Effect of Coal Contaminants on SOFC Cell Performance

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Accomplishments

- Assembled a test fixture for the exposing SOFC button cells for >1000 h exposure.
  - The test fixture was made of YSZ and alumina ceramics to prevent loss of trace-metal species during transport to the anode.
- Determined the effect of 8 trace-level species in a simulated coal gas stream on the anode of an SOFC:
  - Temperature range: 750° to 850°C
  - Contaminant levels: 0.5 ppm to 35 ppm
  - Duration: 100 to >1000 h

Summary of Observed Degradation in Short Term Tests

Contaminant	Level (ppm)	Observed Degradation (%) after 100 h at 750°C	800°C	850°C
As ($As_2(g)$)	10	10	Cell Failure	
P ($HPO_2(g)$)	40	7.5	10	
Cd(g)	5		<1	8
$CH_3Cl(g)$	40		<1	4
HCl(g)	40	<1	<1	
Hg(g)	7	<1	<1	
Hg(g)	0.18	<1	<1	<1
Sb (SbO(g))	8	<1	<1	1
Zn(g)	10		<1	<1

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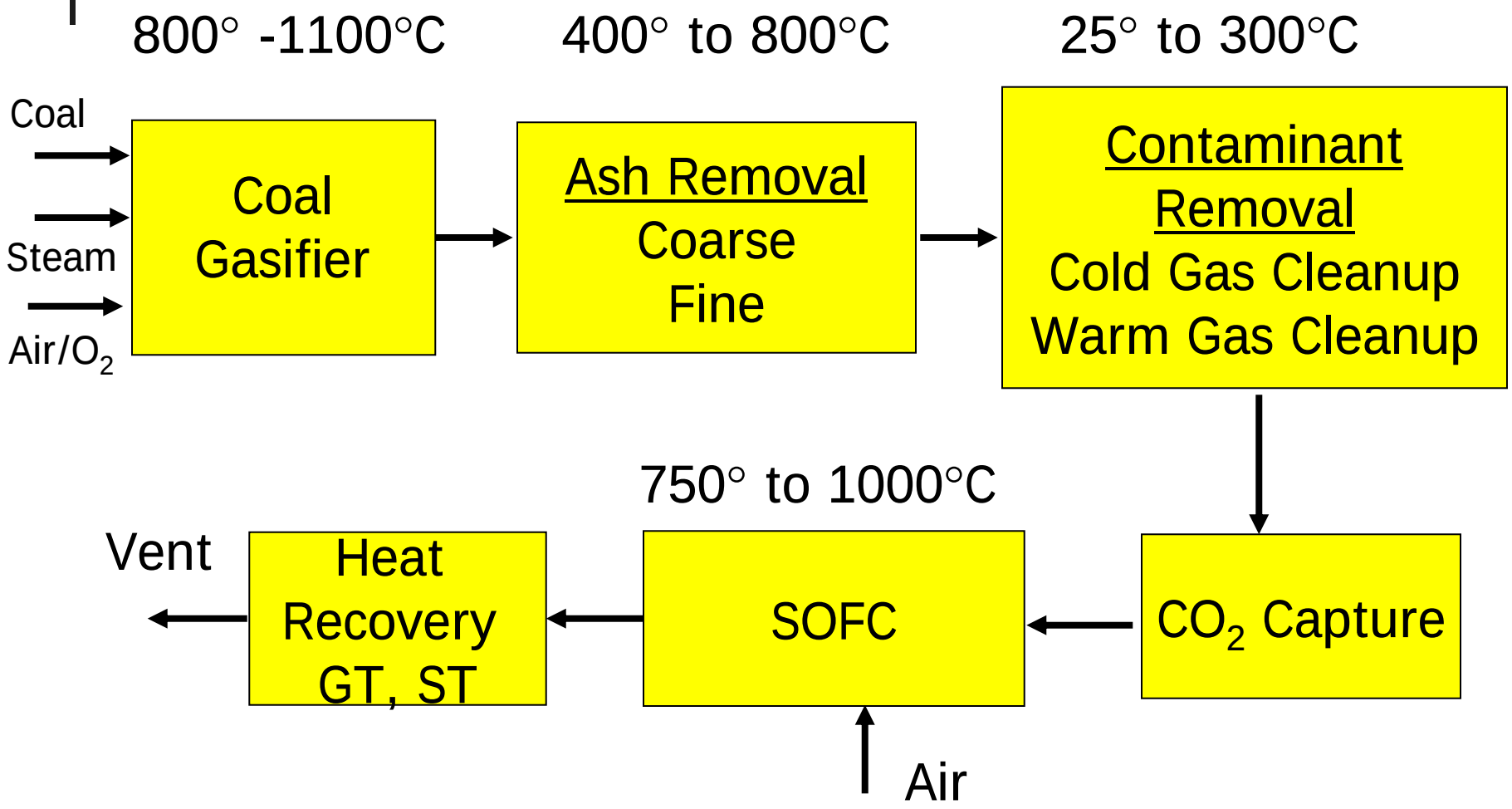
Long-Term Test Data

- AsH_3 exposure at 750°C at 0.5 ppm for 1000 h and at 1 ppm for 600 h did not degrade the cell performance.
- Experiments with PH_3 is continuing

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

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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.
- Condensed species (solid or liquid) may be effectively removed effectively by cold gas cleanup with a solvent such as Selexol or Rectisol.

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	

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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 phosphate
- Affect the electrical conductivity
  - Formation of alloys or bulk phases such as sulfides or arsenides

Experimental Determination of the Effect of Trace Elements on SOFC Performance

- We are concentrating on contaminants other than H_2S.
- Scoping experiments to determine the effect of following contaminants on SOFC performance:
  - HCl, CH_3Cl
  - As, P, Sb, Cd, Hg, and Zn species
- Long-term experiments with selected species:
  - H_2S, AsH_3, PH_3, and CH_3Cl

Experimental Setup

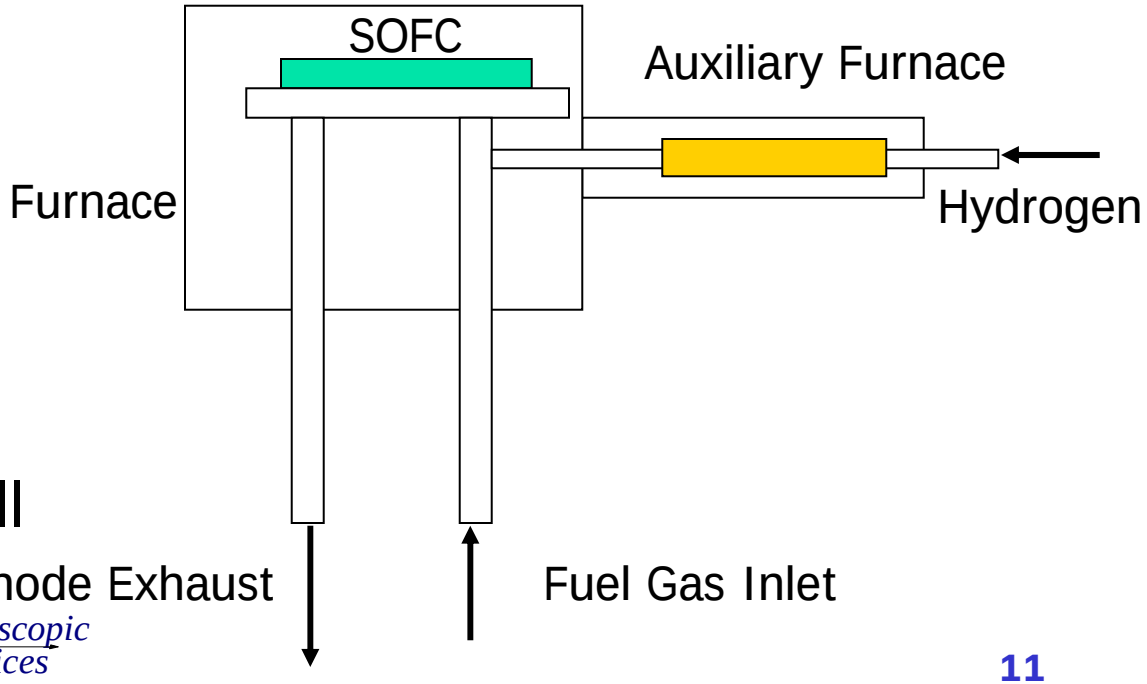
InDec B.V. Cells; 1 in Dia; 4-6μm electrolyte;

