Effect of Coal Contaminants on SOFC Cell Performance

Annual SECA Meeting

Pittsburgh, PA

August 7, 2008

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Accomplishments

- Determined the performance of SOFC button cells to synergistic effect of contaminants.
  - H_2S and PH_3
  - PH_3, and AsH_3
  - H_2S, PH_3, and AsH_3
- Determined the chemical nature of contaminants using a high temperature mass spectrometer:
  - PH_3 in the presence of water vapor
  - CH_3Cl in the presence of water vapor
  - AsH_3 in the presence of water vapor
  - Compare the experimental data with equilibrium calculations

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Phase I Accomplishments

- Phase I:
  - Literature review of the effect of contaminants on SOFC performance.
  - Determined the effect of several impurities in accelerated tests.
    - HCl, CH_3Cl, As, P, Hg, Cd, Sb, and Zn at levels of 5 to 10 ppm and at temperatures 750-850 C.
    - At this contamination level, HCl, Hg, Sb, and Zn did not affect the SOFC performance.
    - As, P, and CH3Cl degraded the cell performance.

Experimental Setup

InDec B.V. Cells; 1 in Dia; 4-6μm electrolyte;

5 to 10 μm Ni-YSZ anode; 520 to 600 μm anode support; 30 to 40 μm LSM-YSZ cathode;

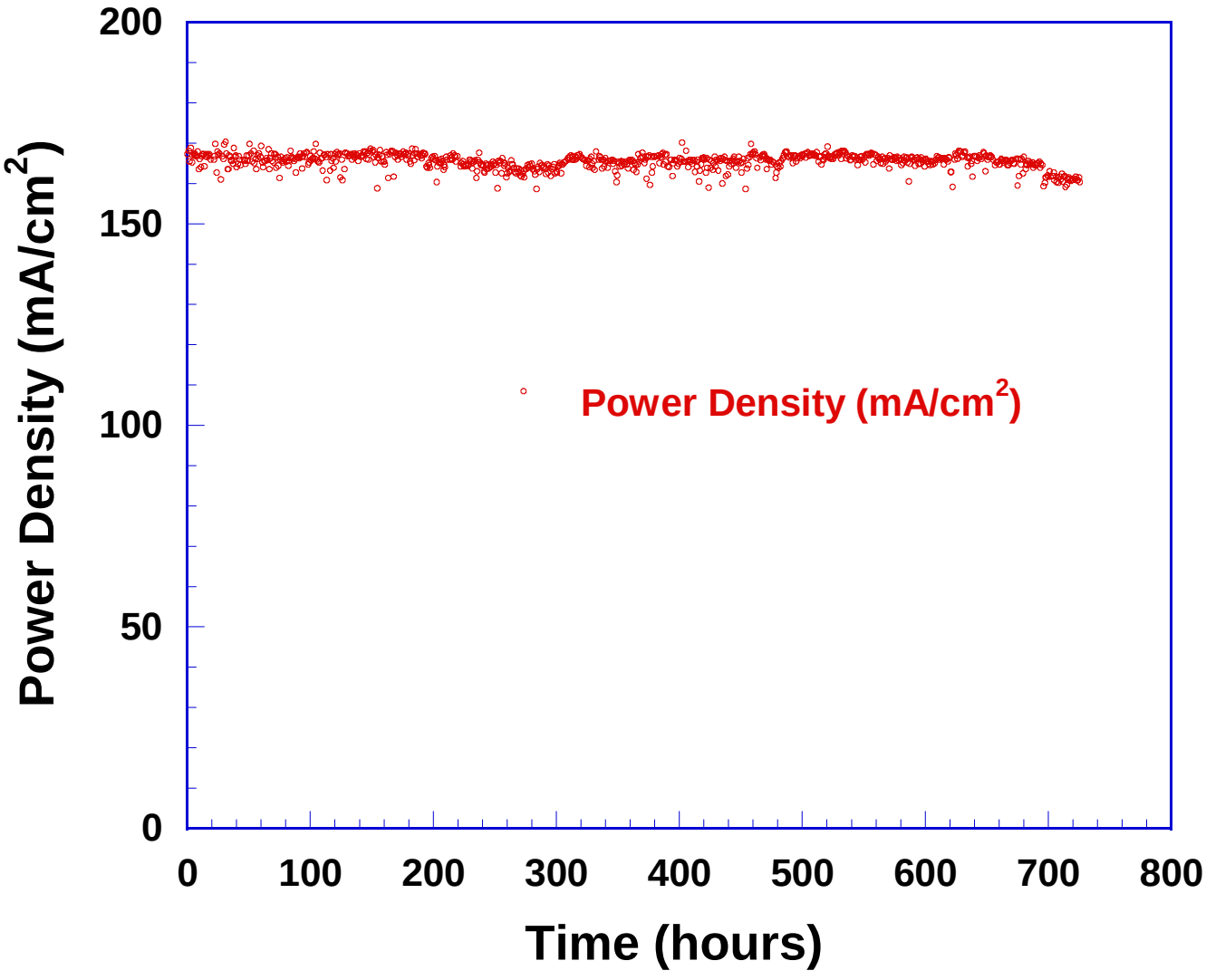
Peak power: 0.15 W/cm^2 at 700°C; 0.35 W/cm^2 at 800°C <10% degradation over 2000 h;

Gas Composition: 30.0% CO, 30.6% H_2, 11.8% CO_2, 27.6% H_2O.

