NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

Coal Syngas Testing and Evaluation at NETL

2009 SECA Workshop

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U.S. DEPARTMENT OF ENERGY

Goal

Identify the effects of trace coal syngas species on SOFC anodes, and identify the trace material exposure levels that will be acceptable to fuel cell operation.

Prior to SECA, no data existed to guide developers on how to design coal syngas cleanup systems suitable for SOFC operation.

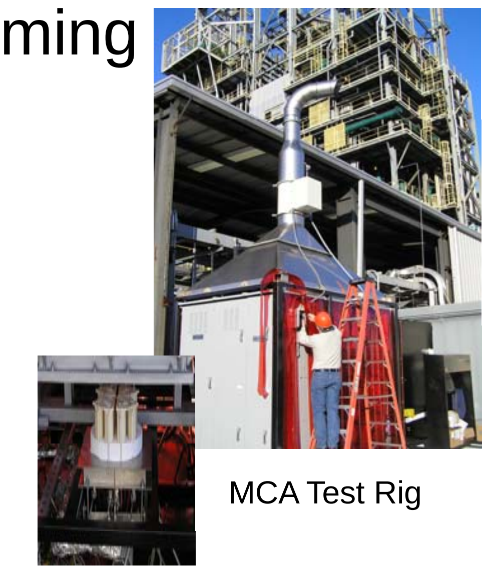
Trace species: <1000ppm (Ref. Speight)

Possible Effects of Trace Species on SOFC Anode

- **Affect the ability of Ni to promote the electrochemical reactions**
  - Trace species on Ni surface inhibit the adsorption of H_2, CO, or dissociation of H_2
- **Affect the ability of YSZ to transport oxygen ion**
  - Formation of secondary zirconia phases
- **Affect the electrical conductivity**
  - Formation of secondary nickel phases such as nickel-phosphide
- **Affect the transport of reactants in/out of electrode**
  - Formation of condensed phases that fill electrode pores

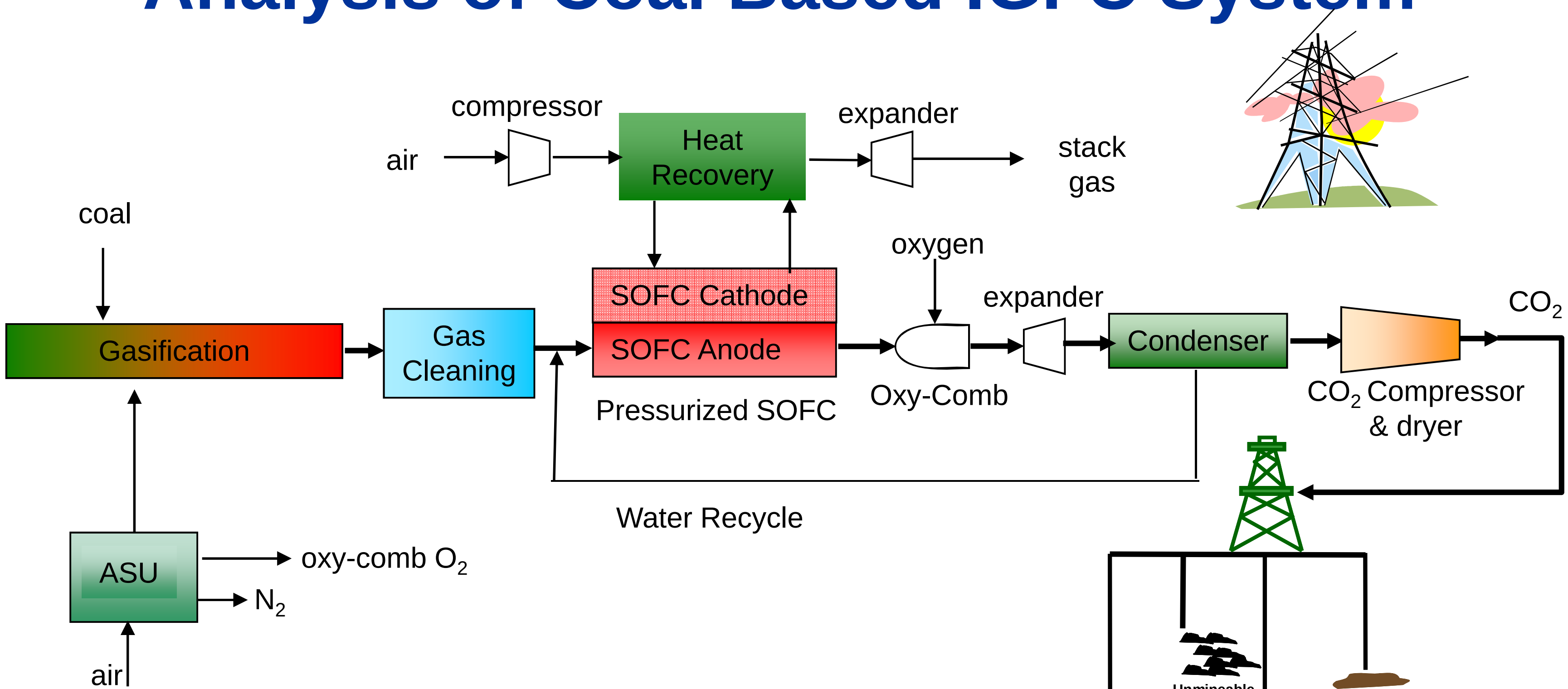
Outline

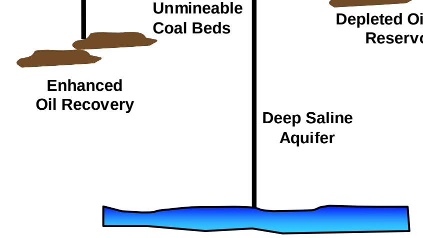
- **Analysis**
  - Identify sensitivity of gasification technology on trace species attack
- **Experimental**
  - Individual trace specie evaluations
  - Direct coal syngas testing—next test coming in August.



MCA Test Rig

Analysis of Coal Based IGFC System





Key Assumptions for All Cases:

•Same contaminant loading (constant carbon to contaminant ratio, Z')

•Same FU (80%)

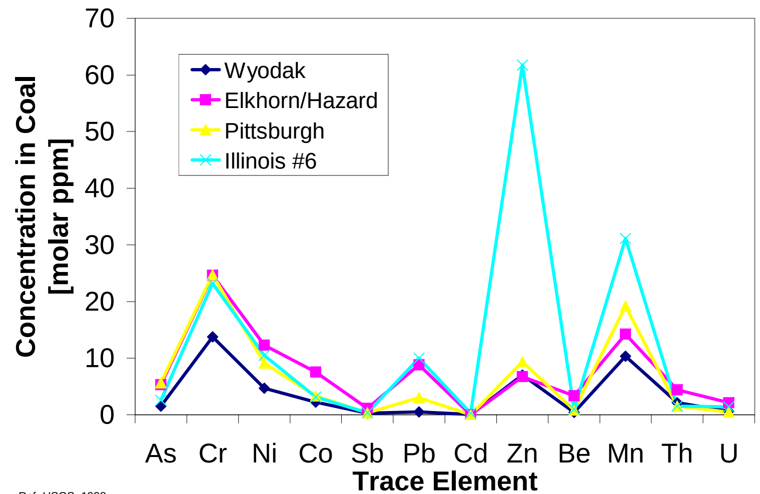
•Same power, P, from fuel cell stack operated at 80% efficiency

•Different syngas compositions affect stack performance through Nernst Potential (effective cell resistance fixed)

•Carbon deposition control through water addition

Trace Metal Contaminants
(Coal-Type Dependency)

- **USGS analysis of trace elements in coals.**
- **Different coals have different levels of given a given contaminant.**