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

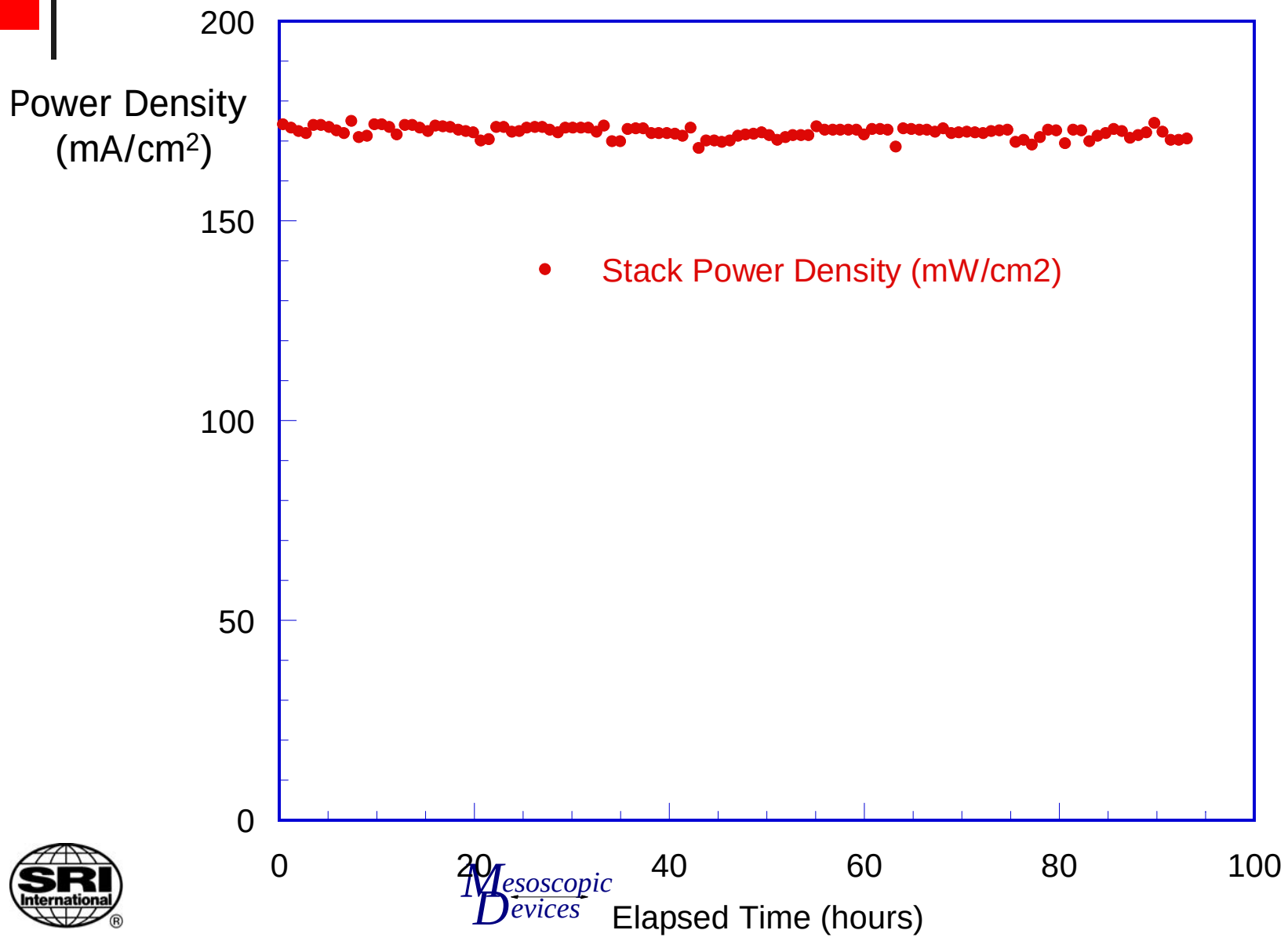
YSZ Holder with the cell



Degradation on Exposure to Trace-Metal Species

- Last year:
  - Degradation data on exposure to HCl, CH_3Cl, Zn, and P species.
- Current Data:
  - Degradation due to Hg, Cd, Sb, As, and P.

Performance of SOFC with 7 ppm Hg Vapor at 800°C (~0.7V and 0.2A/cm^2)