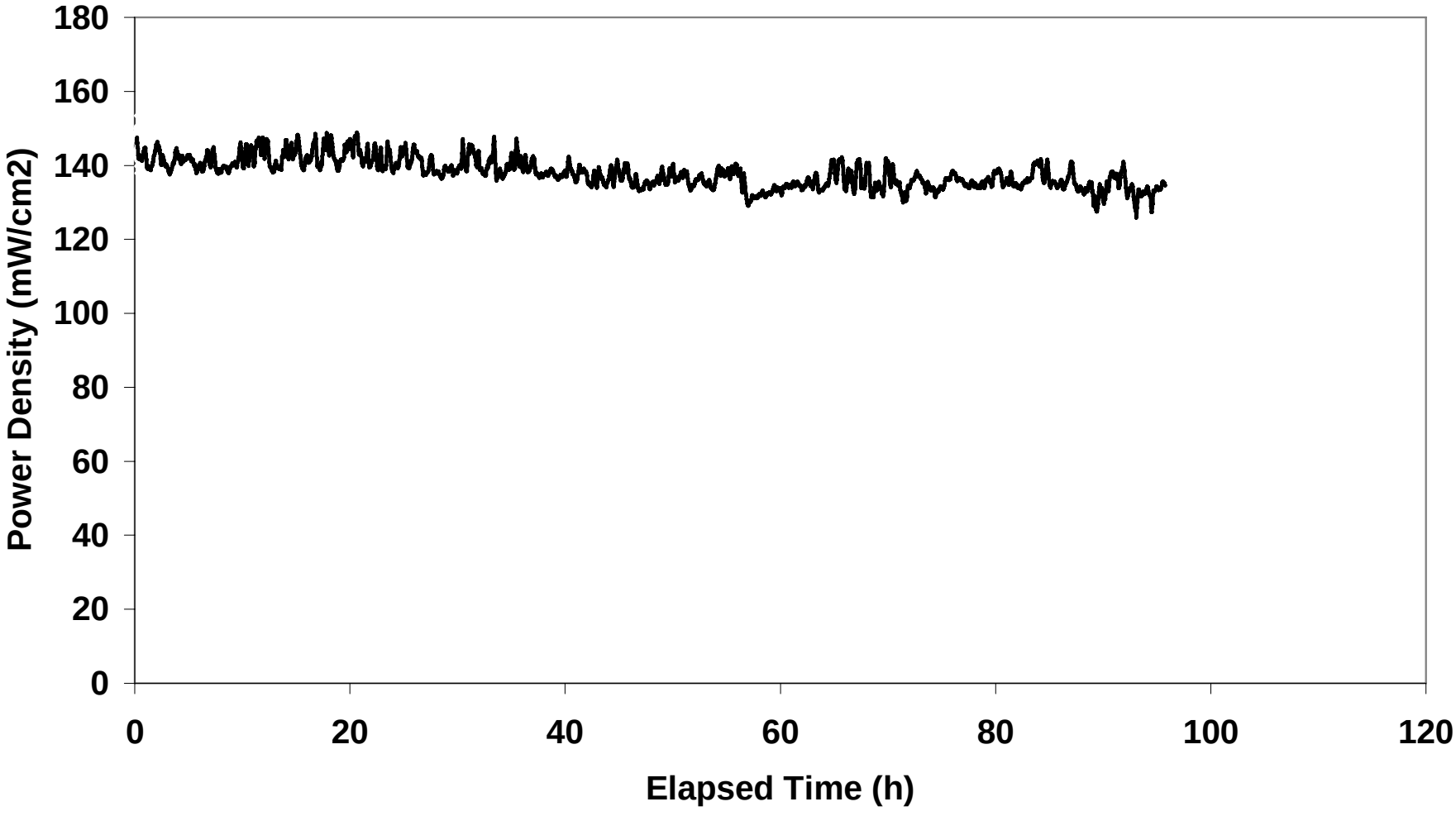
Contaminants: Premixed gas cylinders or permeation cells (VICI Metronics)

