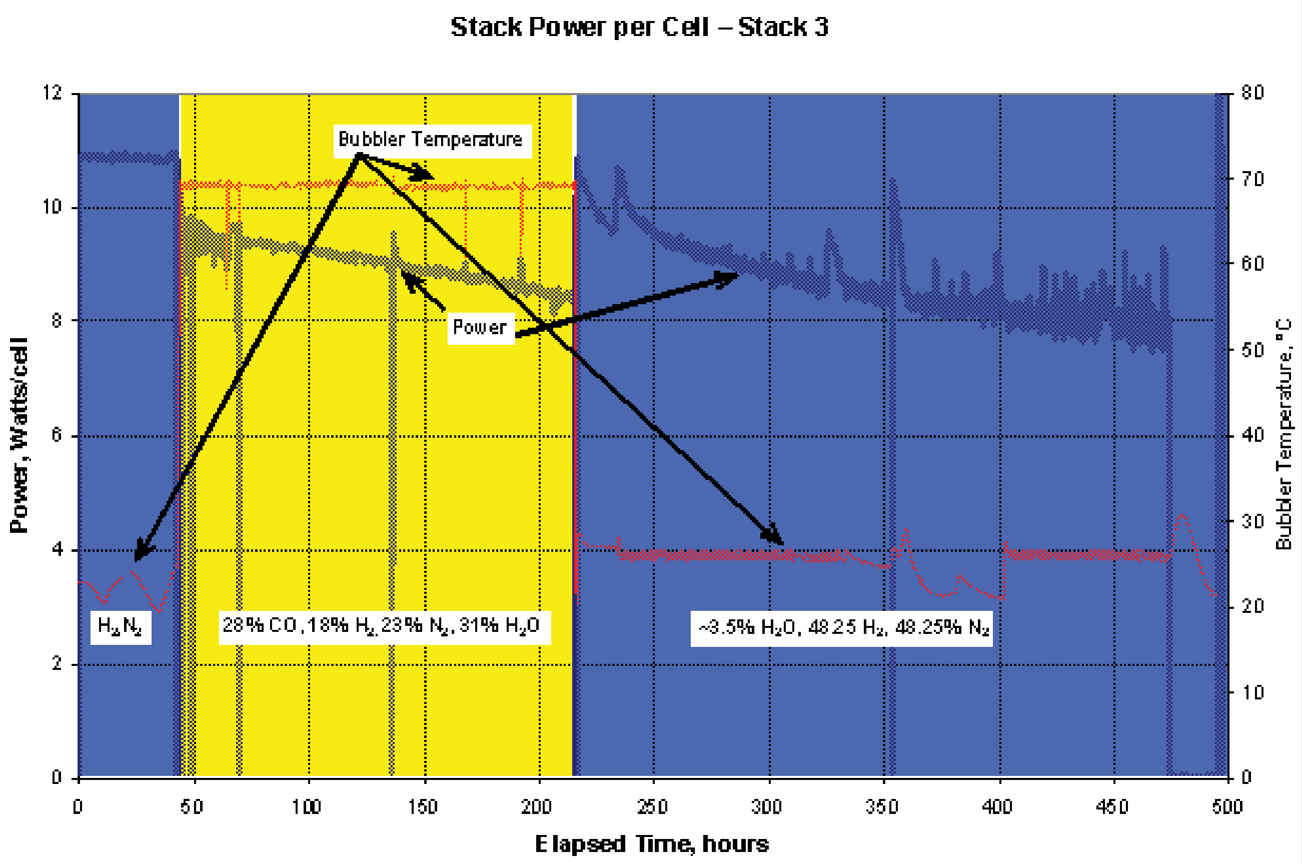
- PSOFC Area Specific Resistance (ASR) measured by completing V-I scans; ASR histories plotted and studied

- 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.

