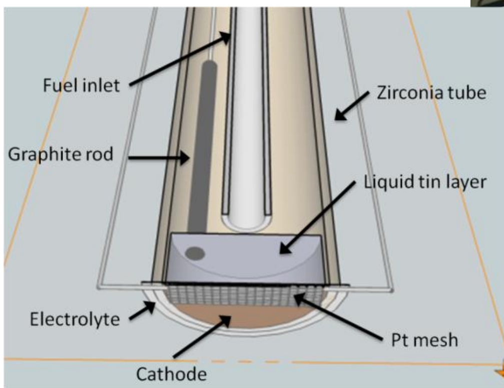
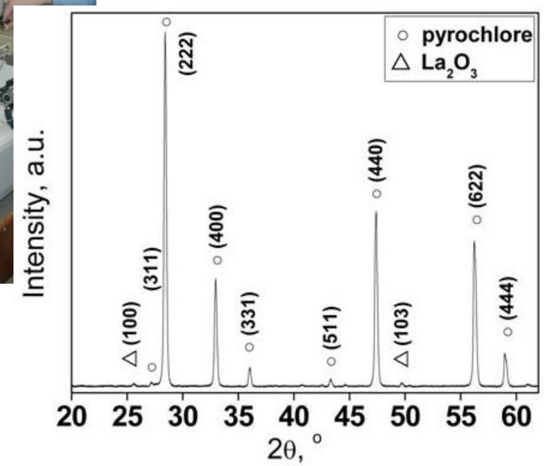
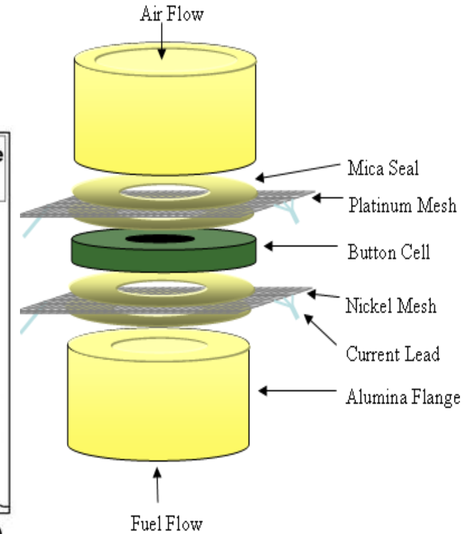
NATIONAL ENERGY TECHNOLOGY LABORATORY







Exposure Limits of Higher Hydrocarbons for SOFC

SECA 2010 Workshop

NETL Fuel Cell Group

July 29, 2010

Kirk Gerdes

Research Group Leader, Fuel Cells

NETL Morgantown

Overview

- **NETL FC Group Background**
- **Discussion of Coal Syngas Exposure Results**
  - Individual contaminants testing protocol
    - Mercury
    - Naphthalene, Benzene
    - PEG/DME
- **Conclusions**
- **FY11 planned research**

NETL Fuel Cells Group

- **Federal activity**
  - 5 federal research projects
    - Anode contaminates and liquid metal anode
    - Cathode infiltration
    - Hybrid gas turbine / FC operation and controls
    - GC-ICP/MS
  - 4 federal researchers and 5 post-doctoral research associates

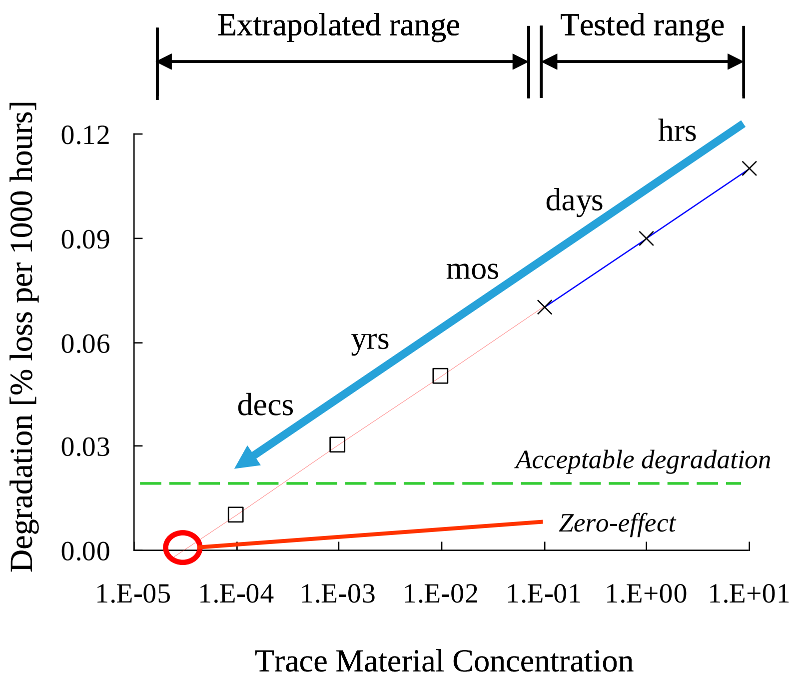
- **University activity**
  - 5 university research projects (CMU and WVU)
    - Cathode crystallographic evolution
    - Cathode infiltration and microstructural modeling (2 projects)
    - Fundamentals of oxygen reduction reaction (ORR)
    - Hybrid controls

- **Contract labor support**
  - Research management and support activities

Contaminants - Problem Outline

- Analyze the interaction of trace materials in direct syngas with the solid oxide fuel cell (SOFC) anode

- **Thermodynamic analysis**
  - Elements present
    - As, Cd, Hg, Pb, Sb, Se
  - Elements interacting
    - As, Sb
    - Stable secondary phases
- **Laboratory results**
  - As, P, S, Se



A. Martinez, K. Gerdes, R. Gemmen, and J. Poston, Journal of Power Sources, 195, (2010) p5206–12.

- Additionally interested in higher hydrocarbons and process materials (benzene, naphthalene, ethylene, Selexol)

Contaminants - Background

- **Trace material can attack the anode by any (or all) of three primary degradation mechanism classes**

- **<u>Class I</u> – Physical blocking of fuel feed pores**
  - Carbon whiskers (graphite), incombustible materials (Si)

- **<u>Class II</u> – Surface adsorption**
  - Deactivation of catalytic sites (S, Se)

    J. Hansen, "Correlating Sulfur Poisoning of SOFC Nickel Anodes by a Temkin Isotherm" Electrochem. Solid-State Lett., Volume 11, Issue 10, pp. B178-B180 (2008)

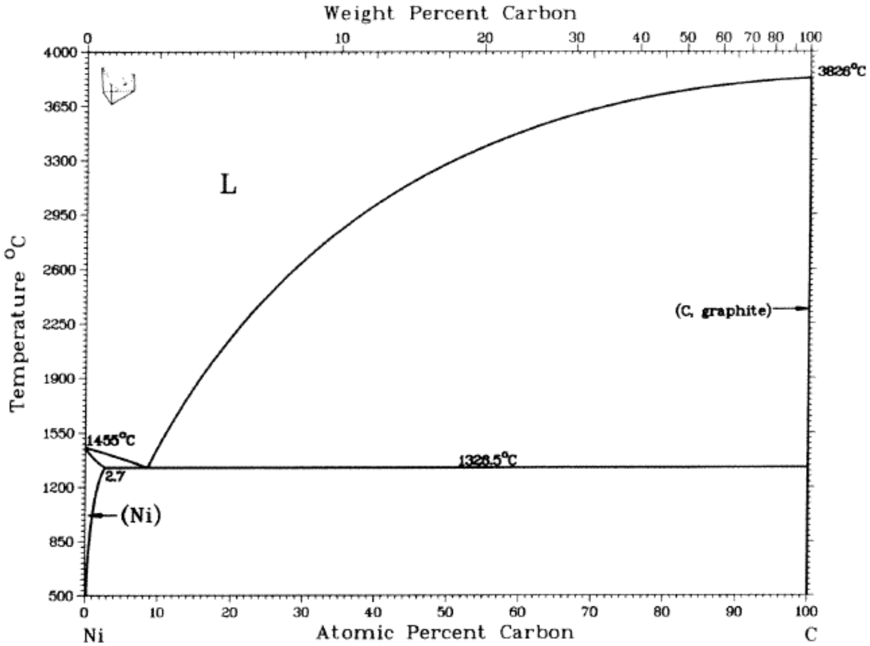
- **<u>Class III</u> – Chemical reaction**
  - Class IIIA – Formation of secondary metal phases (P, As, Sb)
  - Class IIIB – Formation of metal solutions (C)

