Effect of Coal Contaminants on SOFC System Performance and Service Life

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OBJECTIVE

- Determine the sensitivity on the performance of SOFC to trace level contaminants present in a coal-derived gas stream in the temperature range 750° to 900°C.
- Assess short-term risk and long-term cumulative effect of the trace-level contaminants.
- Assess the life-time expectancy of SOFC systems fueled with coal-derived gas streams.

Coal and SOFC

- Coal is an abundant fuel in the U.S.
- Integrated coal gasification-fuel cell system $\Rightarrow$ Efficient and potentially low cost generation of electricity from domestic sources.
- Contaminants in the coal-derived gas can degrade the performance of SOFC.

Trace Elements in Coal-Derived Gas

- Coal contains nearly 80 elements!
- In the gas stream leaving a coal gasifier, many of these elements are present at various levels in the gas stream.
- Components of a coal-derived gas:
  - Major: H_2, CO, CO_2, H_2O (% level)
  - Minor: H_2S, NH_3, HCl (10 to 10,000 ppm)
  - Trace: As, P, Hg, Cd, Zn, Sb, Pb, Bi, Na, K, Fe, and Ni (<1 to 10 ppm)
  - Fine ash particulates (fume) – contains several condensed trace element species

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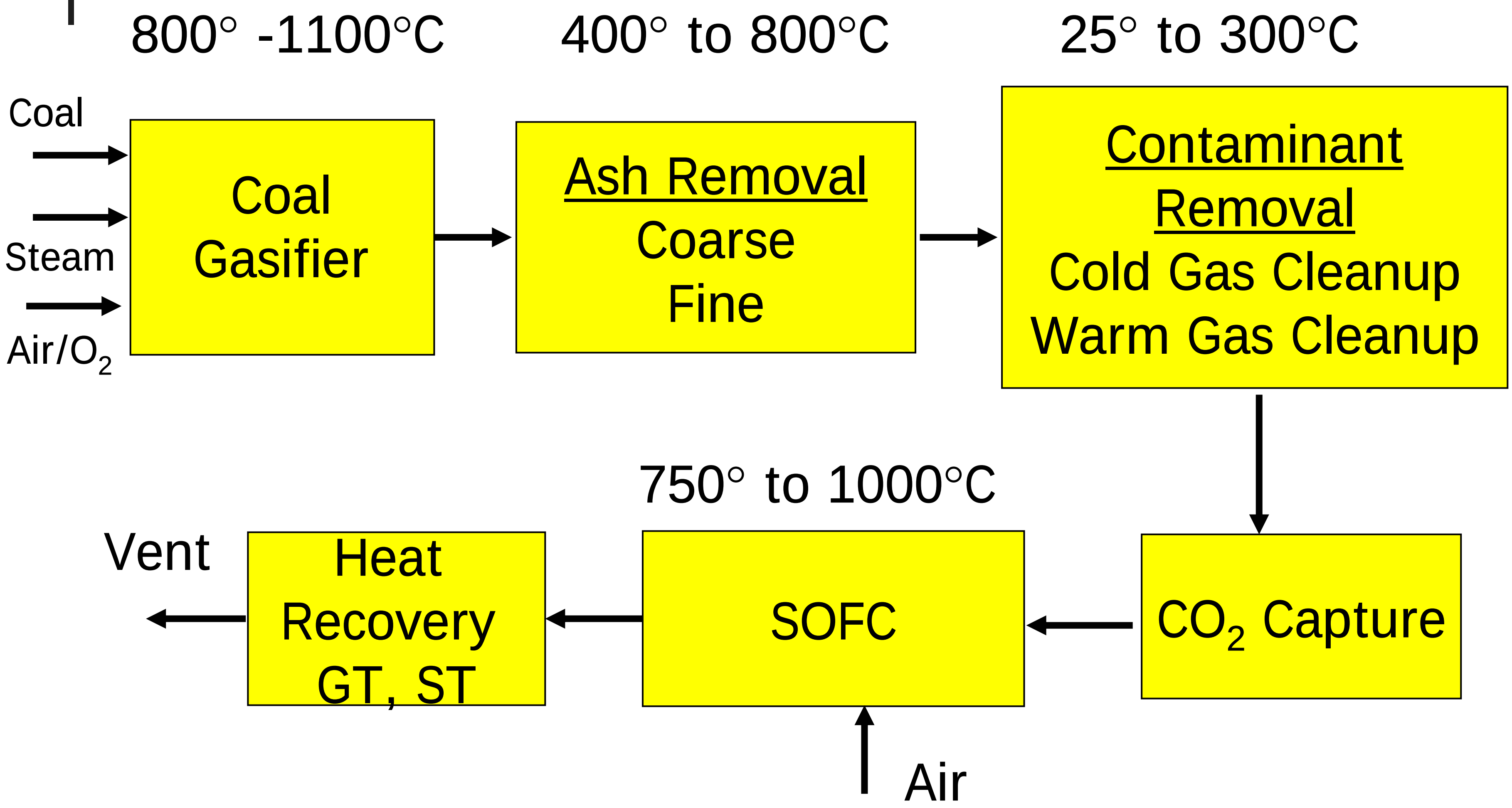
Technical Approach

- Literature review.
- Thermodynamic calculations.
- Determine the performance of small SOFC samples to simulated coal gas containing trace element vapor.
  - Individual contaminants;
  - Synergistic effect of multiple contaminants;
  - Effect of coal ash fumes.
- Assess the SOFC degradation and recommend tolerance limits.