Stack Testing – Effect of H_2S

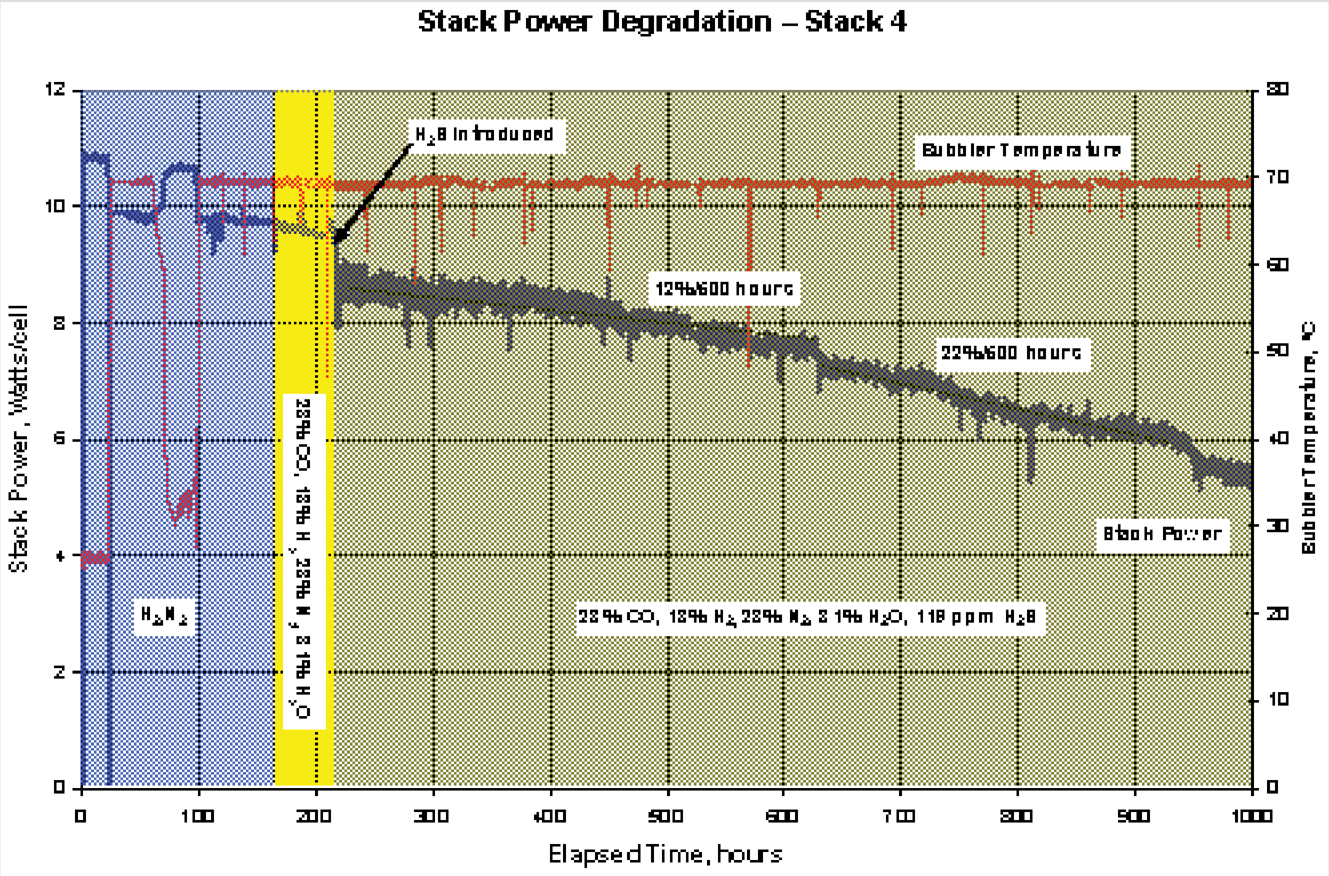
Results



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

Stack Testing – Effect of H_2S

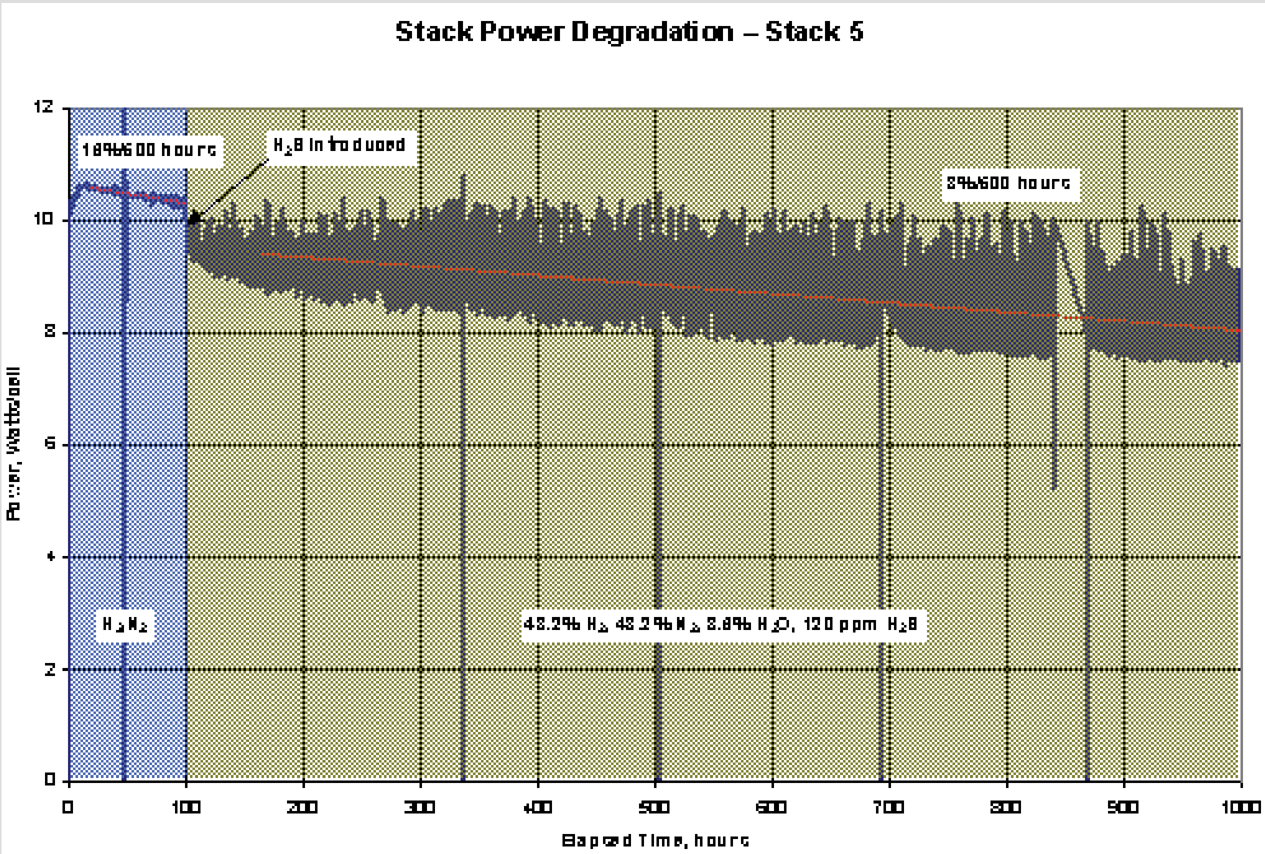
Results



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

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.

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.

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

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.

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

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**

Effect of Trace Contaminant Species

Thermodynamic Evaluation

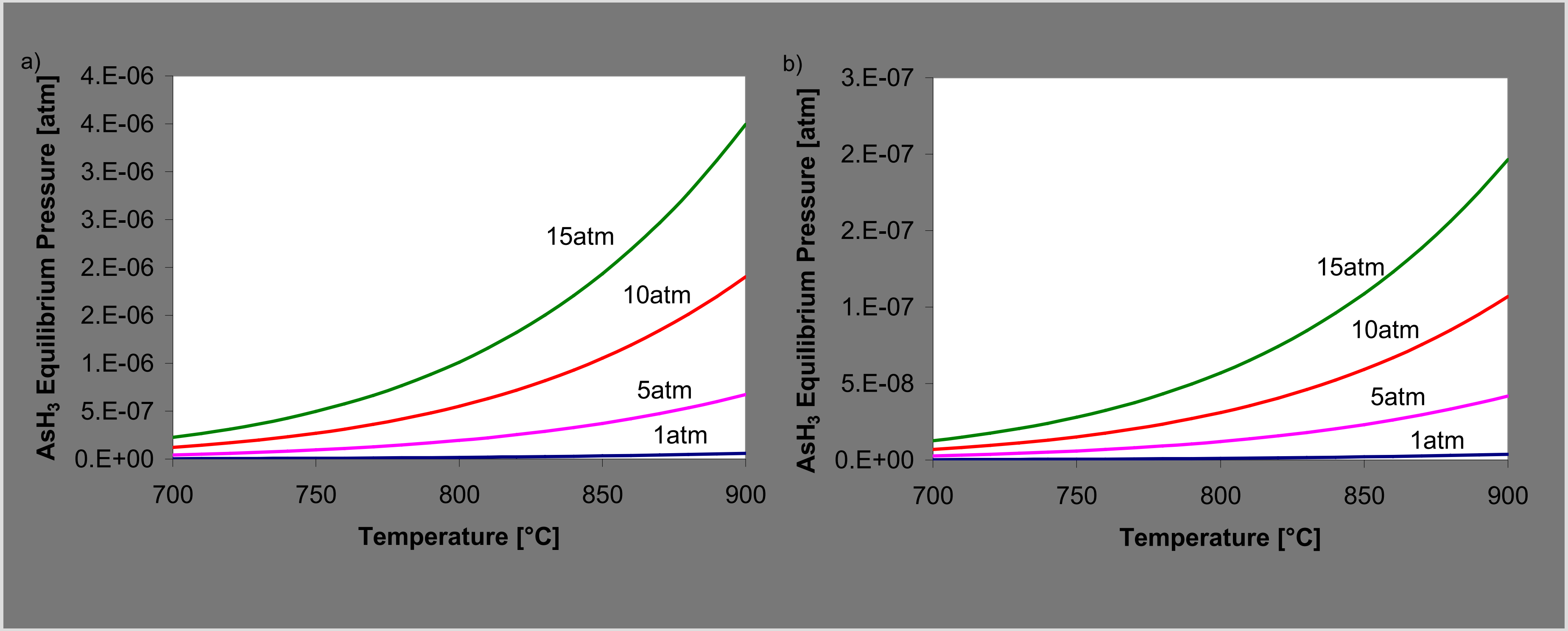
Trace Species Behavior [10].