HHC Contaminants - Background

- **Standard cell is purchased commercially**
  - Ni/YSZ anode; YSZ electrolyte; LSM cathode
- **Cell is exposed to precisely controlled mass of trace material**
  - Benzene @ 15 and 150 ppm
  - Naphthalene @ 100 and 500 ppm
  - PEG/DME @ 1 and 3.5 ppm
  - Mercury @ 1 and 10 ppm

    ** Exposure significantly exceeds gasifier effluent concentration*

- **Electrochemical reaction monitored**
  - Temporal voltage, EIS
- **Post-operational microscopy**
  - SEM/EBSD, XPS, TEM

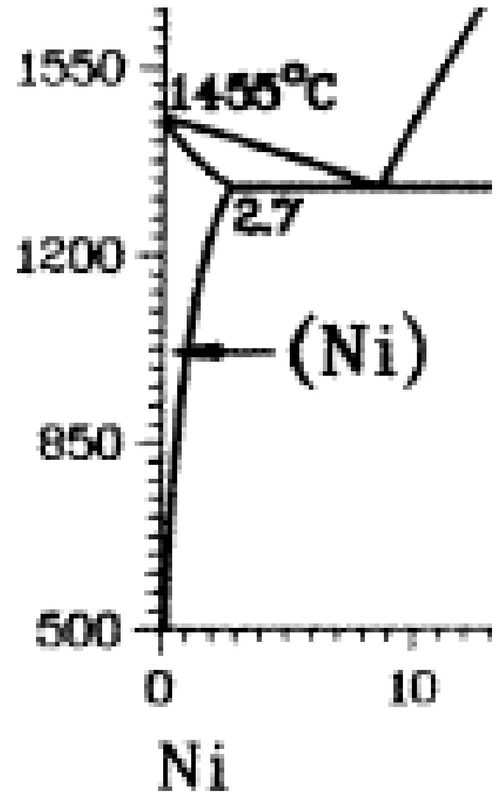


M.F. Singleton and P. Nash

HHC Contaminants - Background

- **Standard cell is purchased commercially**
  - Ni/YSZ anode; YSZ electrolyte; LSM cathode
- **Cell is exposed to precisely controlled mass of trace material**
  - Benzene @ 15 and 150 ppm
  - Naphthalene @ 100 and 500 ppm
  - PEG/DME @ 1 and 3.5 ppm
  - Mercury @ 1 and 10 ppm

    **** Exposure significantly exceeds gasifier effluent concentration***
- **Electrochemical reaction monitored**
  - Temporal voltage, EIS
- **Post-operational microscopy**
  - SEM/EBSD, XPS, TEM



M.F. Singleton and P. Nash

Test Parameters

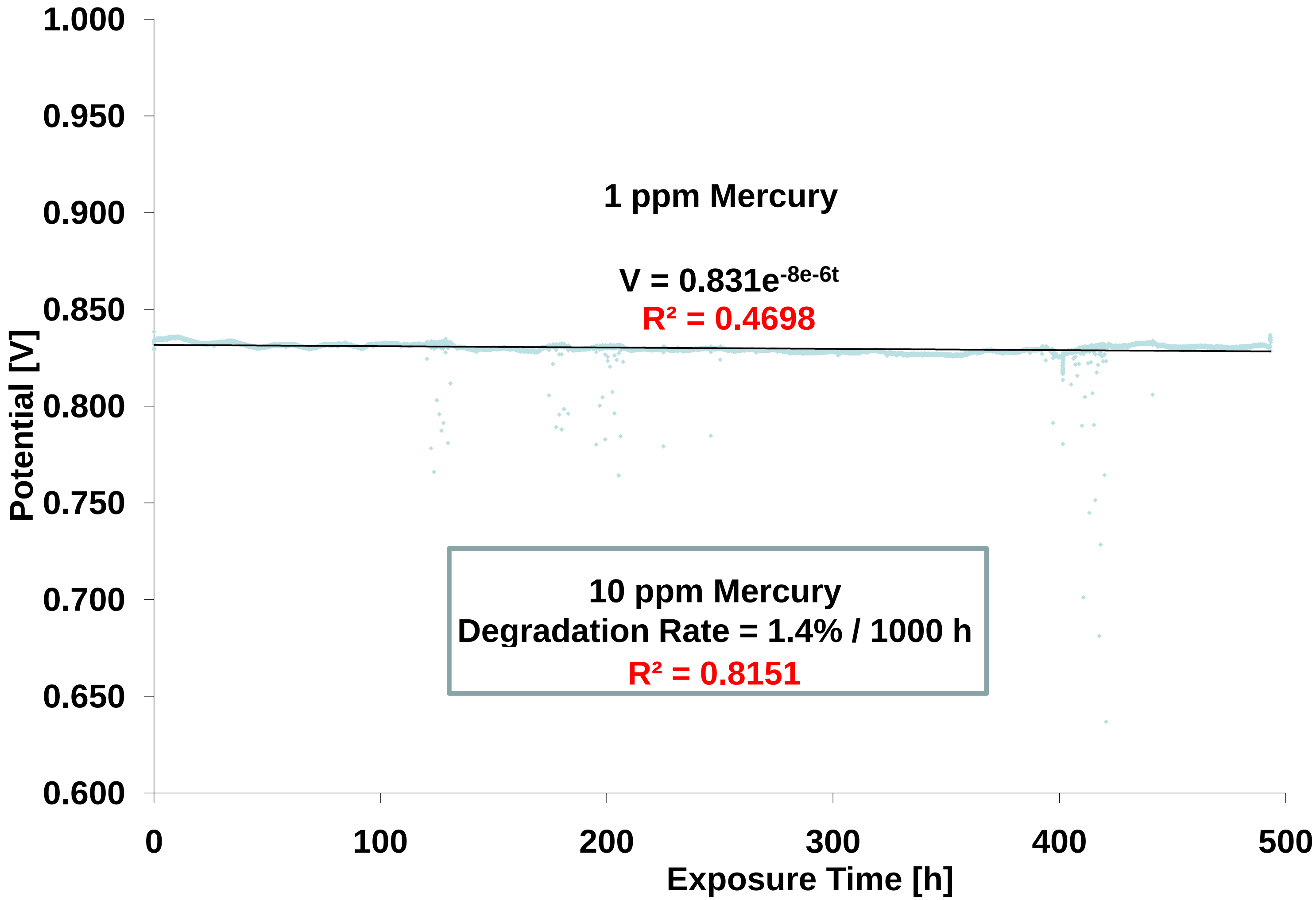
- **Cathode – Air @ 1000 mL/min**

- **Anode:**
  - Hydrogen: 87.3 mL/min (29.1%)
  - Carbon monoxide: 85.8 mL/min (28.6%)
  - H_2O: 81.8 mL/min (27.3%)
  - Carbon dioxide: 36.0 mL/min (12.0%)
  - Nitrogen: 9.6 mL/min (3.2%)