Coal-Derived Gas Stream Processing



Nature of the Trace Element Vapor Species (Equilibrium Thermodynamic Estimate)

Element	>1000°C	400° to 800°C	100° to 400°C	<100°C
As	AsO, As_2	AsO, As_4	As_2,	AsH3,
Be	$Be(OH)_2$	Condensed Species	Condensed Species	Condensed Species
Hg	Hg	Hg	Hg, $HgCl_2$	Hg, $HgCl_2$
B	HBO	HBO	HBO	-
V	VO_2	Condensed Species	Condensed Species	Condensed Species
Se	H_2Se, Se, SeO	H_2Se	H_2Se	H_2Se
Ni	NiCl, $NiCl_2$	Condensed Species	$Ni(CO)_4$	$Ni(CO)_4$
Co	$CoCl_2$, CoCl	Condensed Species	Condensed Species	Condensed Species
Sb	SbO, Sb_2	SbO, Sb_2	Sb_4	Condensed Species
Cd	Cd	Cd	$CdCl_2$	Condensed Species
Pb	Pb, $PbCl_2$	PbS, Pb, $PbCl_2$	Condensed Species	Condensed Species
Zn	Zn	Zn, $ZnCl_2$	Condensed Species	Condensed Species

Concentrations of Trace-Level Contaminants

- The concentrations of many trace contaminants in coal-derived gas stream are not known accurately.
- The expected levels depend on:
  - Type of coal
  - Coal gasifier
  - Gas stream cleanup technology.

Estimate of Trace Level Contaminant Levels in Coal-Derived Gas

Contaminant	Concentration (ppmv) at the Kingsport Facility	UND-EERC Estimate
As (AsH_3)	0.15 to 0.58	0.2
Thiophene		1.6
Chlorine		120
CH_3F	2.6	
CH3Cl	2.01	
HCl	<1	
$Fe(CO)_5$	0.05 to 5.6	
$Ni(CO)_5$	0.001 to 0.025	
CH_3SCN	2.1	
PH_3	1.9	
Antimony	0.025	0.07
Cadmium		0.01
Chromium	<0.025	6.0
Mercury	<0.025	0.002
Selenium	<0.15	0.17
Vanadium	<0.025	
Lead		0.26
Zinc	9.0	

Effect of Coal Contaminants on SOFC Anode Performance

- Affect the ability of Ni crystallites to promote electrochemical reactions
  - Sulfur atoms on the surface poison Ni to dissociate H_2 molecules or adsorb CO
- Affect the ability of YSZ to transport oxygen ions
  - Formation of other phases such as zirconium silicate
- Affect the electrical conductivity
  - Formation of alloys or bulk phases such as sulfides

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Known Effect of Contaminants

- Published literature indicate the effect of H_2S, NH_3, and HCl on SOFC performance.
- Tolerance limits for SOFC:
  - H_2S and HCl: Few ppm; NH_3: 5,000 ppm
- Catalyst literature on Ni-based catalysts indicate:
  - H_2S reduces the steam reforming actiivity;
  - As (1 ppm) affect the steam reforming activity;
  - Cl reduces H_2 and CO adsorption on Ni;
  - P inhibits H_2 uptake by Ni;
  - Bi reduces CO chemisorption;
  - Addition of Zn to Ni prevent agglomeration of Ni/alumina catalysts.
  - Most of the catalyst studies were performed at temperatures lower than the SOFC operation.

Experimental Determination of the Effect of Trace Elements on SOFC Performance

- We are concentrating on contaminants other than H_2S.
- We are exposing SOFC samples at 750° to 850°C to simulated coal-derived gas containing various contaminants (10 to 50 ppm)
- Scoping experiments to determine the effect of following contaminants on SOFC performance:
  - HCl, CH_3Cl
  - Zn, P
  - As

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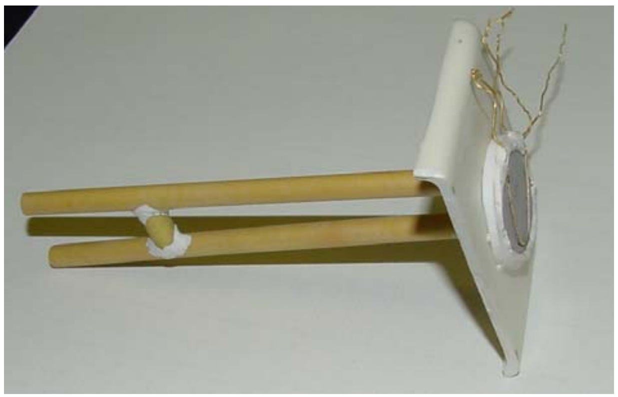
Experimental Setup

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

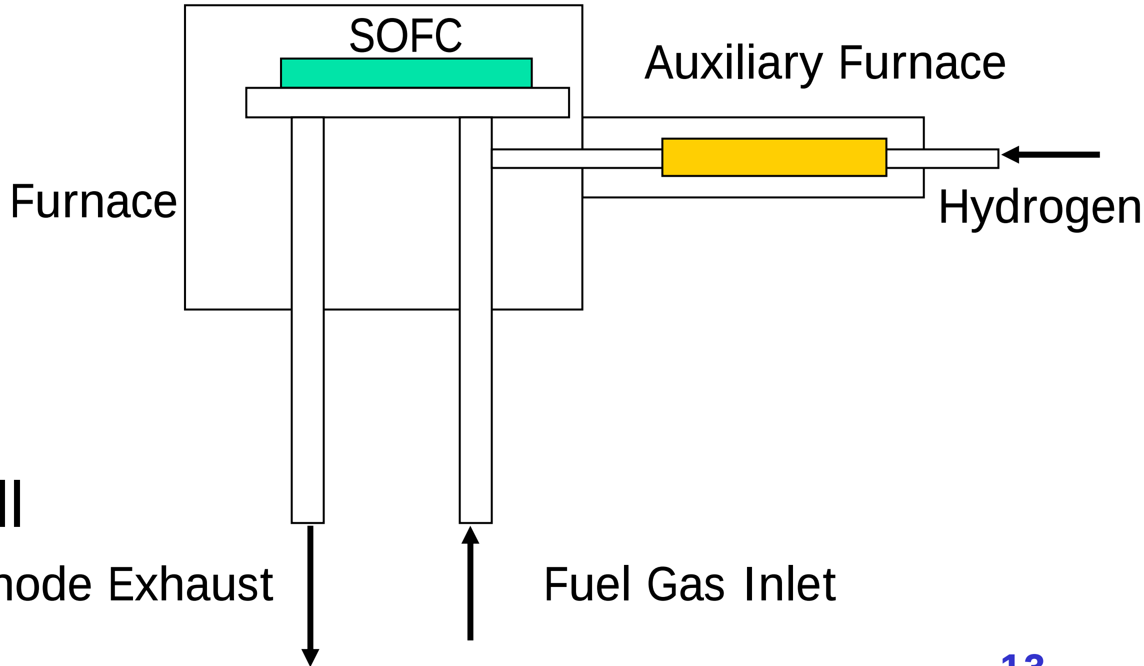
5 to 10 μm Ni-YSZ anode; 520 to 600 μm anode support; 30 to 40 μm LSM-YSZ cathode;