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**

Effect of Trace Contaminant Species

As/Anode Interactions

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

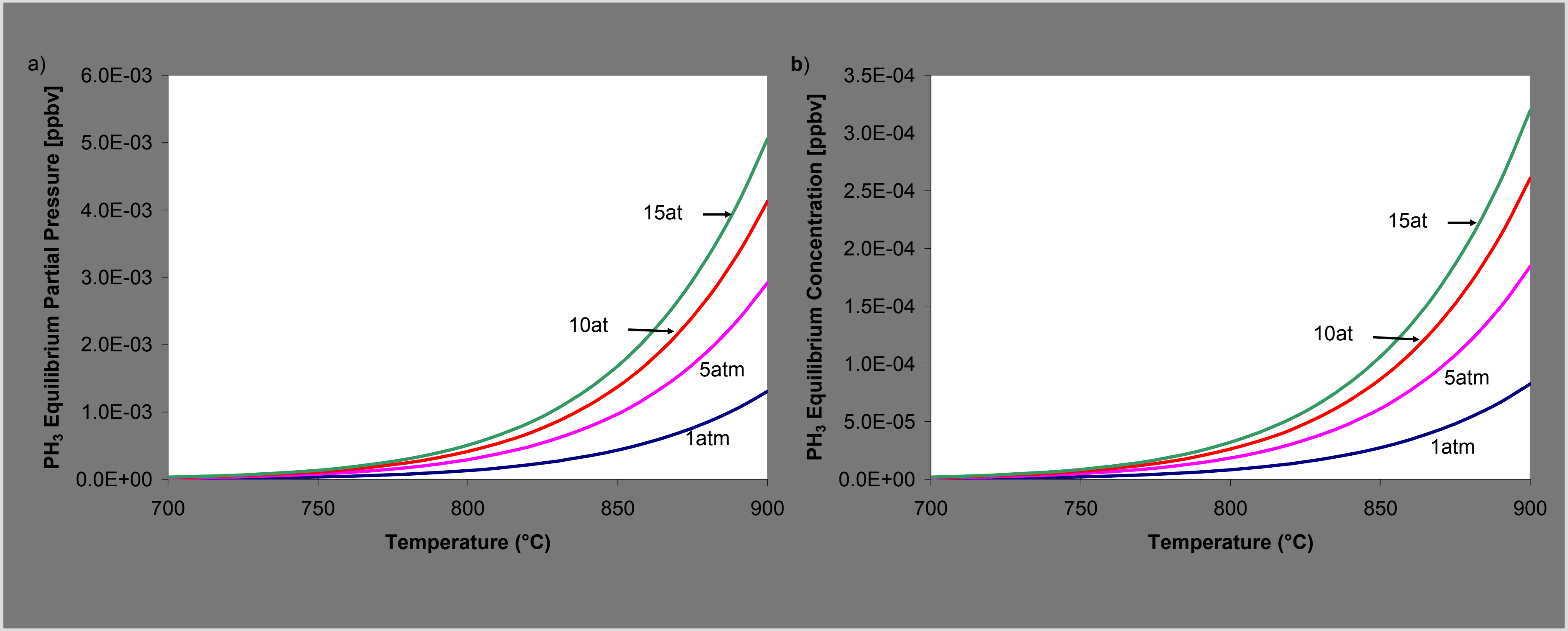


Equilibrium Pressures of AsH_3 at SOFC Operation Conditions at the Inlet (a) and Outlet (b) [10].

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].

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**

Effect of Trace Contaminant Species

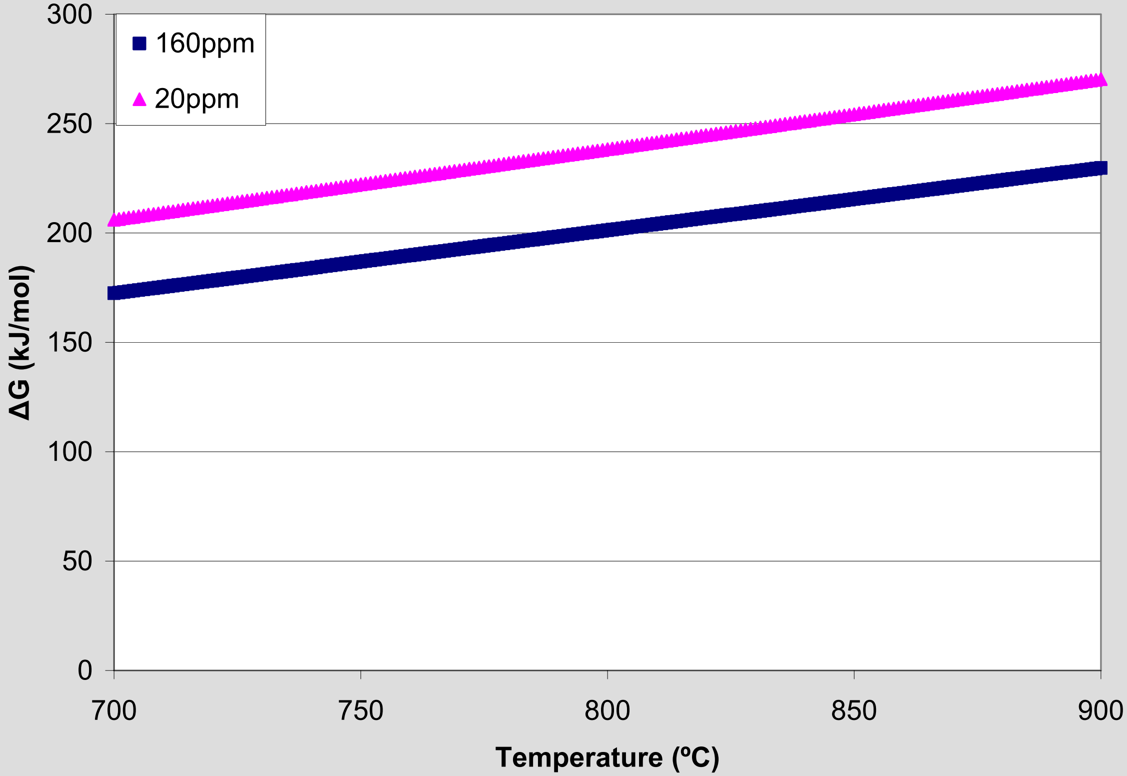
Chlorine in Syngas

- 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].

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.