- **Temperature - 800 C**

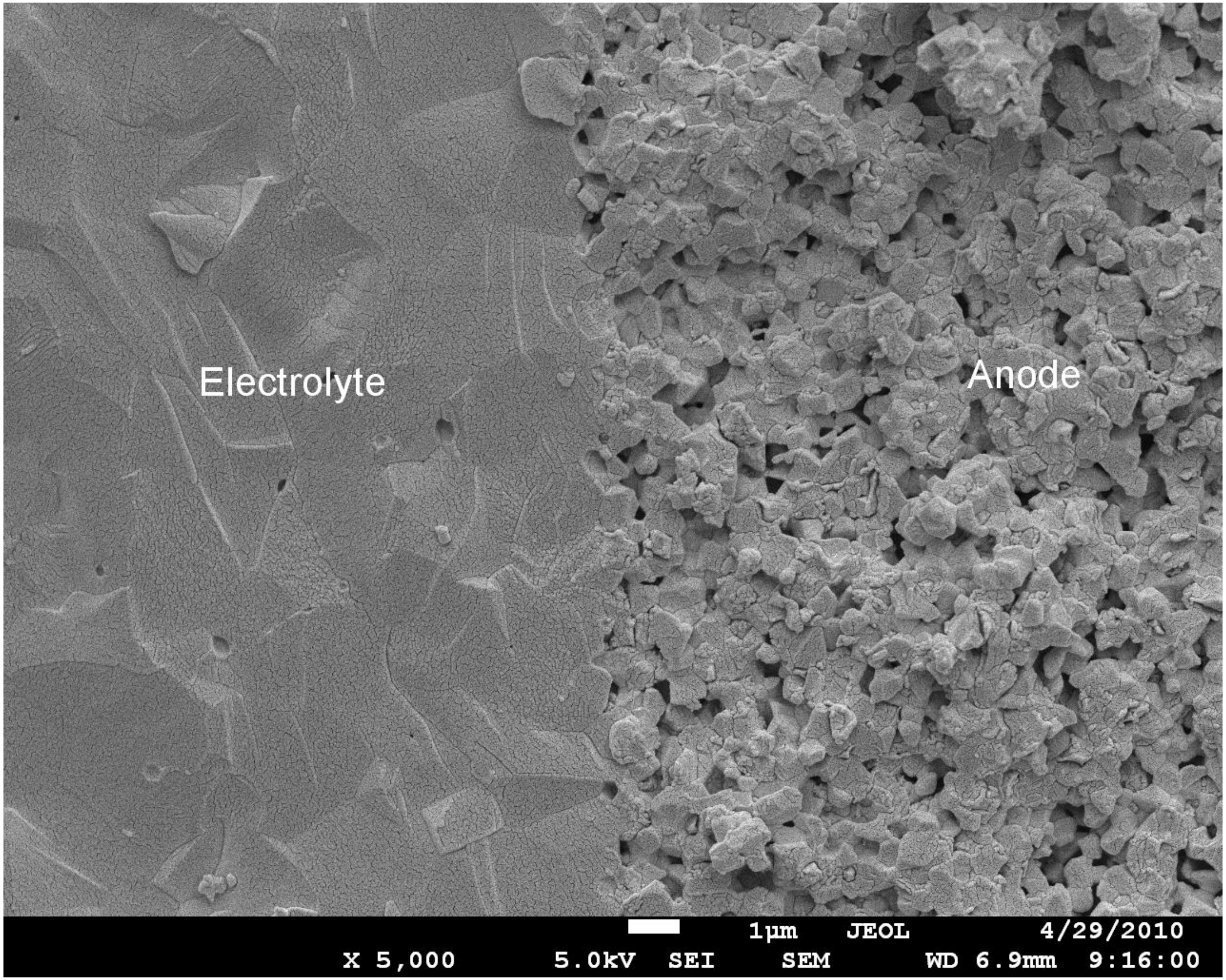
- **Operating condition – 250 mA/cm^2**

Mercury Overpotential



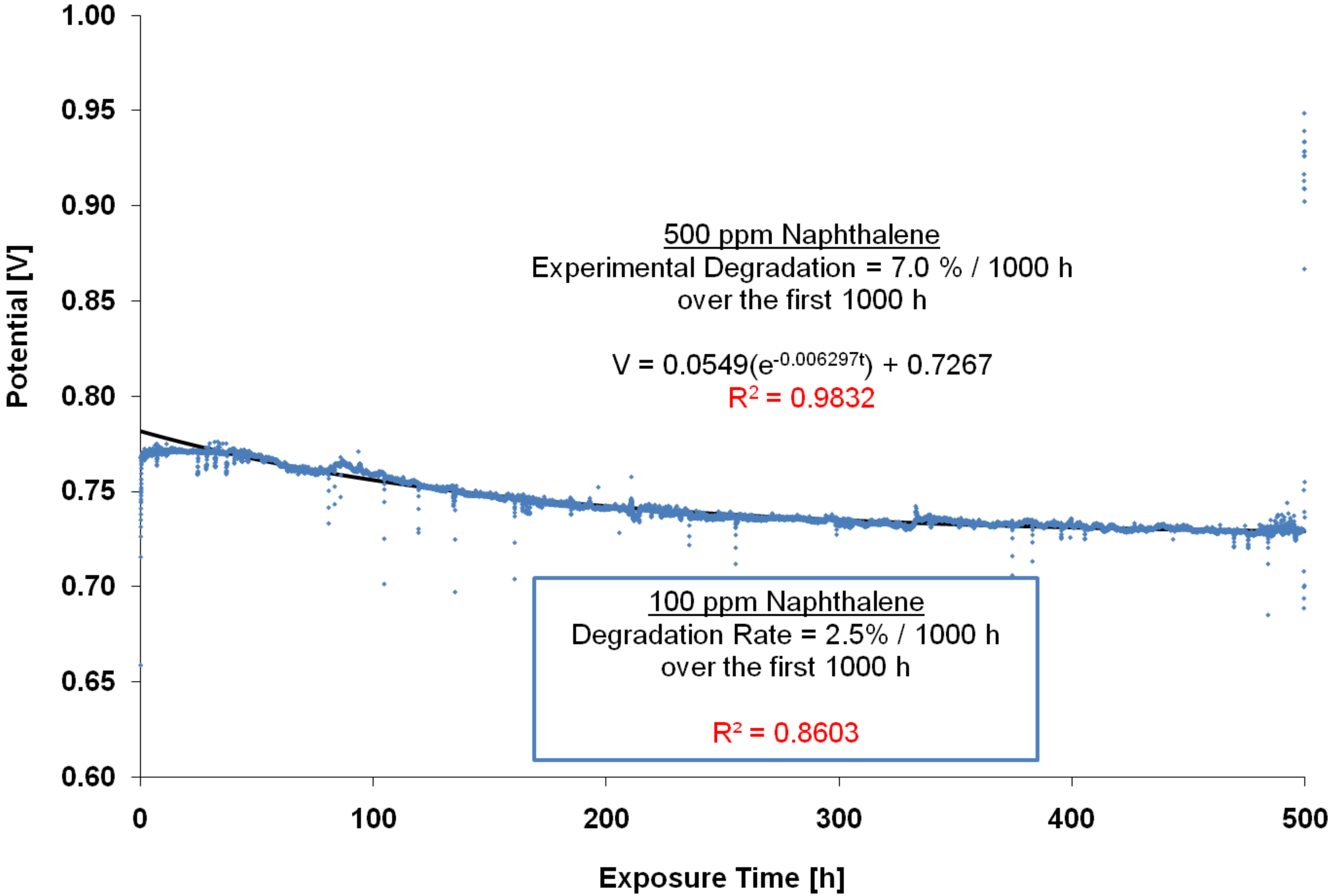
Mercury Data (1 ppm data/equation shown)