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

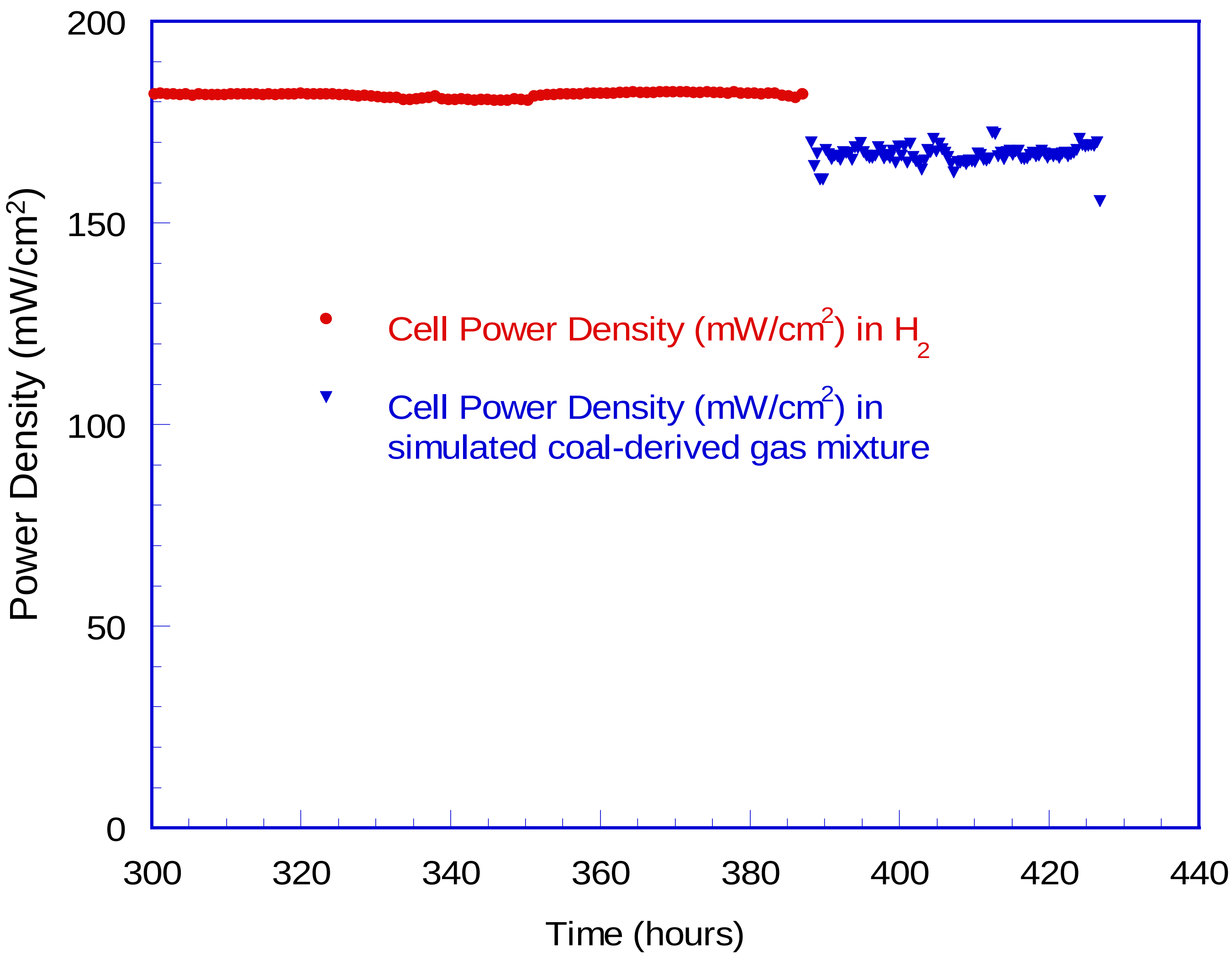
Gas Composition: 30.0% CO, 30.6% H_2, 11.8% CO_2, 27.6% H_2O