Ref. USGS, 1998

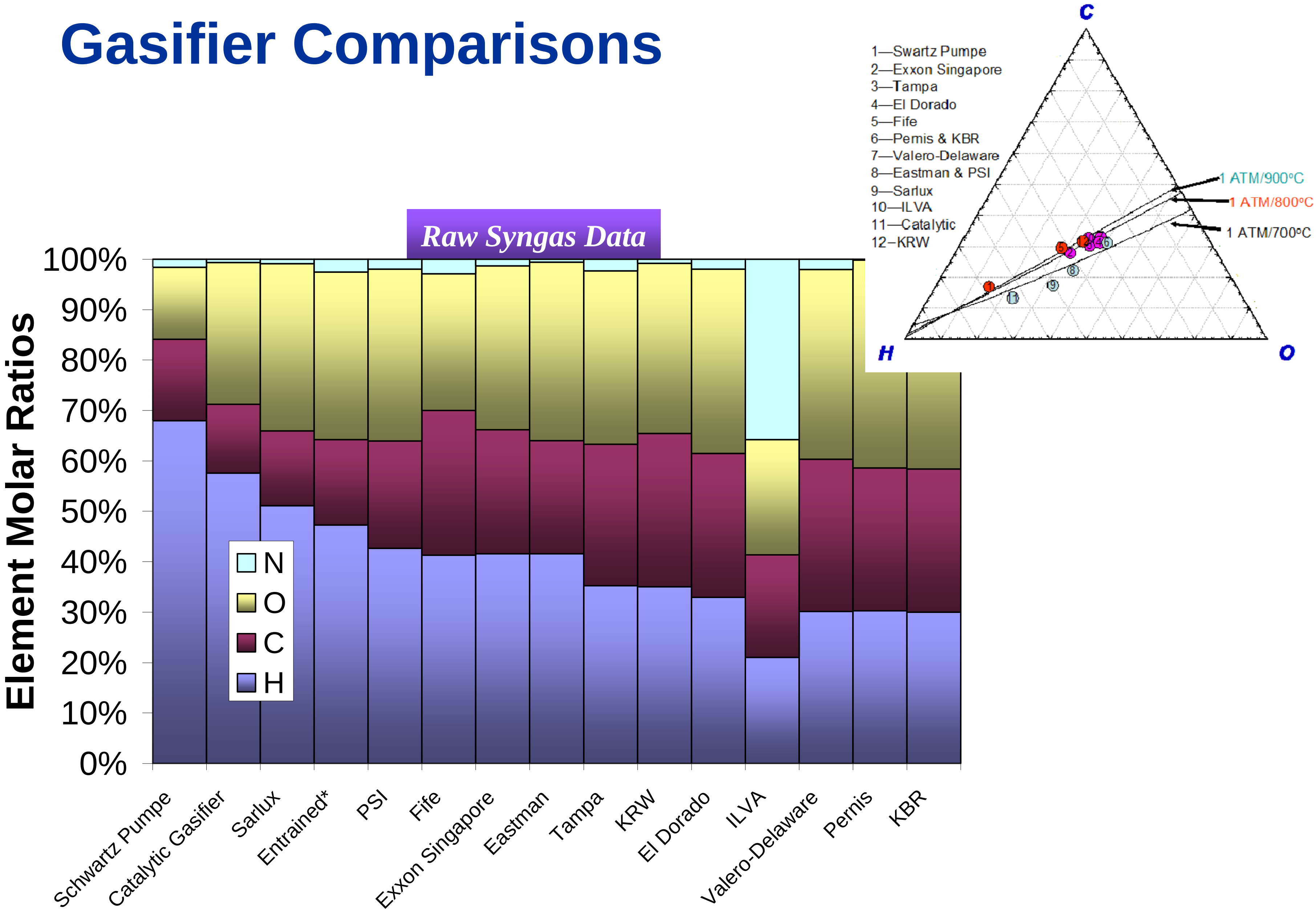
Table 2
Trace specie concentrations

Component	Concentration (ppmv)	Volatility class
AsH_3	0.6	II
HCl	1	III
PH_3	1.91	II
Sb	0.07	II
Cd	0.011	II
Be	0.025	II
Cr	6	II
Hg	0.025	II
K	512	I
Se	0.15	II
Na	320	I
V	0.025	II
Pb	0.26	II
Zn	9	II

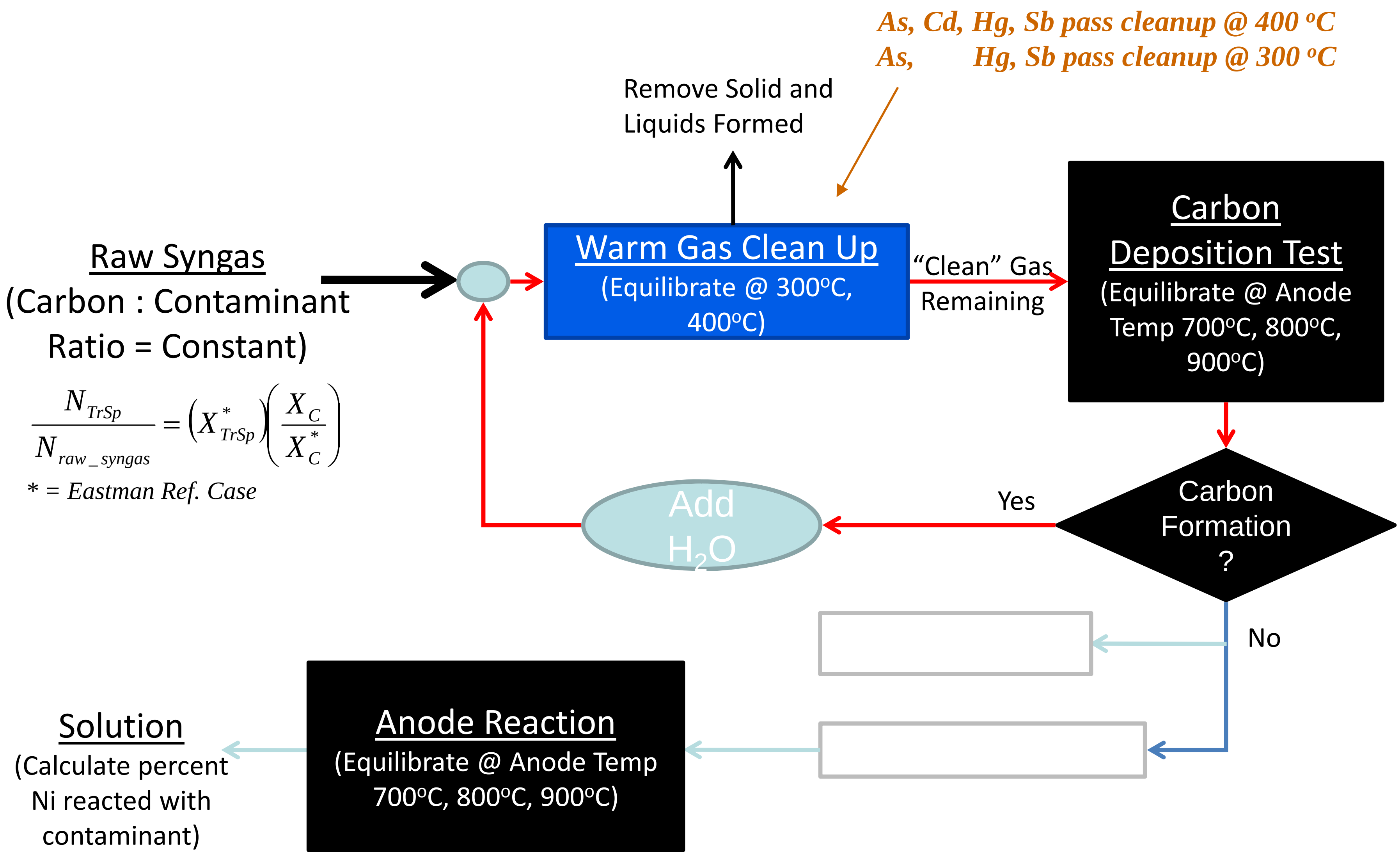
J.P. Trembly et al. / Journal of Power Sources 163 (2007) 986–996

Contaminant for Eastman Gasifier. Other gasifier cases have same trace loadings (by assuming constant Carbon/Contaminant ratio)

Gasifier Comparisons



Computational Procedure



N_{Ni} to N_{fuel} Ratio Calculation

$$\begin{cases} P = A_{cell} i'' V_{cell} N_{cells} \\ N_{cells} A_{cell} i'' = FU \dfrac{N_{fuel} n_{fuel} F}{t} \\ V_{cell} = V_{Nernst} \eta_{cell} = (V_{Nernst} - V_{act} - i'' R_{ohmic}) \\ A_{cell} = \dfrac{I}{i''} \\ N_{Ni} = A_{cell} T_{cell} \hat{\rho}_{\mathrm{Ni}} N_{cells} \end{cases}$$

Specified:

η_{cell} = Cell Efficiency (80%)

R_{ohmic} = Ohmic Resistance (0.1 ohm - cm²)

FU = Fuel Utilization (80%)

V_{act} = Activiation Loss (0.1 V)

t = time (5000 h)

$\hat{\rho}_{\mathrm{Ni}}$ = Electrode Ni Density (0.15 mol/cm³)

$\mathrm{T_{cell}}$ = Anode Thickness (1 mm)

From Syngas Composition:

V_{Nersnt} = Nernst Potential

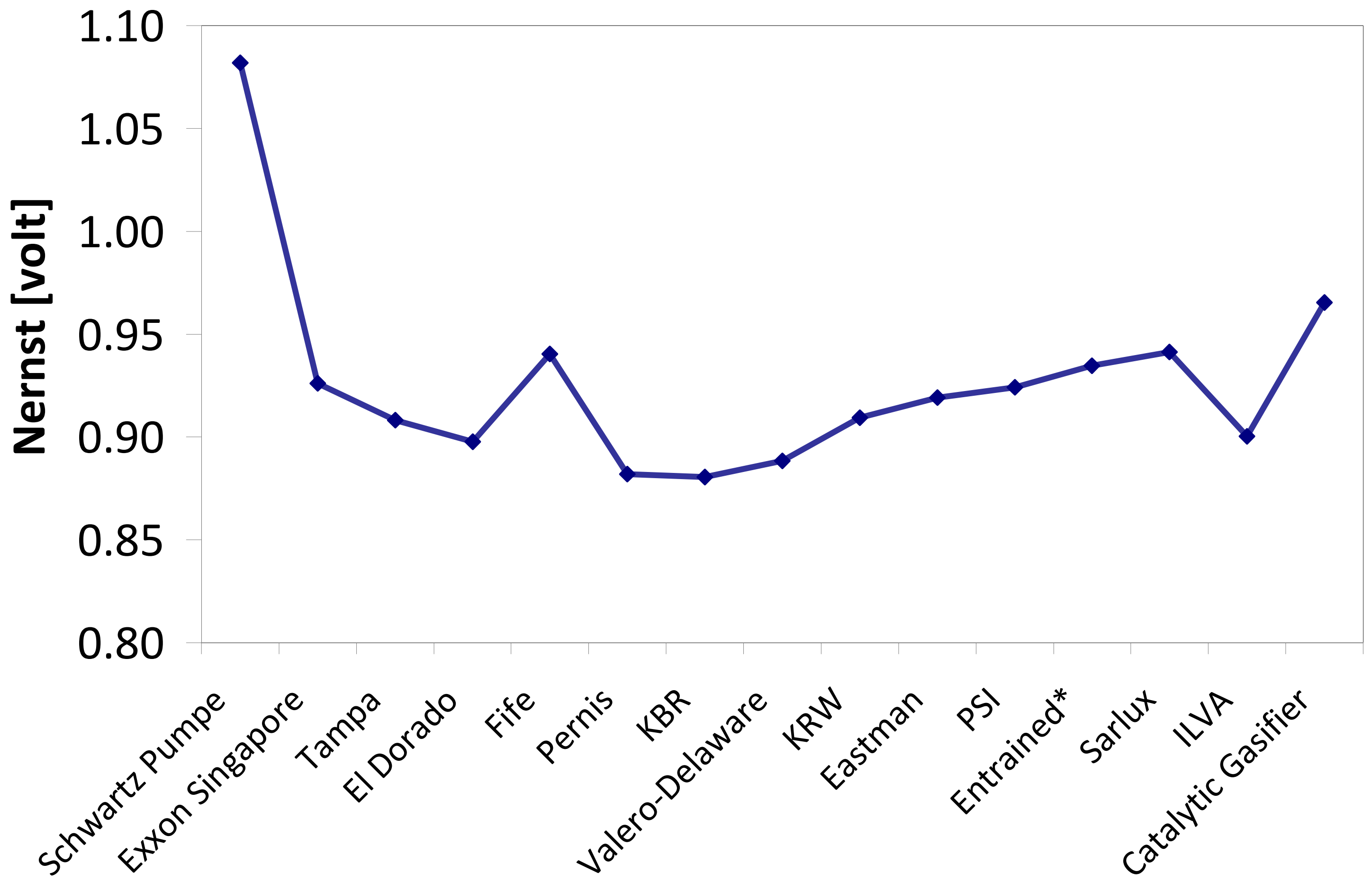
$\mathrm{n_{fuel}}$ = Charge Number (electrons/mole of fuel)