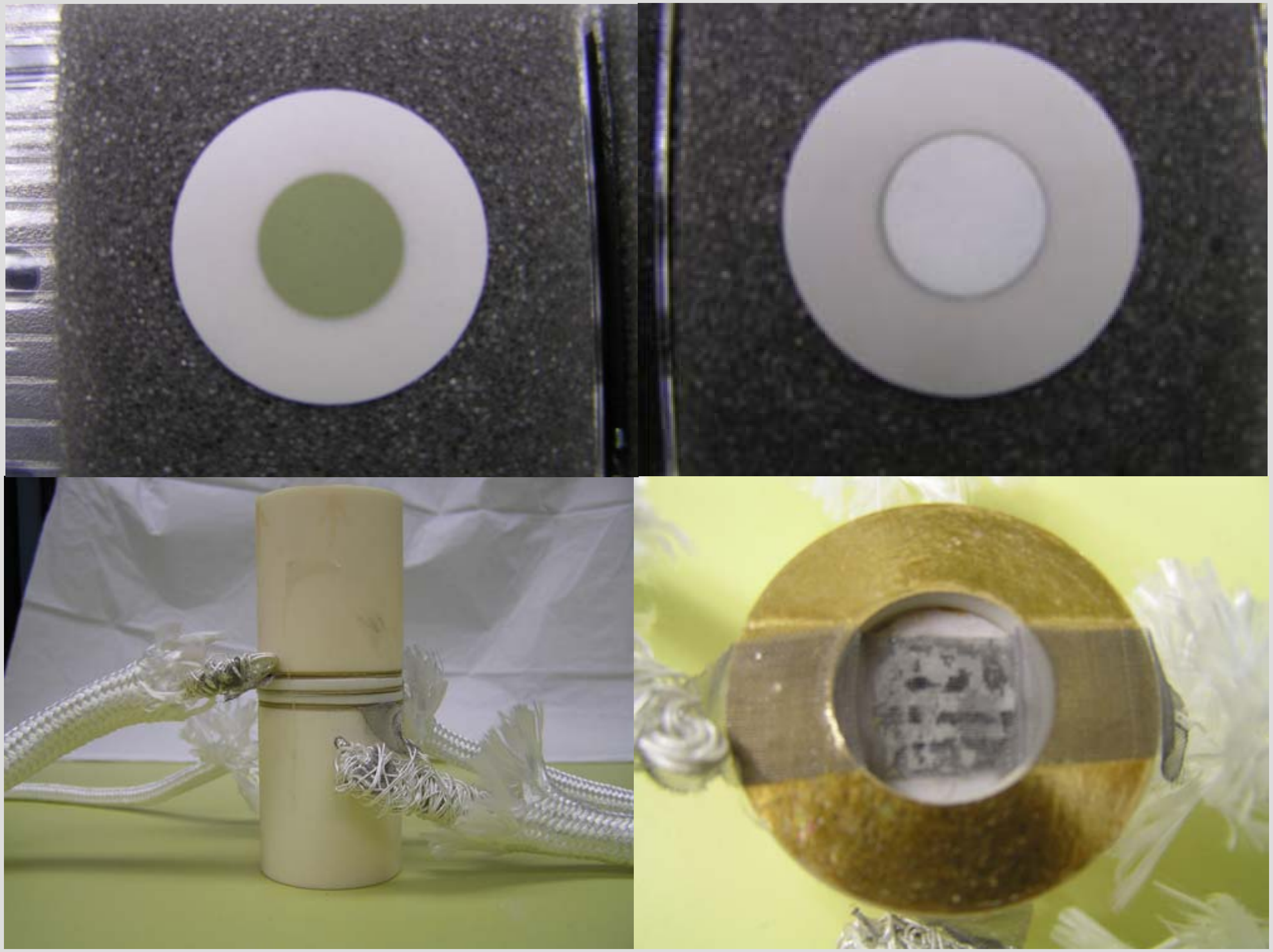
Experimental

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

Experimental

Button Cells



Screen Printed Top Layer and Button Cell Setup

Effect of Trace Contaminant Species

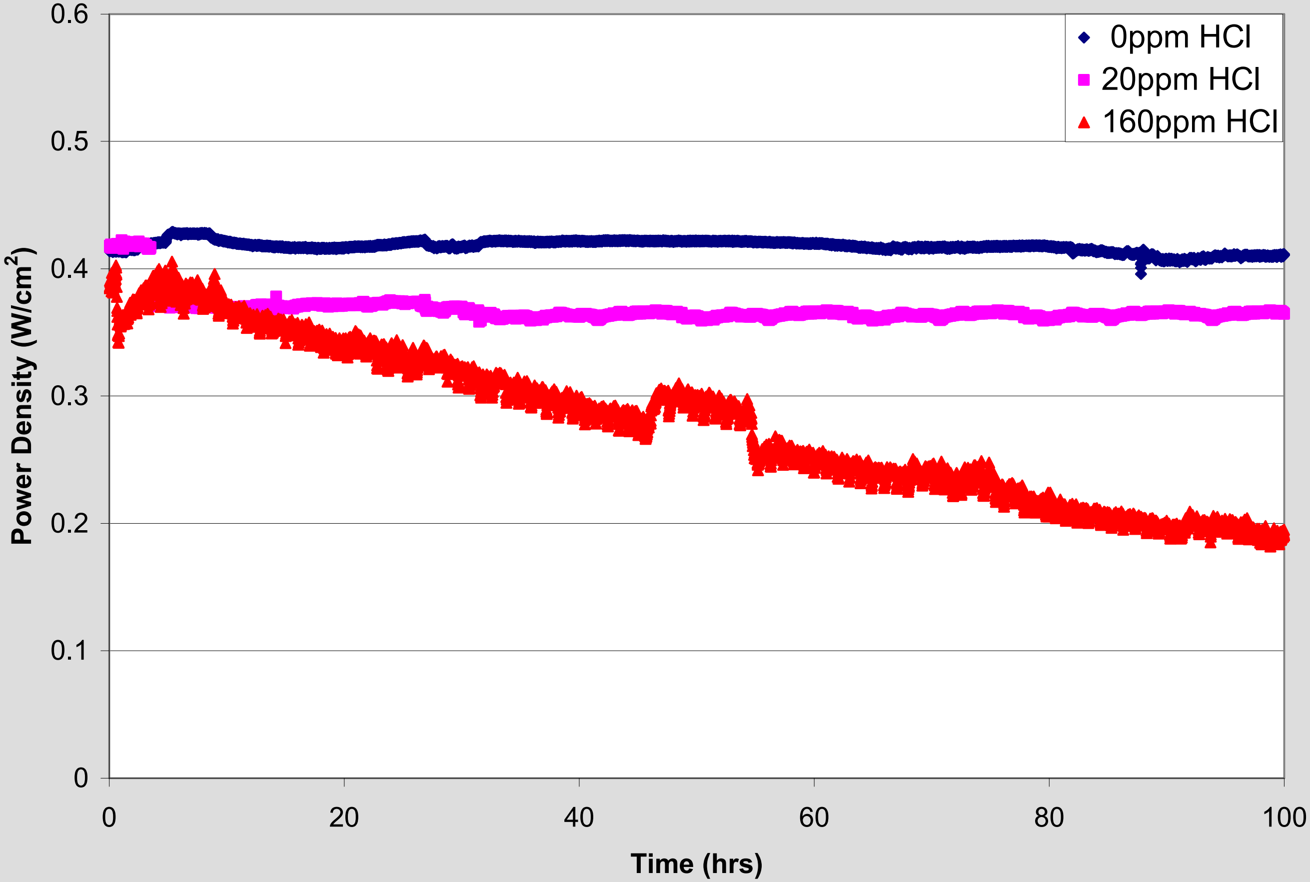
Effect of HCl on SOFCs

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

Effect of Trace Contaminant Species