YSZ Holder with the cell

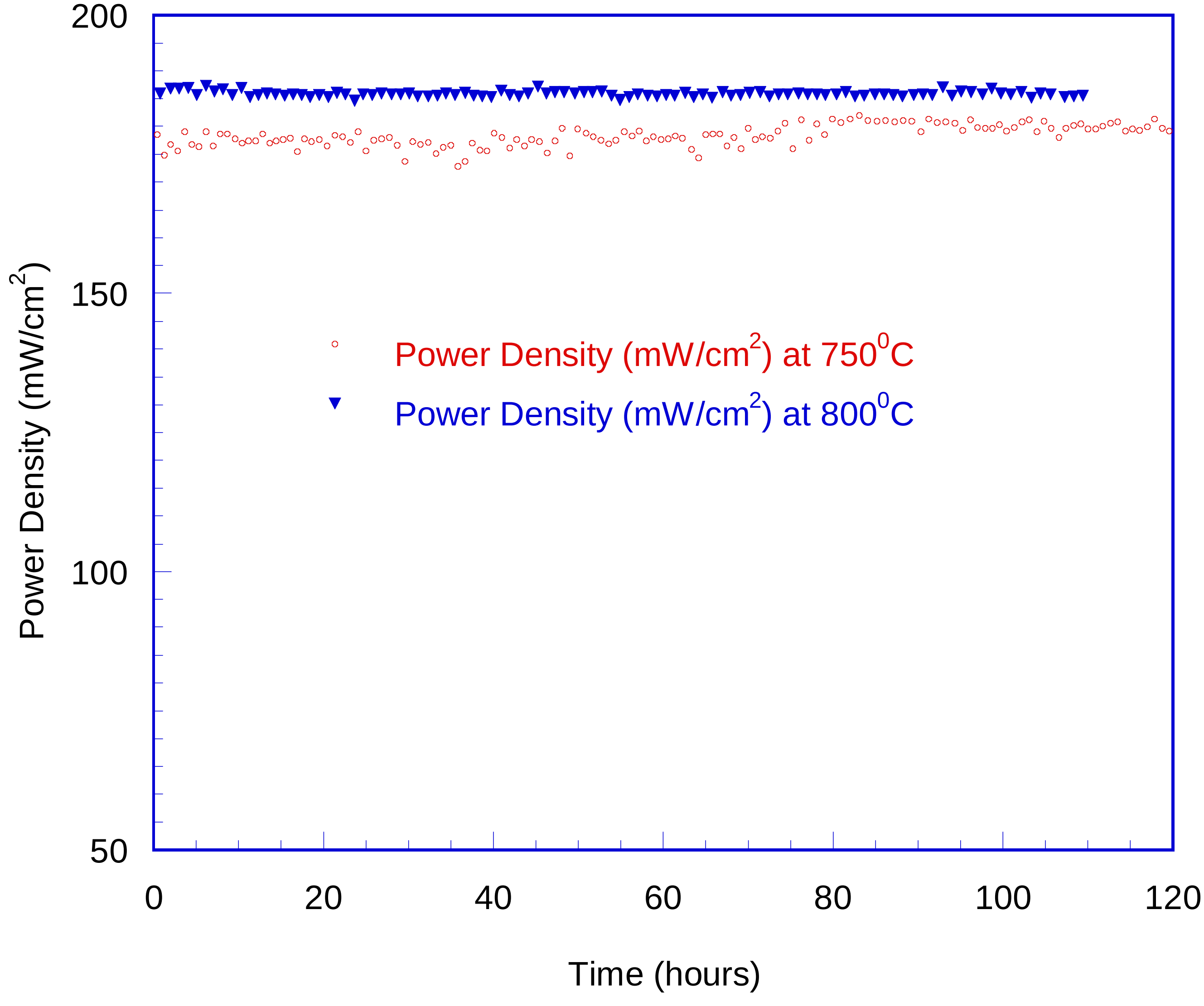


Performance of SOFC in Clean Gas (800°C, ~0.7V and 0.2A/cm^2)