(Ni to Syngas Molar Ratio at Operating Time 't')

$$\frac{N_{Ni}}{N_{fuel}} = \frac{FU \cdot T_{cell} \cdot n_{fuel} F \cdot R_{ohmic} \cdot \hat{\rho}_{Ni}}{\left[V_{Nernst} (1 - \eta_{cell}) - V_{act} \right] \cdot t}$$

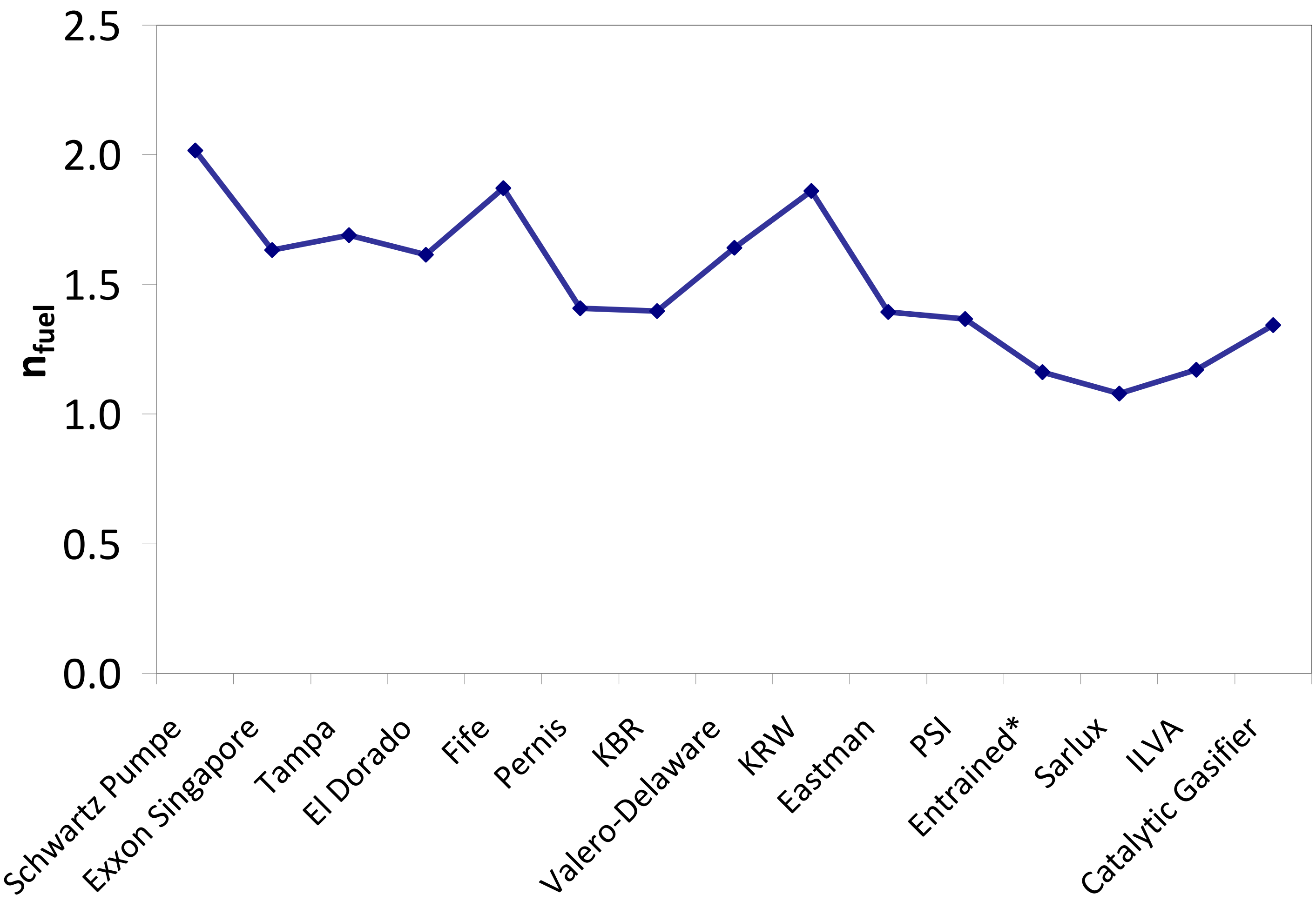
Cell Inlet Nernst Voltage

(400 deg. C cleanup; 800 deg. C Anode)



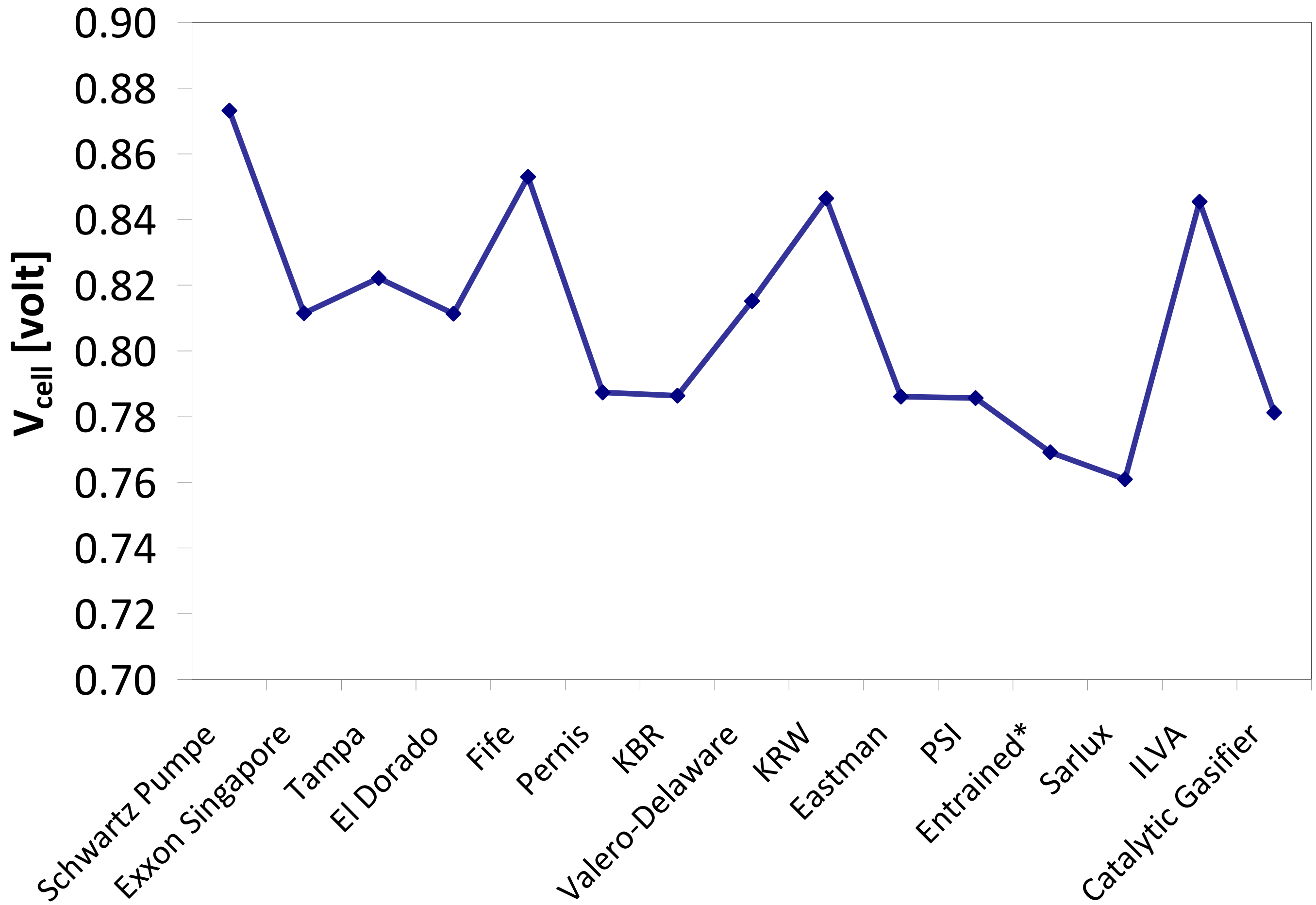
Charge Number

(400 deg. C cleanup; 800 deg. C Anode)