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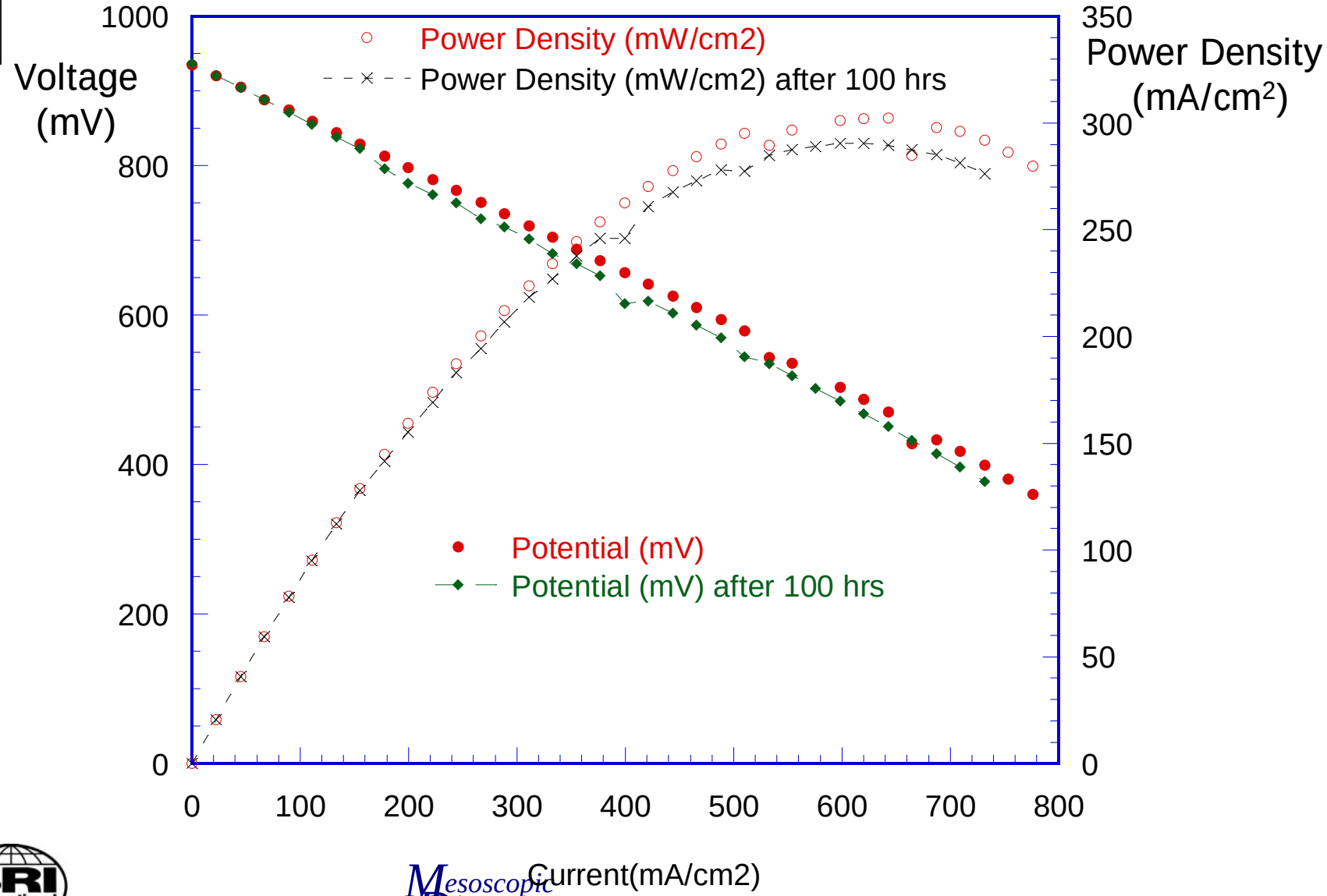
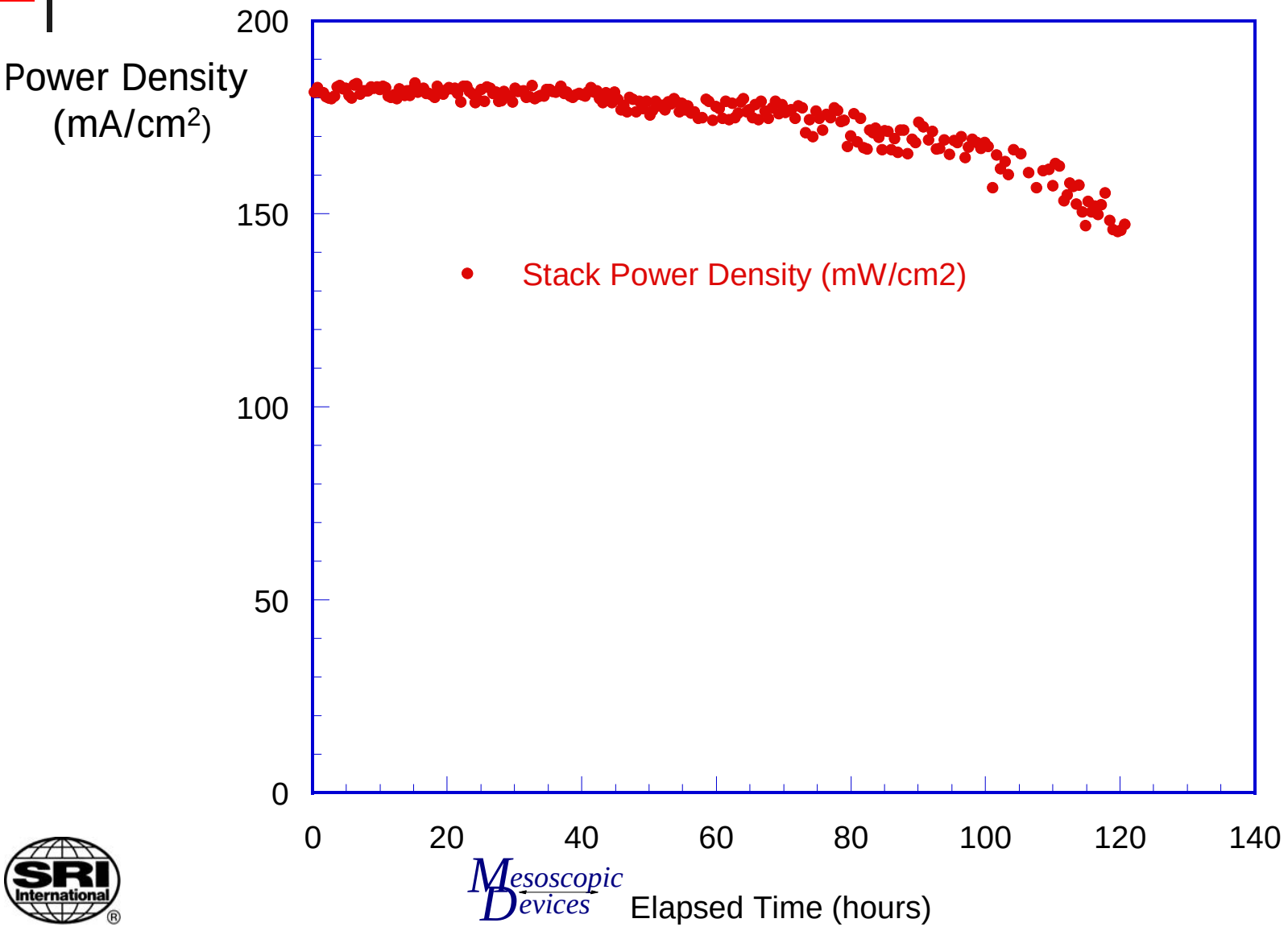
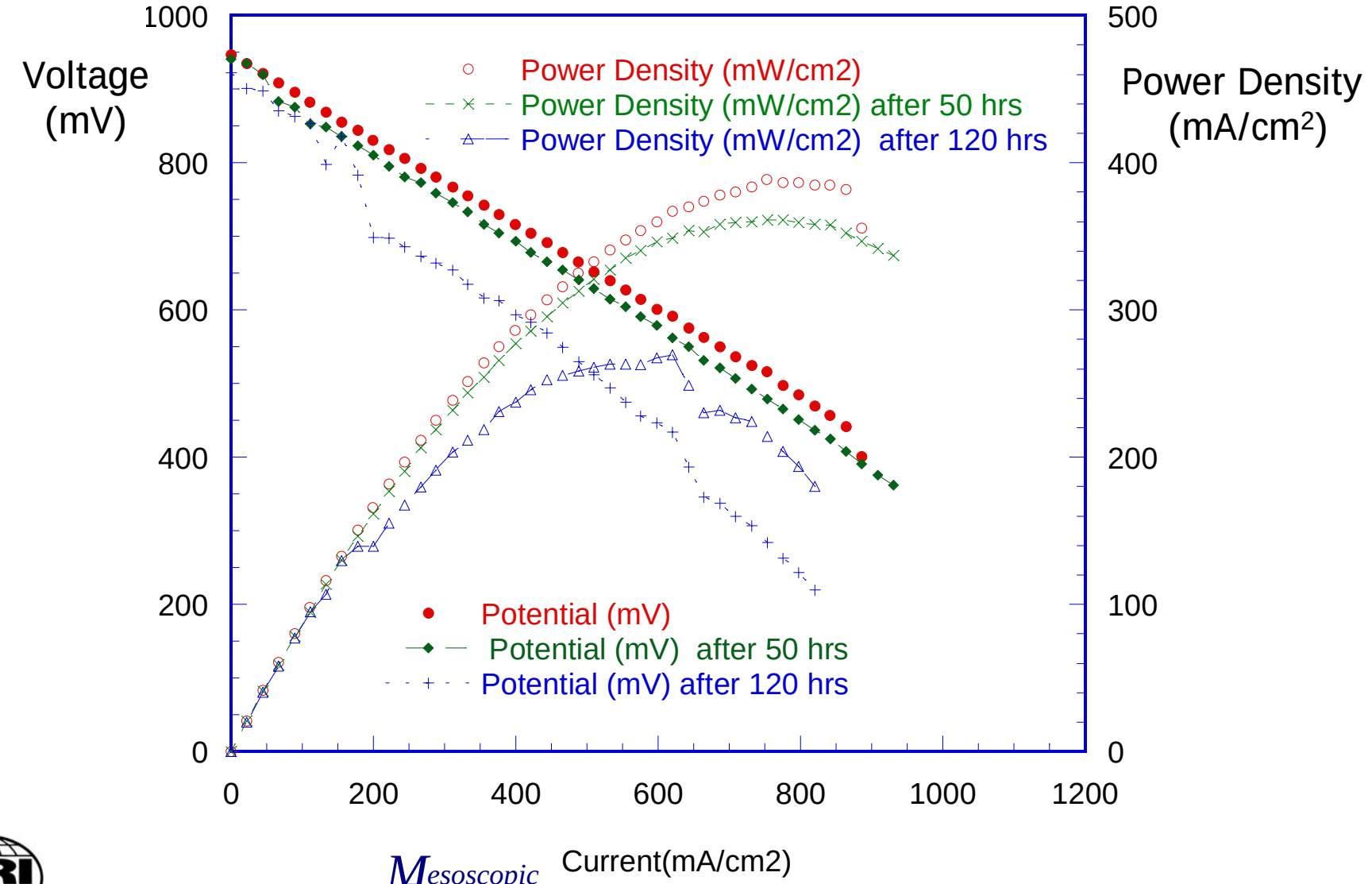


