SOFC Operation on Hydrogen and Coal Gas in the Presence of Phosphorus, Arsenic and Sulfur Impurities

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Outline

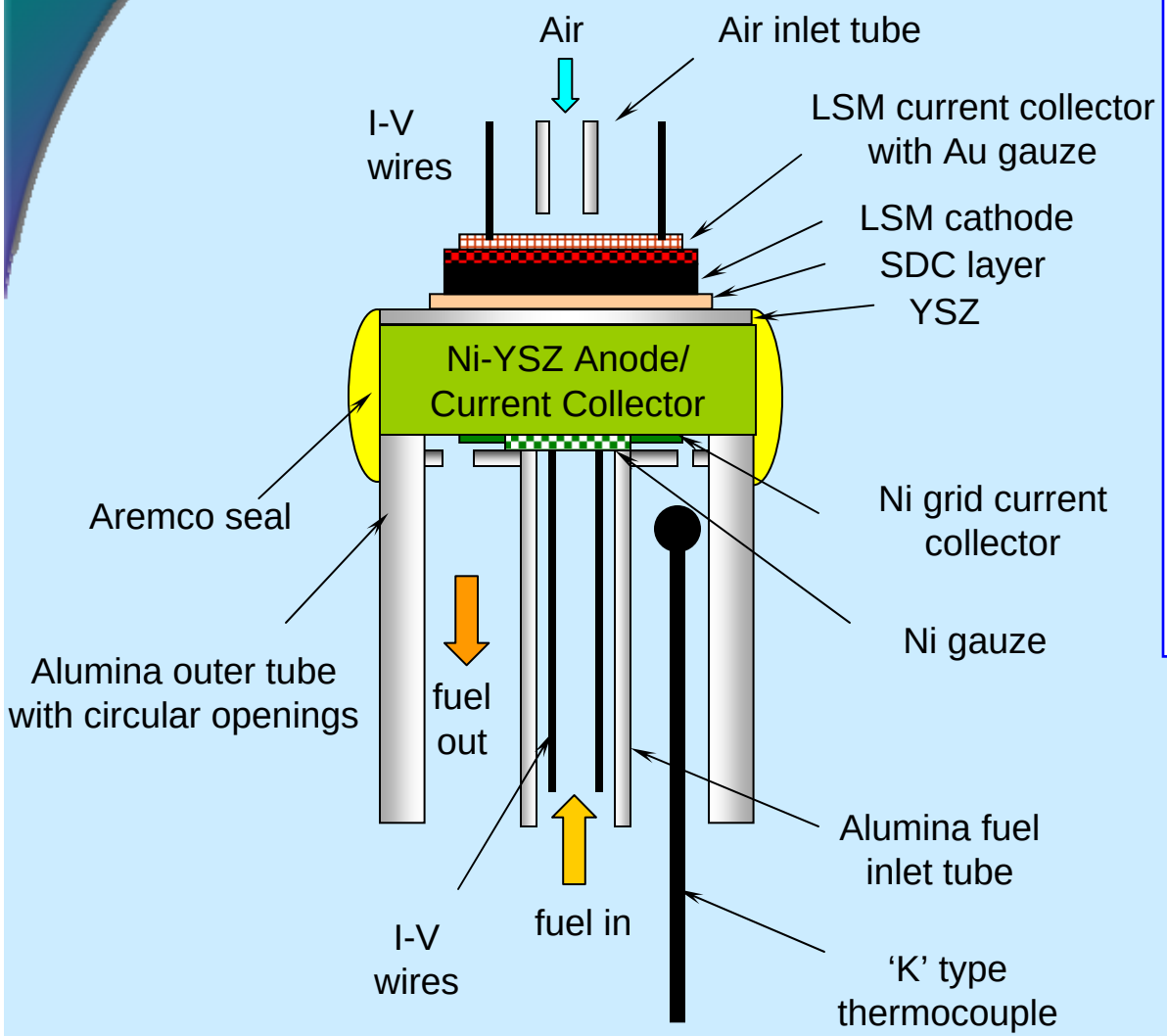
- Objective
- Experimental Results
- Post-mortem cell investigations using SEM/EDS, TEM, EBSD, XPS, ToF-SIMS, and XRD
- Summary

Objective and Approach

- Evaluate performance of SOFCs operating on coal gas assuming warm gas clean-up

- Phosphorus, arsenic, and antimony are potentially the most harmful to the Ni/YSZ anode because of possible second phase formation with Ni
- Studies also were performed with key contaminants in hydrogen to aid in poisoning mechanism understanding
- Adsorption studies on small Ni, Ni/YSZ, Ni/SDC coupons were performed to determine the interactions between Ni and P or As as a function of exposure time

Schematic of Button Cell Test Stands



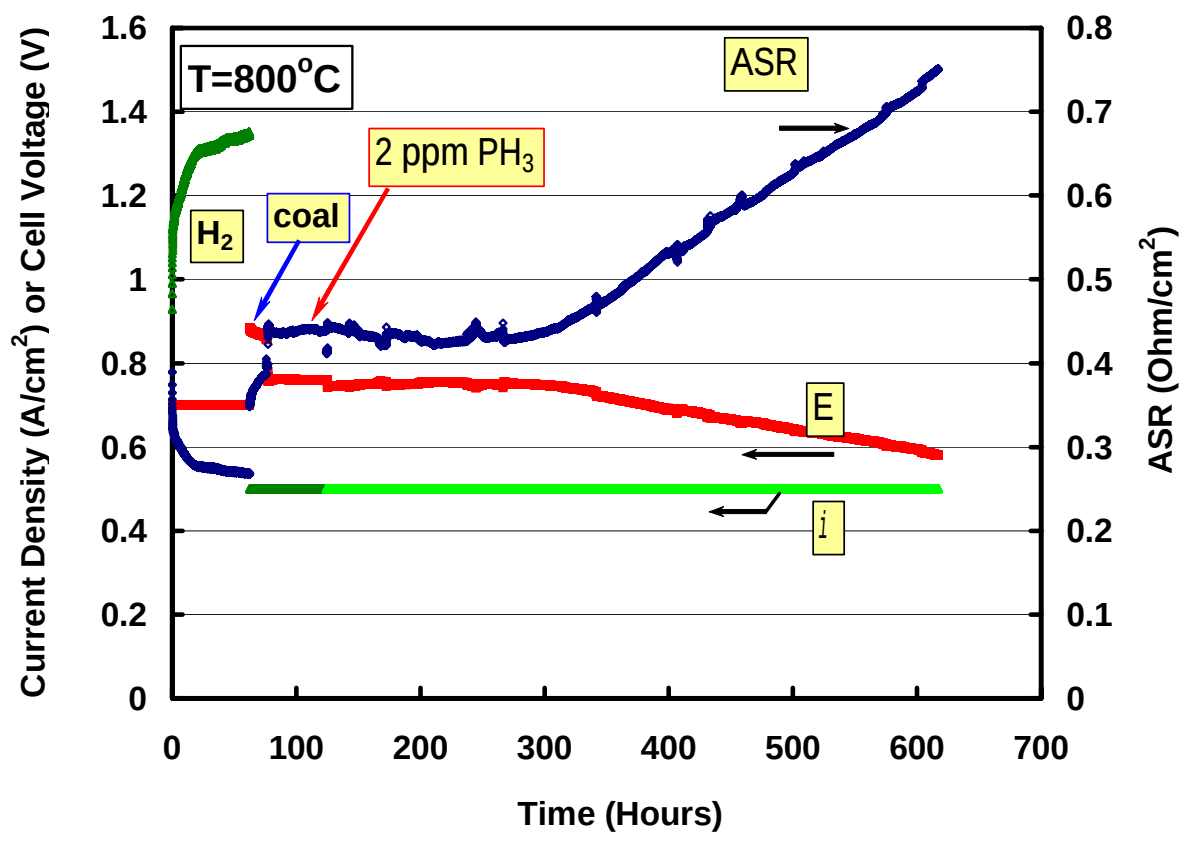
Test Conditions:

- 700 and 800°C
- Fuel (at equilibrium): H_2/H_2O = 97/3 or $H_2/CO/CO_2/H_2O$ = 30/23/21/26
- Initially preconditioned in H_2 at 0.7 V for 24-30 hours followed by 0.5 A/cm^2 in H_2 or coal gas for ~100 hours
- All impurities were added after water bubbler
- Tested at a current of 0.5 A/cm^2

Standard Ni/YSZ anode:

- 50 vol% Ni (solids) active anode (~ 8 µm)
- 40 vol% Ni (solids) bulk anode ~ 800 µm thick