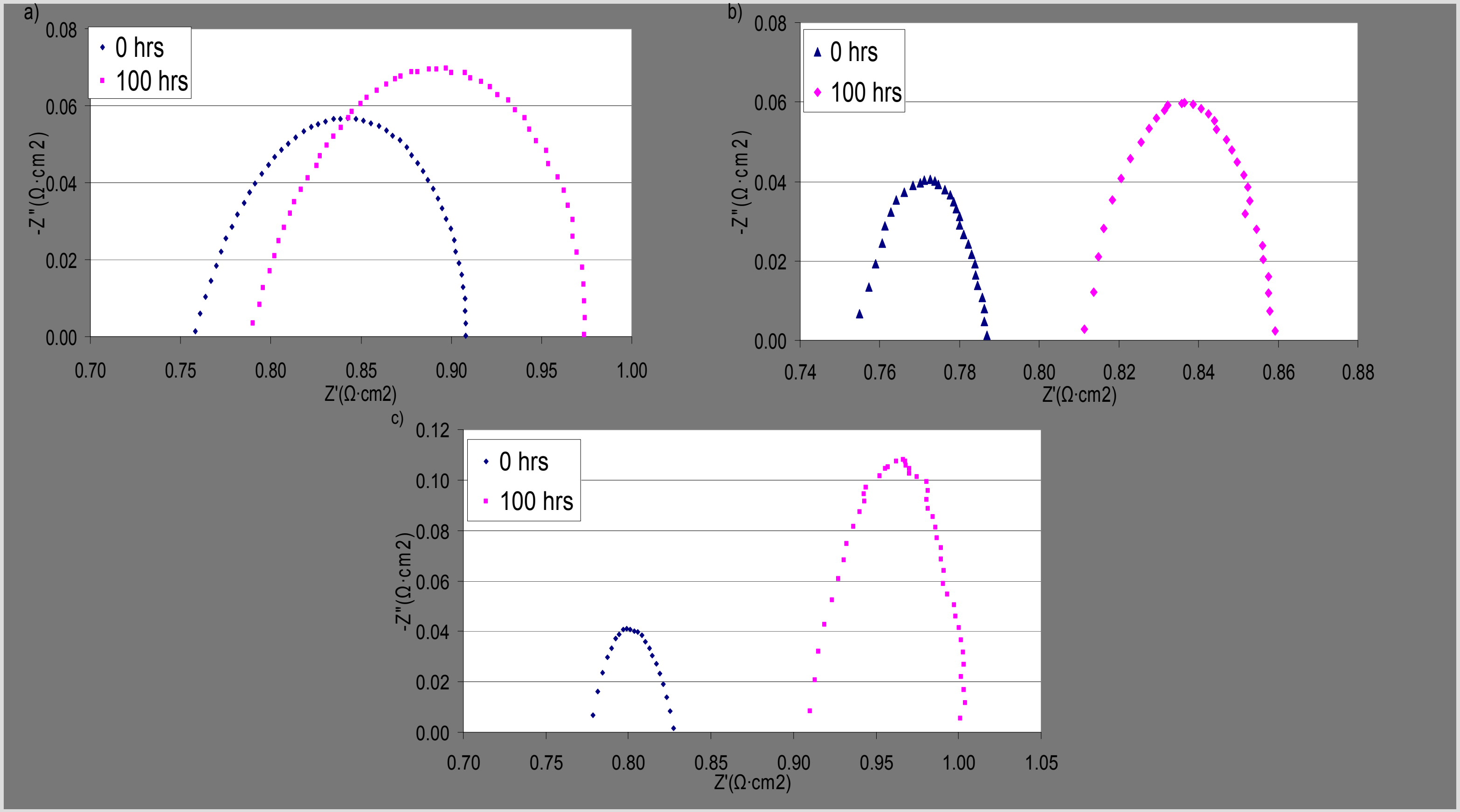
Results: 20ppm and 160ppm HCl



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

Effect of Trace Contaminant Species

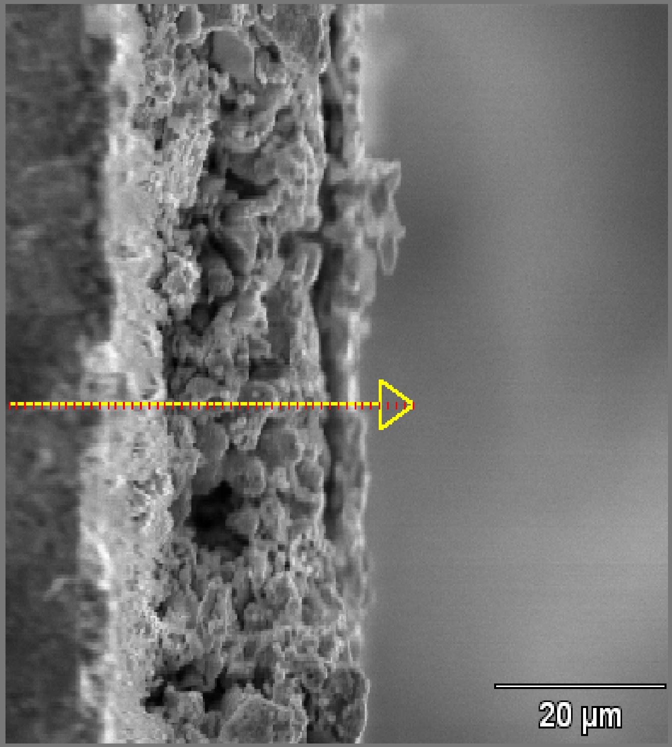
Results: 20ppm and 160ppm HCl

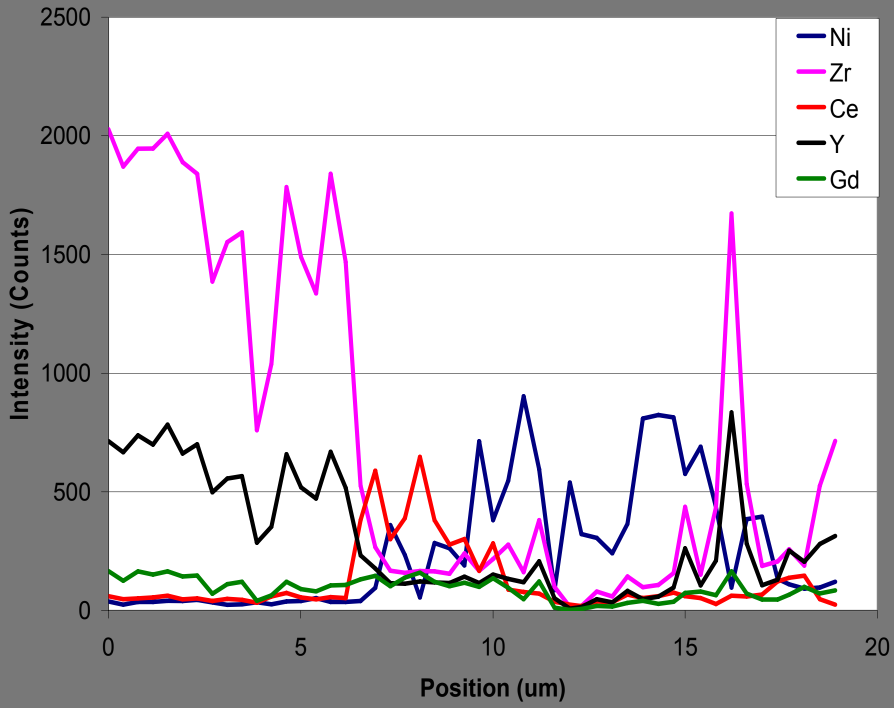


EIS Data for SOFC Operating at 800°C and 0.7V Over Time with HCl Concentrations of 0ppm, 20ppm, and 160ppm [11].