SEM - Mercury



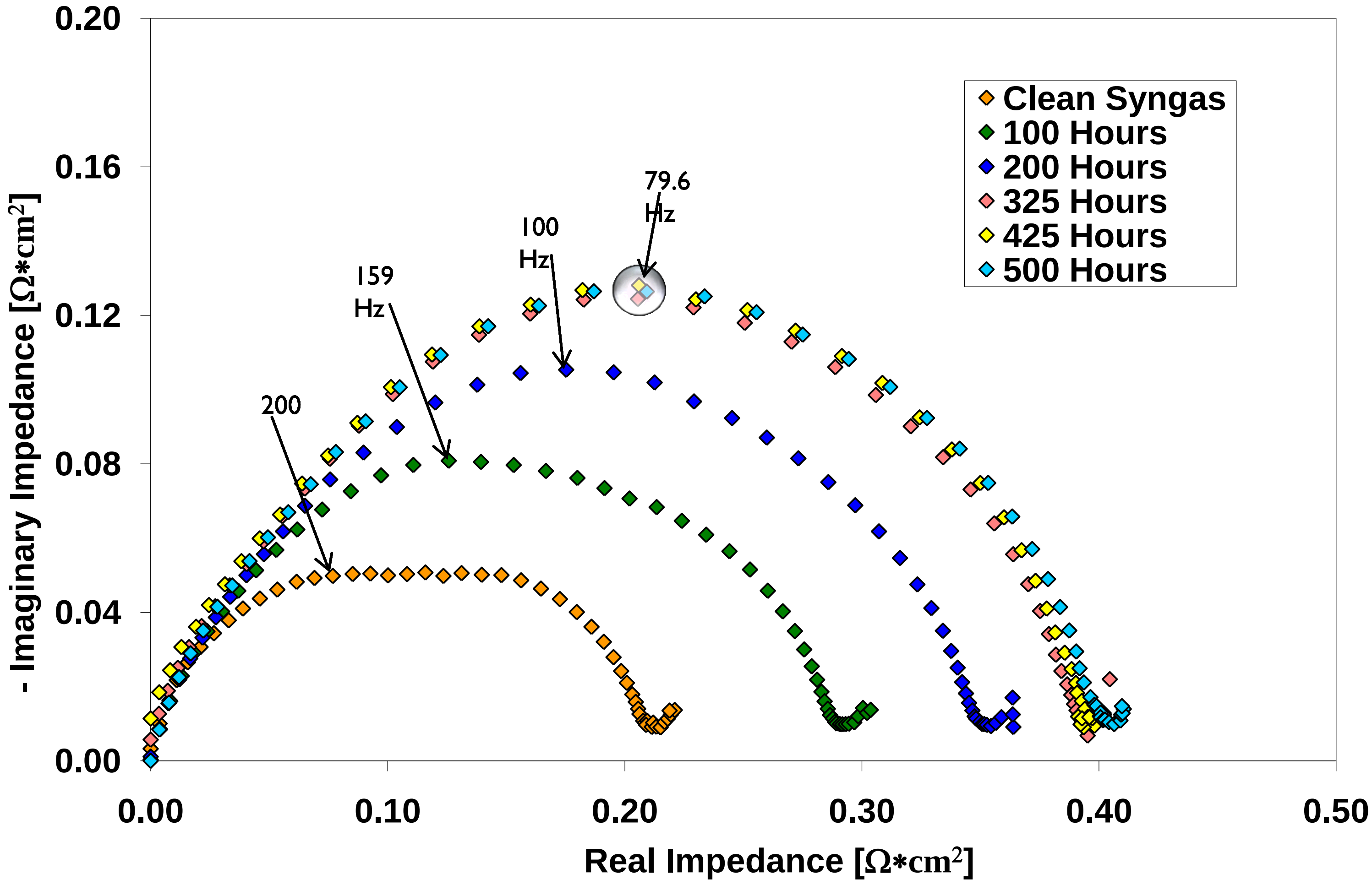
Mercury Exposure (1 ppm)

Naphthalene overpotential



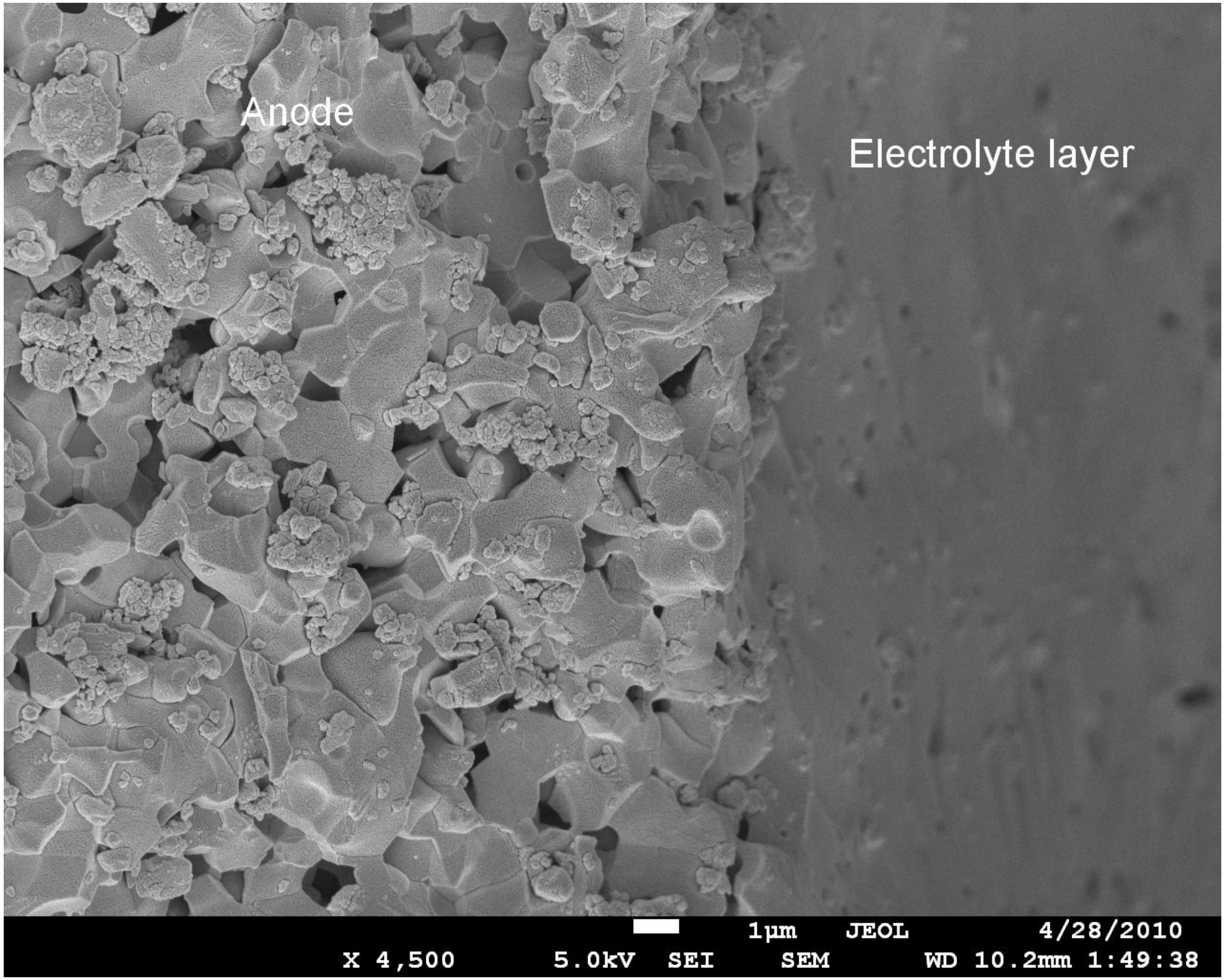
Naphthalene Data (500 ppm data/equation shown)