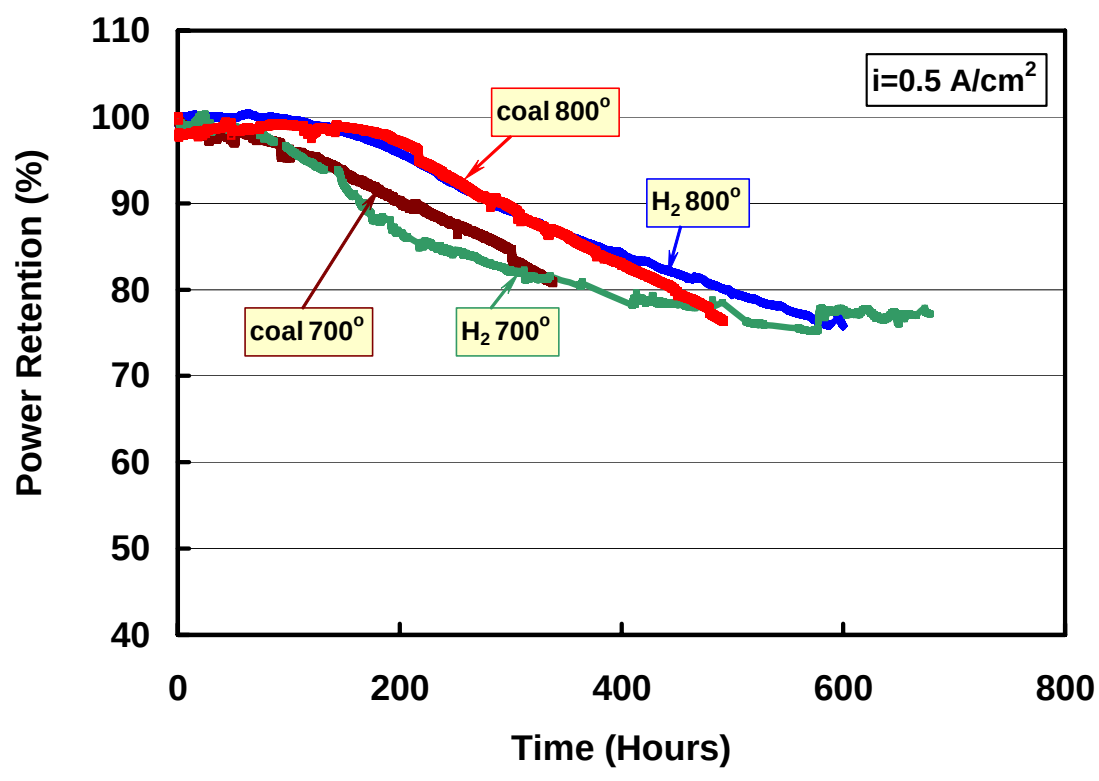
SOFC Performance at 800°C in Coal Gas with 2 ppm of PH_3



- PH_3 exposure leads to cell degradation,

  ~0.13-0.2%/hr increase in ASR
- This degradation is irreversible
- Cells continue to degrade after PH_3 removal from the fuel

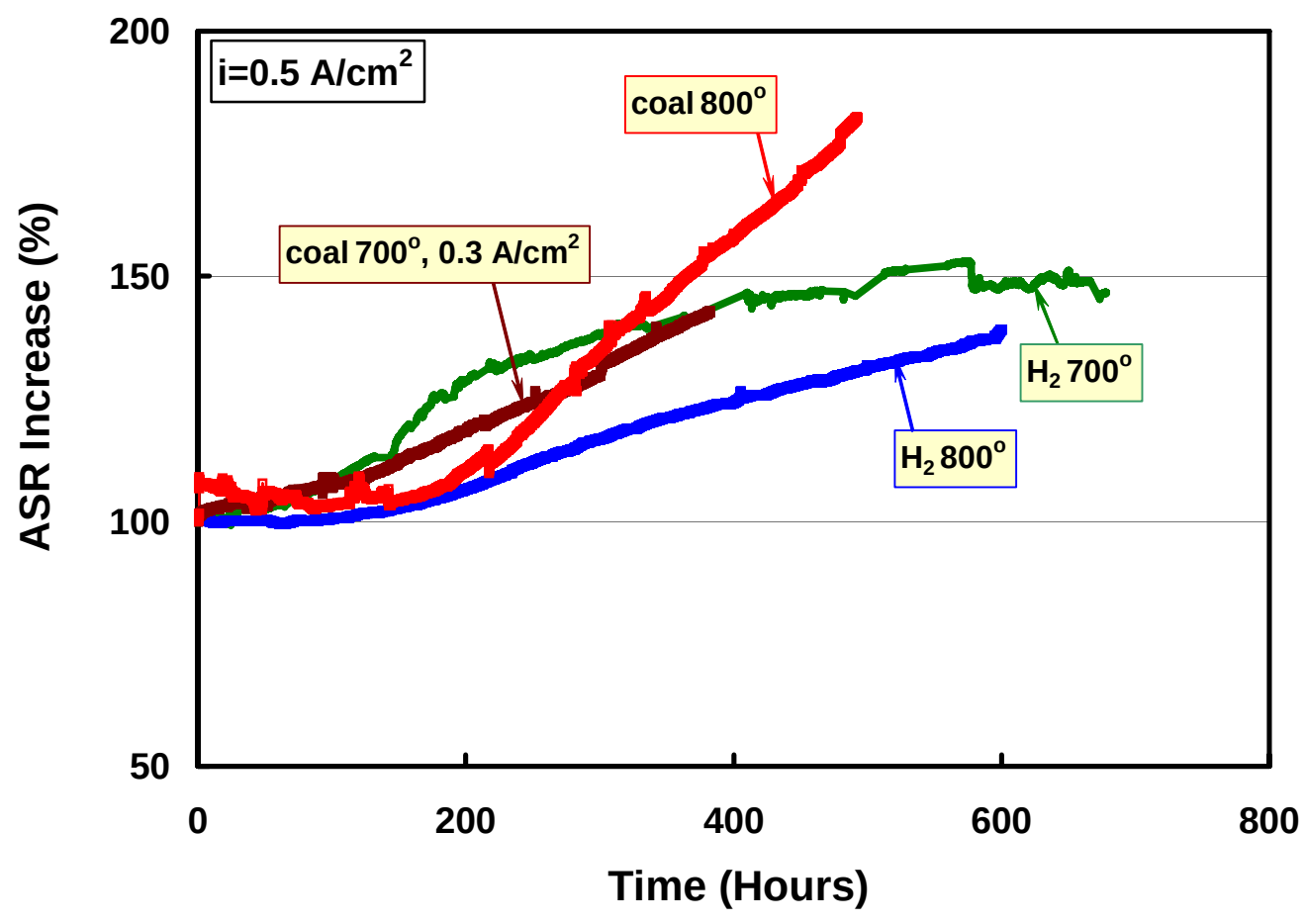
Effect of Phosphorus on Cell Performance