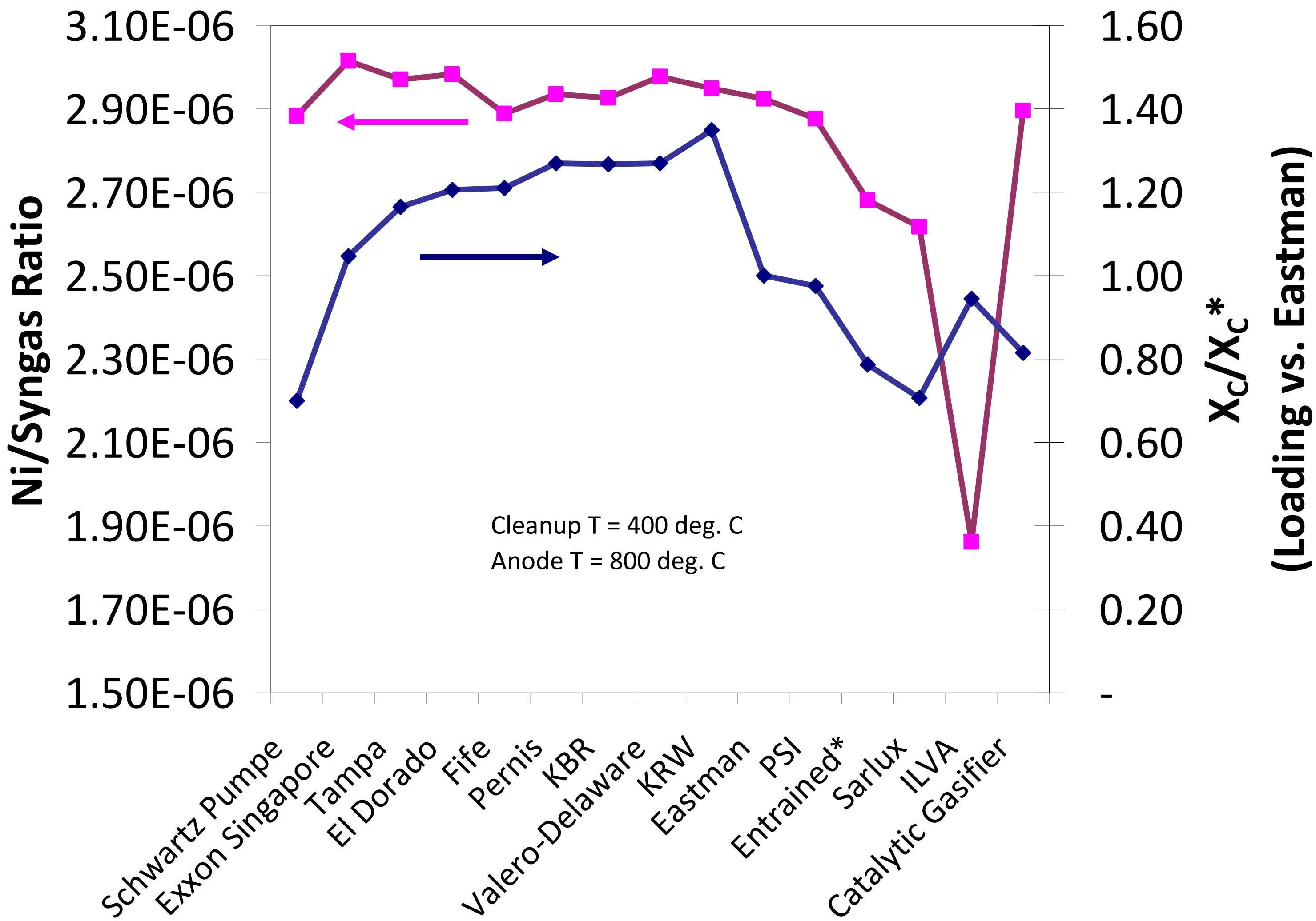
Cell Operating Voltage

(400 deg. C cleanup; 800 deg. C Anode)



Results for 5000h

(400 deg. C cleanup; 800 deg. C Anode)



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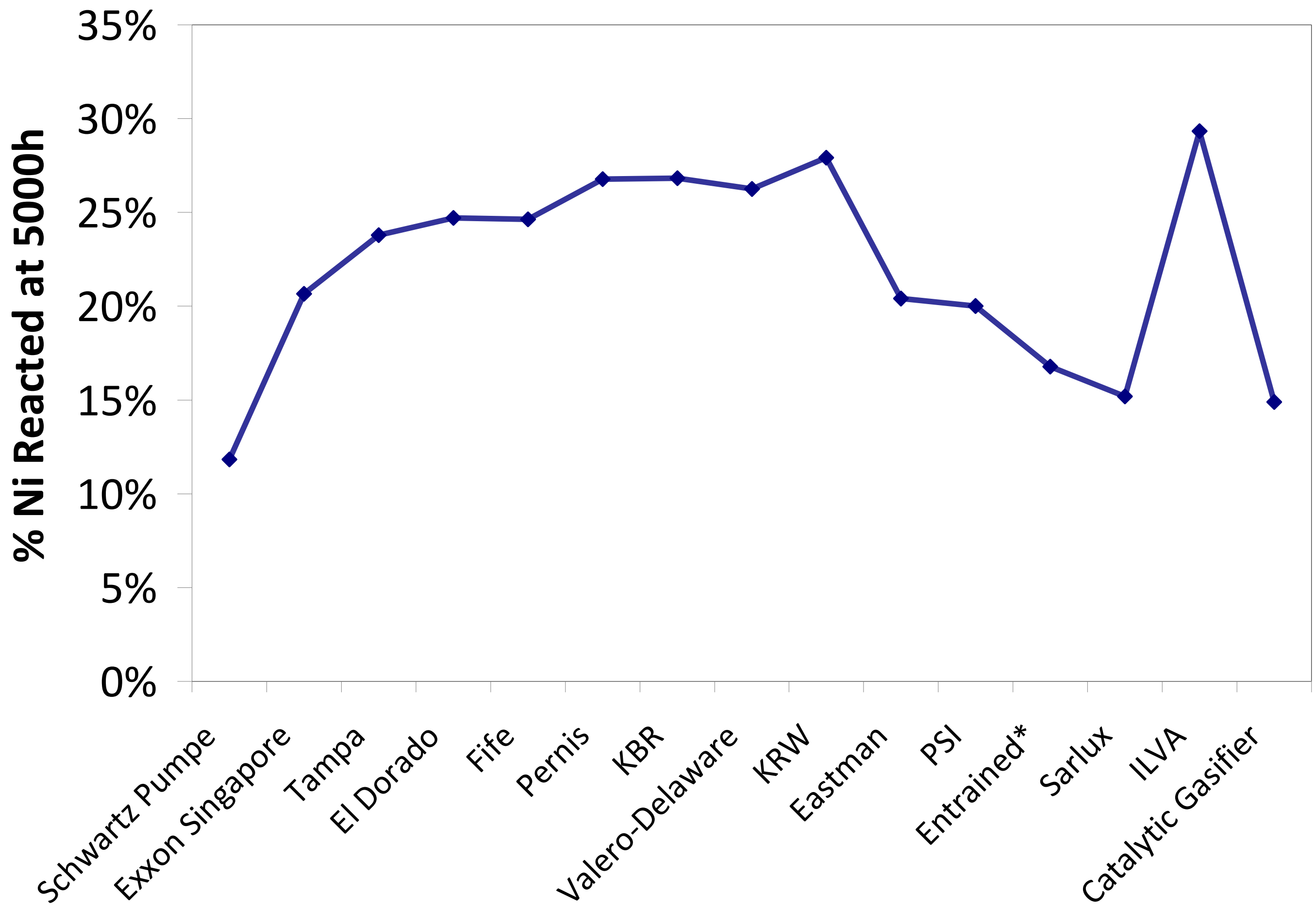

Results for 5000h

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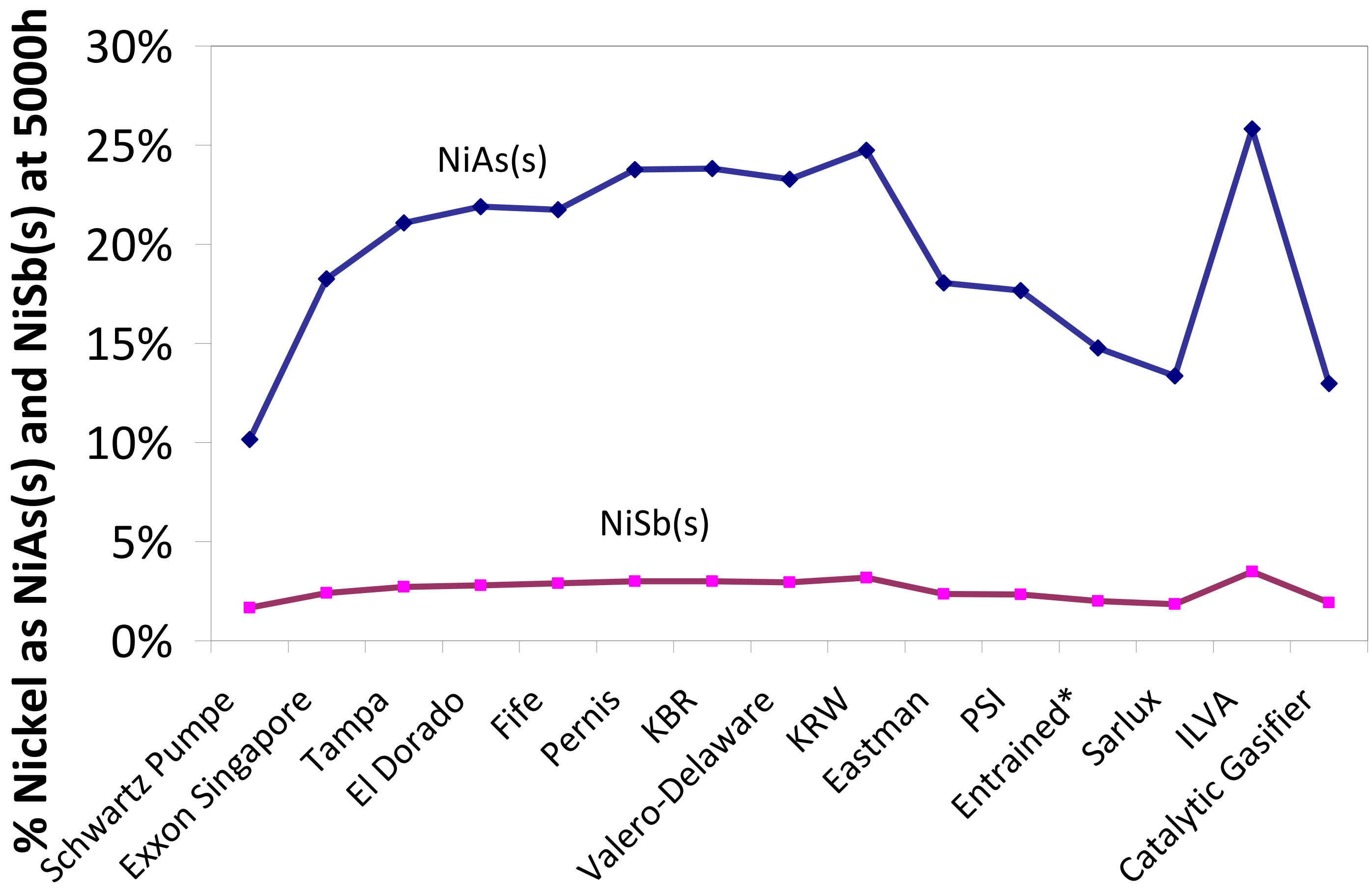