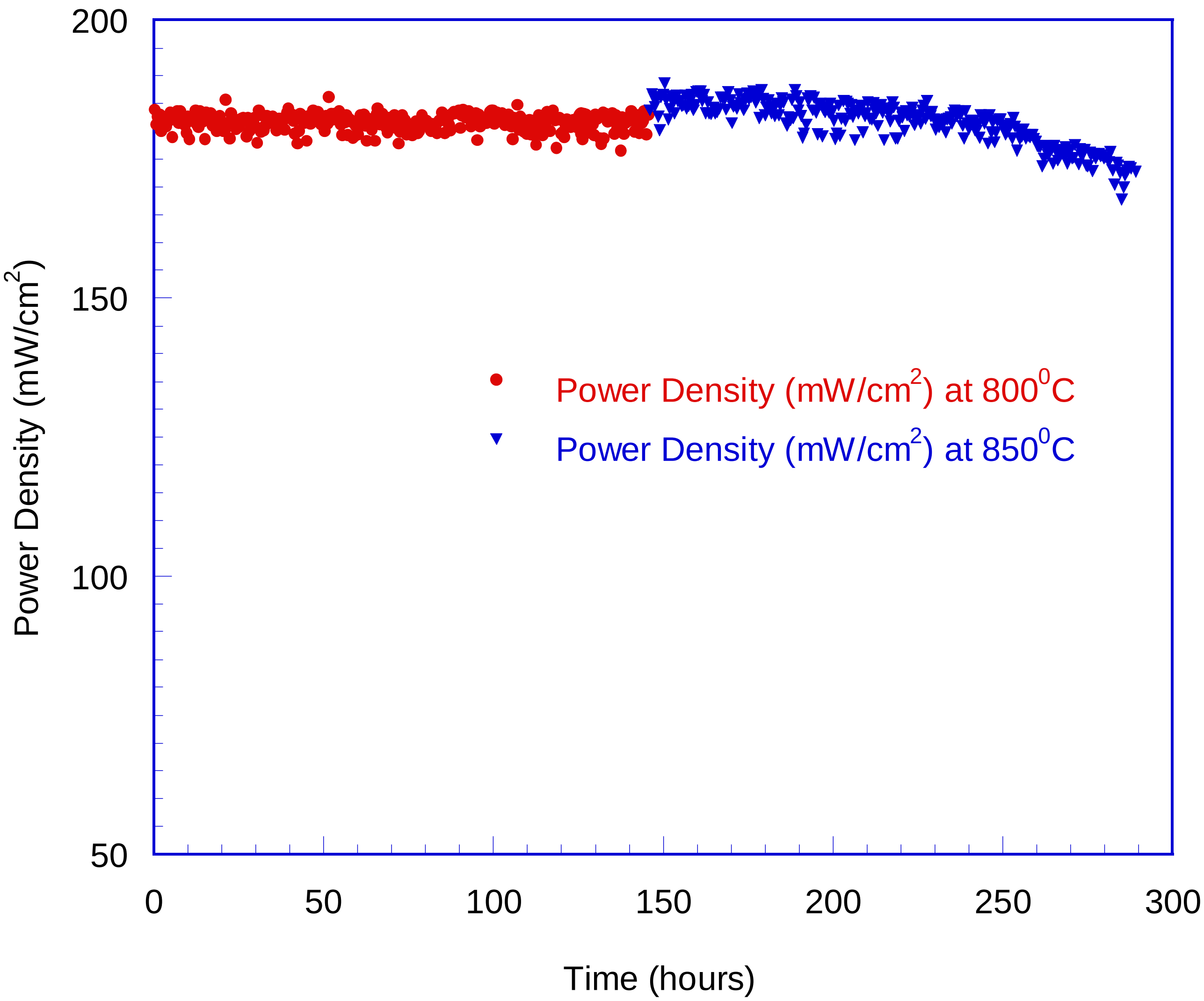


Note: The power density was 182 mW/cm^2 during 0 to 300h.

Performance of SOFC with 38 ppm HCl Vapor at 750° and 800°C (~0.7V and 0.2A/cm²)



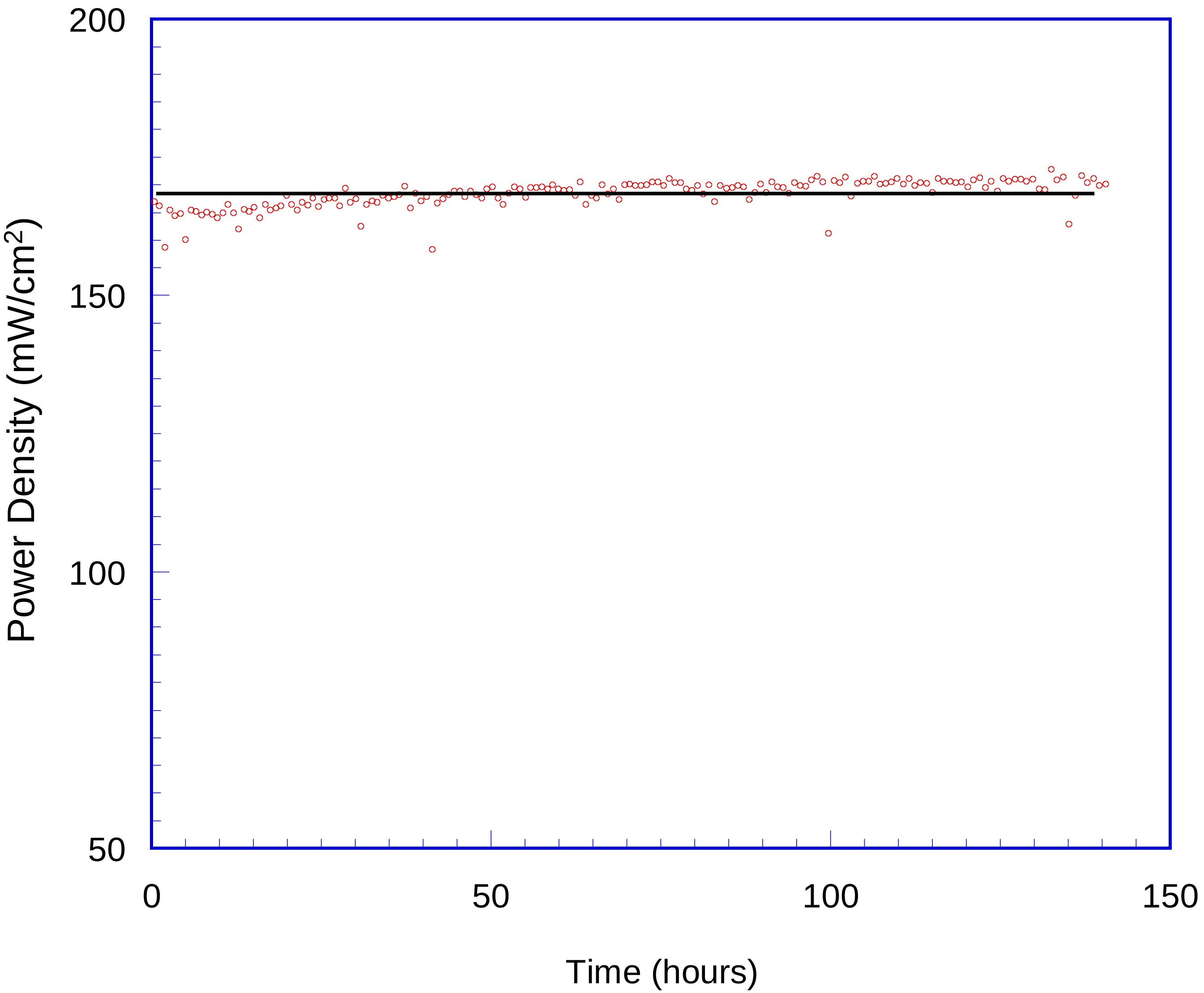
Performance of SOFC with 40 ppm CH_3Cl Vapor at 800 and 850°C (~0.7V and 0.2A/cm²)