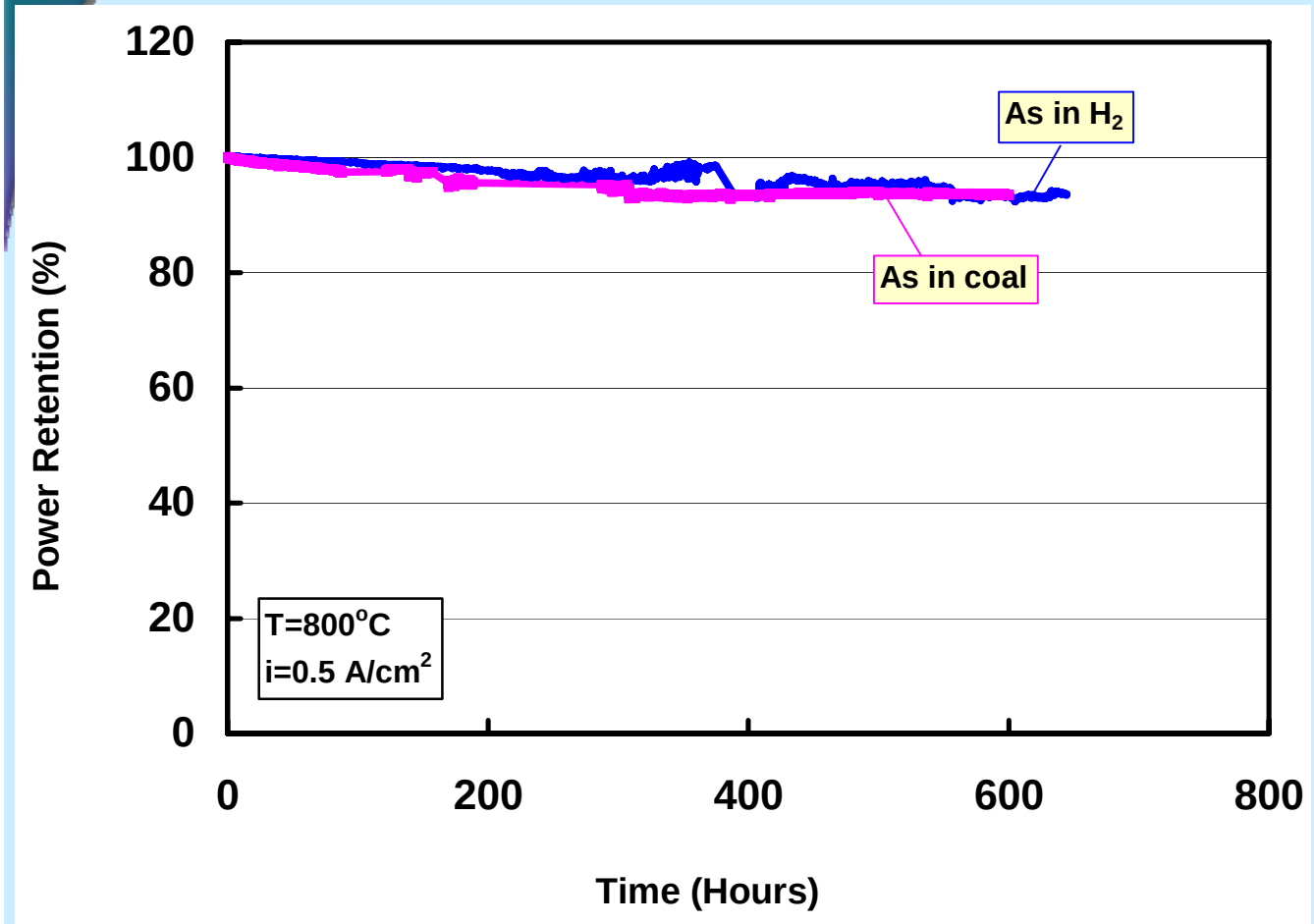
- Power loss onset occurs more rapidly at 700°C
- After onset, degradation rates do not appear to be significantly different at 700 and 800°C

% Power retention calculated after the impurity introduction over power before impurity introduction

More Rapid ASR Increase in Coal Gas



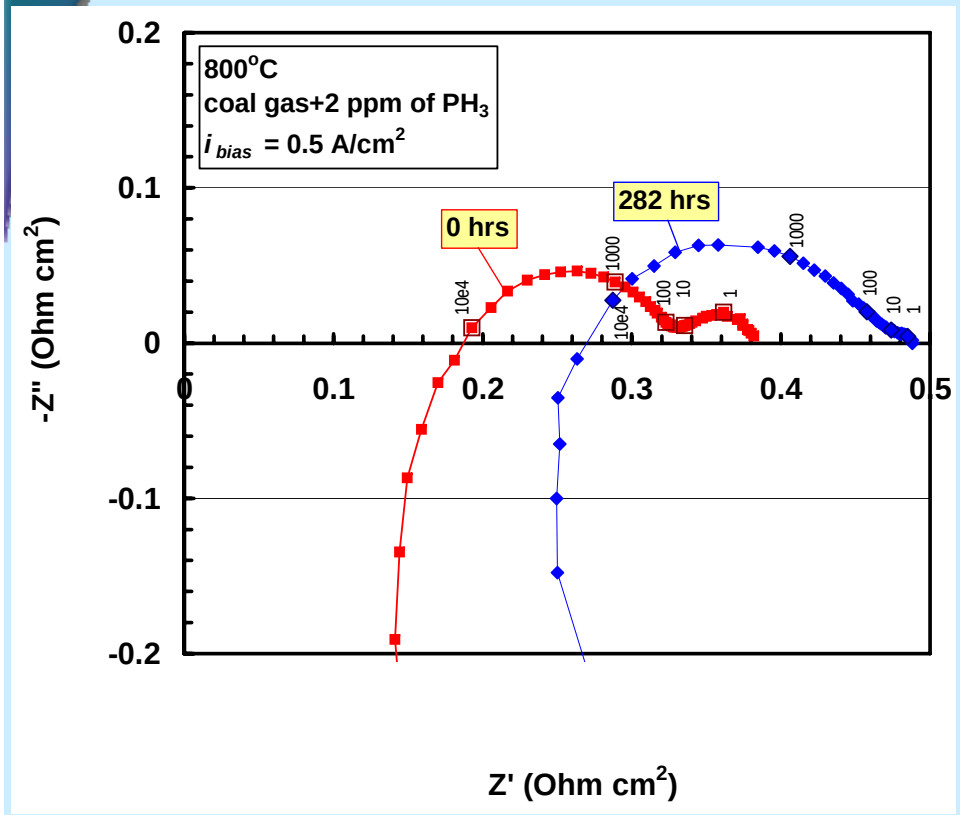
Effect of Arsenic on Cell Performance

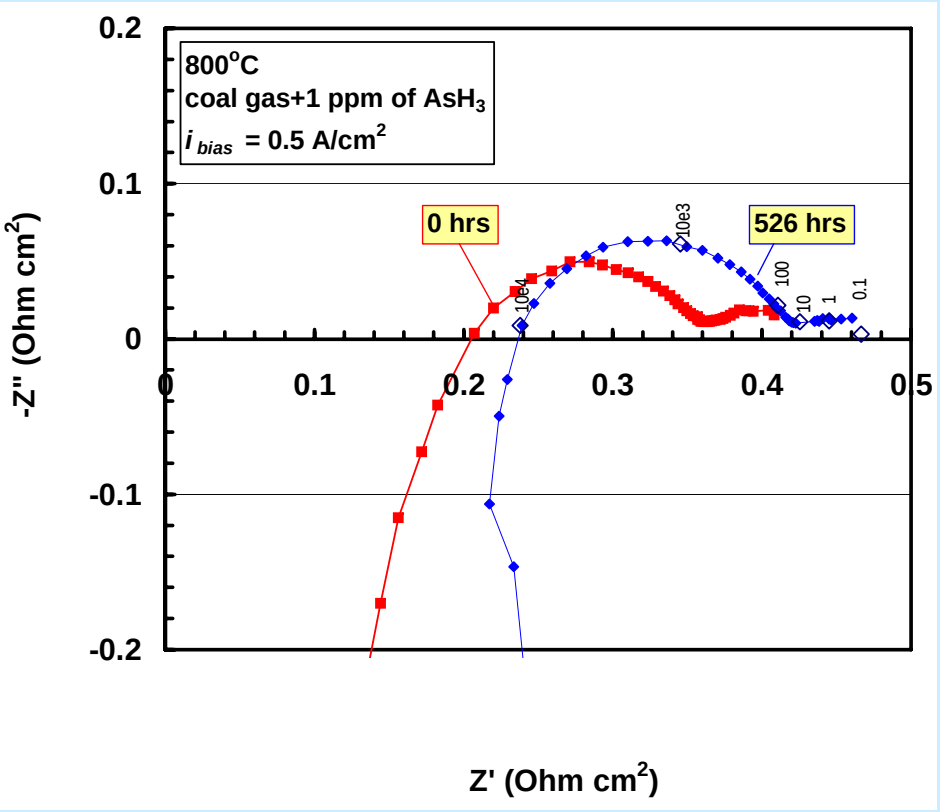


Slow degradation (~1%/100 hr) in the presence of 1 ppm of As in both H_2 and coal gas