YSZ Holder with the cell

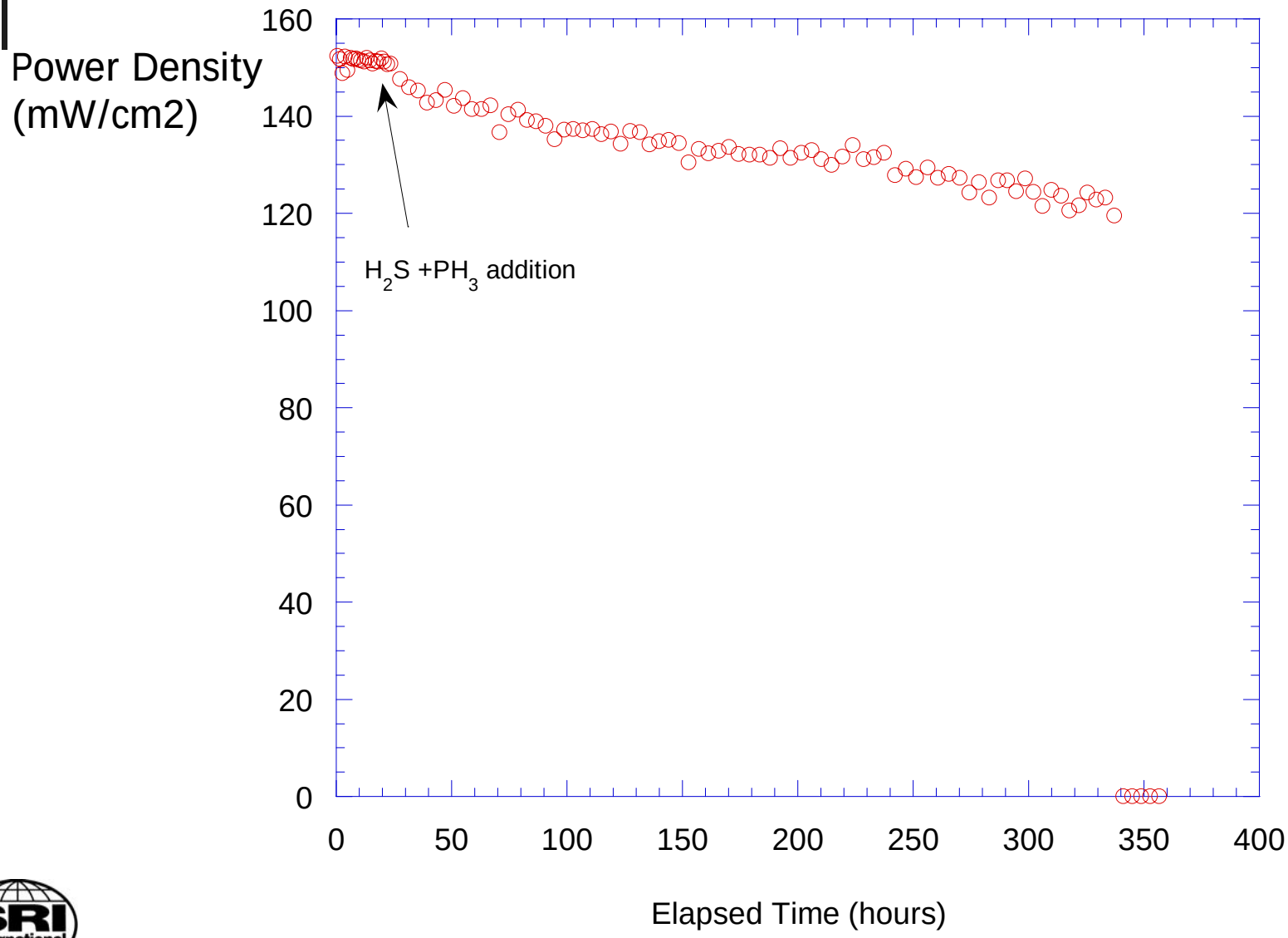
AsH_3 Exposure at 1 ppm Level at 750°C



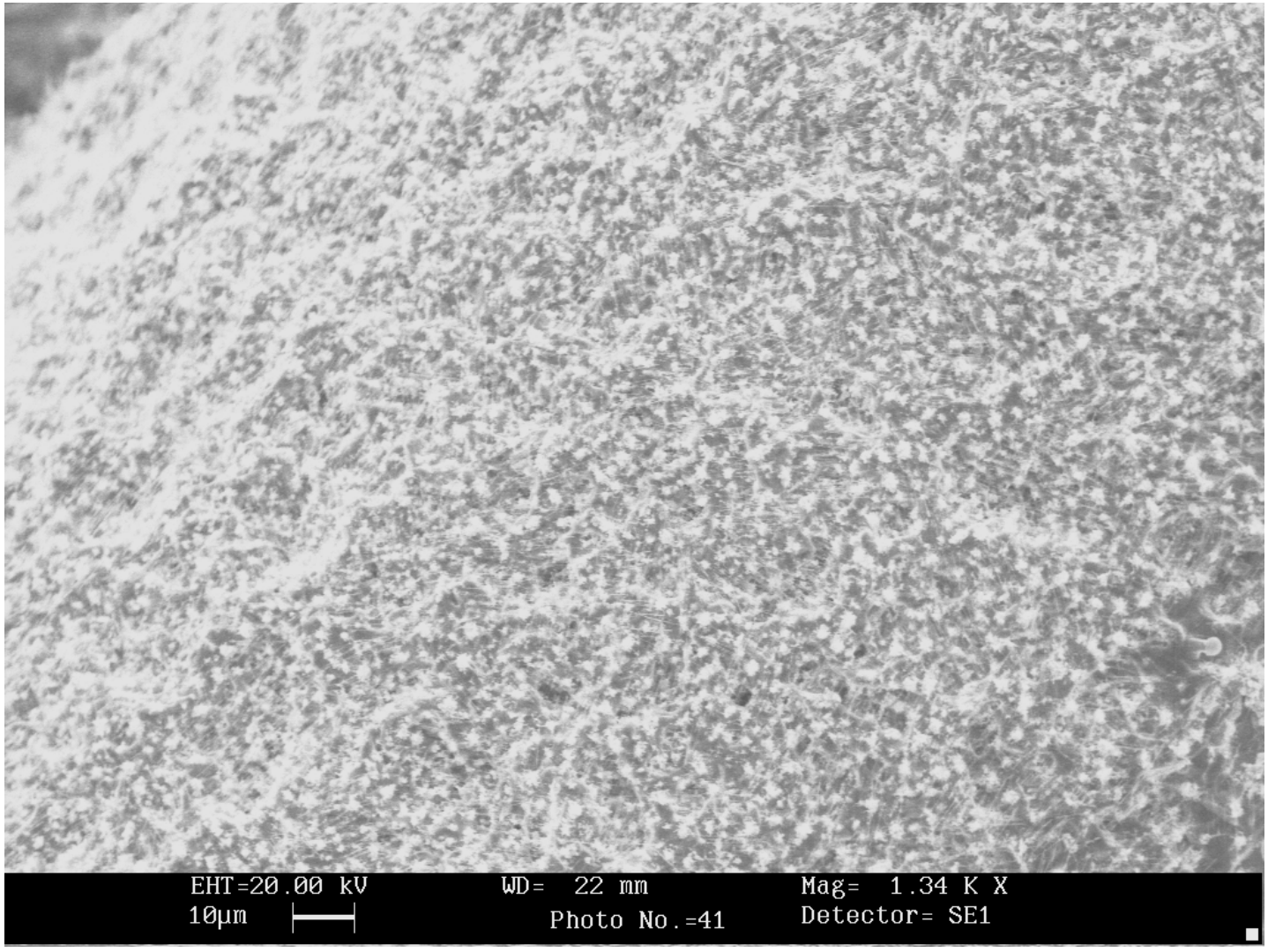