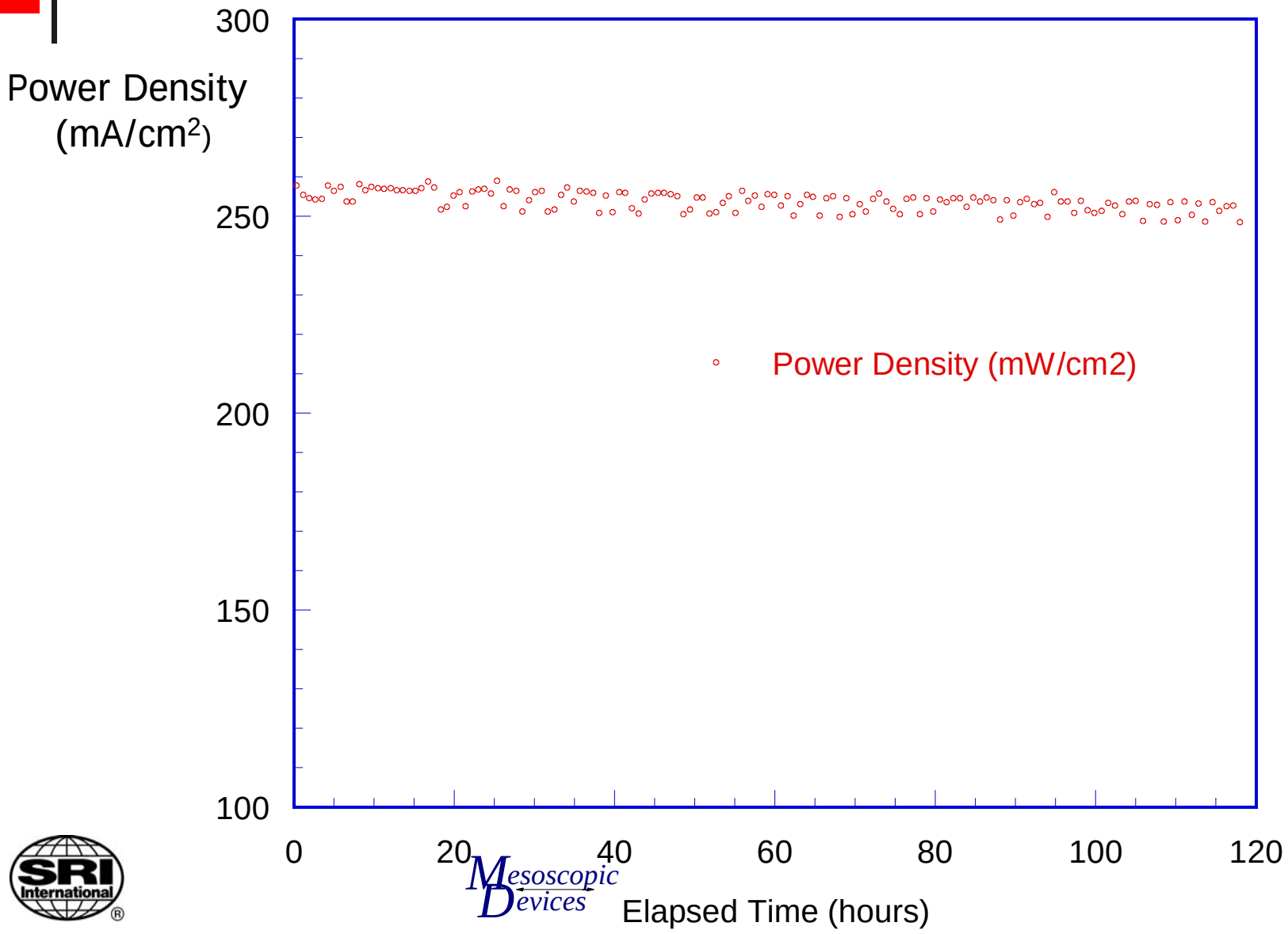
Performance of SOFC with 5 ppm Cd Vapor at 850°C (0.2A/cm^2)



Performance of SOFC with 5 ppm Cd Vapor at 850°C (0.3A/cm²)



Performance of SOFC with 5 ppm SbO Vapor at 850°C (0.3A/cm^2)



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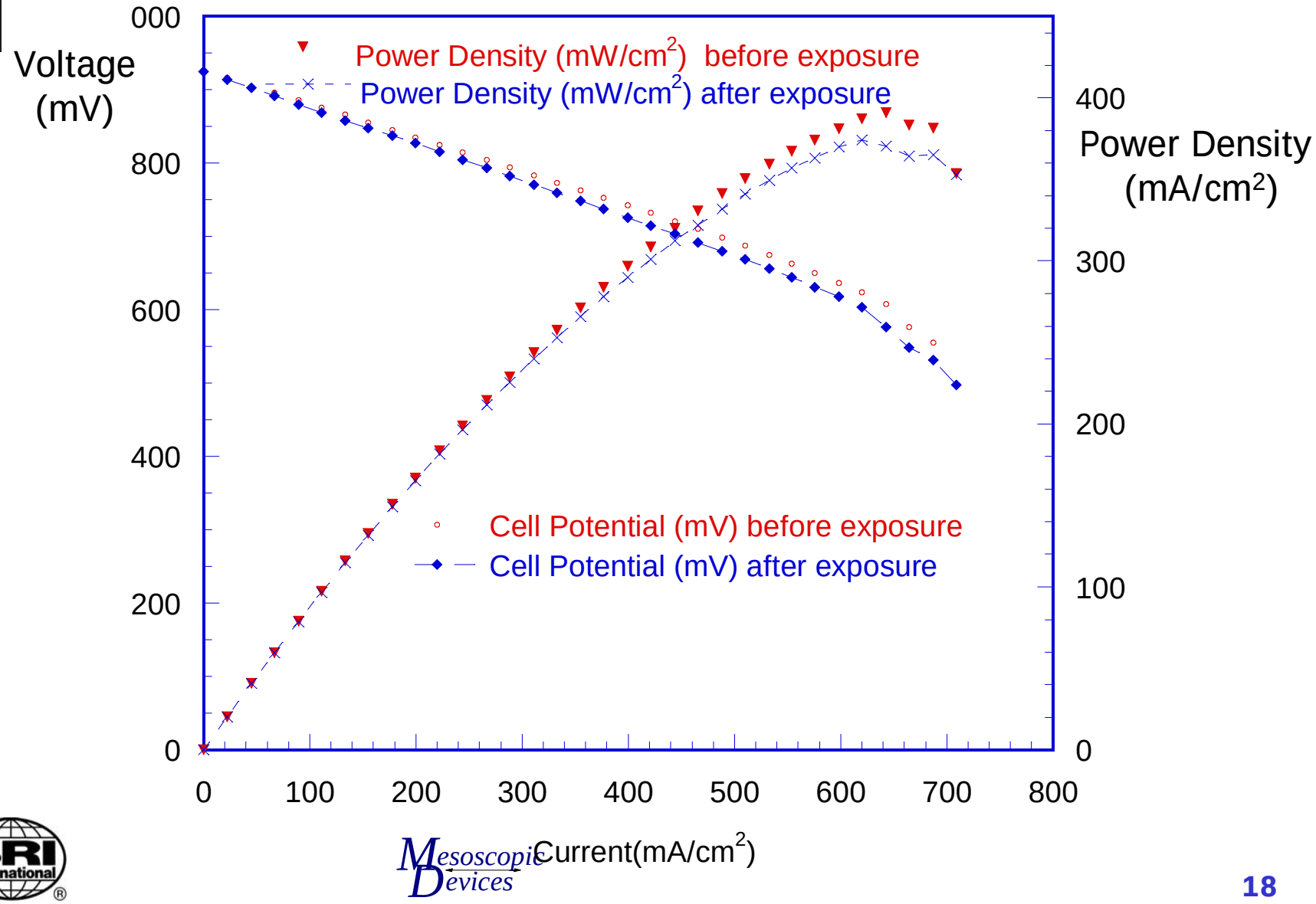
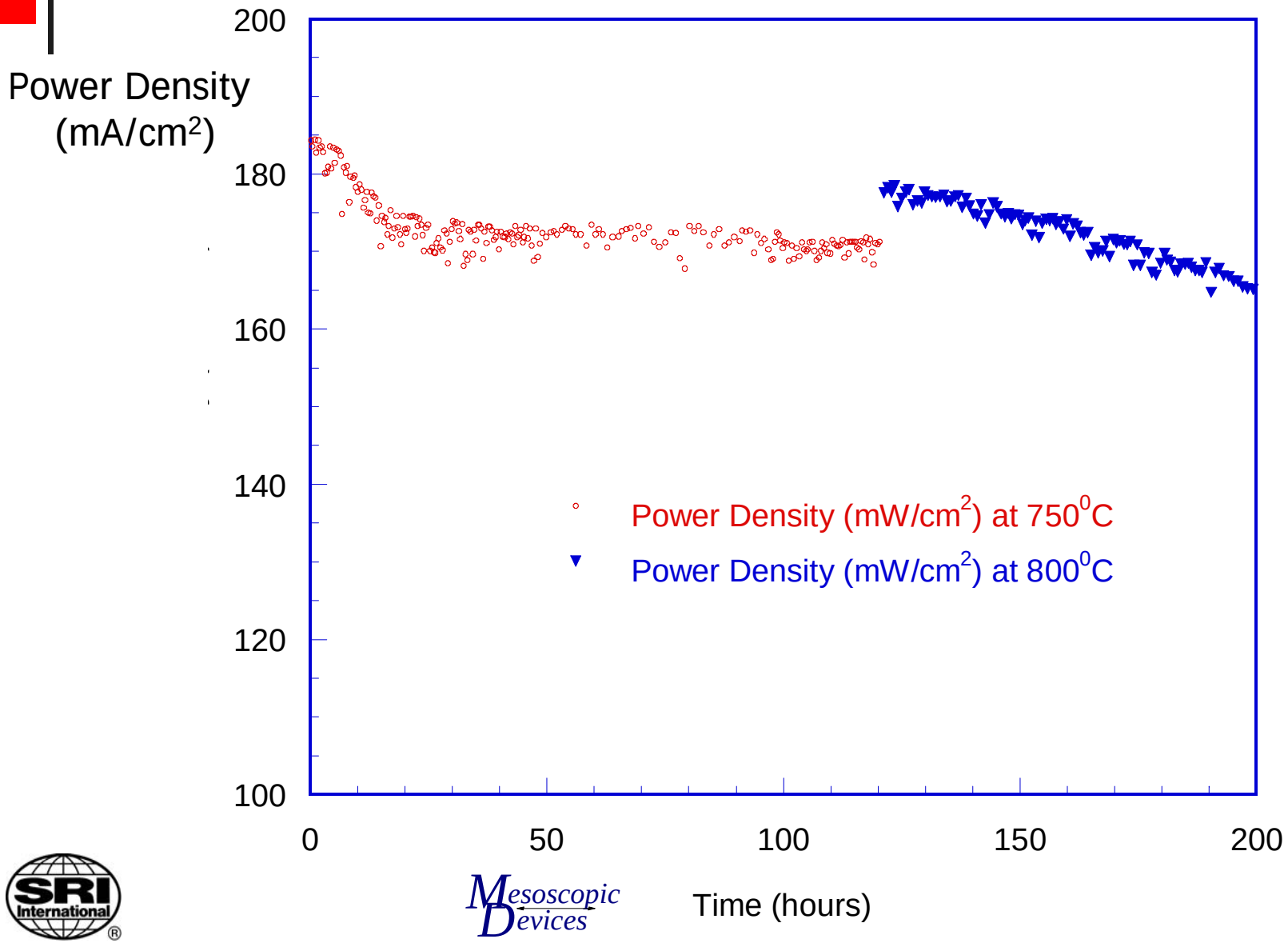
Performance of SOFC with 5 ppm SbO Vapor at 850°C for 120 h (0.3A/cm^2)