1 ppm of AsH_3

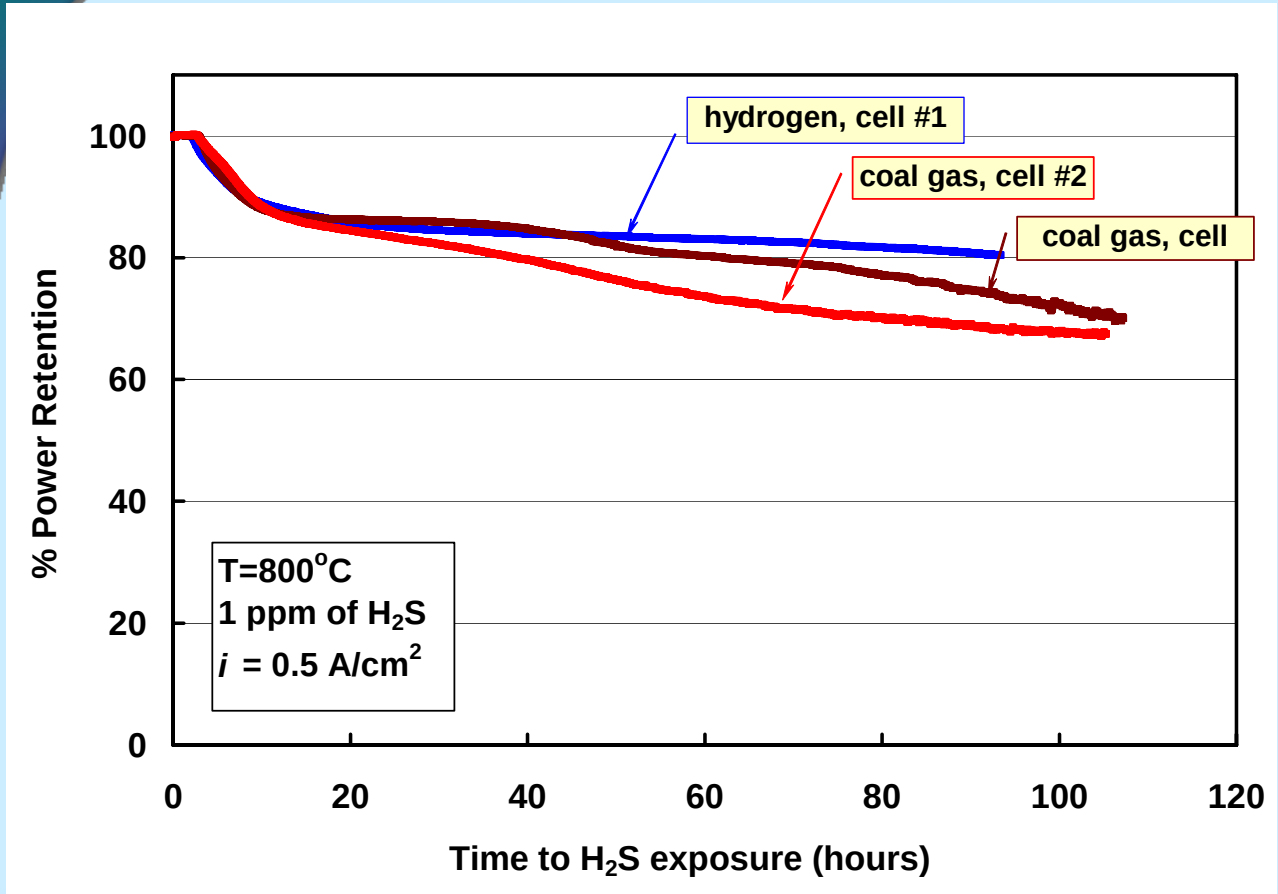
Effect of P and As on Cell Resistance





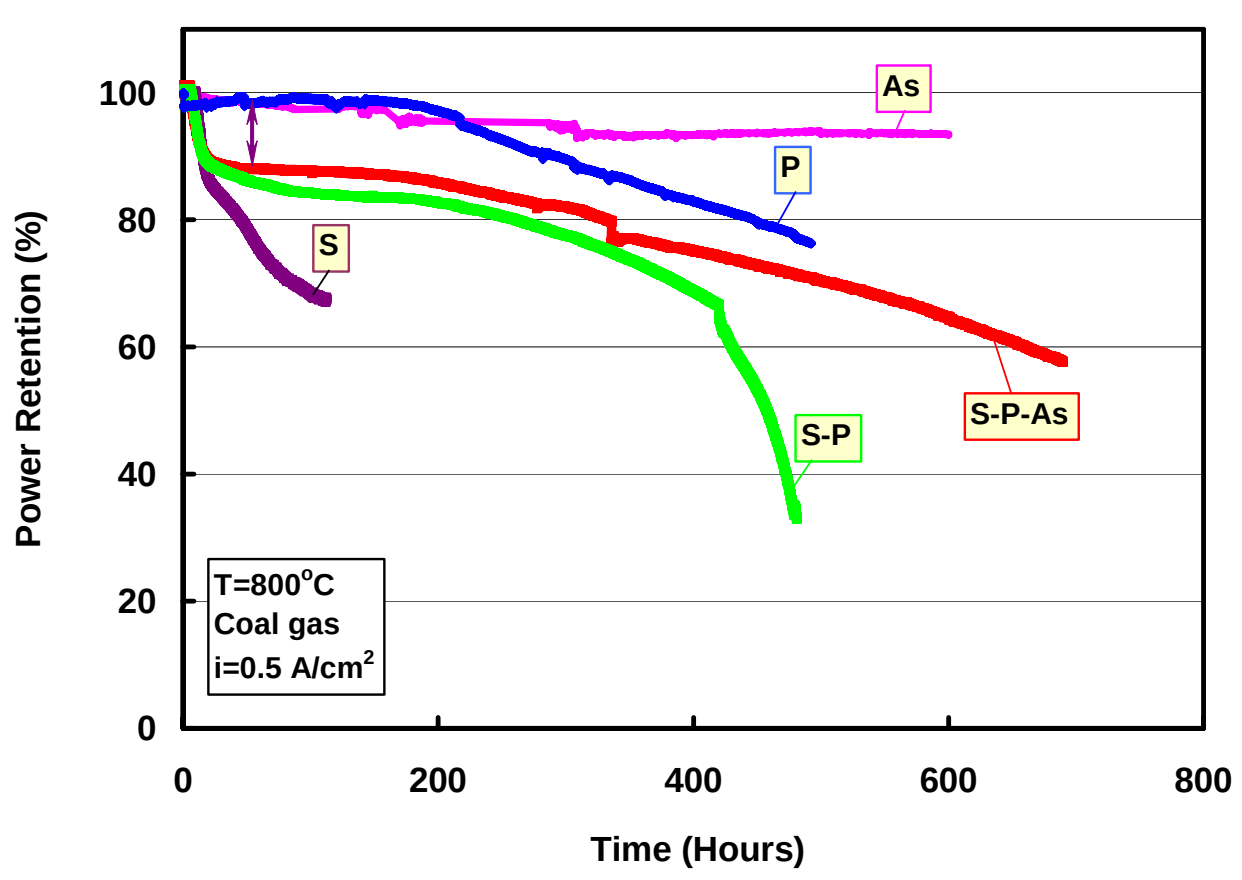
- R_{Ohmic} and $R_{electrodic}$ increase with time of exposure to PH_3
- Change in R_{ohmic} is more significant for AsH_3 exposure

Effect of Sulfur on Cell Performance: Baseline for Tests with Contaminants



- Rapid initial degradation (ca. 15%) during first 30 hours in both H_2 and coal gas
- 2nd stage degradation rate (0.06%/hr in H_2 and 0.26%/hr in coal gas)