CH_3Cl (2 ppm) Exposure at 750°C



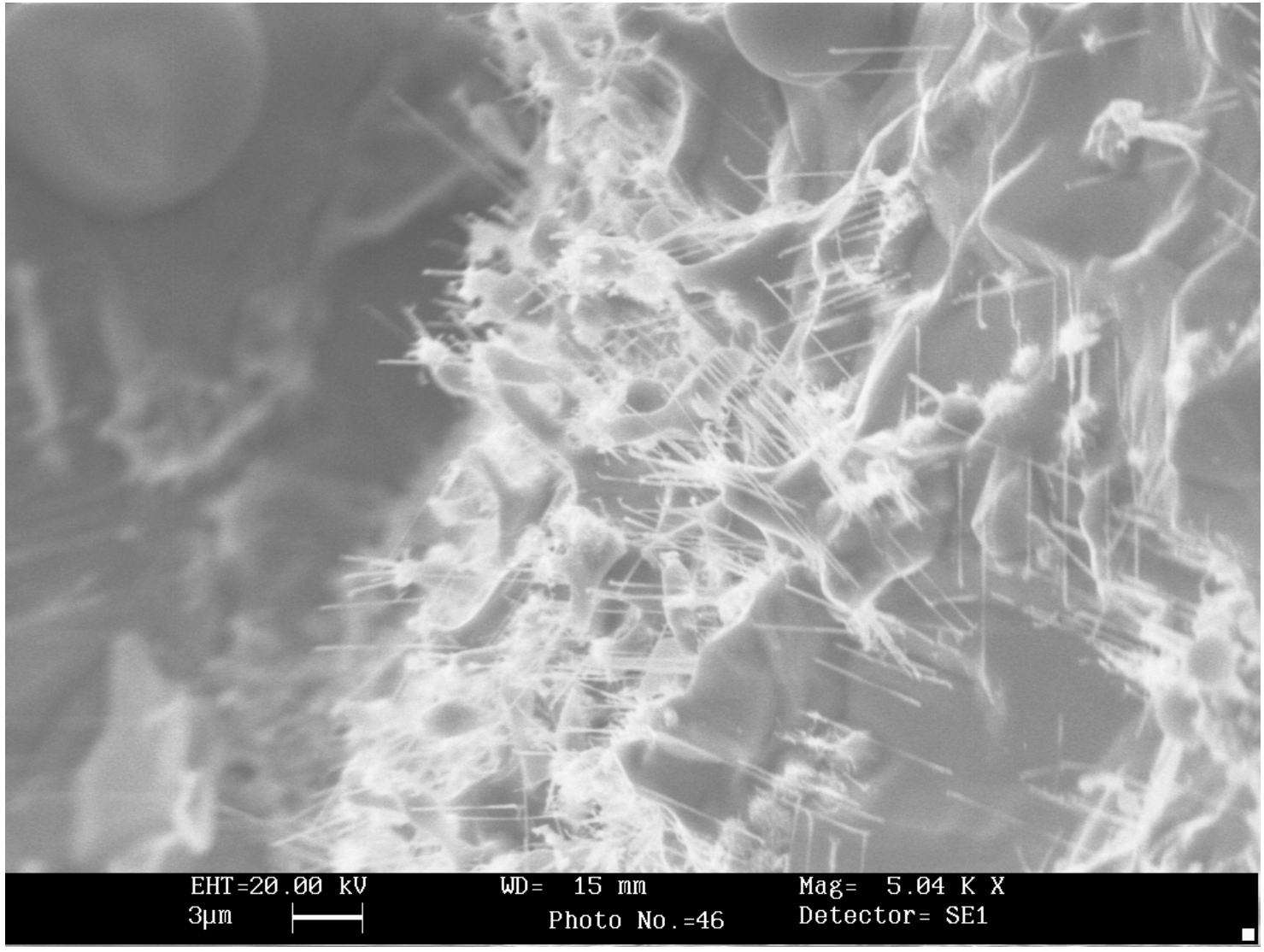
PH_3 (1 ppm) and H_2S (1.3 ppm) Exposure at 750°C