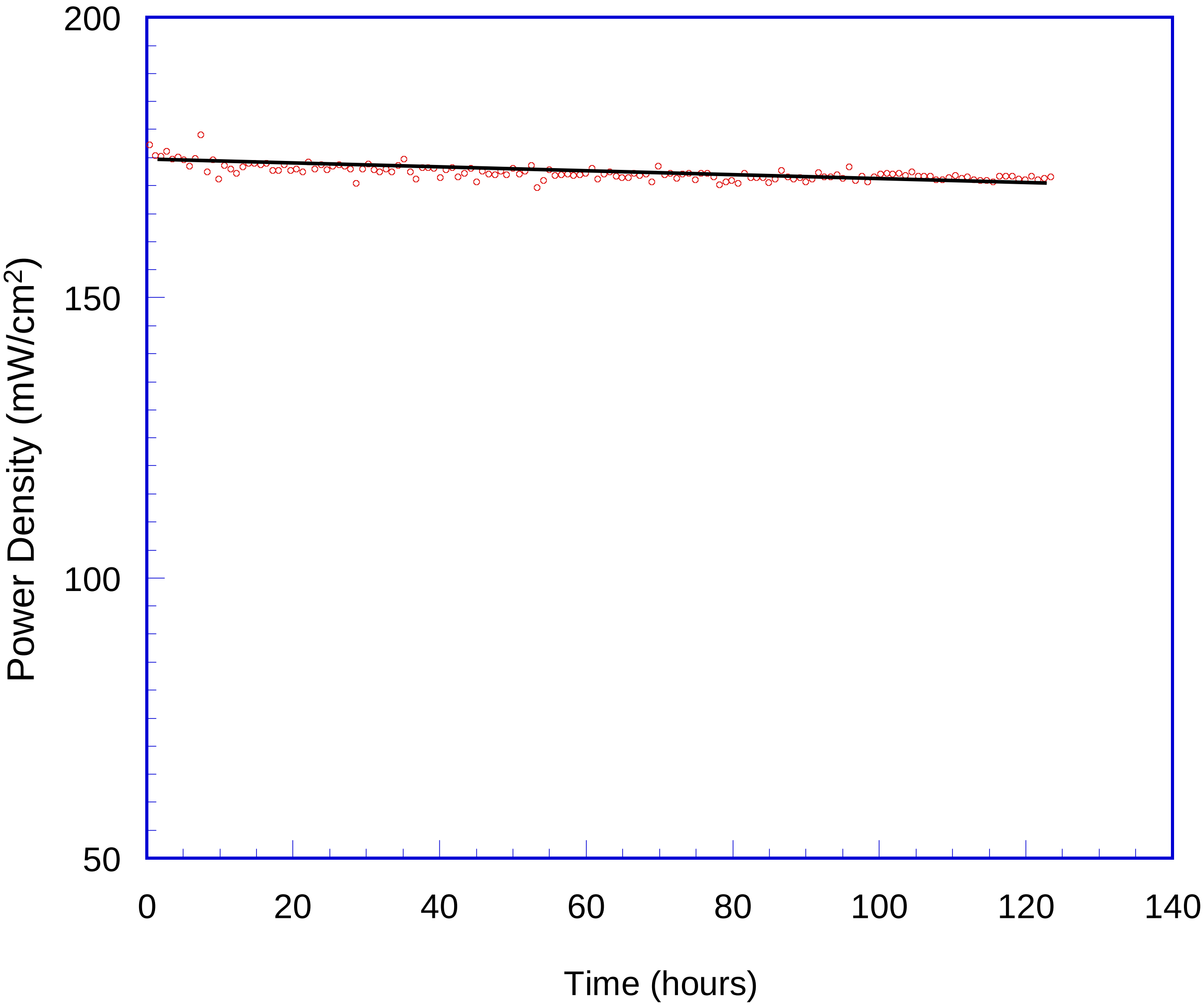
Nature of Zn Vapor Species under SOFC Anode Conditions (10 ppm feed)

Gaseous Species	Partial pressures (atm) 700°C	750°C	800°C	850°C	900°C
H_2(g)	0.38	0.37	0.36	0.35	0.34
CO(g)	0.23	0.24	0.25	0.26	0.27
CO_2(g)	0.19	0.18	0.17	0.16	0.15
H_2O(g)	0.20	0.22	0.23	0.24	0.25
Zn(g)	1.0E-05	1.0E-05	1.0E-05	1.0E-05	1.0E-05
ZnO(g)	7.7E-18	3.9E-17	1.7E-16	6.5E-16	2.2E-15
$Zn(OH)_2$(g)	7.3E-12	8.1E-12	9.0E-12	9.9E-12	1.1E-11

Performance of SOFC with 10 ppm Zn Vapor at 750°C (~0.7V and 0.2A/cm^2)



Performance of SOFC with 10 ppm Zn Vapor at 800°C (~0.7V and 0.2A/cm^2)