Naphthalene impedance



Naphthalene Impedance - 500 ppm

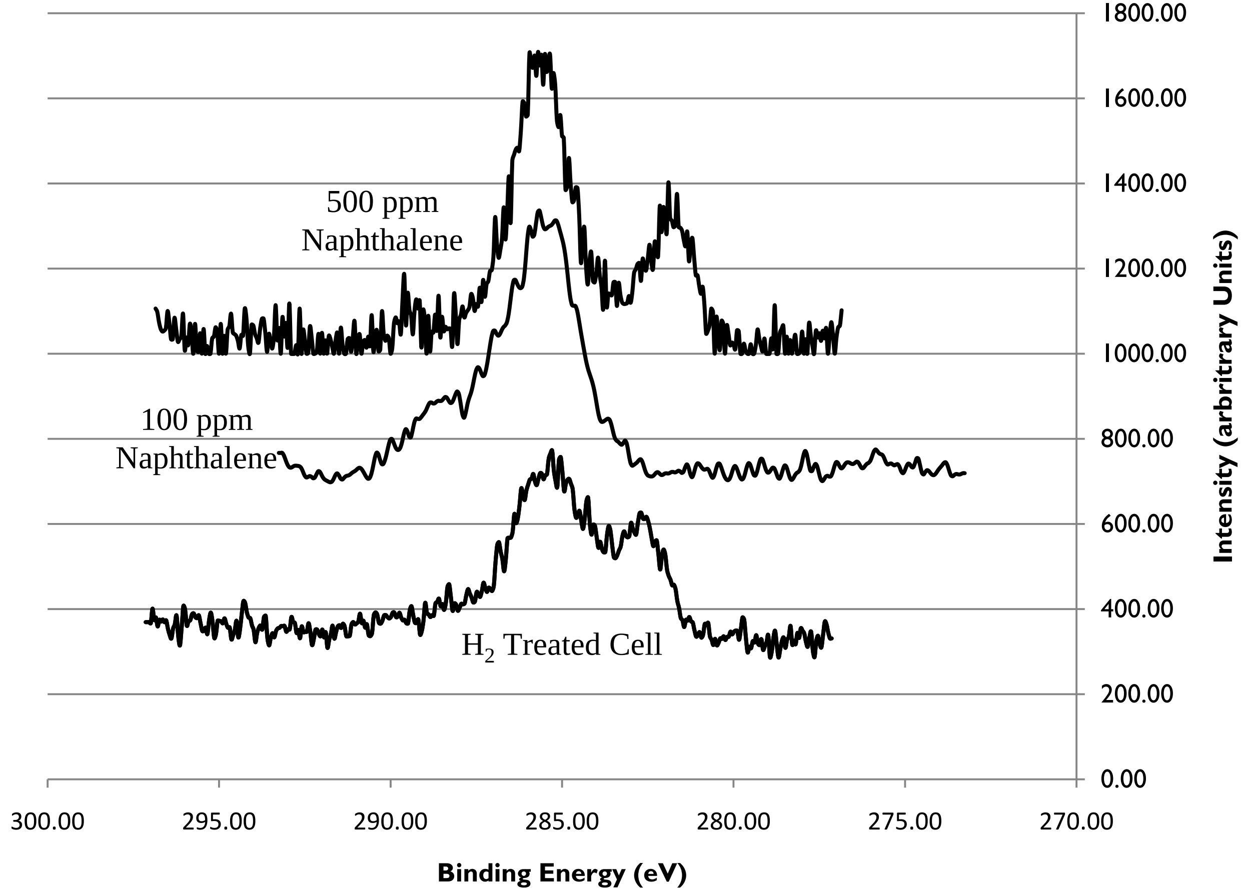
SEM – Naphthalene



Naphthalene SEM Image - 500 ppm

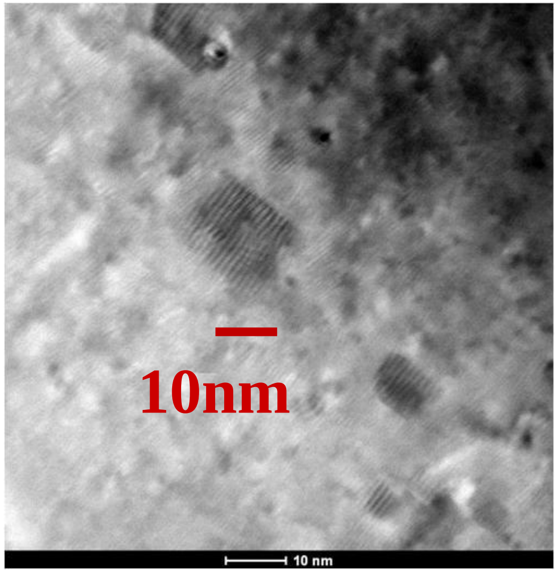
XPS - Naphthalene

- Naphthalene exposed samples showed minimal carbon



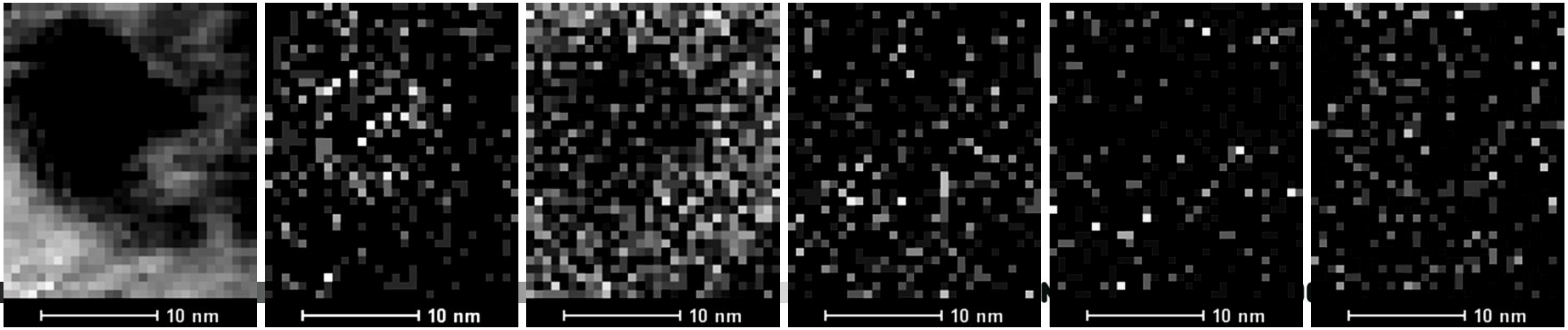
TEM imaging – Naphthalene

- Titan 80-300 (aberration corrected HR-STEM)
  - Accelerating V=300 kV
  - Resolution = 0.07 nm
- The beam size is substantially smaller than the particle (<1 nm)



- Five elements within inclusion: Ni, Al, Si, C, and O

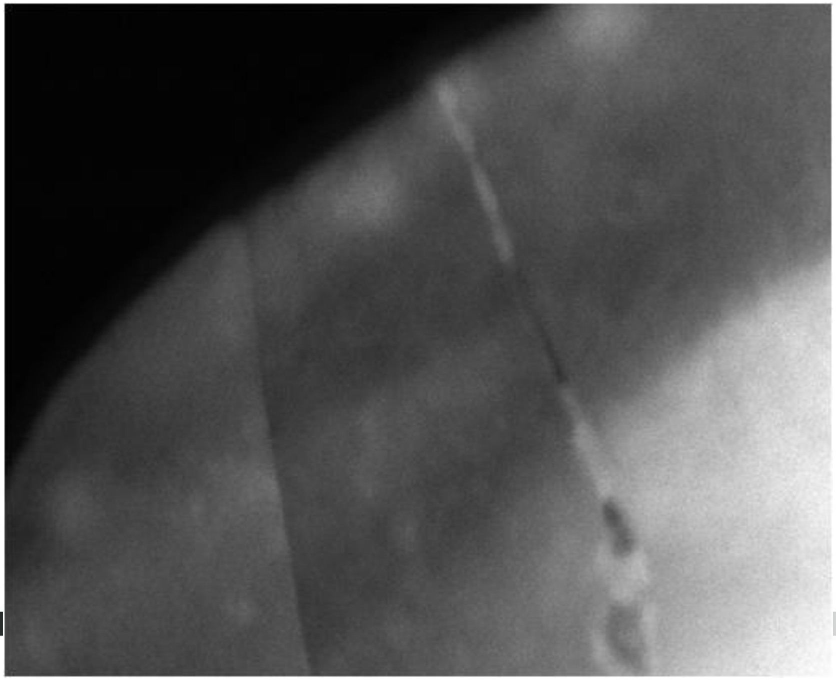
Al Ni C Si O



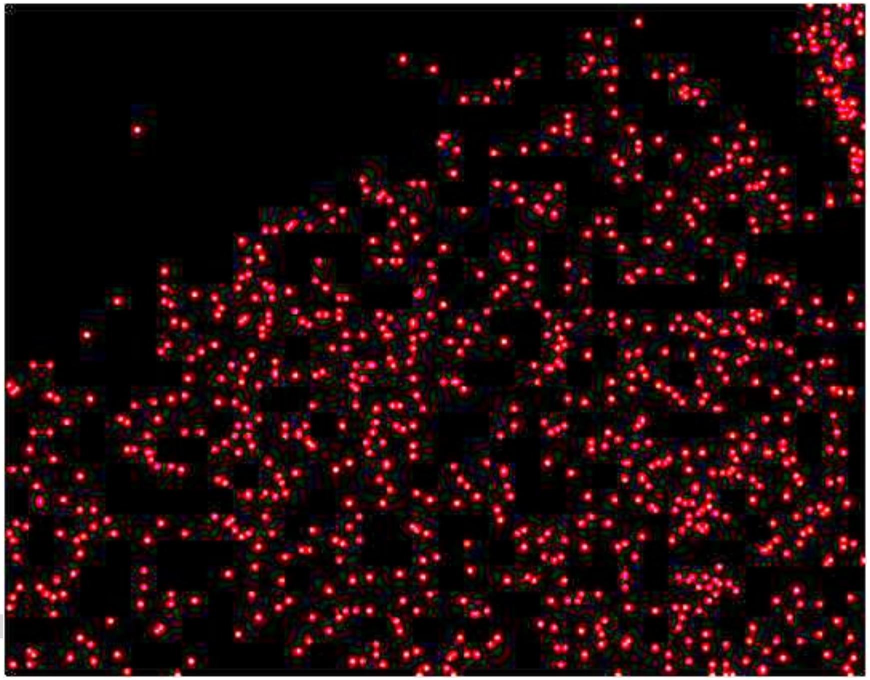
TEM/EDS – Naphthalene

- JEOL 2100F Cs-Corrected STEM (U Michigan, a system which is comparable to Titan system)
- C distributes evenly in the Ni grain.
  - Result is consistent with Titan data.
- C observed everywhere through the 500 ppm sample.
  - Sample is cleaned using ion-mill but C remains.
  - New sample prepared and similar result acheived.
- Preliminary confirmation that C is major solid solution specie.