Synergistic Effect of P+As+S Contaminants in Coal Gas

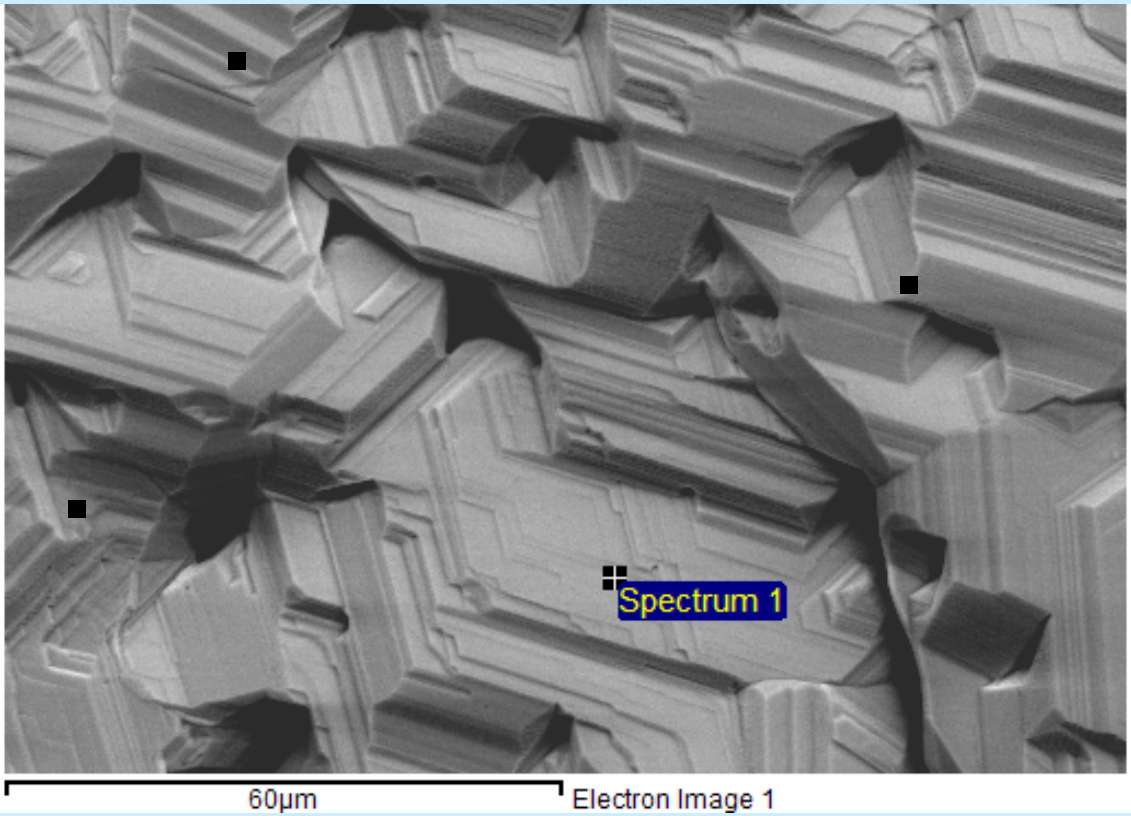


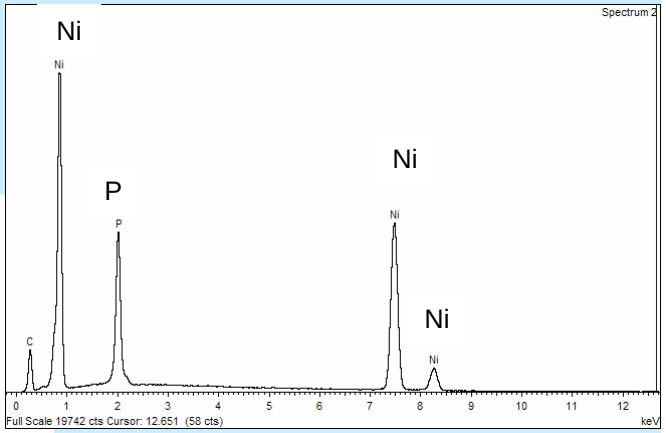
- In the presence of S, initial drop is ca. 15% and appears to be independent of other impurities
  - Effect of S is predominant over first 30 hours
- S-related 2nd stage degradation is suppressed by the presence of P and As
- 2nd stage degradation is similar to that in P

1 ppm of AsH_3, 1 ppm of H_2S, 2 ppm of PH_3

Ni Contact Layer Surface Under the Fuel Inlet after 381 hr Test with 2 ppm of PH_3

All surface Ni under the fuel inlet is converted into Ni_3P. Surface Ni away from the fuel channel is present as the metal.



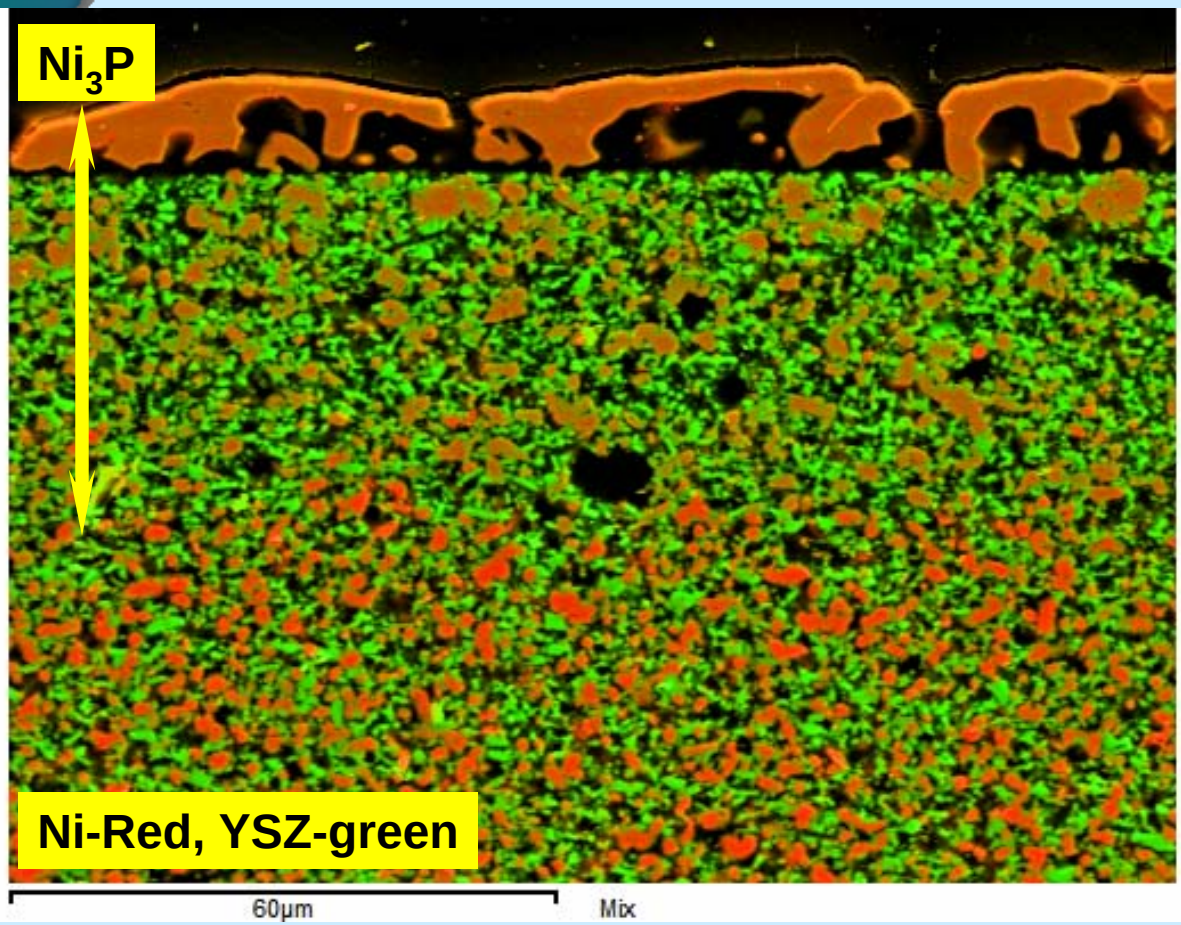


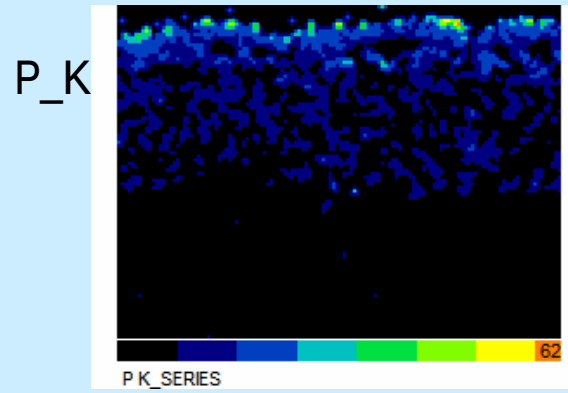
Spectrum	P (at%)	Ni (at%)
Spectrum 1	31.00	69.00
Spectrum 2	30.89	69.11
Spectrum 3	32.67	67.33
Spectrum 4	24.69	75.31

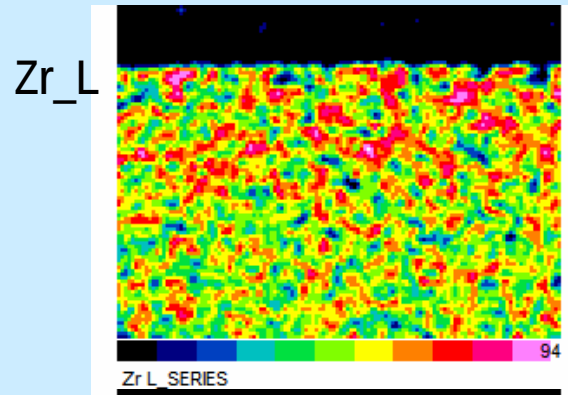
Ni_3P (TEM & XRD confirmed)

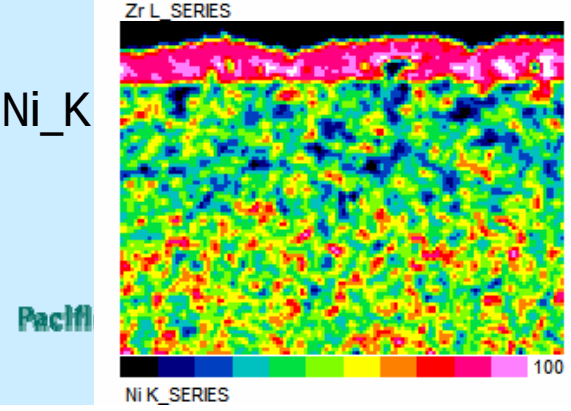
381 hr test in H_2/H_2O=97/3 with 2 ppm of PH_3 at 800°C