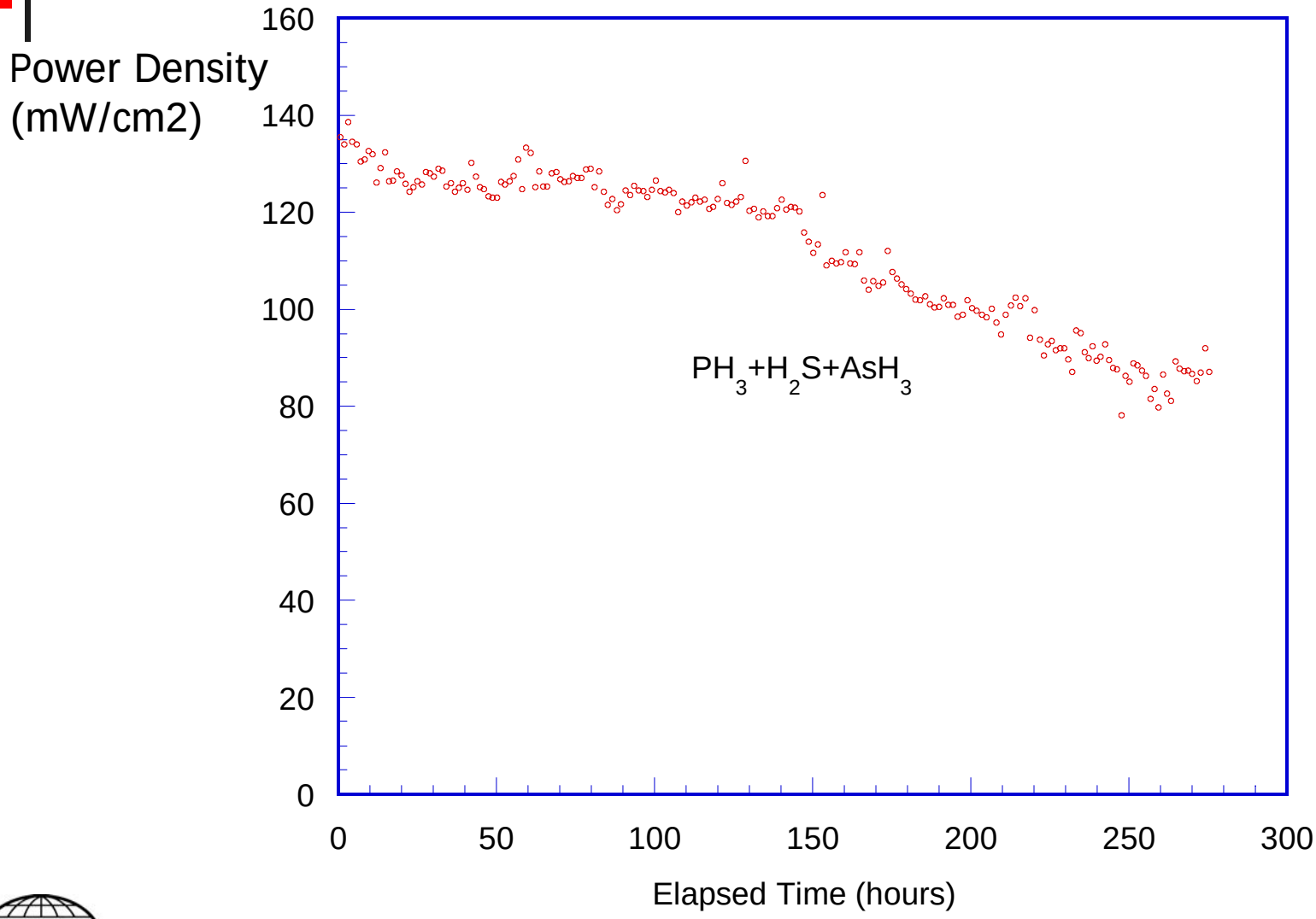
A SEM image of a Ni Mesh After Exposure to PH_3 and H_2S