Effect of Trace Contaminant Species

Results: 20ppm and 160ppm HCl

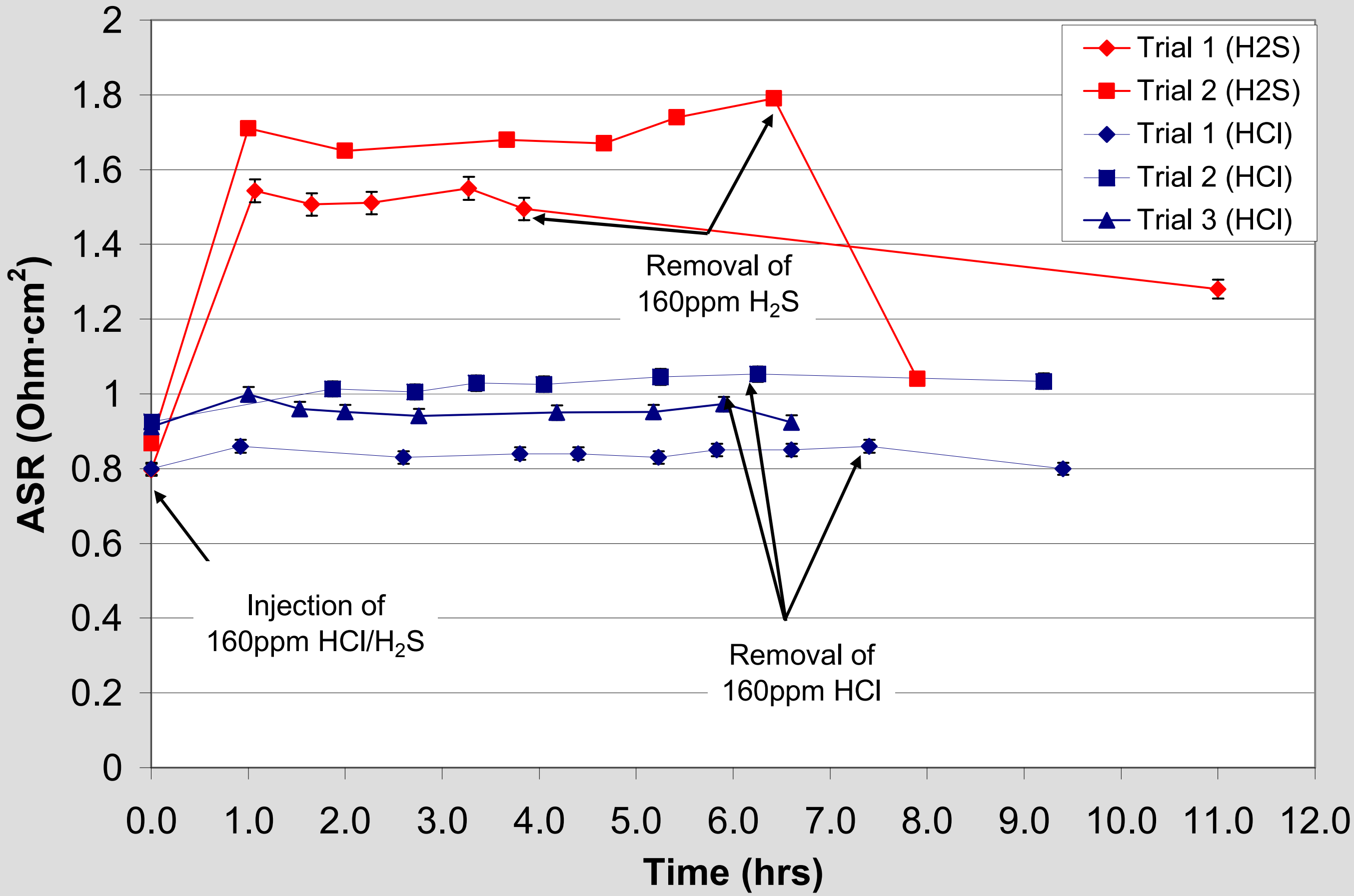




SEM Image of SOFC Cross Section and EDS Linescan. [11].

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].

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.

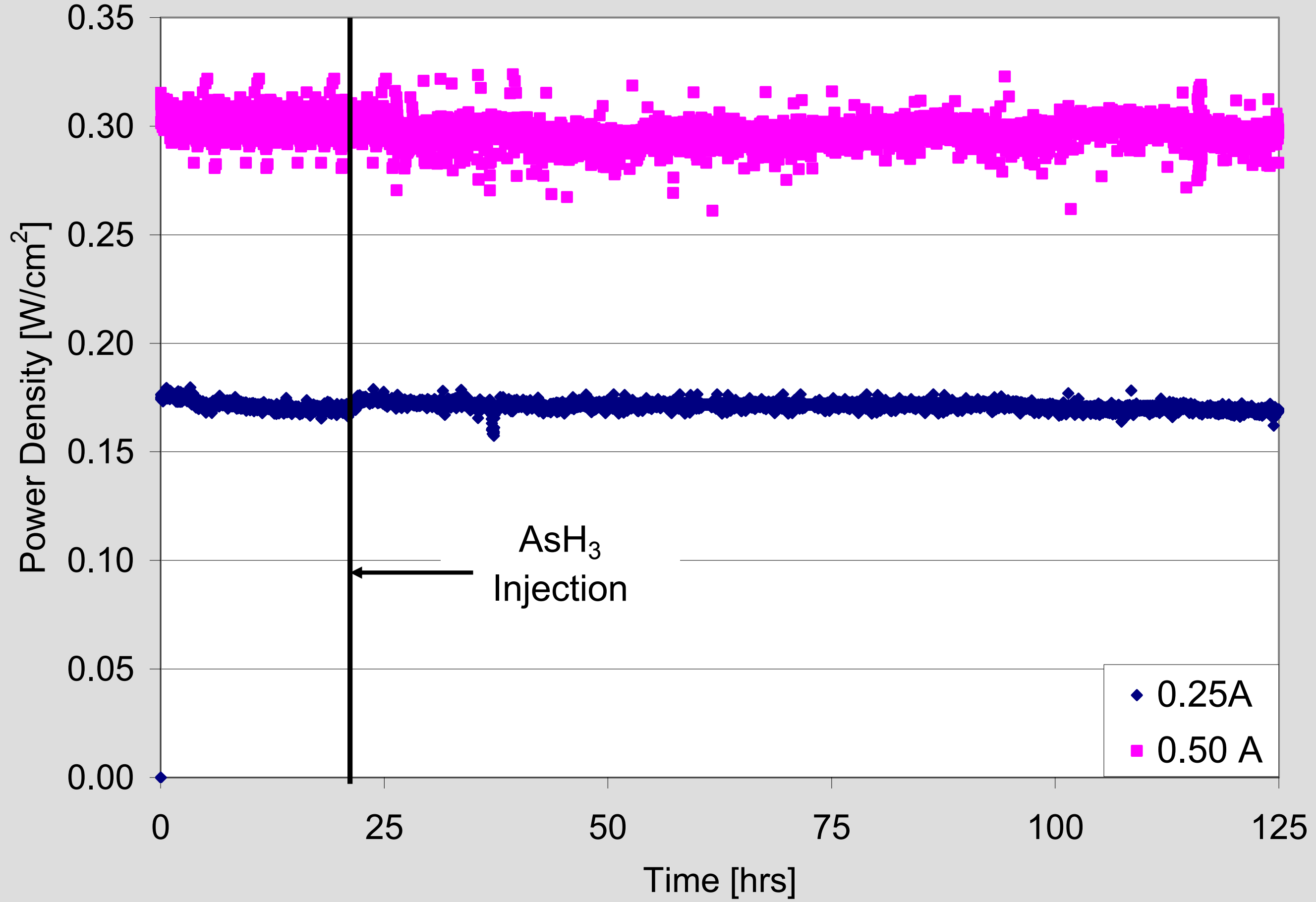
Effect of Trace Contaminant Species

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.