Nature 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

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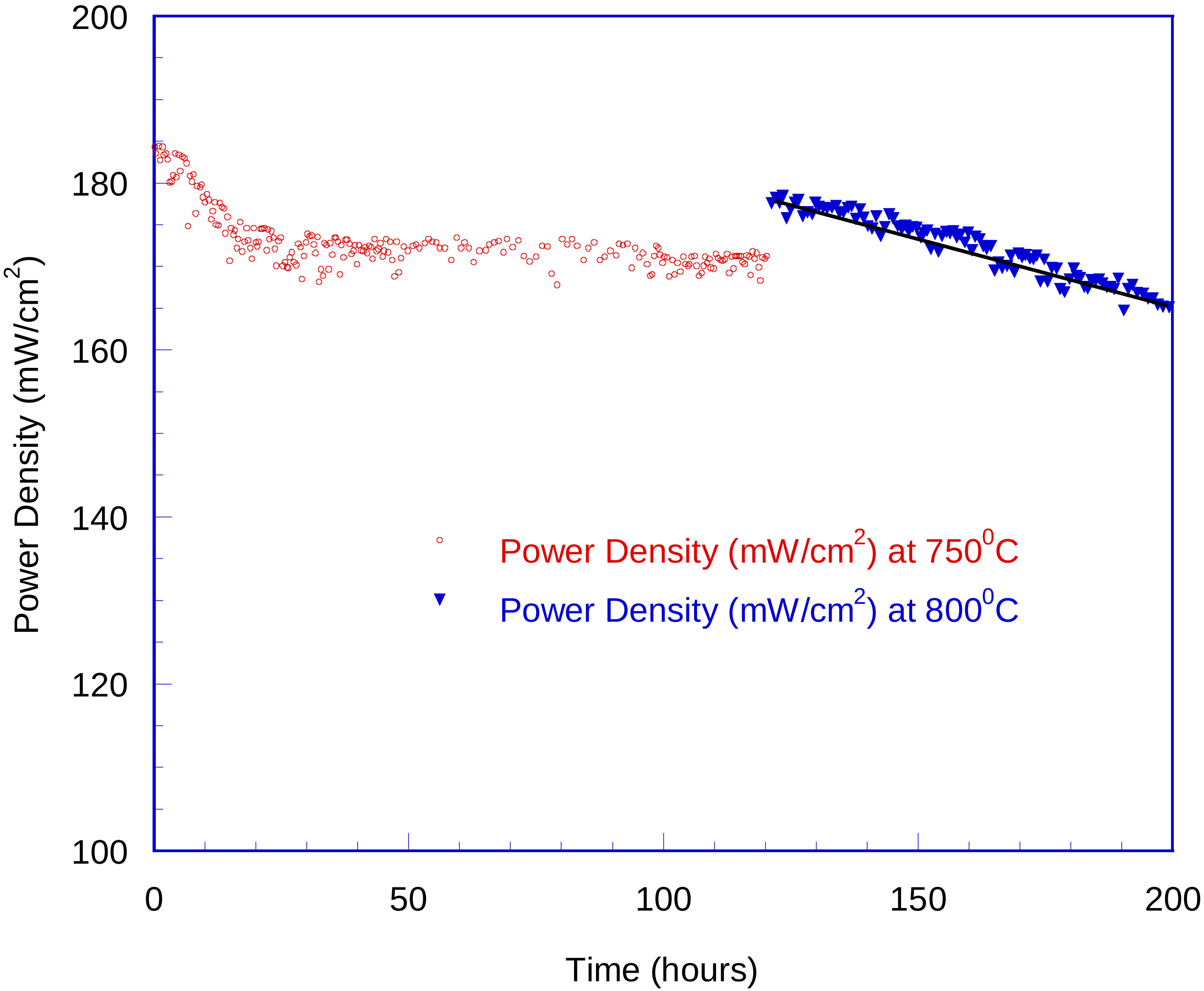
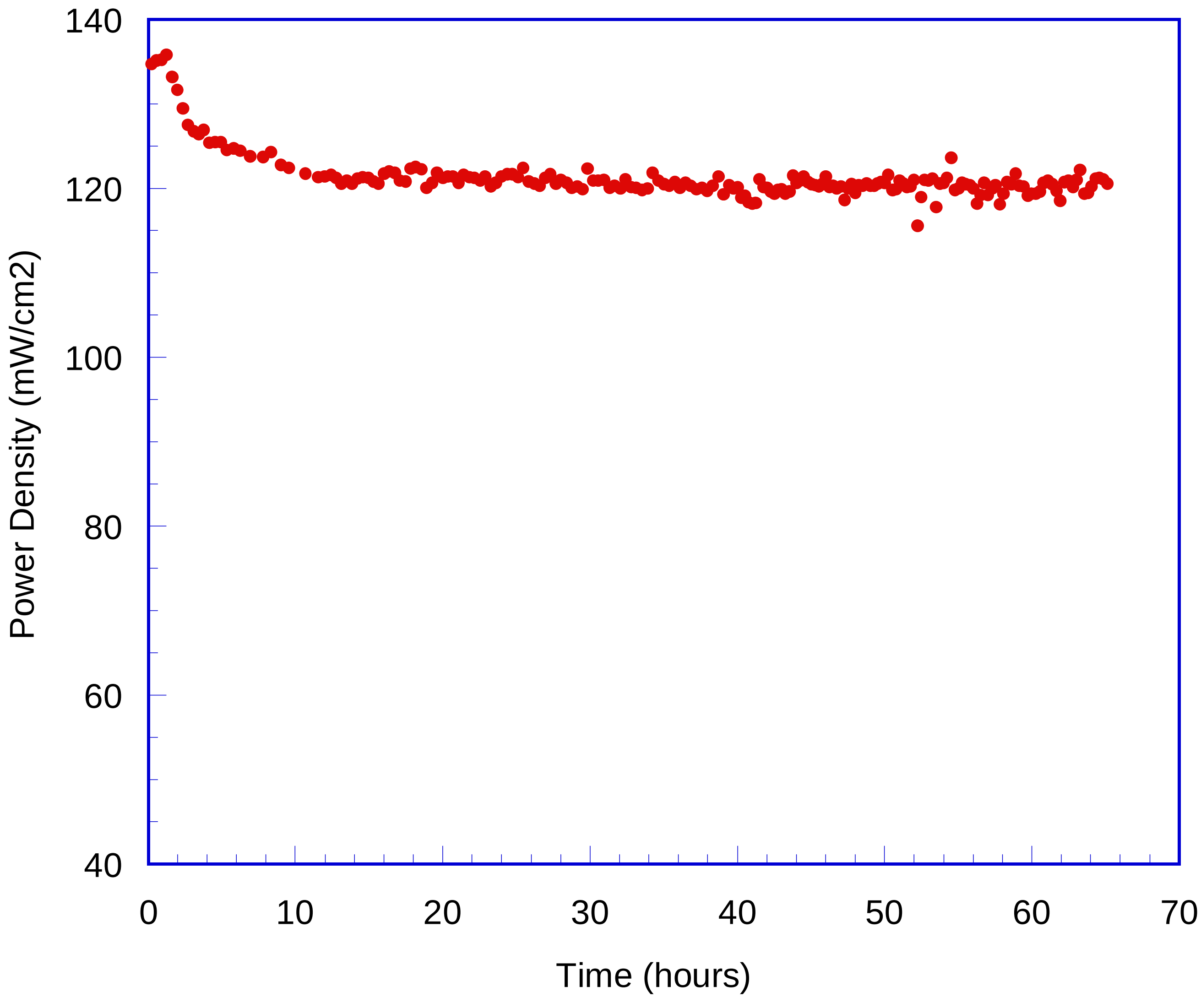
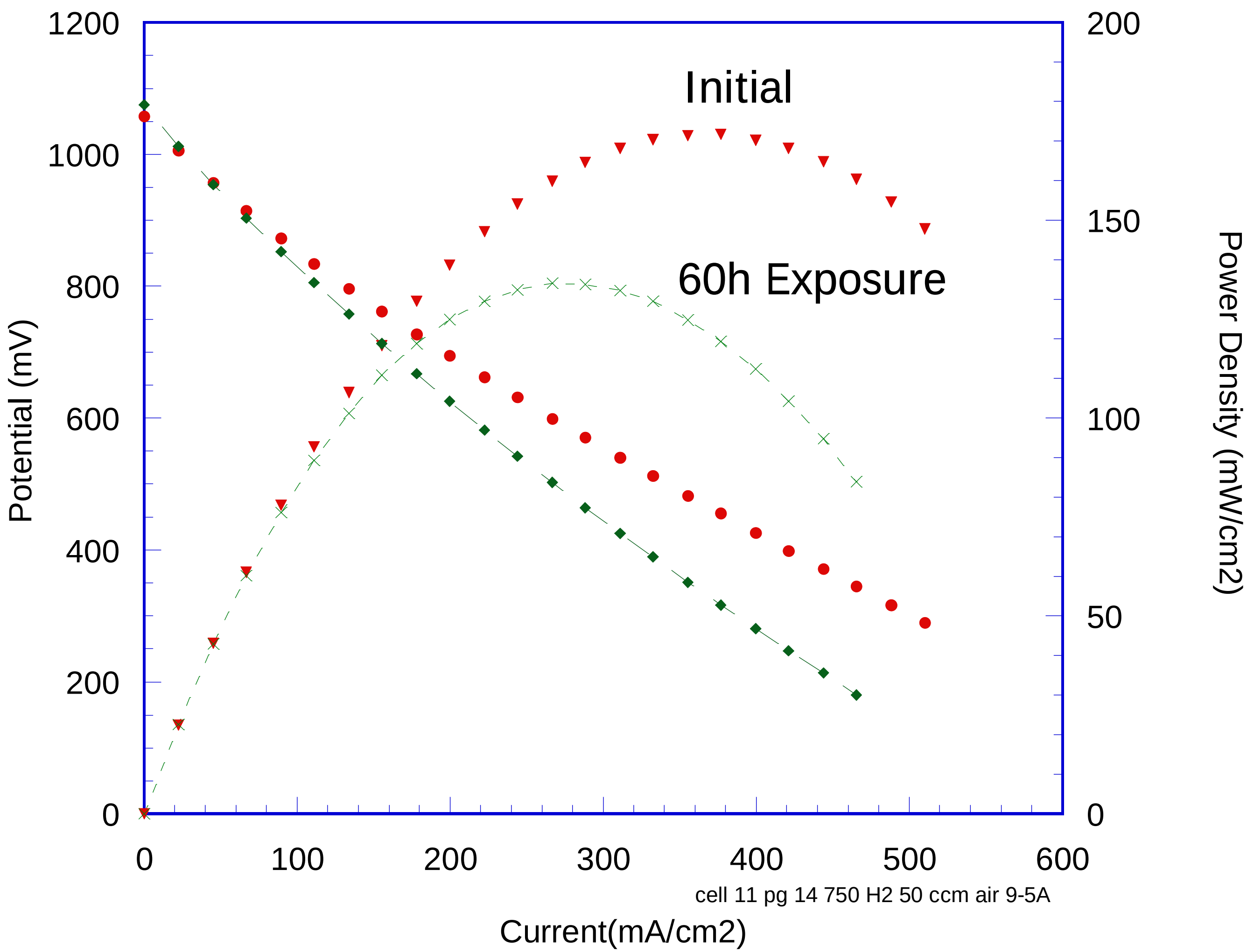
Performance of SOFC with 10 ppm P_2O_5 Vapor at 750° and 800°C (~0.7V and 0.2A/cm²)