Analysis Summary

- **Detailed thermodynamic analysis method applied to determine behavior of different gasification technology on anode attack.**
- **Catalytic gasifier approach appears beneficial compared to other technology regarding potential for contaminant attack.**
- **Several other technologies could also be considered …their gasification efficiencies need to be evaluated.**

Outline

- **Analysis**
  - – Identify potential interactions between trace species and anode across a variety of gasification systems
- **Experimental**
  - – Perform individual trace specie evaluations
    - Naphthalene, Benzene, Hg

Concentrations Tested

- **Overview of contaminant testing and data analysis**
- **Summary of results**
  - Mercury
    - 1 ppm
    - 10 ppm
  - Benzene
    - 15 ppm
    - 150 ppm (in progress)
  - Naphthalene
    - 100 ppm
    - 500 ppm

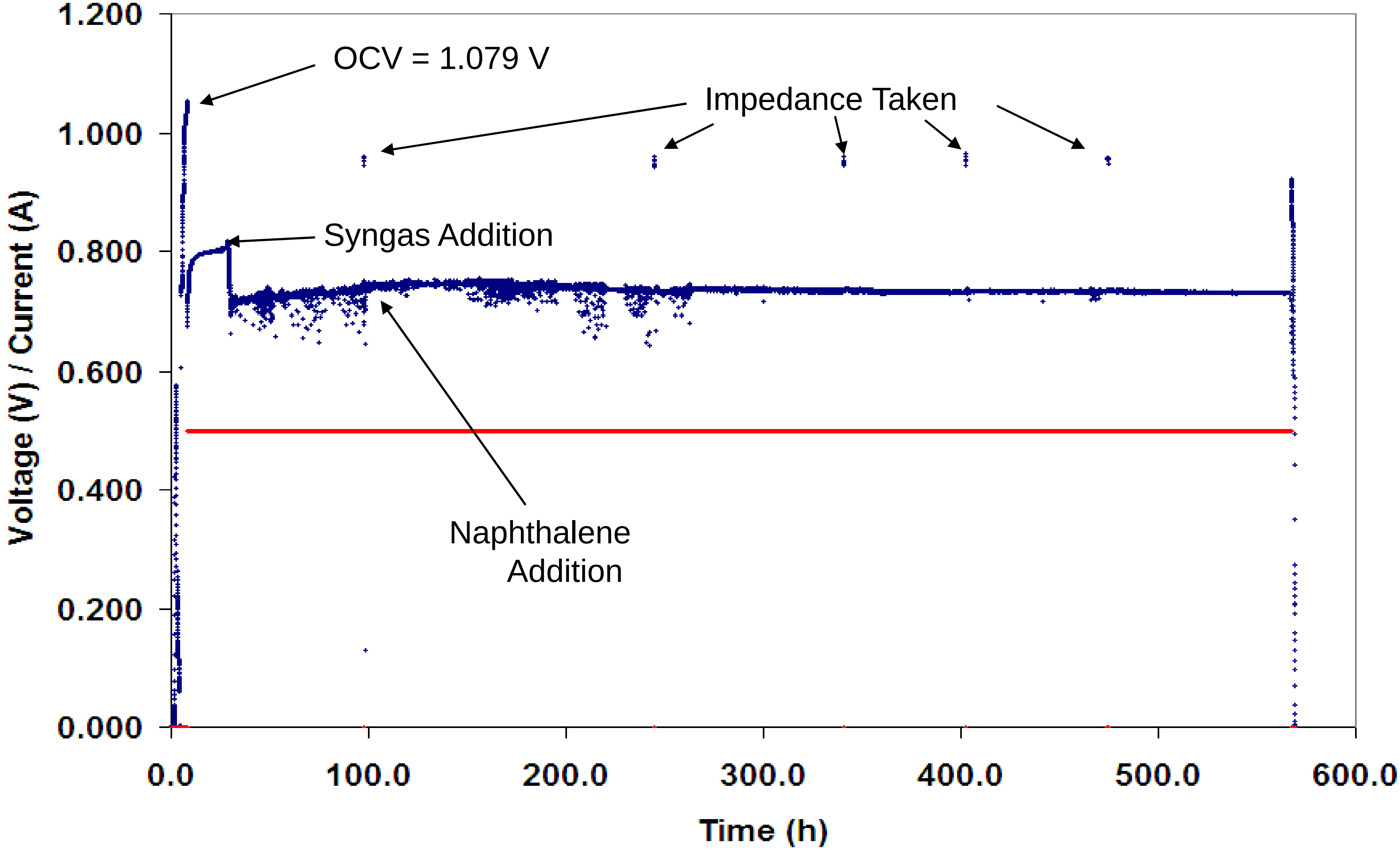
Test Conditions

- **All tests at 800°C and 250 mA/cm^2 load**
- **Gas mixture is simulated syngas**

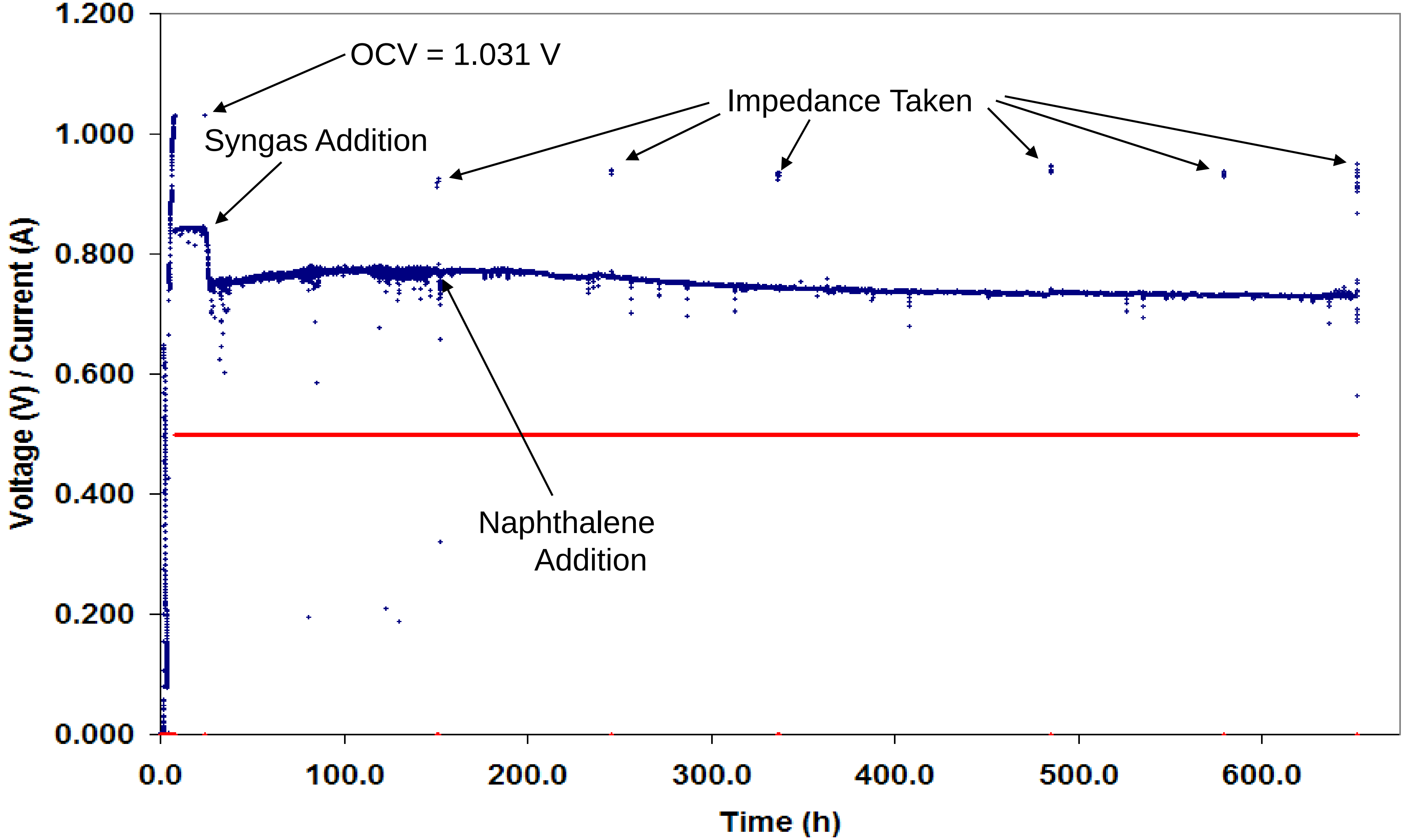
  28.6% CO **29.1% H_2** **27.1% H_2O**

  3.2% N_2 **12.0% CO_2**
- **Cells equilibrated on 3% H_2O / bal H_2 under load for over 12 hours, equilibrated on syngas for 48 hours**
- **Trace contaminant exposure commences after equilibration, 500 hour duration**
- **Cells 'quenched' to preserve trace material, post-operational analysis by SEM/EDS, XRD, XPS**