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

Performance of SOFC with 10 ppm P_xO_y Vapor at 750° and 800°C (~0.7V and 0.2A/cm^2)



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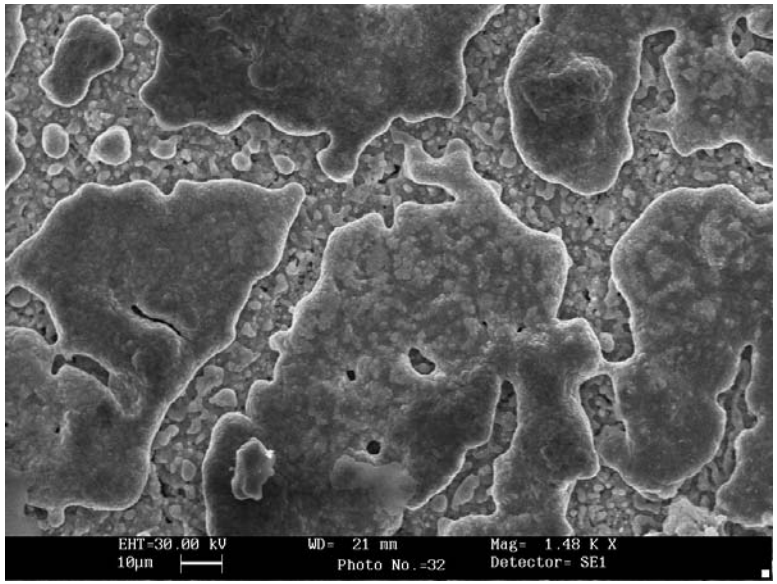
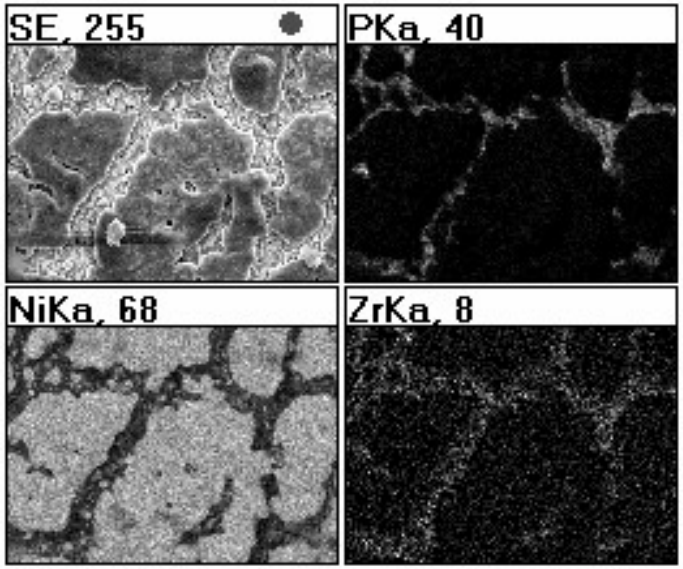
EDX Mapping of P contamination