Cross Section of Top Ni/YSZ Layer after 381 hr Test with 2 ppm of PH_3





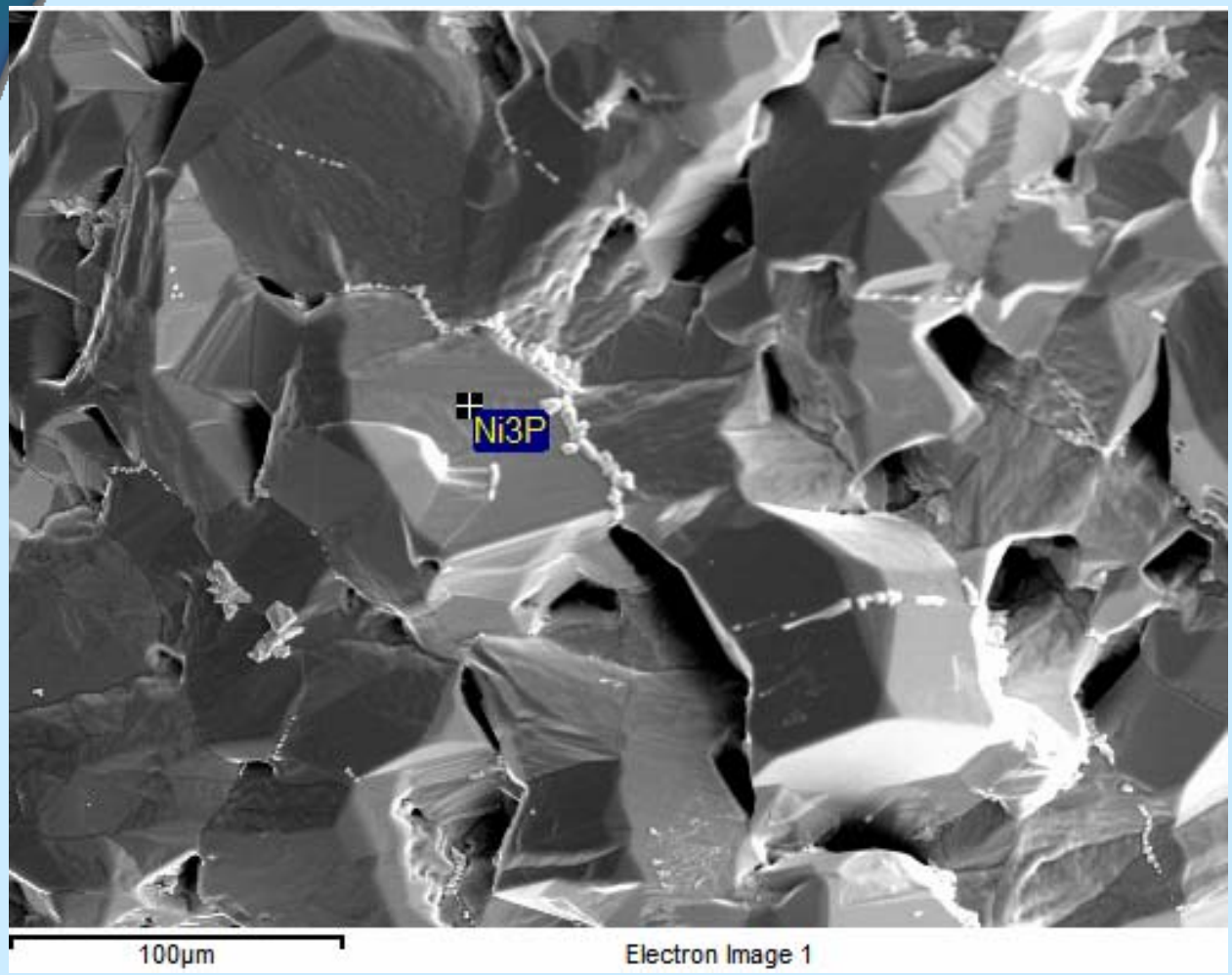




381 hr test in H_2/H_2O=97/3 with 2 ppm of PH_3 at 800°C

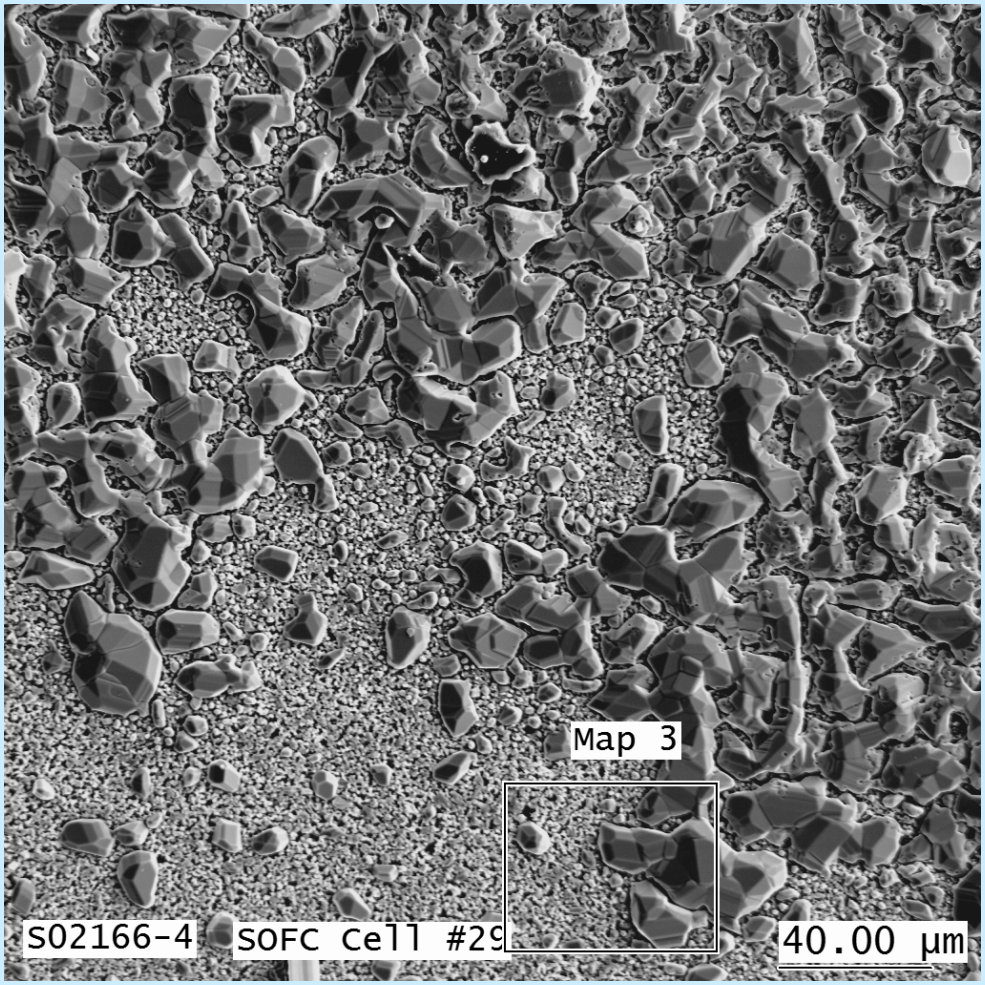
Based on intensity maps, Ni is coarsened and converted into Ni_3P within the top 60 µm.