Effect of Trace Contaminant Species

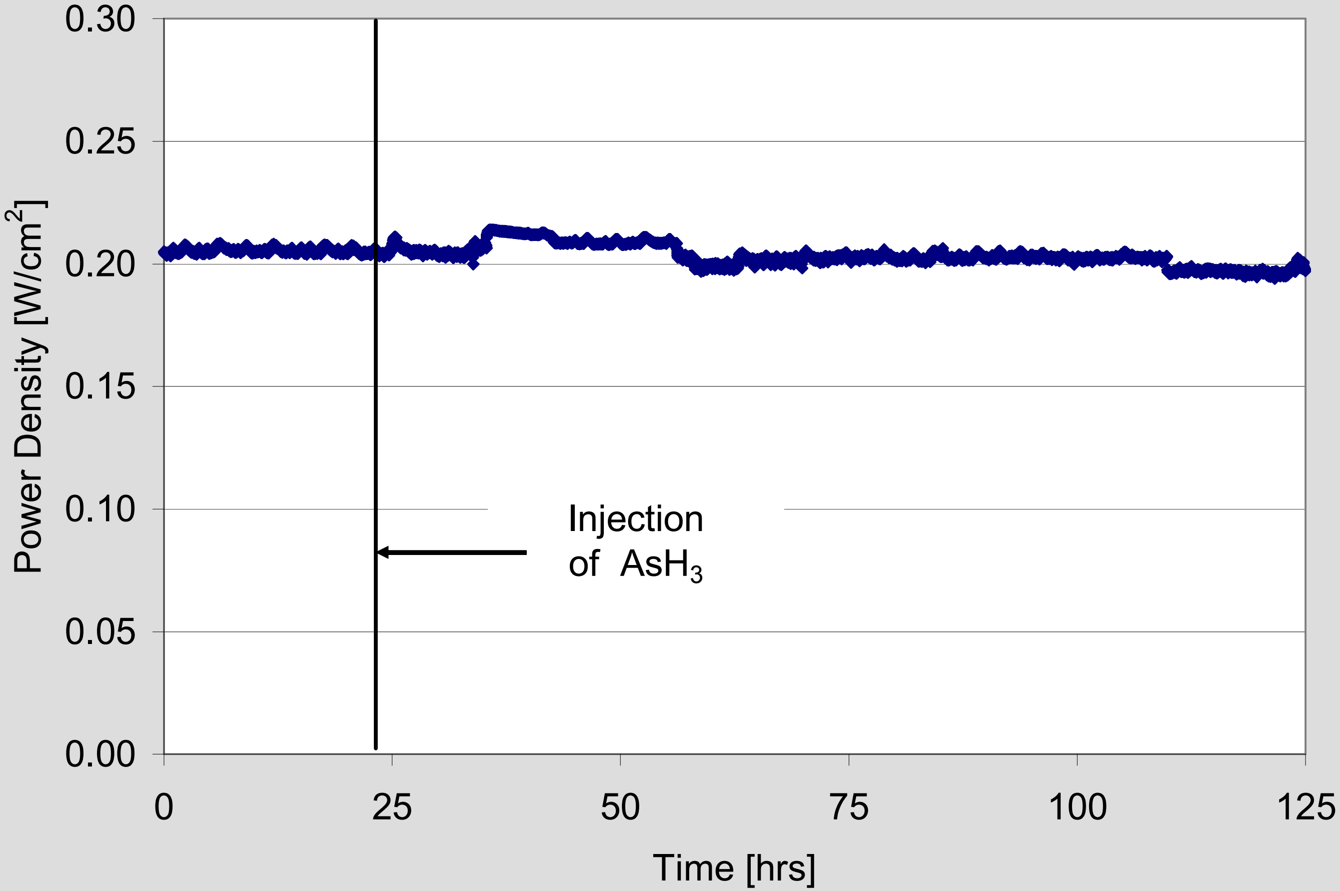
Results: 1 ppm AsH_3



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

Effect of Trace Contaminant Species

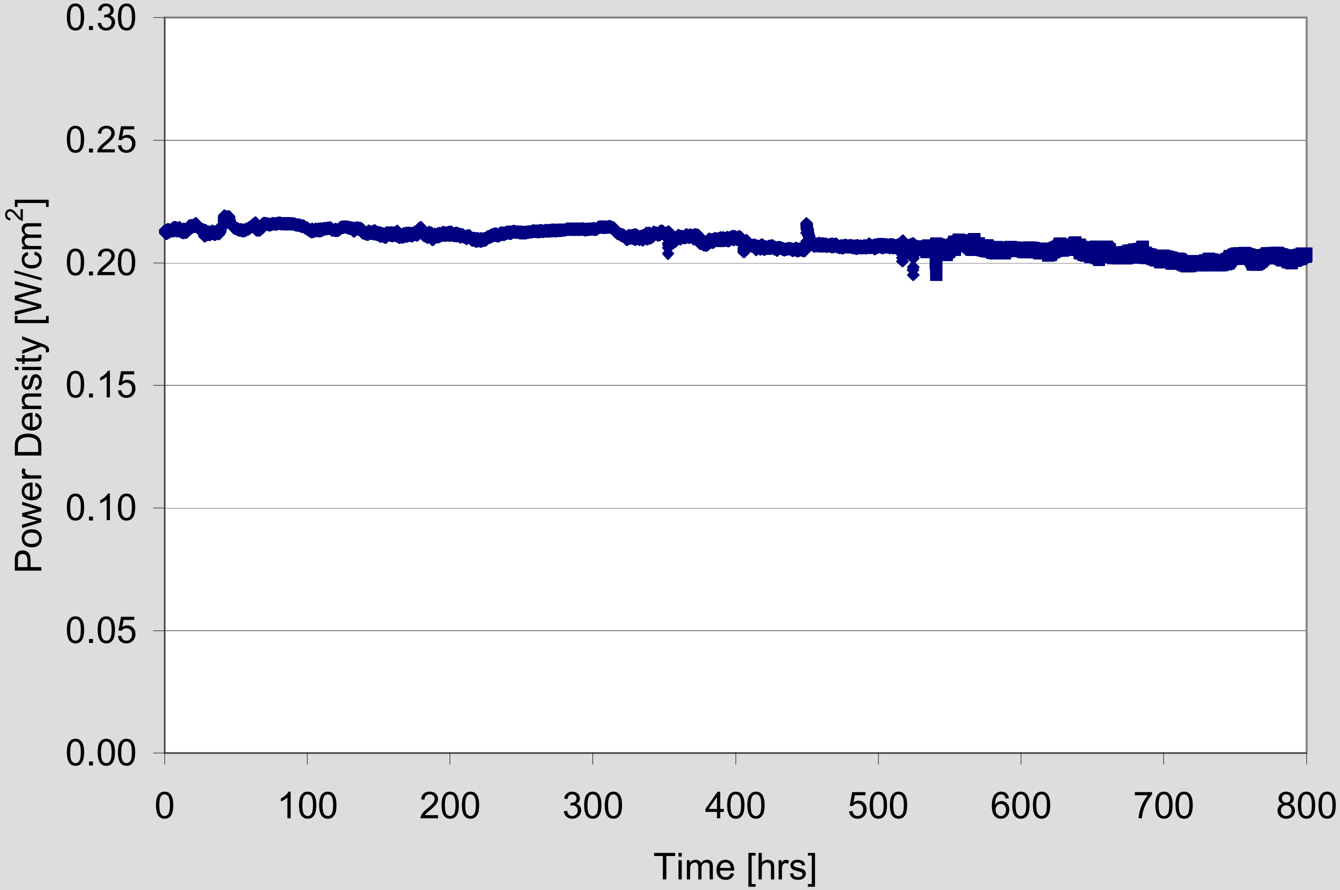
Results: 2 ppm AsH_3



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

Effect of Trace Contaminant Species

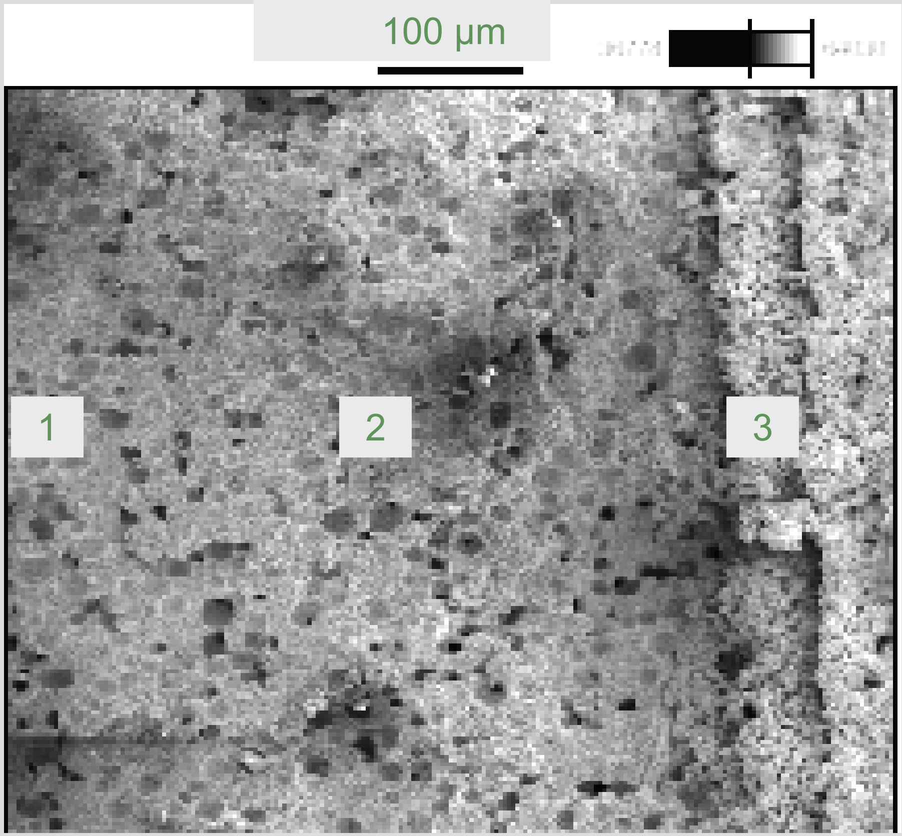
Results: Extended Testing



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