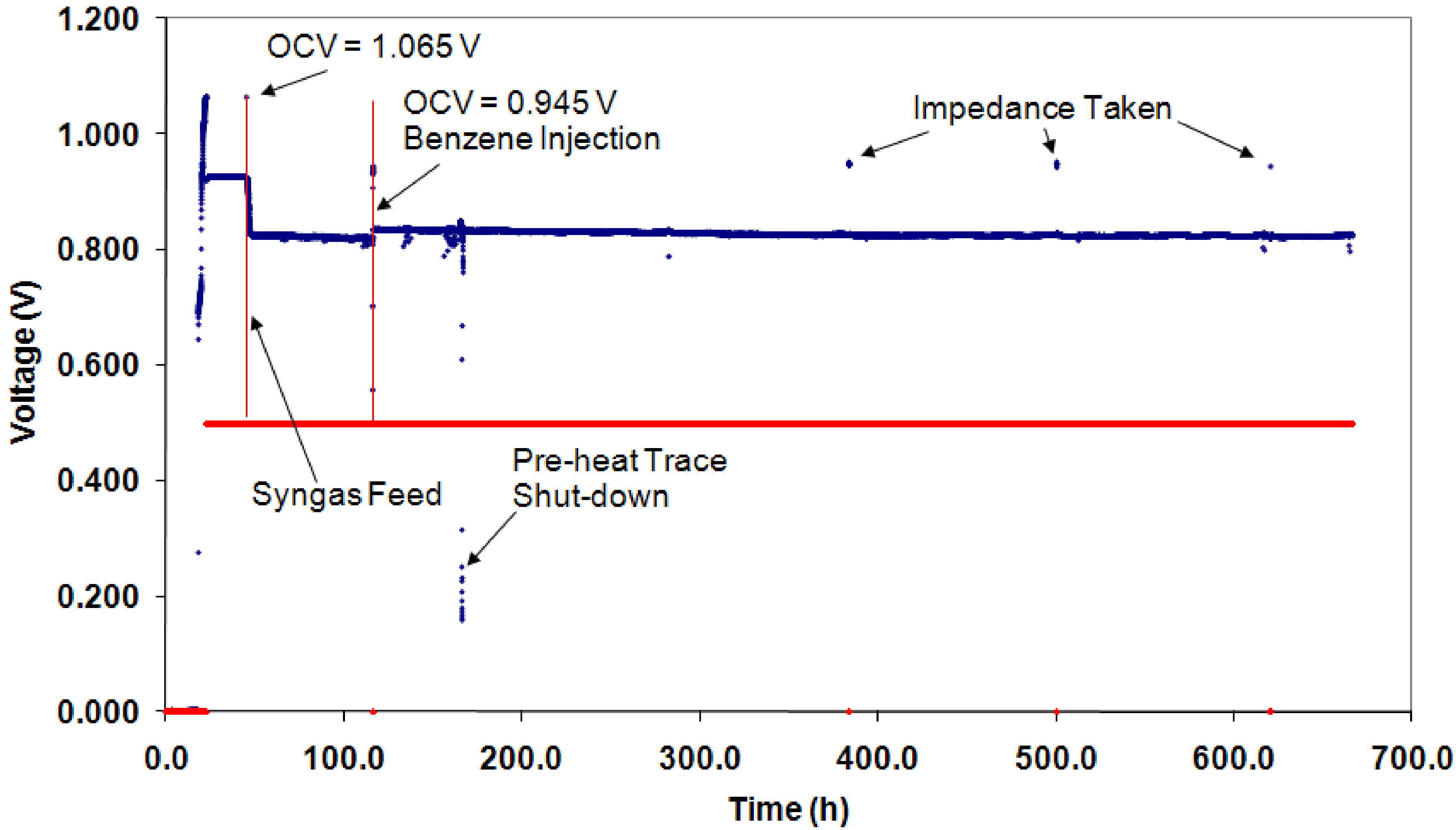
V-I Response of Button Cell on Syngas Doped with 100 ppm Naphthalene



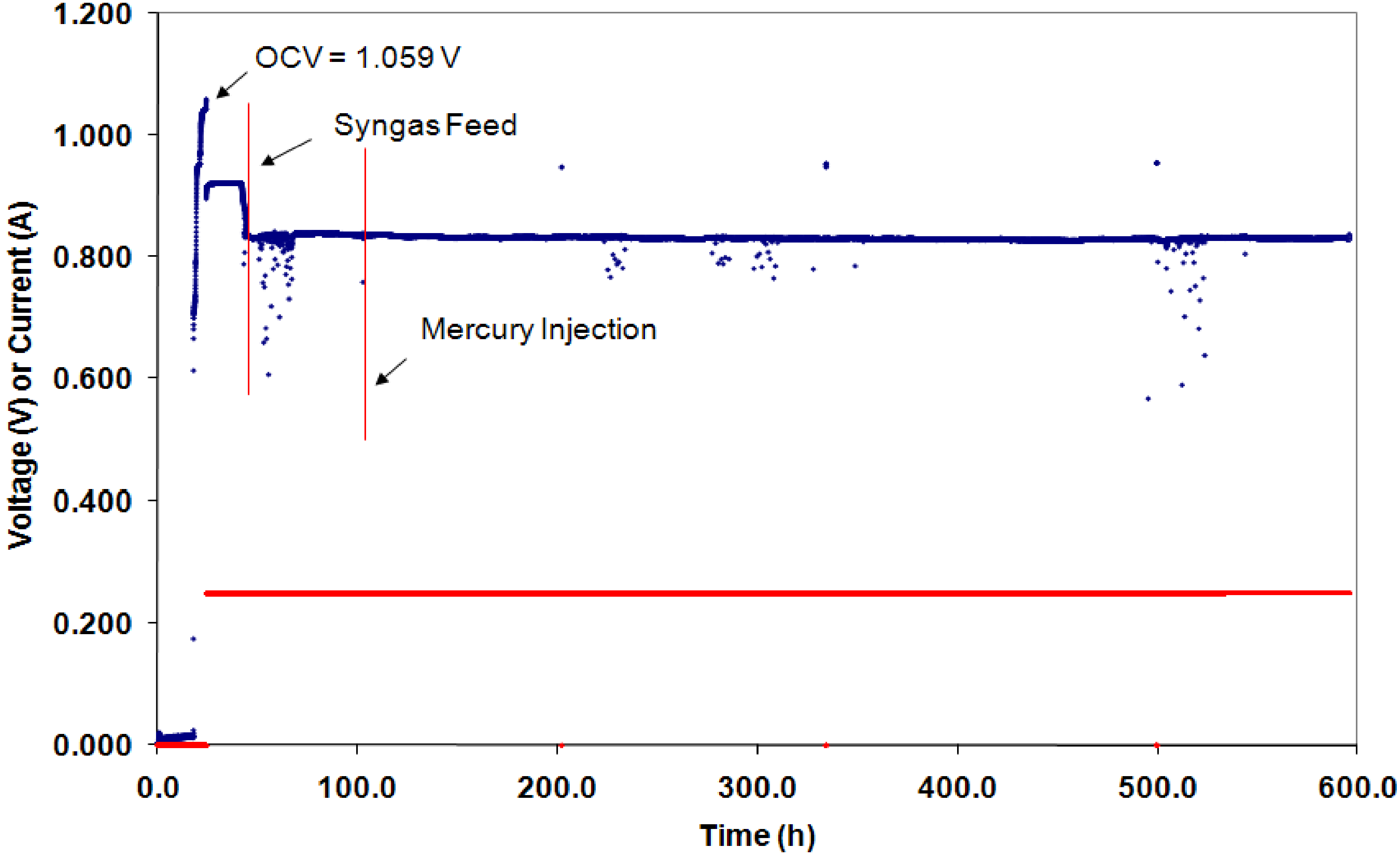
V-I Response of Button Cell on Syngas Doped with 500 ppm Naphthalene



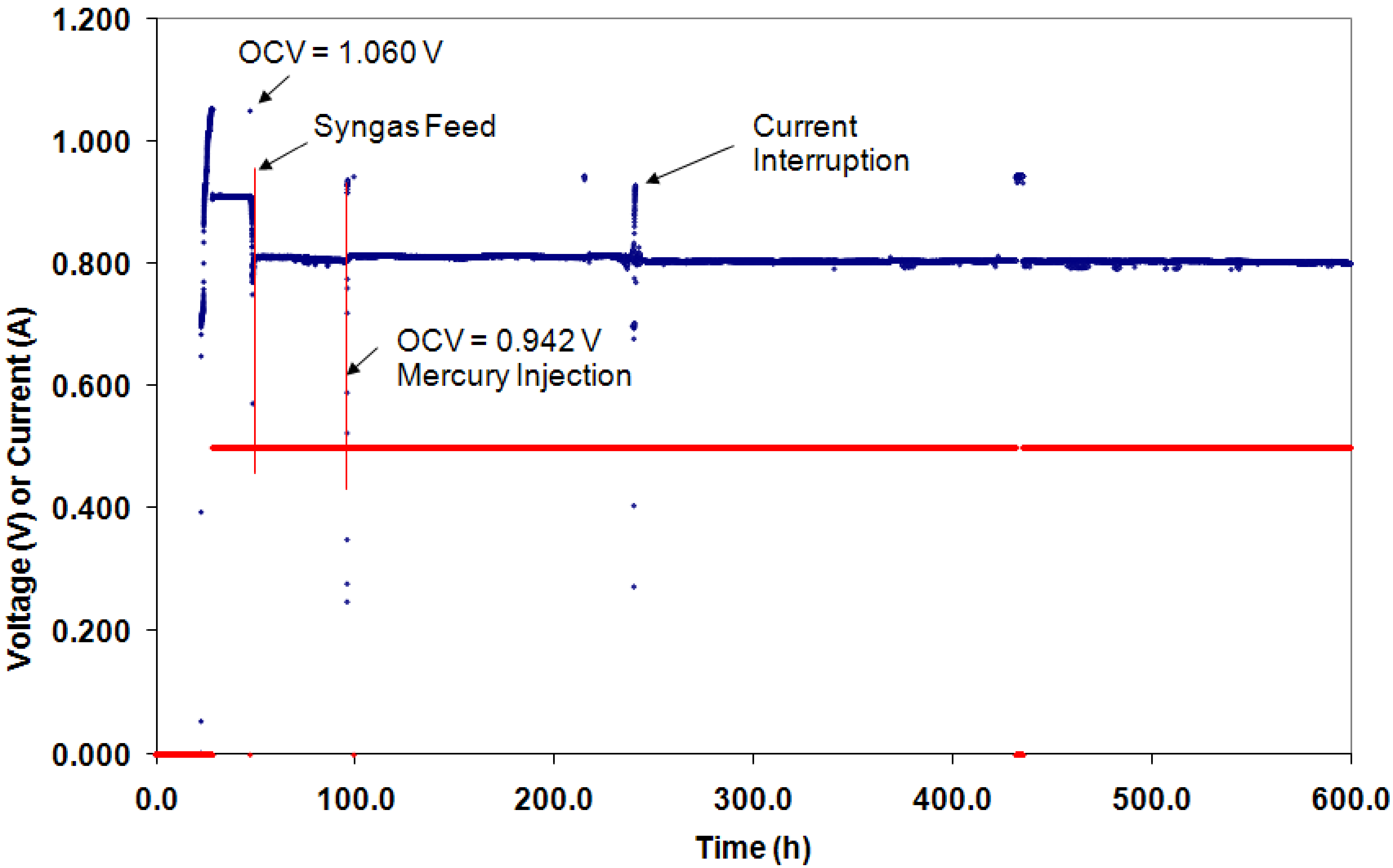
V-I Response of Button Cell on Syngas Doped with 15 ppm Benzene