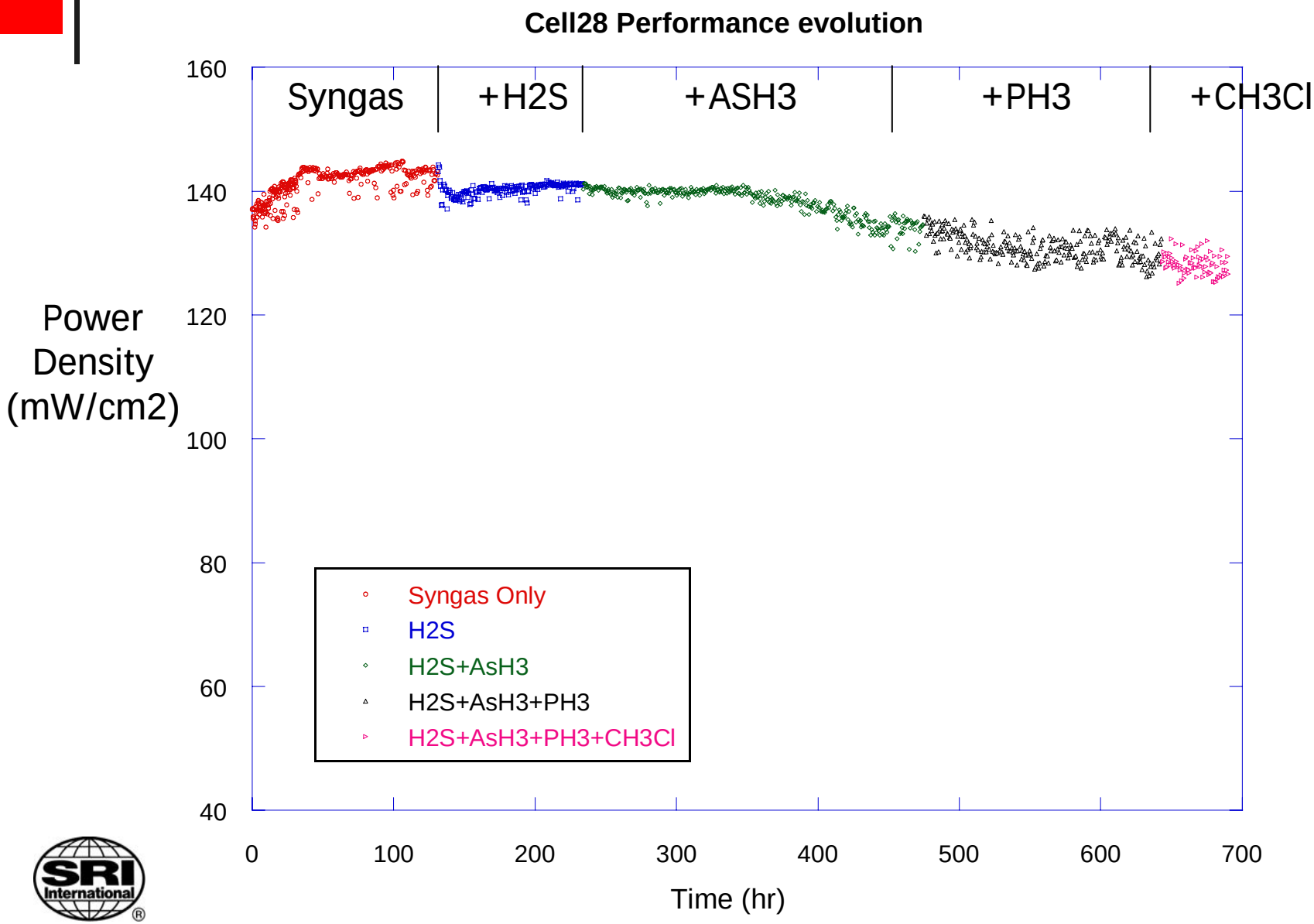
A High Magnification SEM image of a Ni Mesh After Exposure to PH_3 and H_2S



PH_3 (1 ppm) AsH_3 (0.5 ppm) and H_2S (1 ppm) Exposure at 750°C



Synergistic Effects of Contaminants



Equilibrium Concentrations of P Vapor Species under SOFC Anode Conditions

Gaseous Species	Partial pressures (atm) 727°C	777°C	827°C	877°C
CO	0.23	0.24	0.25	0.26
CO_2	0.19	0.17	0.16	0.15
H_2	0.37	0.36	0.35	0.34
H_2O	0.21	0.22	0.23	0.24
→ HPO	6.75E-08	9.33E-08	1.24E-07	1.61E-07
→ HPO_2	2.85E-05	2.83E-05	2.83E-05	2.82E-05
→ HPO_3	1.64E-07	1.82E-07	2.02E-07	2.23E-07
→ PH_3	1.00E-09	7.72E-10	5.96E-10	4.68E-10

HPOx species may affect the YSZ phase whereas PH_3 may react with Ni phase.