Effect of Trace Contaminant Species

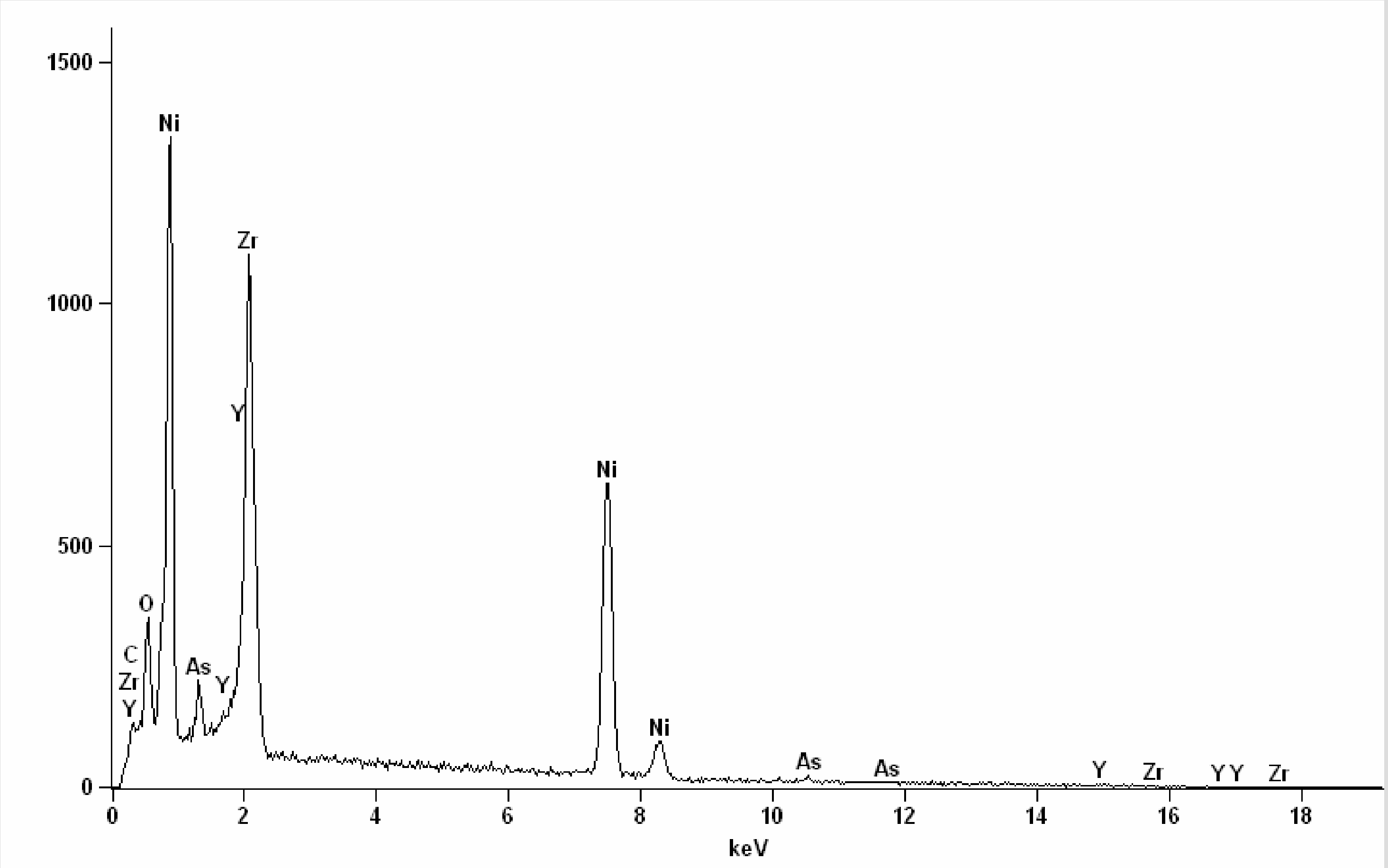
Results: Post Trial Analyses (As)



Representative SOFC anode cross section at 200x.

Effect of Trace Contaminant Species

Results: Post Trial Analyses



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

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.

References

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Acknowledgments

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