Current Collecting Wire after 381 hr Test with 2 ppm of PH_3



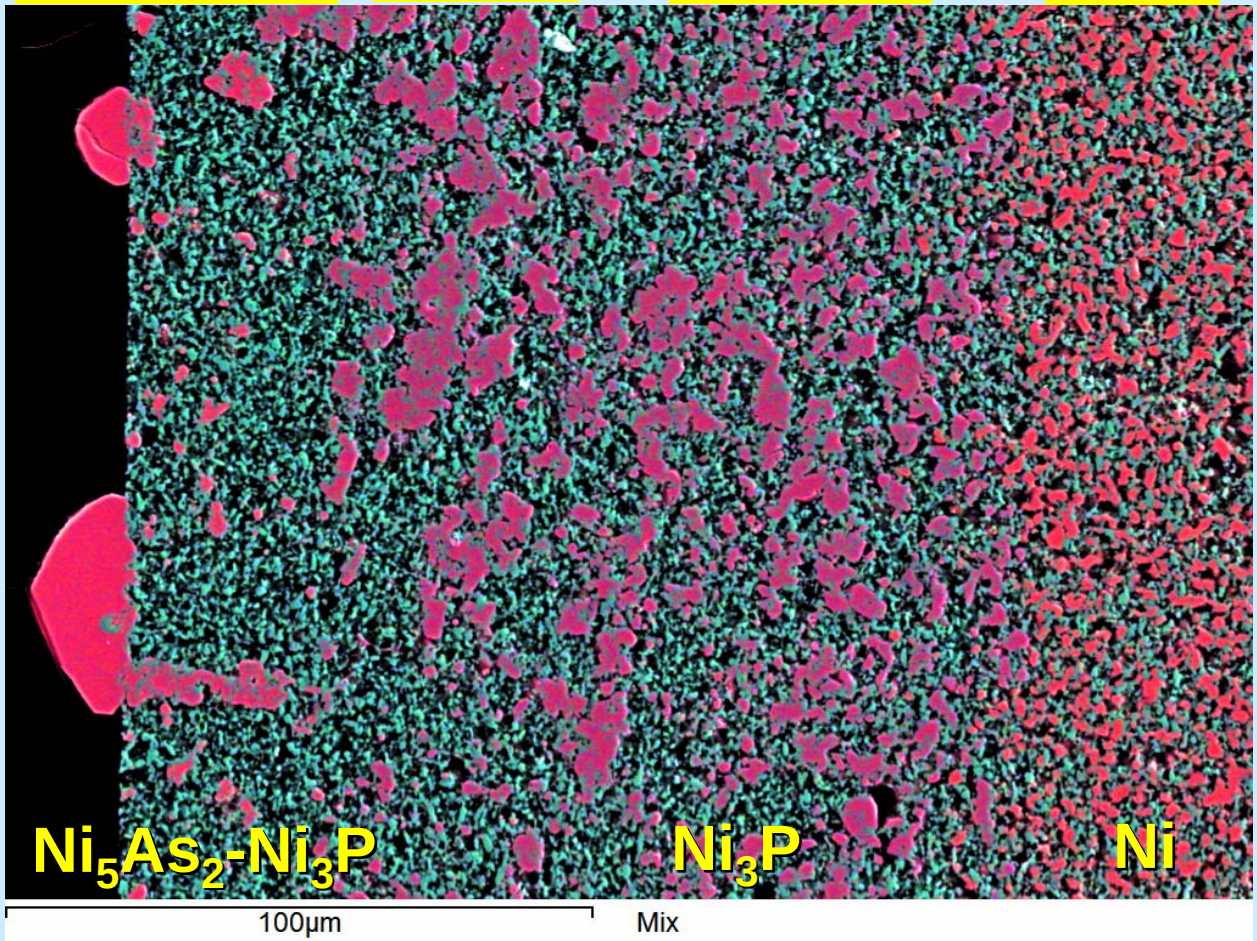
Outer layer of the wire is converted into phosphides

EBSD Reveals Ni_5As_2 Formation after 70 hr Test with 1 ppm of AsH_3



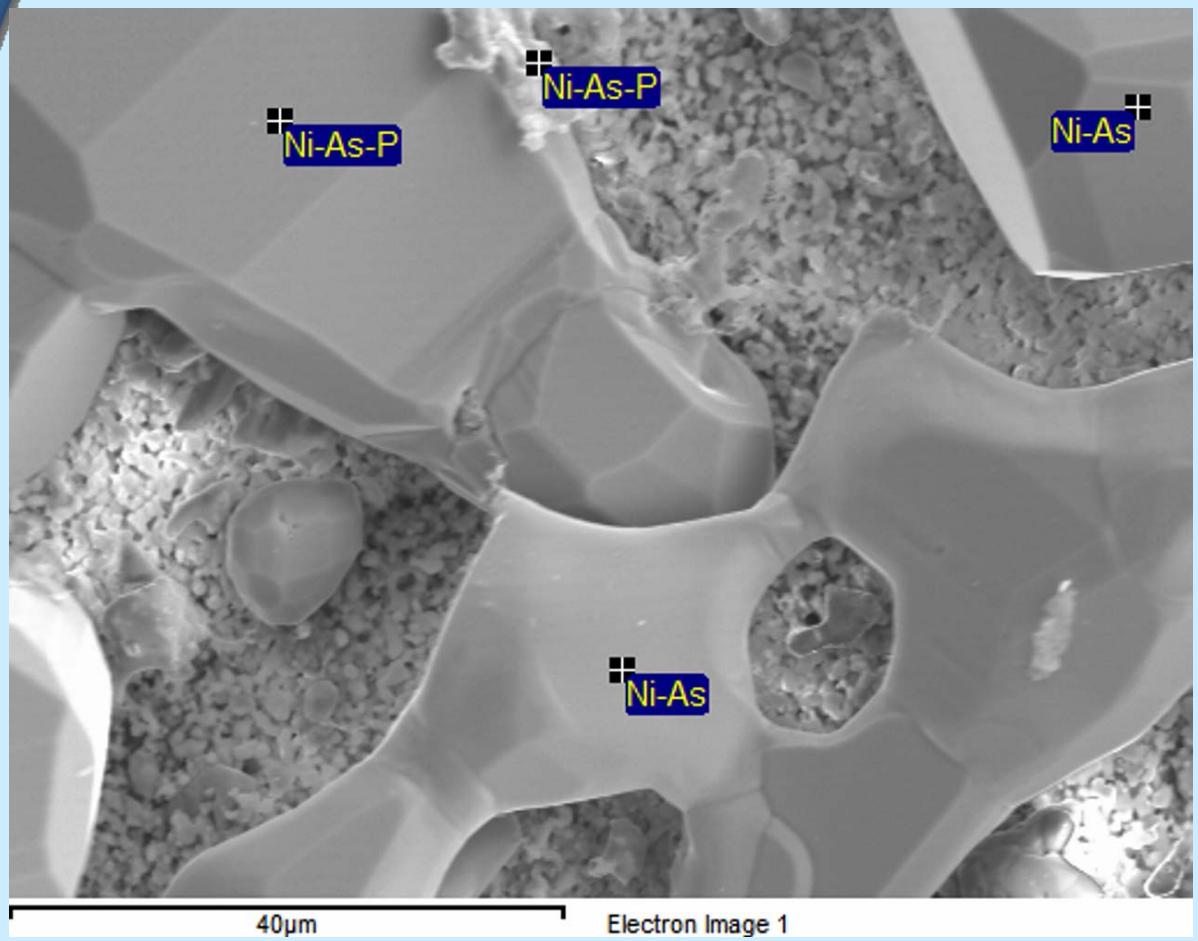
70 hr test in H_2/H_2O=97/3 with 1 ppm of AsH_3 at 800°C

Cross Section of Top Ni/YSZ Layer after 700 hr Test in Coal Gas with $PH_3 + H_2S + AsH_3$



Ni has two phase regions, one rich in As (ca. 45 µm) and the other rich in P (150 µm).

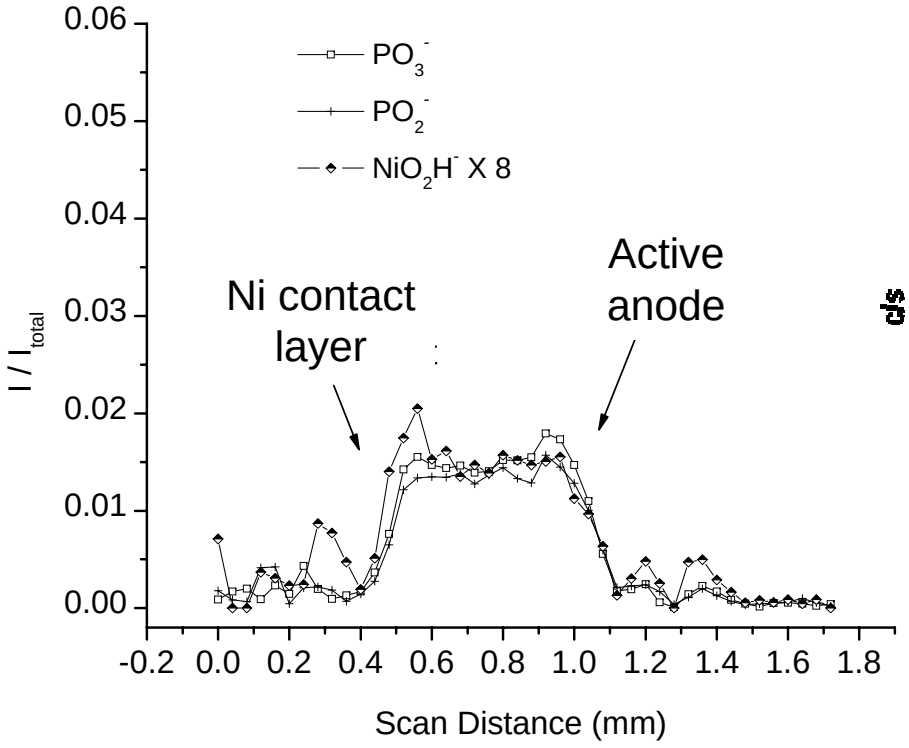
Surface Layer after 700 hr Test in Coal Gas with $PH_3 + H_2S + AsH_3$