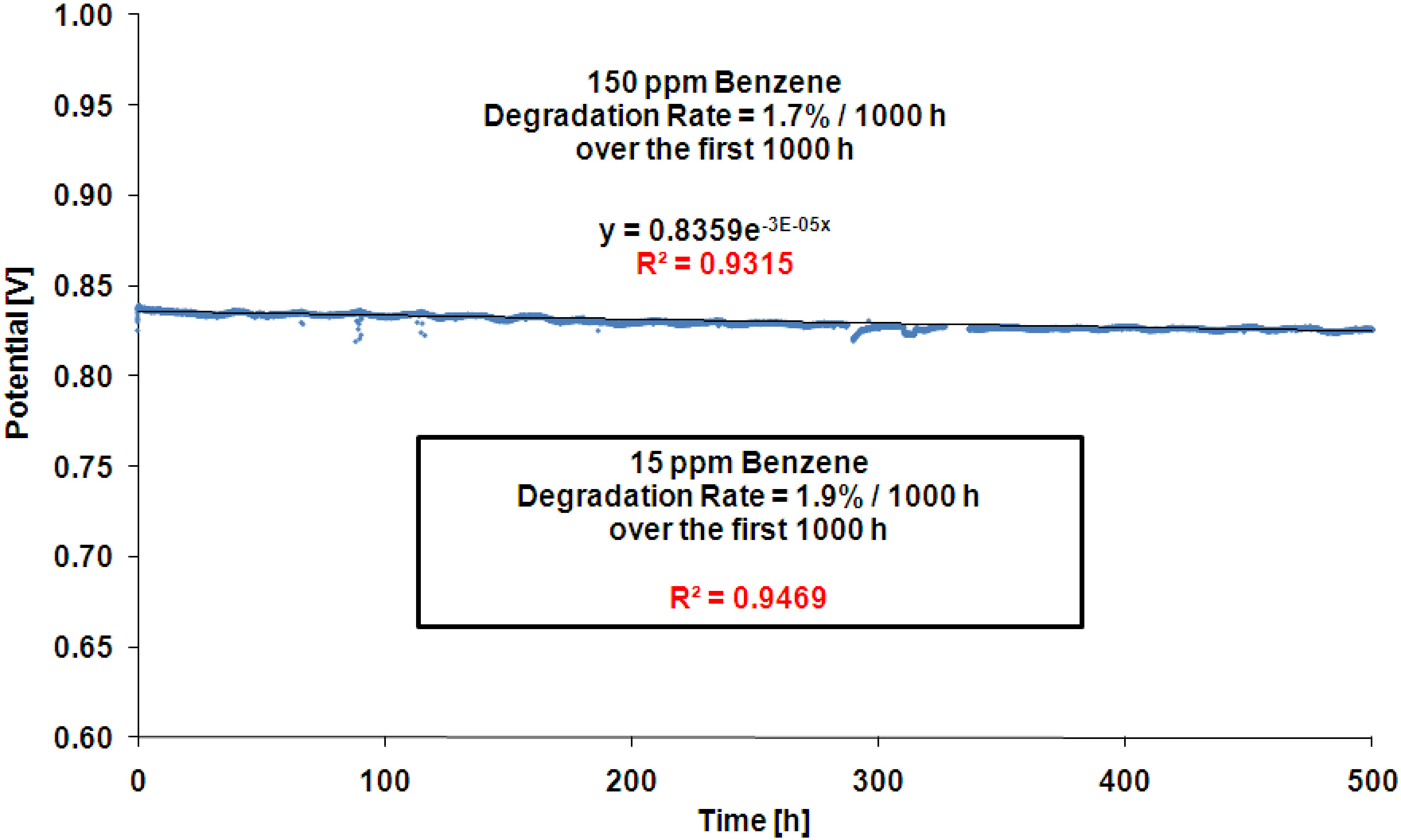
Image



Carbon map

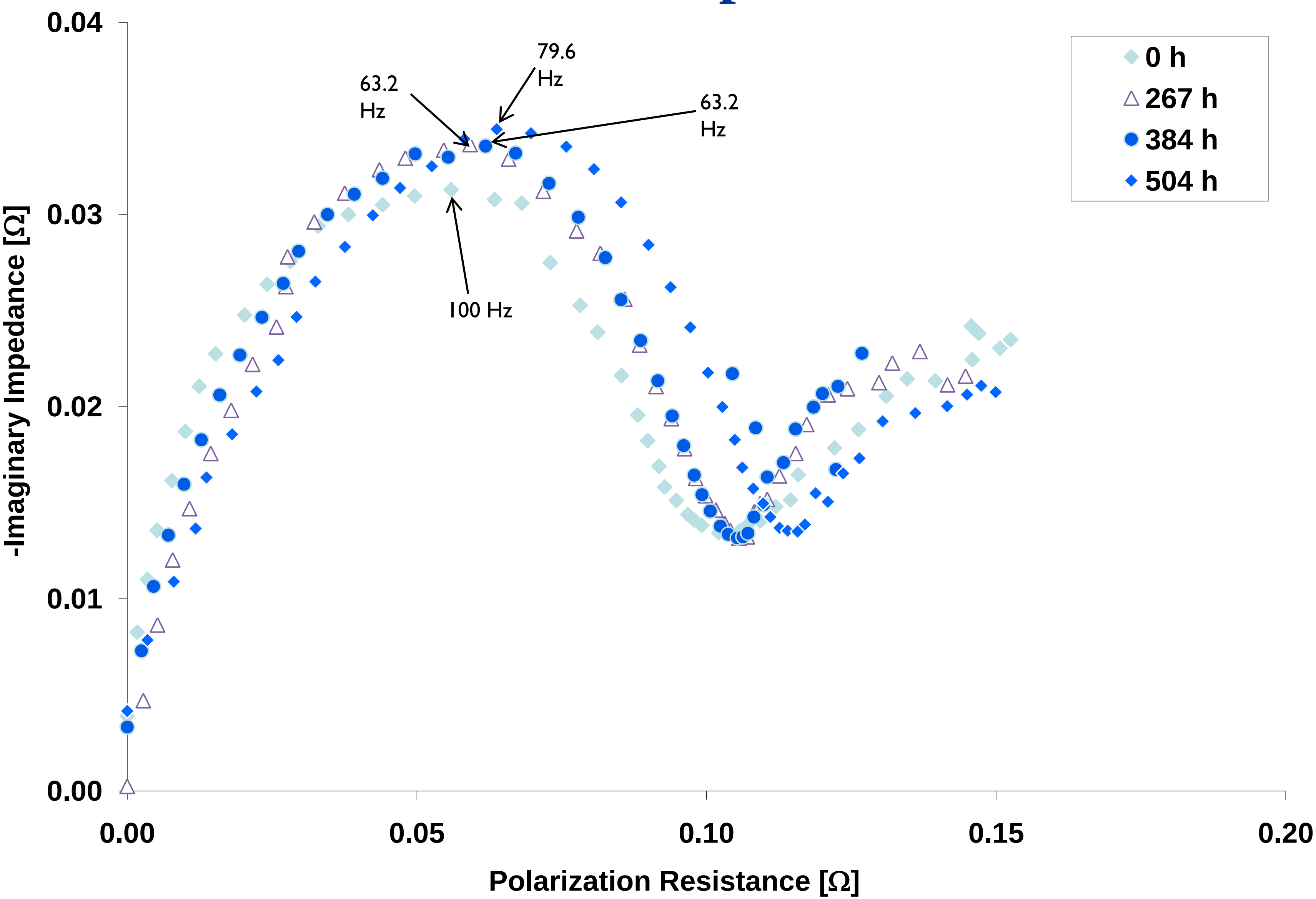


Benzene overpotential



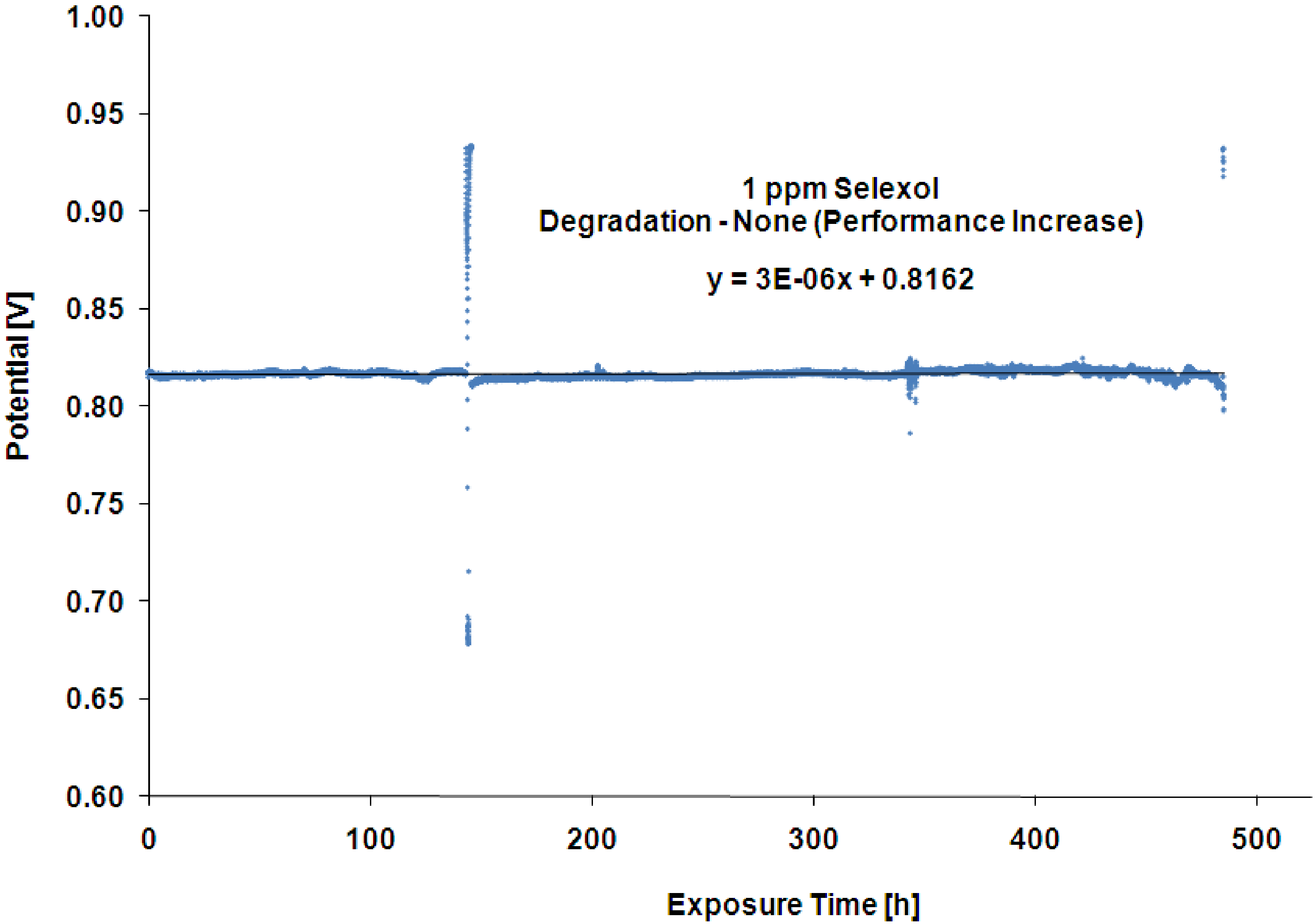
Benzene Data (150 ppm data/equation shown)