Equilibrium Concentrations of As Vapor Species under SOFC Anode Conditions

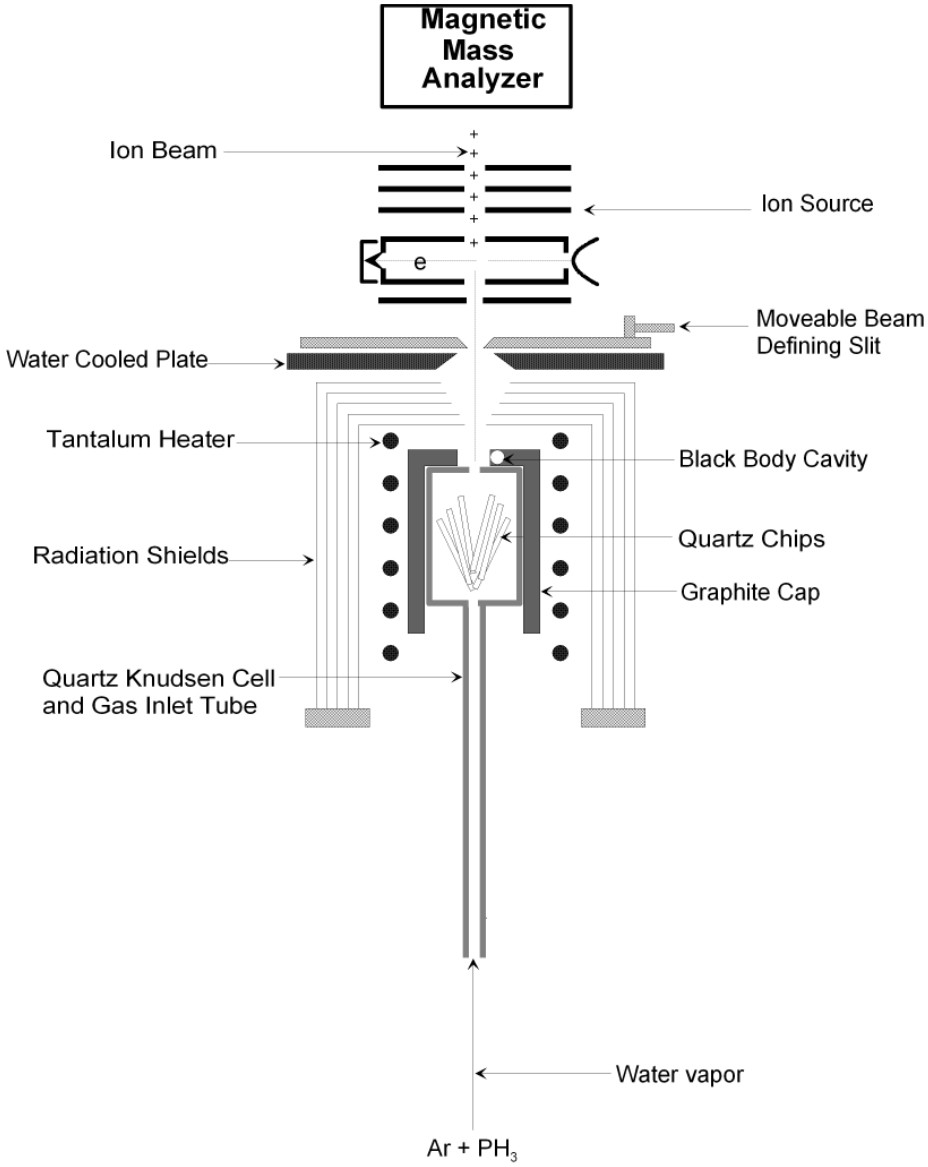
Gas Species	Partial Pressure (atm)		
	1000 K	1100 K	1200 K
CO	2.30E-01	2.54E-01	2.72E-01
CO2	1.88E-01	1.64E-01	1.46E-01
H2	3.70E-01	3.51E-01	3.34E-01
H2O	2.10E-01	2.30E-01	2.48E-01
CH4	2.19E-03	1.62E-04	1.77E-05
As2	4.70E-07	4.81E-07	4.79E-07
AsH3	5.39E-08	3.26E-08	2.10E-08
As4	2.26E-09	2.13E-10	2.86E-11
As	1.46E-10	1.11E-09	5.97E-09
AsH	8.63E-10	3.48E-09	1.10E-08
As3	9.97E-11	7.43E-11	5.63E-11
AsO	4.85E-11	4.95E-10	3.44E-09

AsH_3 decomposes to $As_2(g)$ under equilibrium conditions.