V-I Response of Button Cell on Syngas Doped with 1 ppm Mercury

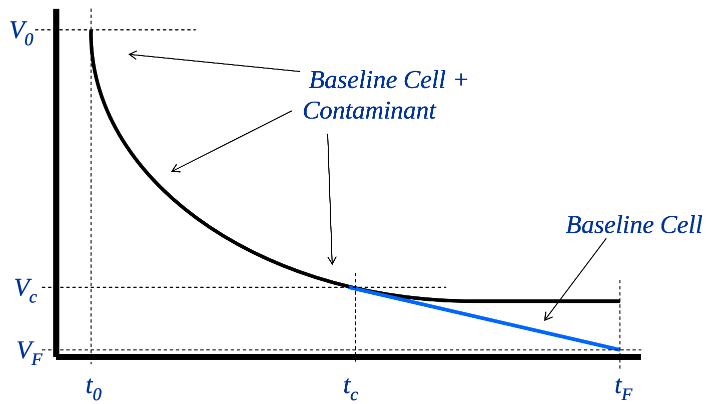


V-I Response of Button Cell on Syngas Doped with 10 ppm Mercury



Observed Behavior

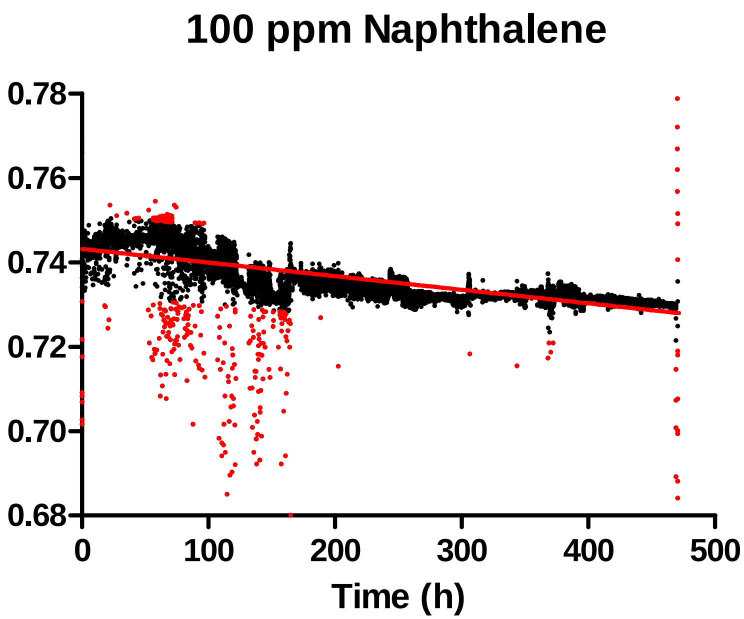
- **Two-phase decay expected**
  - Phase 1:
    - Exponential decay model applied from t_0 to t_c
    - t_c determined at instantaneous decay rate of baseline cell (e.g., 1% / 1000 hours)
  - Phase 2:
    - Linear decay applied from t_c to t_{final}
    - Linear decay rate of baseline cell (1.0%/1000 hours)

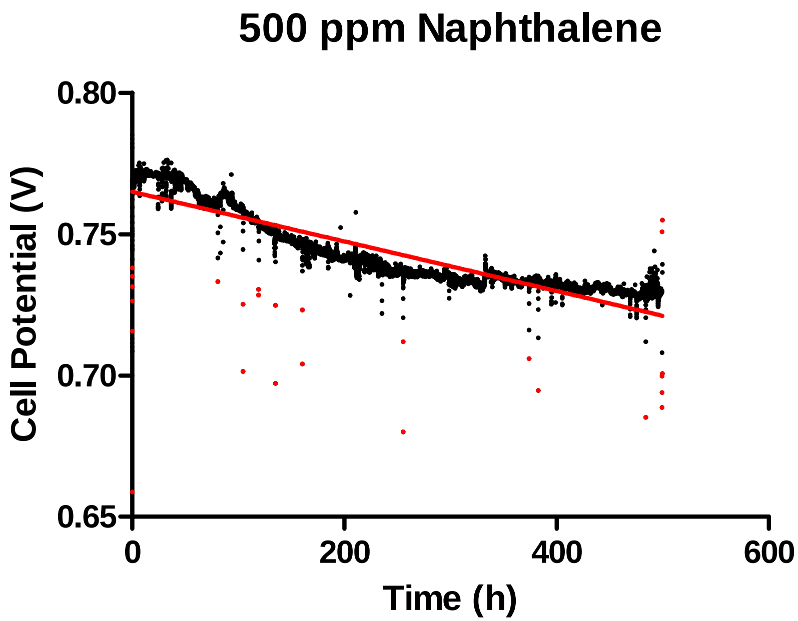


Statistical Data Analysis

- Data are used to fit an exponential or linear decay equation by minimizing the least squares difference through non-linear regression (PRISM)
- Comparisons between 'all data' and 'data with outlier removal'

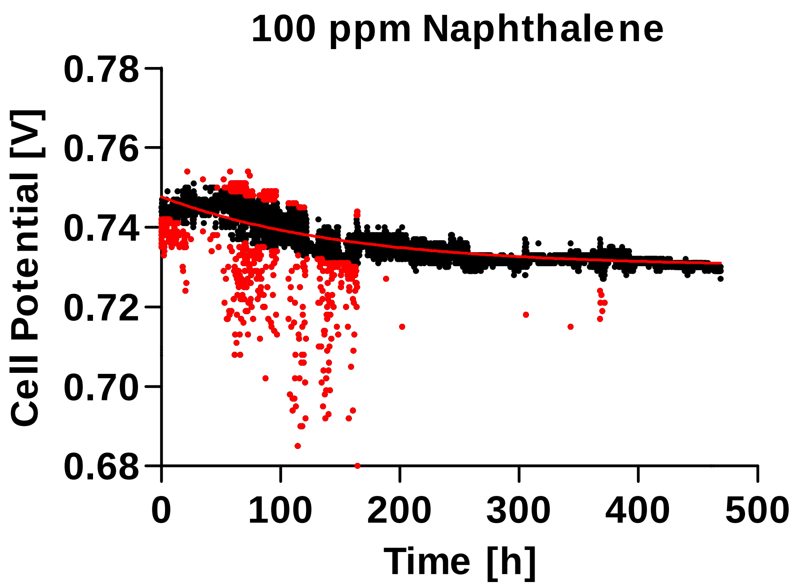
Naphthalene Summary – Linear Decay Approach

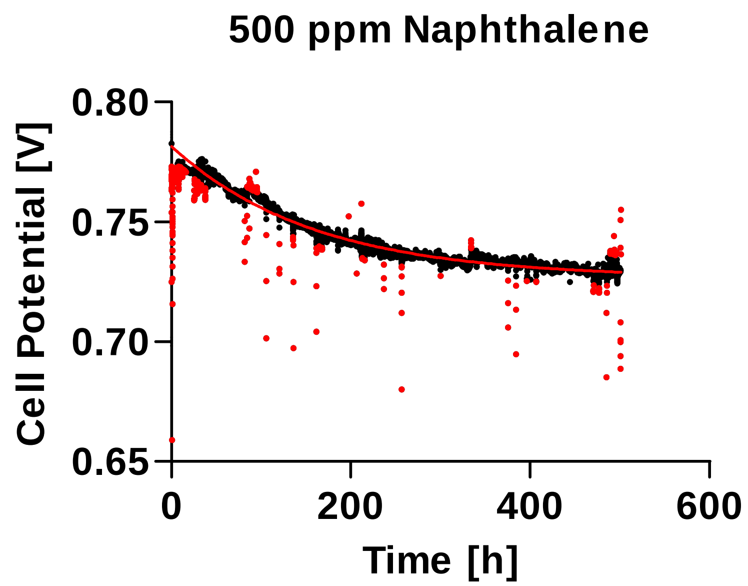




Conc [ppm]	Case	y-int	slope	R^2	Ave. Deg [% khr^{-1}]
100	all data	0.743	-3.11E-05	0.2150	4.19
100	outliers removed	0.743	-3.26E-05	0.7227	4.39
500	all data	0.765	-8.69E-05	0.6370	11.36
500	outliers removed	0.765	-5.91E-05	0.8599	7.73

Naphthalene Summary – Two-phase Decay

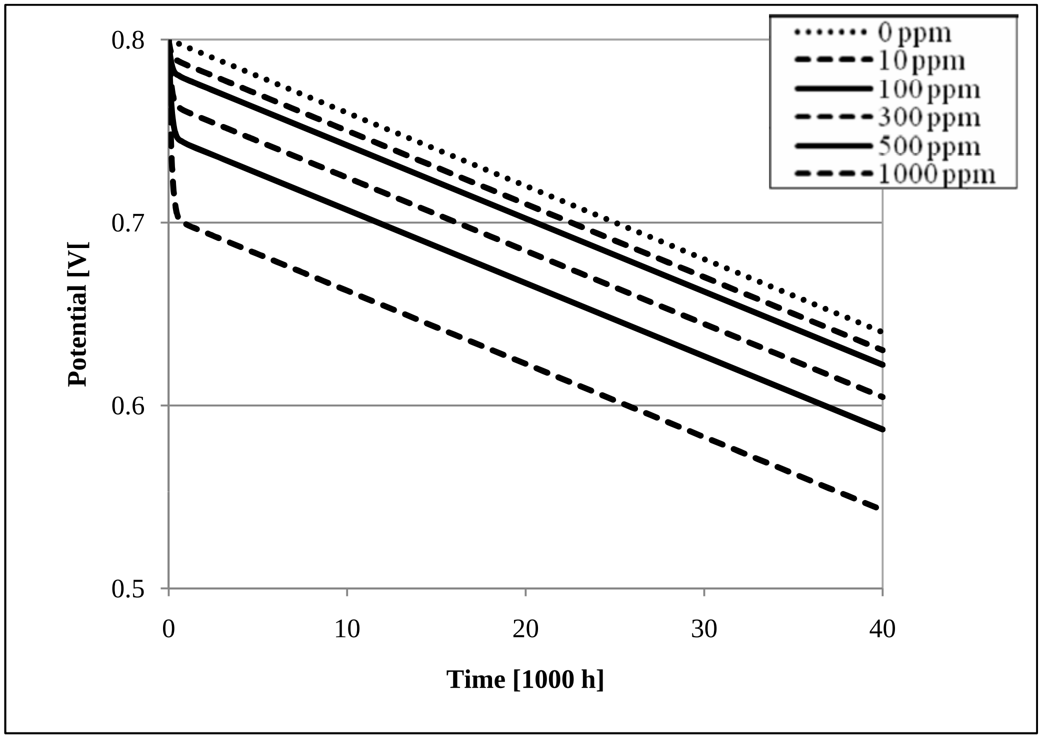




Conc [ppm]	Case	V[V] @ t=0	t_c [h]	V[V] @ t=40khr	Ave. Deg [% khr^{-1}]
100	all data	0.748	408	0.442	1.023
100	outliers removed	0.748	427	0.442	1.024
500	all data	0.778	654	0.441	1.082
500	outliers removed	0.782	598	0.441	1.089