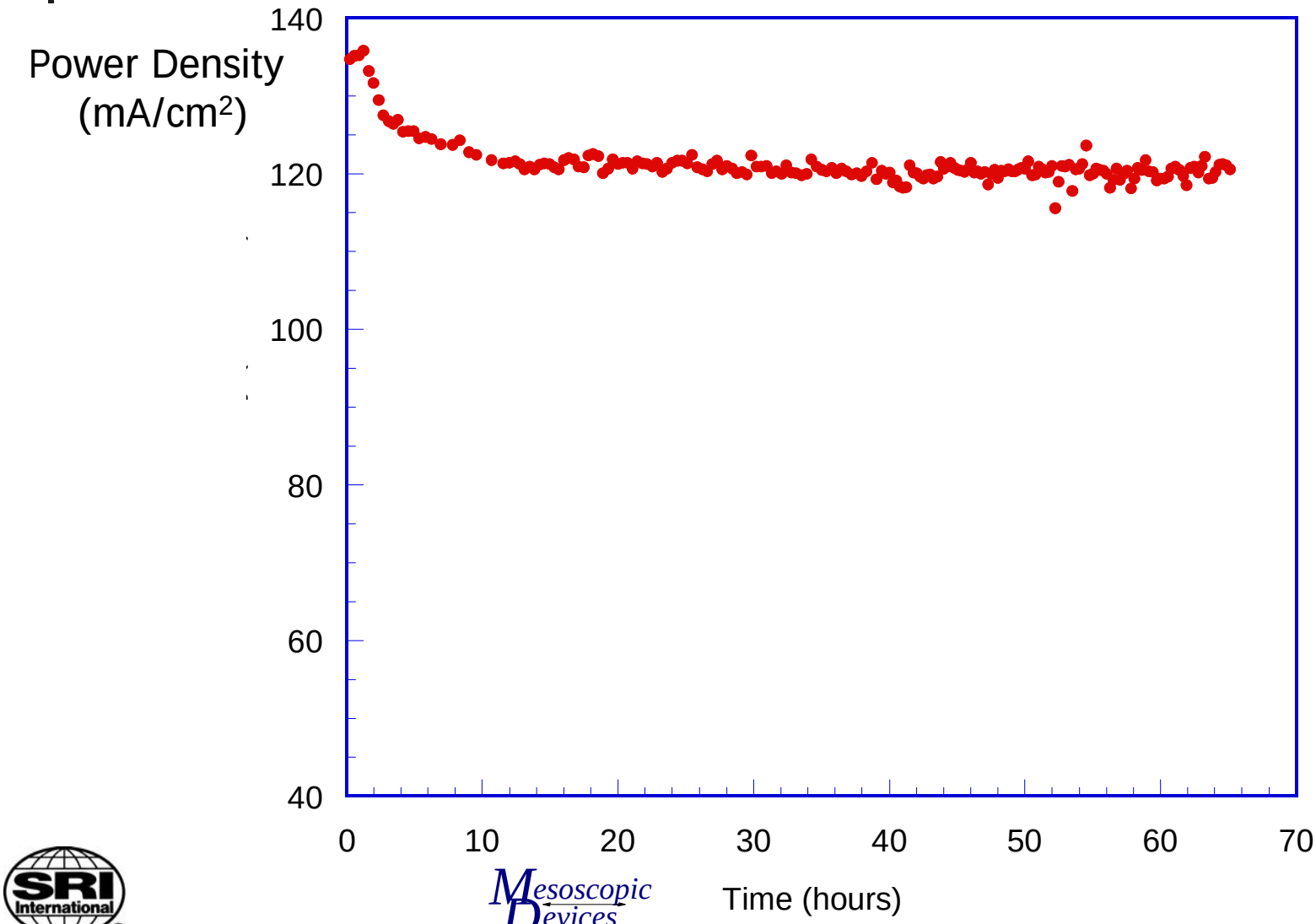


SEM image of anode



X-ray images

Performance of SOFC with 10 ppm $As_2(g)$ Vapor at 750°C (0.2A/cm^2)



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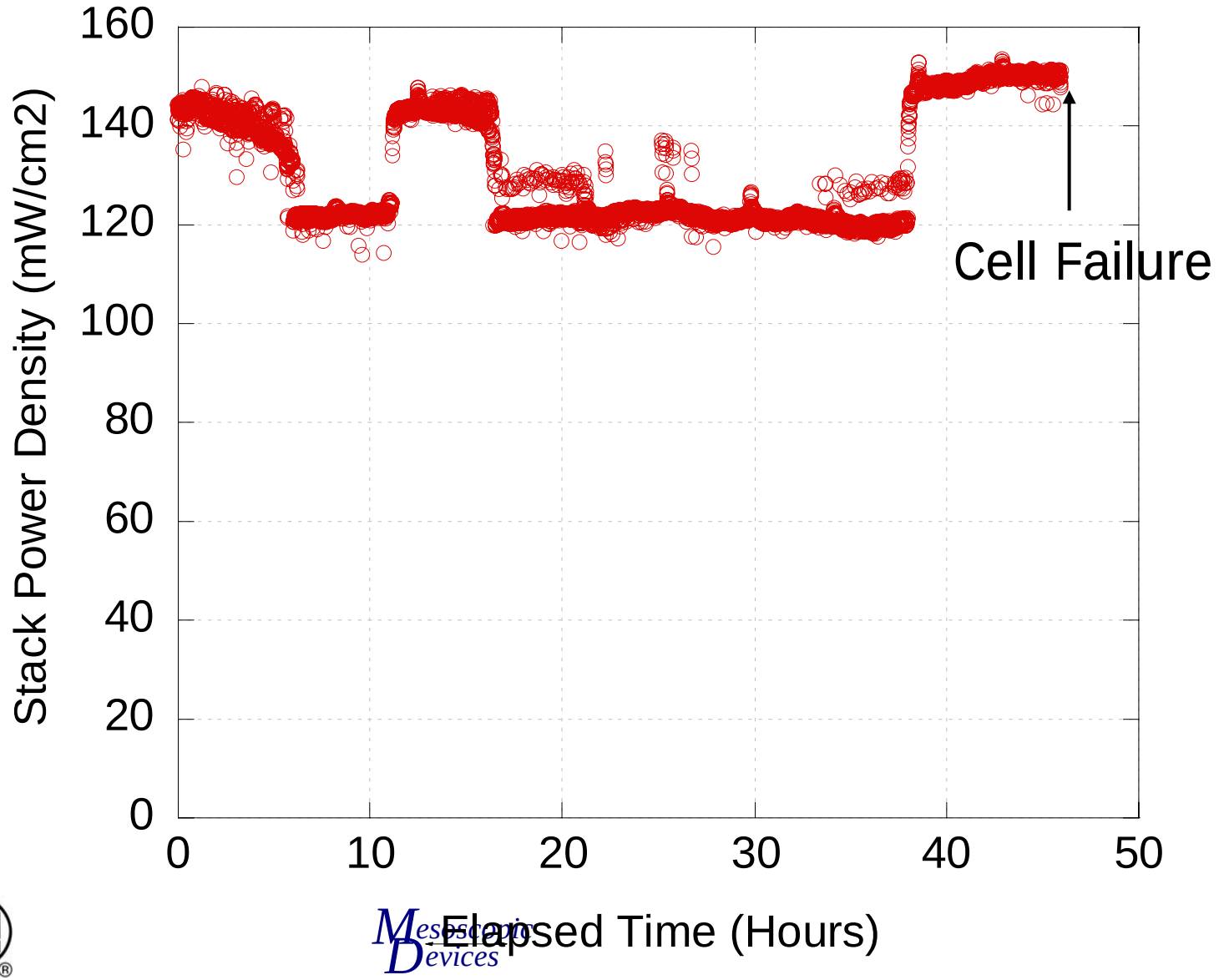
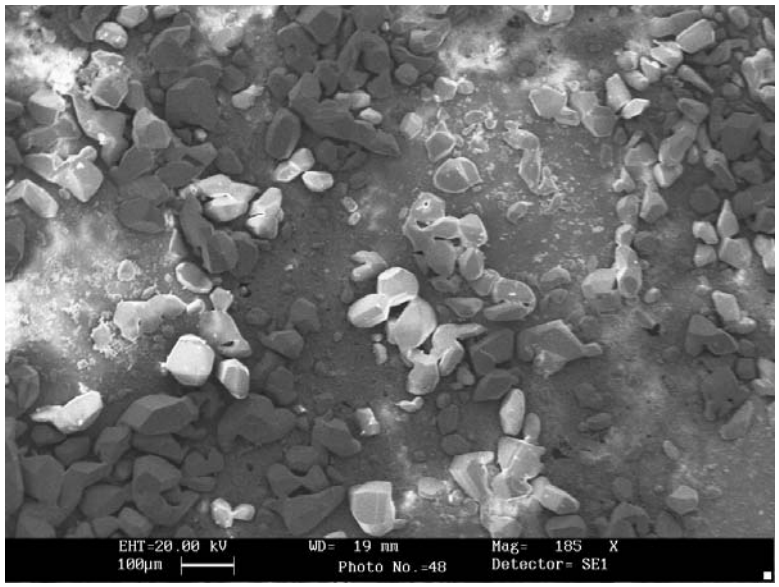
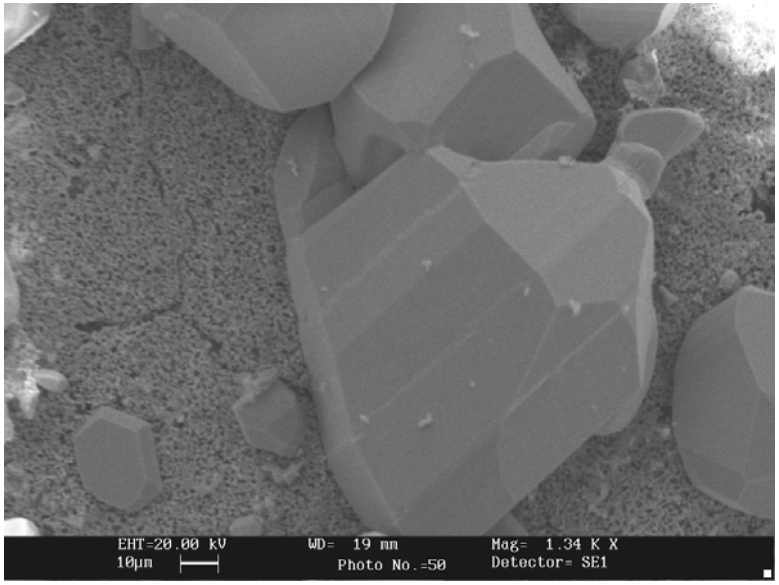
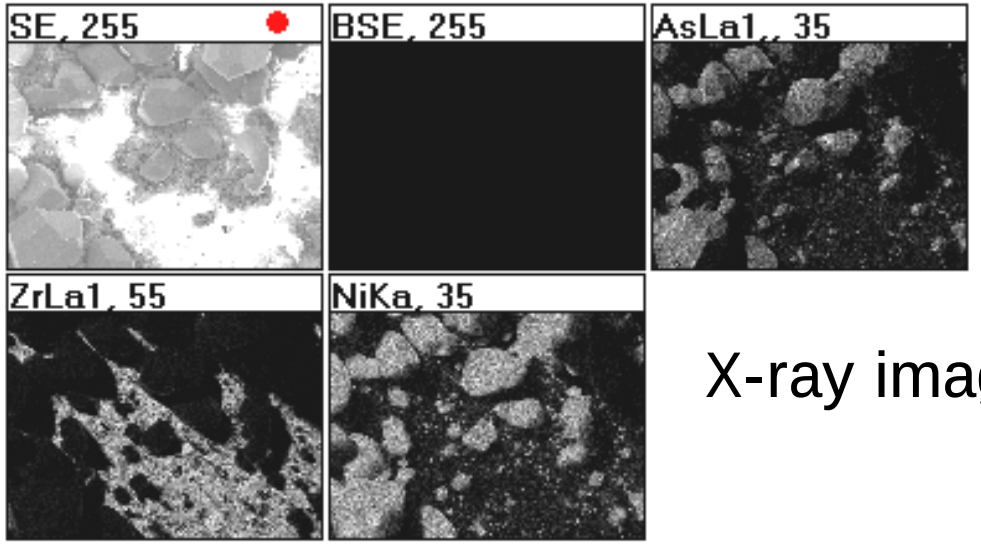
Performance of SOFC with 10 ppm $As_2(g)$ Vapor at 800°C