Performance of SOFC with 10 ppm As(g) Vapor at 750°C (~0.7V and 0.2A/cm^2)



Performance of SOFC with 10 ppm As(g) Vapor at 750°C After 60 h



Summary

- 100 h exposure tests in a simulated coal gas stream at 750° to 800°C show that:
  - HCl and CH_3Cl at 38 ppm level do not have a significant effect. At 850°C, CH_3Cl degrades the SOFC performance steadily.
  - Zn vapor at 10 ppm level leads to a slow decline in performance at 800°C.
  - P vapor (10 ppm) degrades the SOFC anode.
  - As vapor at 750°C affects the performance rapidly initially, but remains steady after 10 h.

Future Work

- Determination of the effect of Hg, Cd, Sb, and Bi.
- Characterize the anode degradation using bulk and surface analyses.
- Relative ranking of the effect of individual contaminants.
- Determination of the effect of coal ash fumes.
- Determination of synergistic effect of contaminants.
- Preliminary determination of the sensitivity of SOFC to contaminants.
- Long term experiments with selected contaminants in large area cells at different concentrations.
- Recommendation of tolerance limits.

PROJECT TEAM

- SRI International
  - Gopala Krishnan, Palitha Jayaweera, Kai-Hung Lau, and Angel Sanjurjo.
- Research Triangle Institute
  - John Albritton, Brian Turk, and Raghubir Gupta
- U.S. Department of Energy (NETL)
  - Shawna Toth, Wayne Sardoval, Ayyakkannu Mannivannan
- Cooperative agreement: DE-FC26-05NT42627.