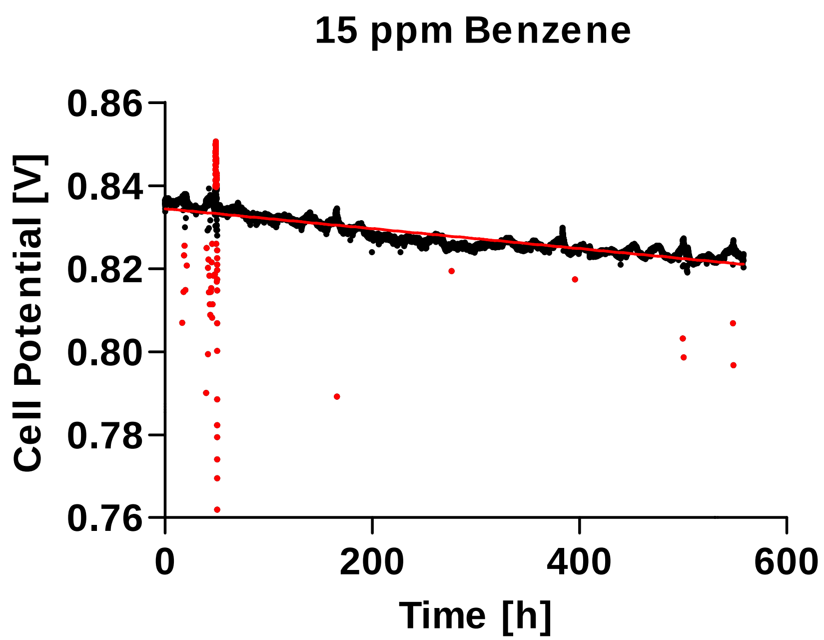
Predicted Naphthalene Cleanup Targets

Based upon 0.50% per 1000 h
Baseline Cell Degradation



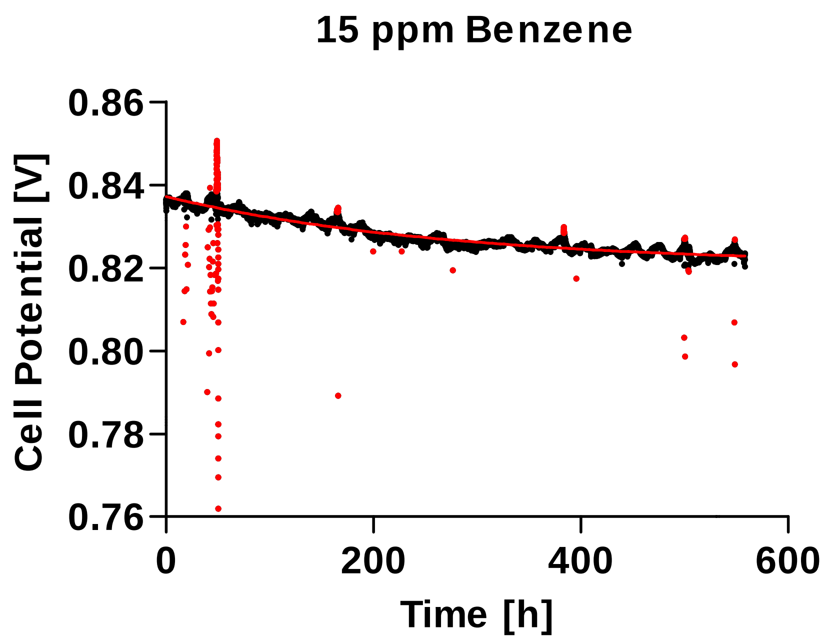
A baseline cell degradation of 0.50% allows a conc. of 360 ppm to produce 0.6 V after 40,000 h of operation.

Benzene Summary – Linear Decay Approach



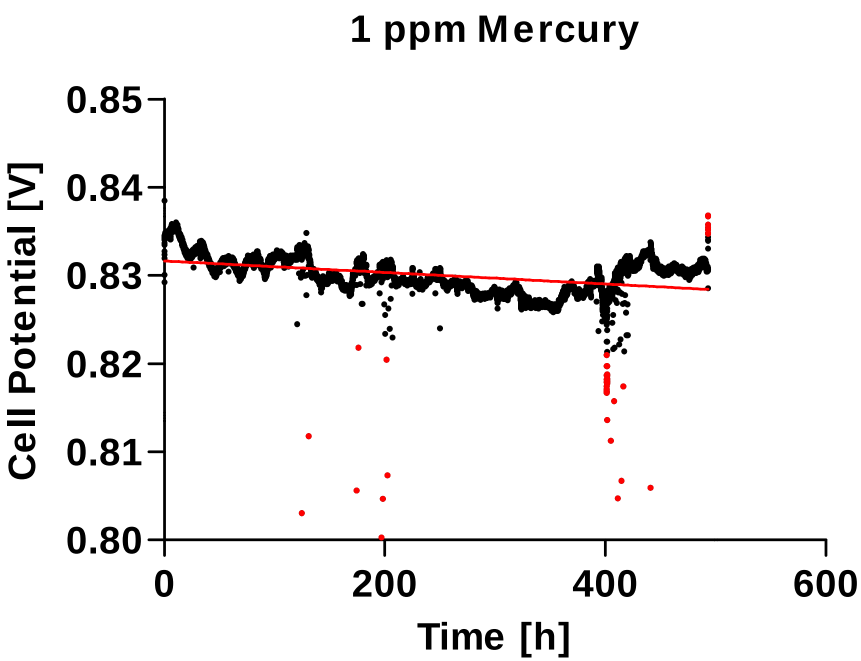
Conc [ppm]	Case	y-int	slope	R^2	Ave. Deg [% khr^{-1}]
15	**all data**	**0.834**	**-2.53E-05**	**0.0345**	3.035
15	**outliers removed**	**0.834**	**-2.40E-05**	**0.8817**	2.880

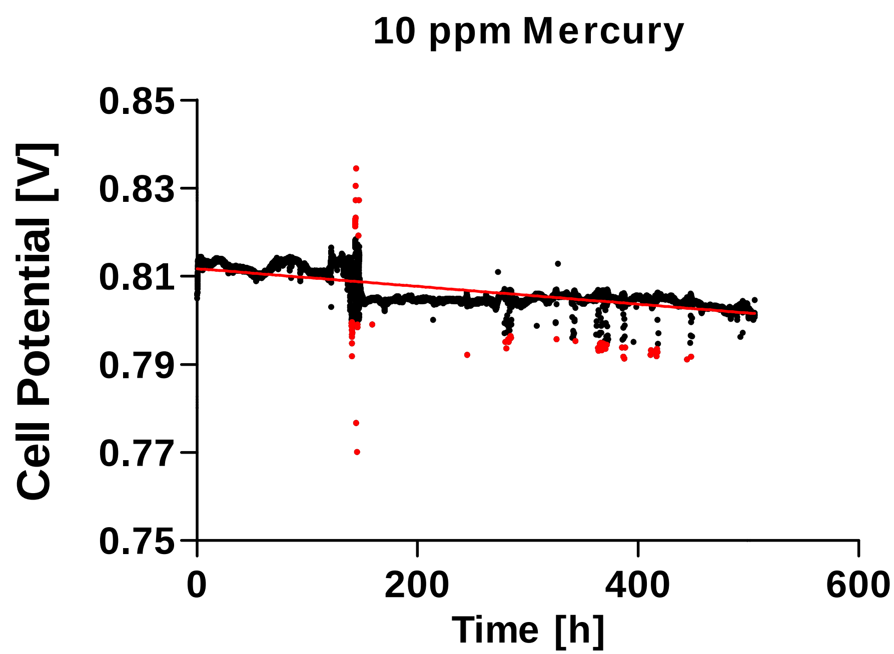
Benzene Summary - Two-phase Decay



Conc [ppm]	Case	V_0 [V]	Tc [h]	V_F [V]	Ave. Deg [% khr^{-1}]
15	all data	0.835	1285	0.497	1.011
15	outliers removed	0.837	519	0.498	1.012

Mercury Summary – Linear Decay Approach





Conc [ppm]	Case	y-int	slope	R^2	Ave. Deg [% khr^{-1}]
1	all data	0.832	-6.73E-06	0.0465	0.809
1	outliers removed	0.832	-6.53E-06	0.2266	0.785
10	all data	0.812	-1.63E-05	0.0319	2.012
10	outliers removed	0.812	2.02E-05	0.6473	2.482

Q4 Testing

- **Collection of baseline cell degradation data**
- **Complete second mercury test at 1 ppm**
- **Repeat 150 ppm benzene test**

Individual Contaminant Summary

- **Mercury effect is small relative to the base cell degradation**
  - Mercury exposure is 10-1000 times greater than raw syngas
- **Naphthalene exposure initially accelerates degradation**
  - Degradation rate slows as test progresses
  - Methods for predicting cleanup targets are under development
- **Benzene exposure initially accelerates degradation**
  - Degradation rate slows as test progresses
  - 150 ppm exposure test pending
- **Results valid for conditions tested**
  - Postulated to be sensitive to current density and temperature