High Temperature Mass Spectrometry

- Molecular effusion beam source.
- Line of sight from the gas source to the ionization chamber.
- Species are identified by
  - M/e ratio, isotope abundance.
  - 3 eV above the IP to minimize fragmentation.
- Partial pressure, Pi is evaluated from:
  - $Pi = k/\sigma * I^{+} * T$
  - K = instrument constant, σ = relative ionization cross section, I^{+} = Measured signal, T = temperature.
- The instrument constant, K, is determined by vaporization of pure Au or Sn.

Knudsen Effusion Cell Assembly



Photograph of the High Temperature Mass Spectrometer

Mass Spectrum of Ar + PH_3 Gas Mixture at 725 C

Ion	AP (eV)	Neutral	AP + 3 eV (293 K)	30 eV (293 K)
PH_3^+	10.0	PH_3	0.34	1.5
PH_2^+	13.4	PH_3	0.12	0.45
Ar^+	15.7	Ar	7640	a
P_2^+	10.6	P_2	b	0.015
P_4^+	10.0	P_4	b	0.05
H_2^+	15.4	H_2	?0.1	a

Notes a: Not measured; b: Too small to measured.

Comparison of the Measured and Calculated Partial Pressures of the Observed Vapor Species for Ar + PH_3 Mixture

	Partial Pressure (atm)	
Species	**Measured**	**Calculated**
Ar	3.96×10^{-4}	5.00×10^{-4}
PH_3	2.36×10^{-8}	8.63×10^{-19}
P_2	5.57×10^{-11}	1.00×10^{-8}
P_4	2.13×10^{-9}	1.07×10^{-12}
H_2		3.00×10^{-8}

Comparison Of The Measured And Calculated Partial Pressures Of The Observed Vapor Species For Ar + PH_3 + H_2O Mixture At 725 C

Species	Partial Pressure (atm)		
	Measured (with out H_2O)	Measured (Add H_2O)	Calculated
Ar	3.96×10^{-4}	3.96×10^{-4}	4.17×10^{-4}
PH_3	2.36×10^{-8}	1.26×10^{-8}	1.51×10^{-28}
H_2O		7.60×10^{-5}	8.33×10^{-5}
HPO			1.22×10^{-15}
HPO_2		1.70×10^{-9}	1.20×10^{-9}
HPO_3		7.20×10^{-9}	1.54×10^{-8}
H_2			6.55×10^{-8}
O			1.27×10^{-16}
OH			4.30×10^{-12}
O_2			8.97×10^{-14}
PO			1.12×10^{-14}
PO_2			3.20×10^{-12}
P_2	5.57×10^{-11}		2.95×10^{-27}
P_4	2.13×10^{-9}		9.29×10^{-51}

Comparison Of The Measured And Calculated Partial Pressures Of The Observed Vapor Species For Ar + AsH_3 + H_2O Mixture At 725 C

Species	Partial Pressure (atm) No H_2O	With H_2O	Calculated
AsH_3	5.82×10^{-9}	1.66×10^{-9}	1.19×10^{-13}
H_2	3.84×10^{-4}	3.36×10^{-4}	3.36×10^{-4}
H_2O	0	2.72×10^{-4}	8.92×10^{-5}
As_2	0	2.31×10^{-10}	3.01×10^{-9}

AsH_3 decomposes to $As_2(g)$ only partially even under quasi-equilibrium conditions.

Comparison Of The Measured And Calculated Partial Pressures Of The Observed Vapor Species For H2 + 500ppm CH_3Cl + H_2O Mixture At 750 C

	Partial Pressure (atm)		
Species	**Measured (with out H_2O)**	**Measured (with H_2O)**	**Calculated**
CH_3Cl	2.12×10^{-7}	9.54×10^{-8}	3.05×10^{-17}
H_2	2.56×10^{-4}	2.59×10^{-4}	2.18×10^{-4}
$P(CH_3Cl)/P(H_2)$	8.29×10^{-4}	3.65×10^{-4}	
CH_4	3.49×10^{-8}	9.89×10^{-8}	3.69×10^{-9}
HCl	8.43×10^{-8}	1.57×10^{-7}	6.82×10^{-8}
CO	0	1.84×10^{-7}	8.18×10^{-5}
CO_2	0	0	2.43×10^{-9}
H_2O	0	3.91×10^{-5}	4.97×10^{-9}

Calculation was based on $C/H_2/H_2O/CH_3Cl$ = 1/1/0.6/500 ppm mole ratio for using graphite Knudsen cell and at 3.0×10^{-4} atm total pressure

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Summary

- Synergistic effects of the contaminants appear to be more severe than individual contaminants alone.
- Combination of PH_3, AsH_3, and H_2S at ppm levels appear to degrade the cell rapidly.
- PH_3 and CH_3Cl in the absence of water vapor appear to be more stable than the thermodynamic equilibrium calculations indicate.
- The above species in the presence of water vapor appear to oxidize at elevated temperatures.

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Future Work

- Continue long-term tests with multiple contaminants (H_2S, AsH_3, PH_3 and CH_3Cl) to confirm the synergistic effects.
- Use the results of the program to recommend the sensitivity limits for SOFC operation.
- Submit Phase III final report.