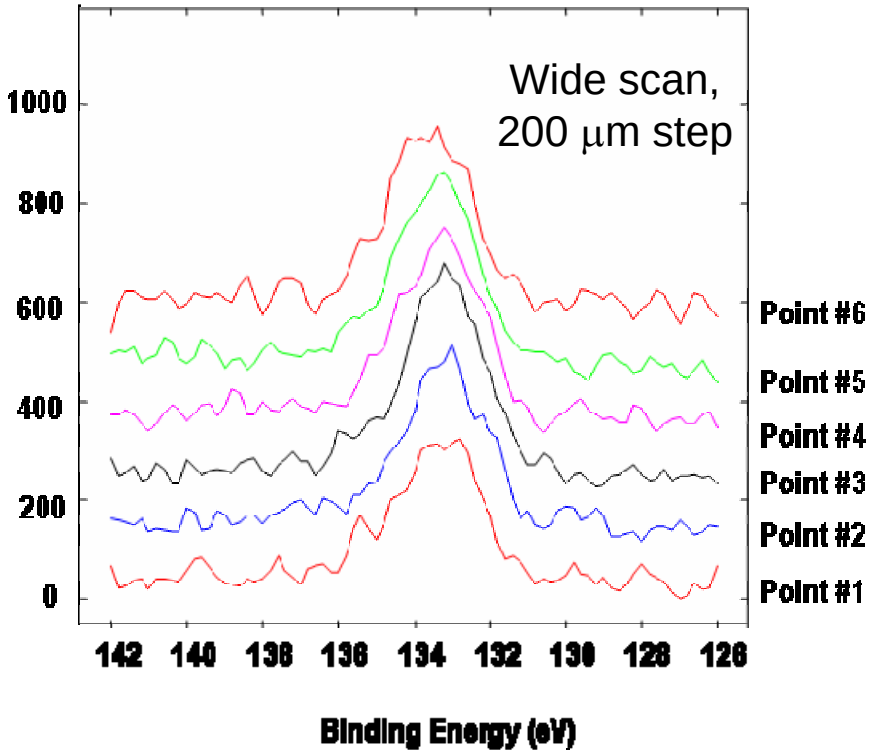


Ni is converted into a mix of Ni_5As_2 and Ni_3P

Ni Grain Surfaces Uniformly Covered with P Throughout Ni/YSZ

This is likely an adsorption layer undetectable by SEM/EDS





ToF-SIMS line-scan of the cross-section of button SOFC after test at 800°C in coal gas with H_2S, PH_3 and AsH_3.

High resolution photoemission spectra of the P 2p region

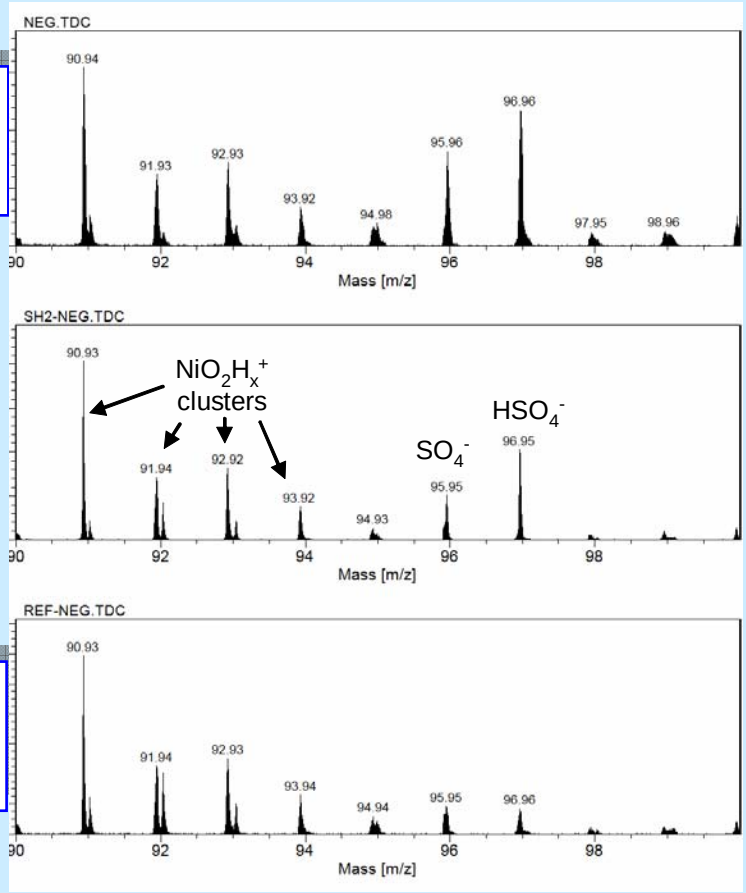
Surface Probe Shows Presence of Adsorbed Sulfur on Ni

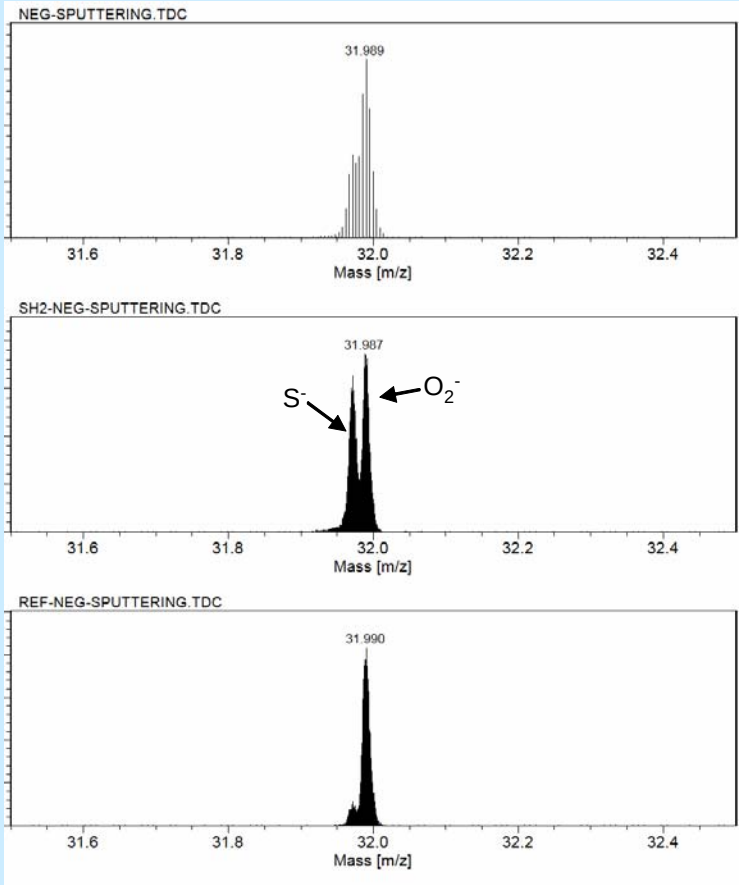
- Ni/YSZ anodes tested in coal gas with H_2S have higher S concentrations than the reference.
- No second Ni-S phase found

$PH_3+H_2S+AsH_3$
700 hrs

1 ppm H_2S
850 hrs

No impurities
(Reference)





Post Test Analysis Summary: Ni Interactions with P, S, and As

- S, P, and As adsorb on the Ni surface
- Affinity for Ni increases in the order S < P < As
  - Phosphorus displaces absorbed sulfur
  - Arsenic displaces adsorbed phosphorus
- Unlike sulfur, P and As form secondary phases, nickel phosphides and nickel arsenides. This transformation is irreversible.

Summary

- Ni/YSZ anodes were tested in simulated coal gas with 1 ppm of H_2S, 2 ppm of PH_3 and 1 ppm of AsH_3 in various combinations at 700-800^oC for up to 800 hours.
- Initial cell degradation, ~ 15 % of the power density, is attributed to the presence of sulfur (effect on the anode resistance).
- Second stage degradation, 0.01-0.07%/hr, is P and As related and is due to the increase in the ohmic resistance and electrode resistance.
  - Ni contact paste, wires and Ni in the top Ni/YSZ later under the fuel inlet were severely affected by the presence of 2 ppm of PH_3. Surface and bulk (~ 150 μm) Ni_3P was formed during 700 hours test at 800^oC.
  - Ni_3P showed extensive agglomeration and self-crystallization followed by the densification of the upper Ni layer. Similar grain orientation of Ni_3P suggests partial liquefaction and re-solidification as a single, continues grain.
  - A nickel deficient layer was formed in the upper part of the Ni/YSZ affecting the Ni percolation.
  - Surface Ni_5As_2 was formed after exposures to 1 ppm of AsH_3 at 800^oC. Arsenide formation alone had insignificant degradation over 700 hour test because of strong Ni-As interaction near the surface (and not at the active interface).

Acknowledgements

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