Benzene impedance



Benzene Impedance - 15 ppm

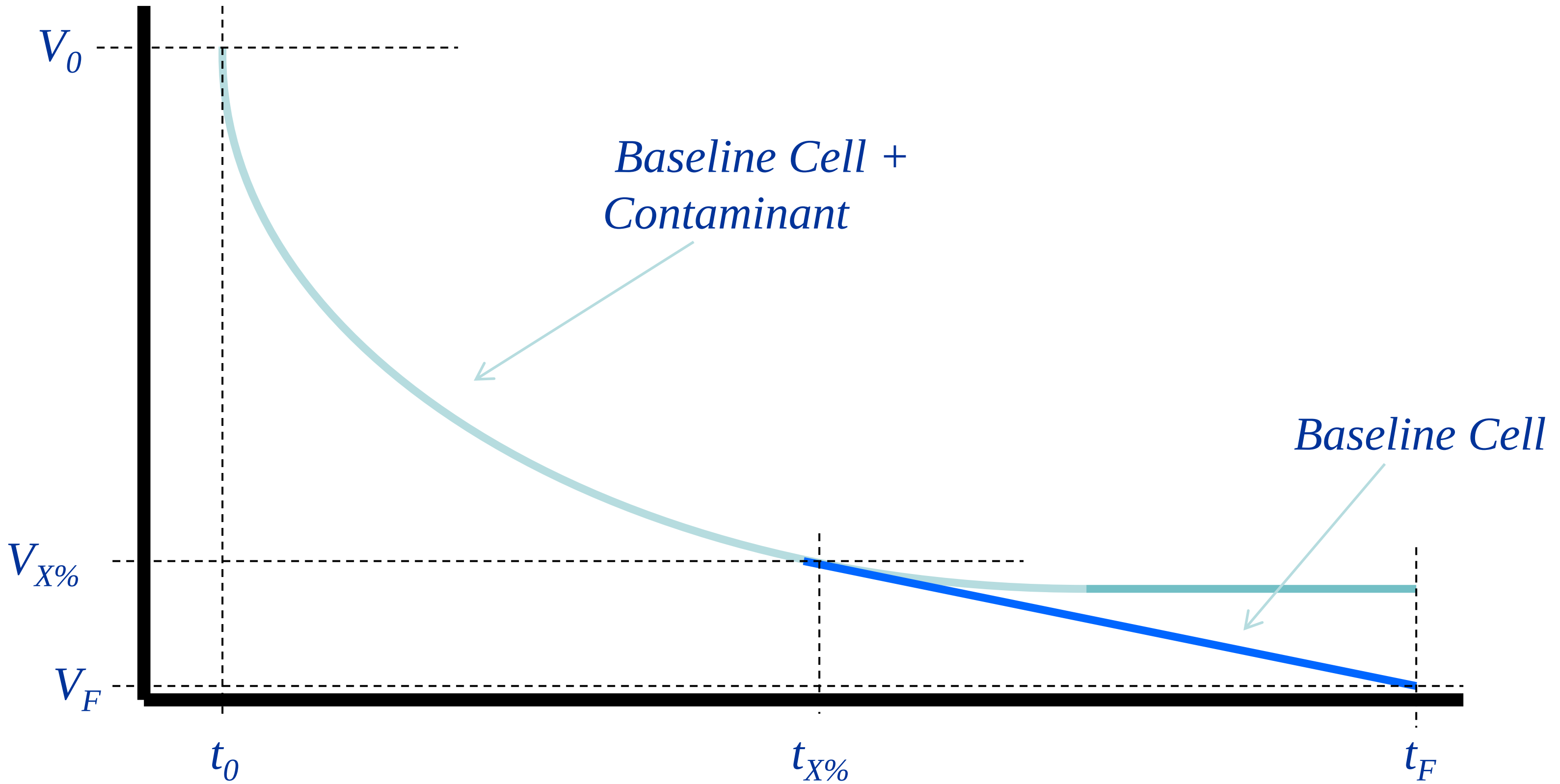
PEG/DME Overpotential



PEG/DME data (1 ppm (g) data/equation shown)
3.5 ppm data inconclusive due to noise