As Contamination

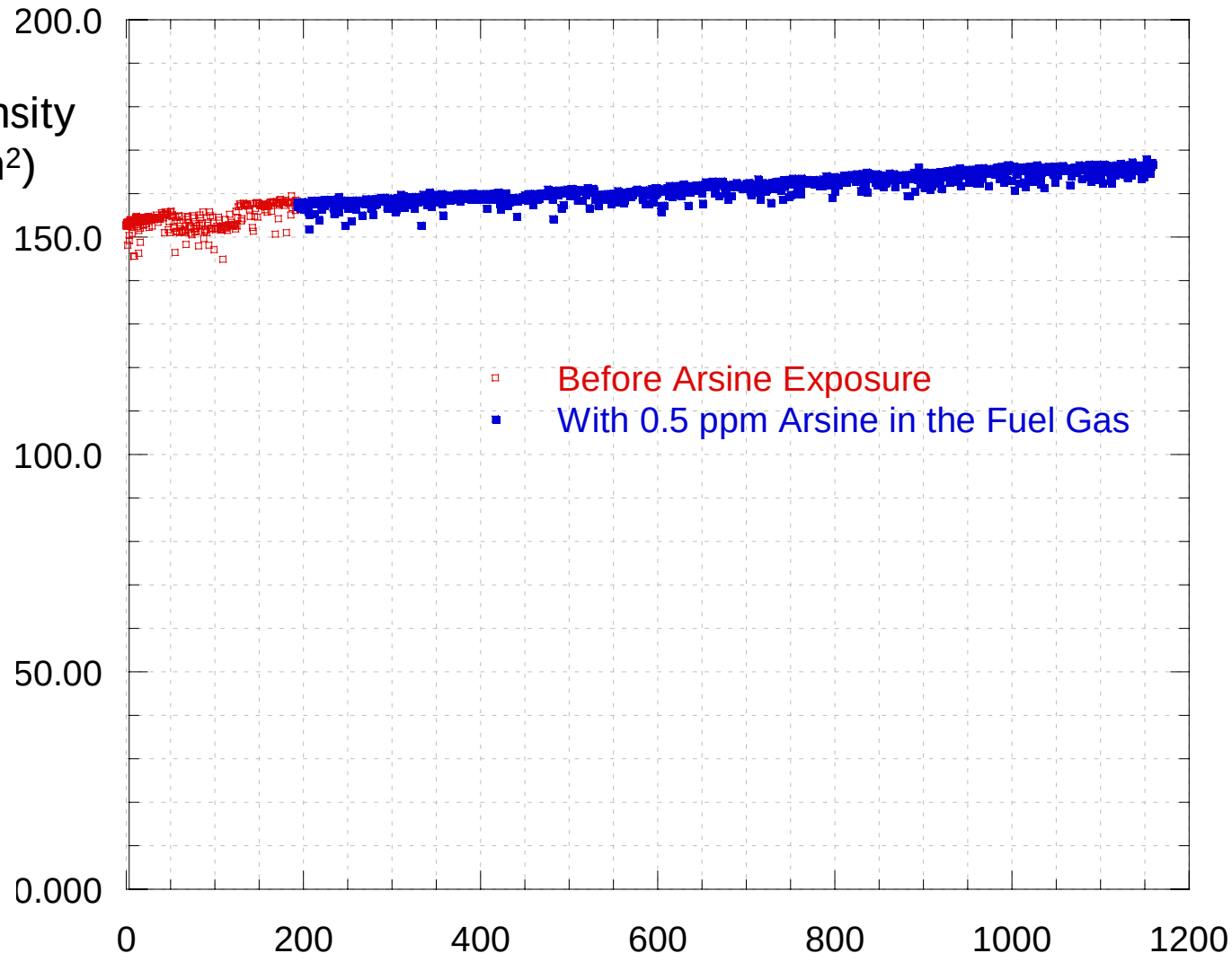






X-ray images

Performance of SOFC with 0.5 ppm AsH_3(g) Vapor at 750°C over 1000 h



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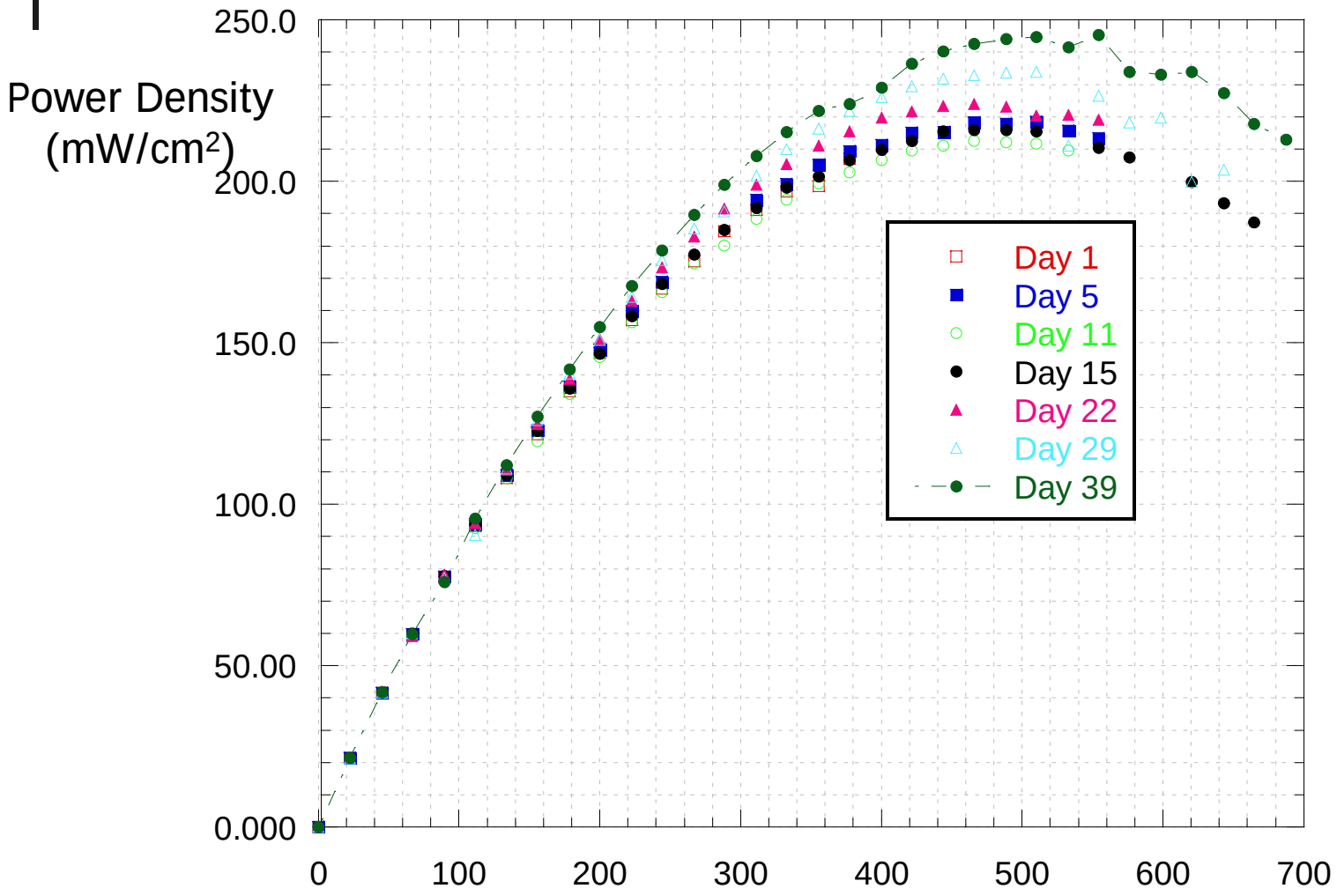

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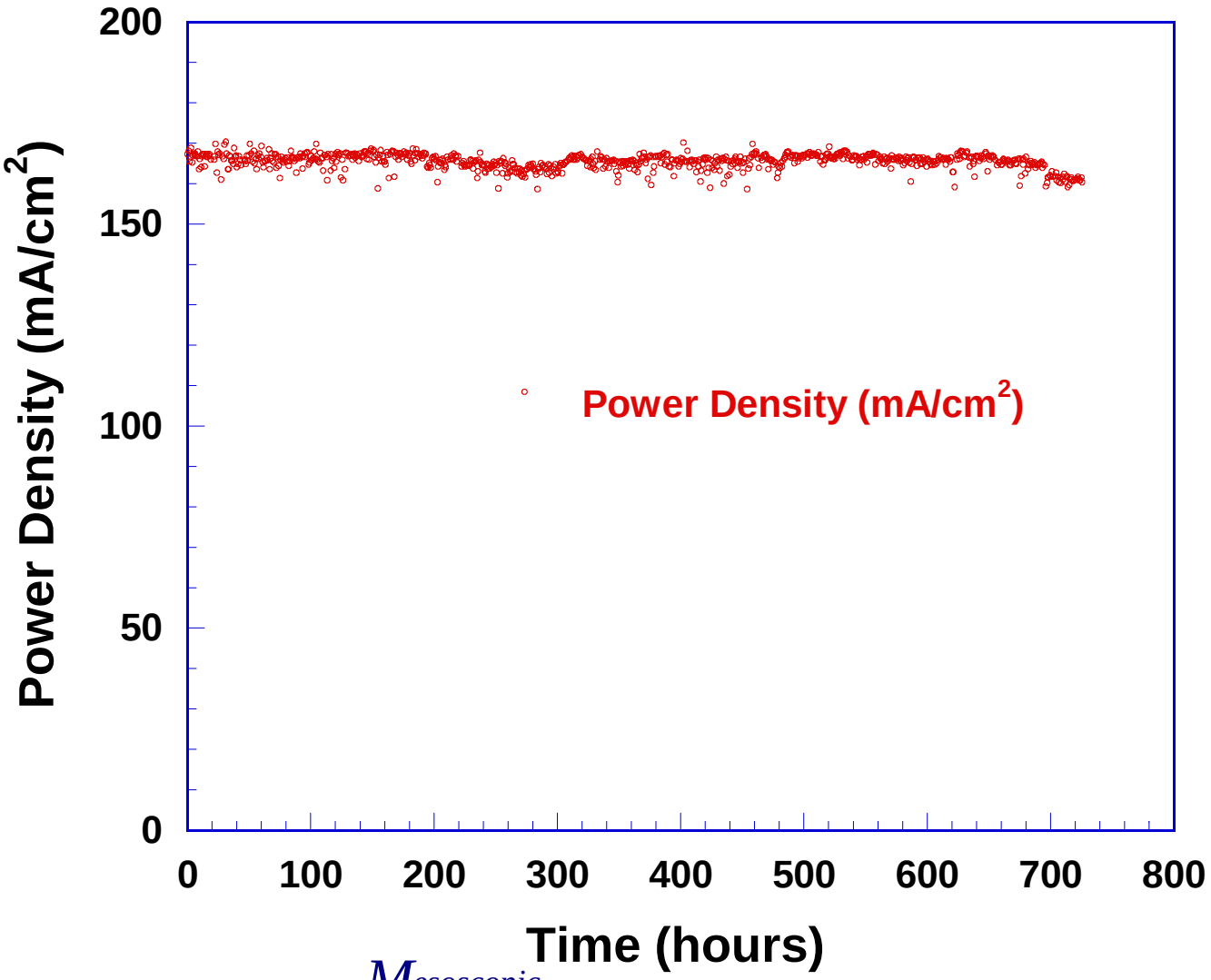
AsH_3 Exposure at 1 ppm Level at 750°C



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Summary

- 100 h exposure tests in a simulated coal gas stream at 750° to 800°C show that:
  - HCl and CH_3Cl at ~40 ppm level do not have a significant effect at 750°C. At 850°C, CH_3Cl degrades the SOFC performance steadily.
  - As vapor at 10 ppm levels degrades the performance by interaction with the nickel phase.
  - HPO_2 vapor degrades the SOFC anode by interaction with the YSZ matrix
  - Zn vapor at 10 ppm level leads to a very slow decline in performance at 800°C.
  - Cd vapor leads to slow degradation at 850°C.
  - SbO vapor at a 8 ppm level did not affect the performance.
  - Hg vapor does not affect the anode performance.

Summary (continued)

- Long-term tests with AsH_3 0.5 and 1ppm levels did not degrade the cell performance.
- Tests with sub-ppm levels are continuing.

Future Work (Phase II)

- Perform long-term tests with multiple contaminants (H_2S, AsH_3, PH_3 and CH_3Cl) at typical of coal-derived gas streams that have undergone gas cleanup using Selexol technology.
- Use the Design of Experiments approach to limit the number of experiments that need to be performed for statistical analysis of the effect of multiple contaminants on the cell performance.
- Identify the chemical nature of the contaminant species at the operating temperature of SOFC and compare them with thermodynamic equilibrium calculations.
- Use the results of the program to recommend the sensitivity limits for SOFC operation

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, Ayyakkannu Mannivannan, Briggs White, Wayne Sardoval.
- Cooperative agreement: DE-FC26-05NT42627.