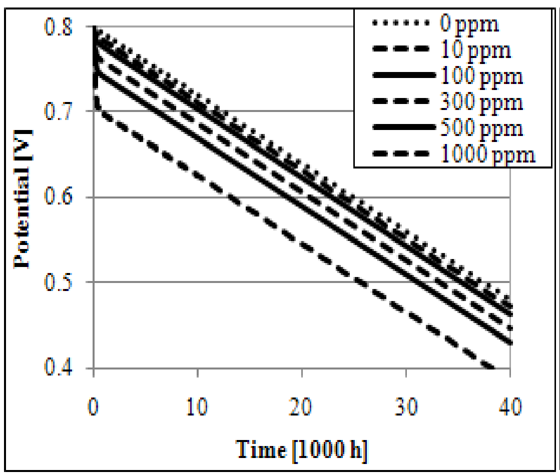
Discussion – Analysis Method

- **Empirical degradation model assumptions**
  - Initial degradation is well modeled by exponential decay
  - Long term (2000 + hours) cell degradation is linear

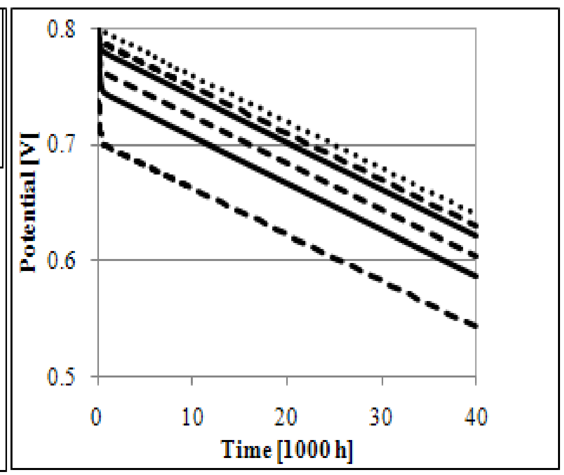


Exposure limit - Naphthalene

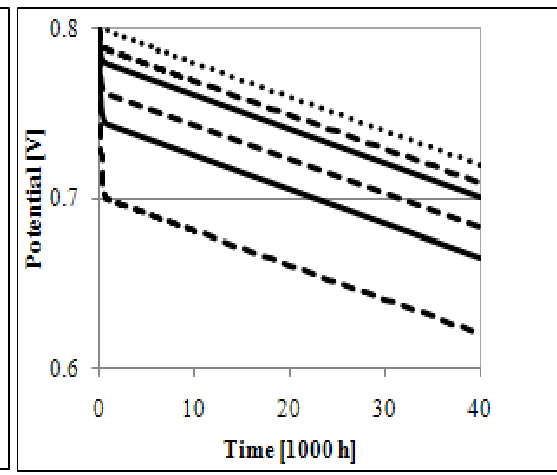
- First order with respect to concentration in range of 100-500 ppm
- Exposure limit depends on
  - Assumed baseline cell degradation rate (1%, 0.5%, 0.25% / 1000 hours)
  - Acceptable final operating voltage



1.0% / 1000 h



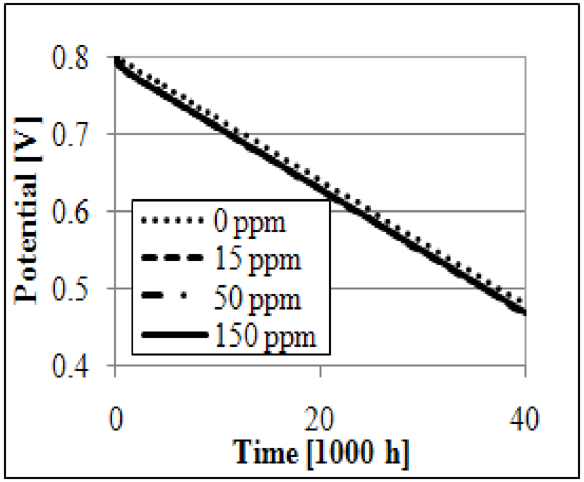
0.50% / 1000 h



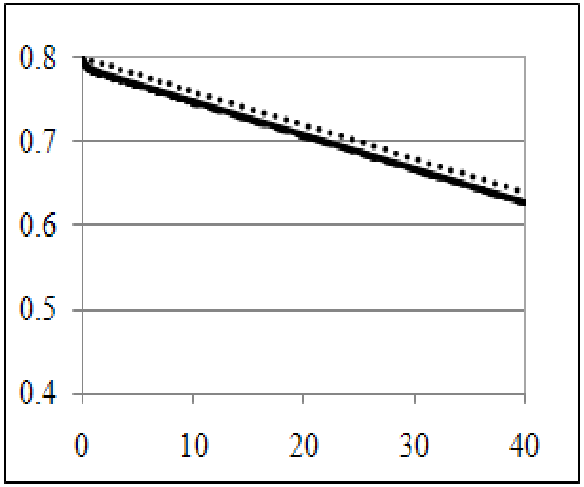
0.25% / 1000 h

Exposure limit - Benzene

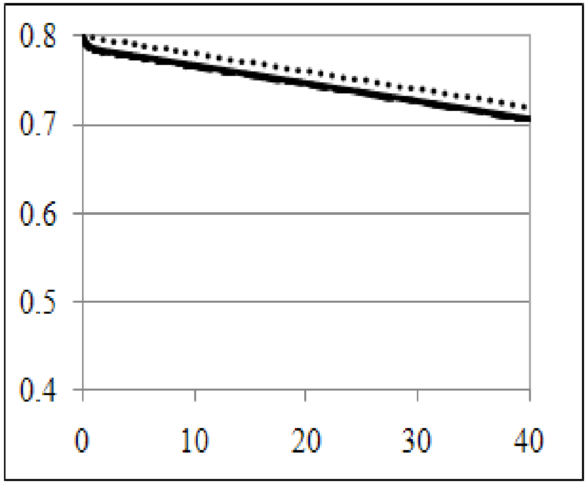
- Zero order with respect to concentration in range of 15-150 ppm
  - Degradation rate too similar b/n two concentrations to extrapolate limit



1.0% / 1000 h



0.50% / 1000 h



0.25% / 1000 h

Conclusions

- **Naphthalene**
  - SOFC exposed to naphthalene at 150 and 500 ppm demonstrated obvious performance degradation
    - Rates greater than those for benzene.
  - After 40,000 h, the SOFC will produce usable potential of :
    - **0.7 V at 110 ppm** @ base cell degr rate of 0.25% per 1000 h.
    - **0.6 V at 1200 ppm** @ base cell degr rate of 0.25% per 1000 h.
    - **0.6 V at 360 ppm** @ base cell degr rate of 0.50% per 1000 h

Conclusions

- **Mercury**
  - SOFC exposed to mercury at 1 and 10 ppm shows no performance degradation
  - Results agree with thermodynamic analyses and literature
  - Mercury cleanup is not required for fuel cell

- **Benzene**
  - SOFC exposed to benzene at 15 and 150 ppm showed noticeable performance degradation.
  - Cleanup to <u>less than 150 ppm</u> is recommended

Continued HHC Exposure testing

- **Complete tests on PGE/DME (3.5 ppm repeat)**
- **Initiate Ethylene tests at 100-1000 ppm**
  - Predict exposure limitations
- **Carefully monitor grain growth**
  - Record sufficient microstructure observations to ensure statistical relevance
- **Spot check literature results for H_2Se and AsH_4**

Acknowledgements

- Principal Investigator

  Gregory Hackett (NETL)

- Microscopy

  Yun Chen (WVU), Xueyan Song (WVU), Jim Poston (NETL)

- Discussion

  Harry Finklea (WVU), Xingbo Liu (WVU), John Zondlo (WVU), Harry Abernathy (NETL)

- SECA