Novel Approaches to the HyS SDE Anode

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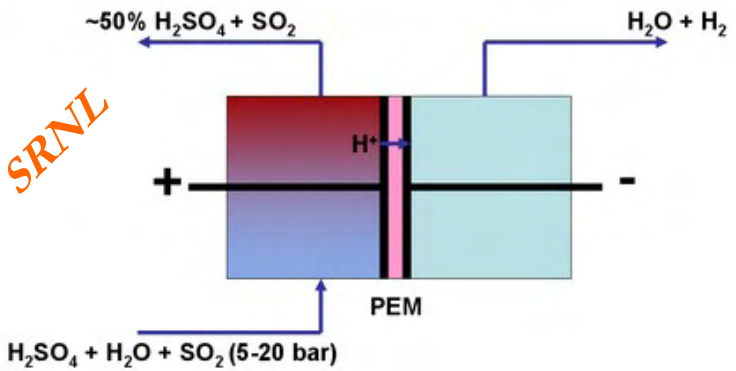
Giner Electrochemical Systems, LLC

April 20, 2009

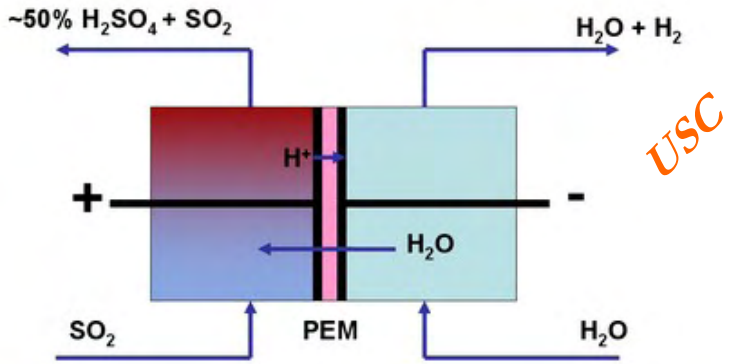
Hybrid Sulfur Electrolyzers ('SDEs')

Liquid Feed



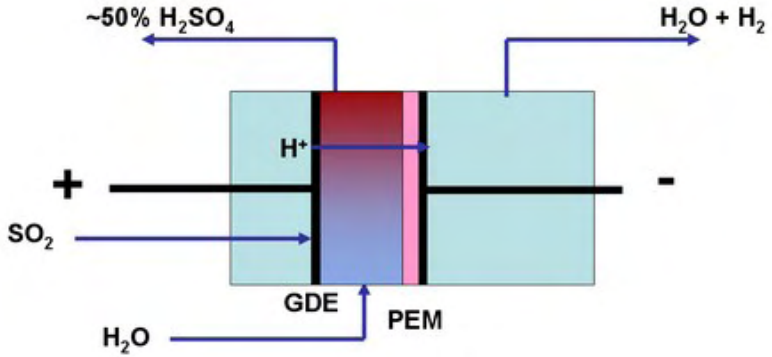
SRNL

Direct Feed

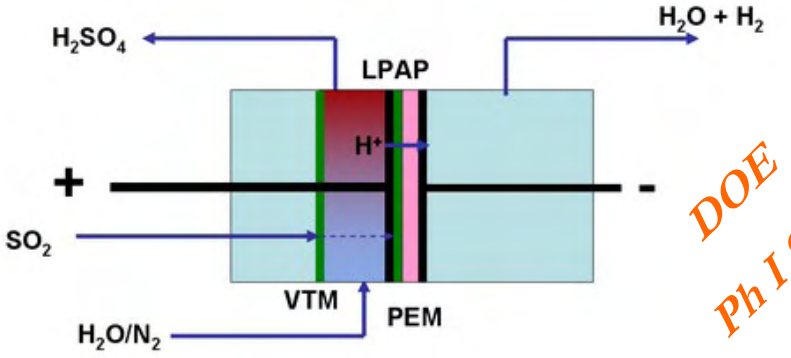


USC

GES Narrow-Gap Anode



GES VTM / LPAP



DOE
Ph I SBIR

Narrow-Gap Anode for HyS Electrolyzer

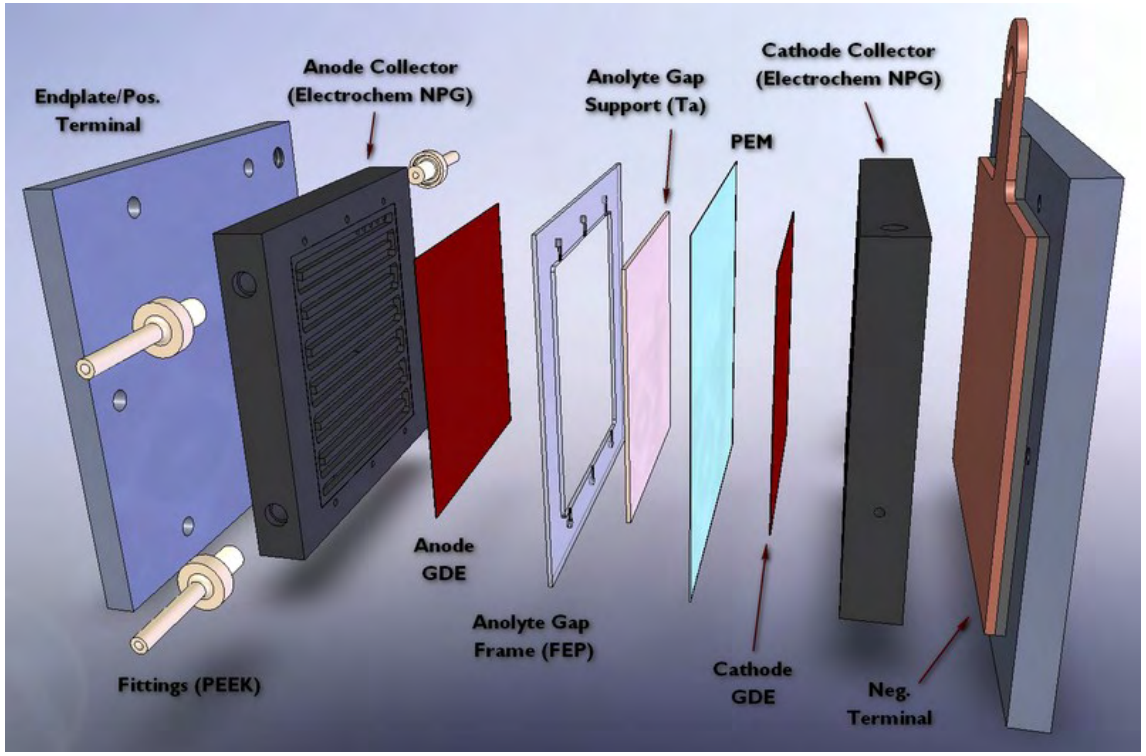
- *US Publ. Pat. Appl.* ***2009/0045073***
- *SRNL Subcontract* ***AC54775O***

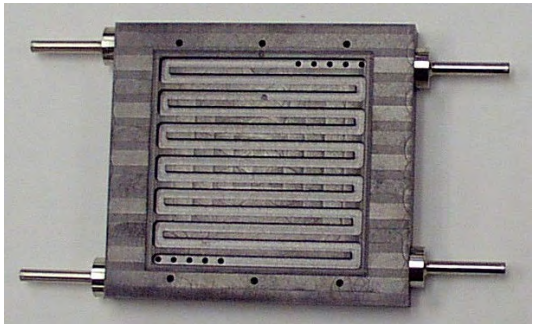
Objectives:

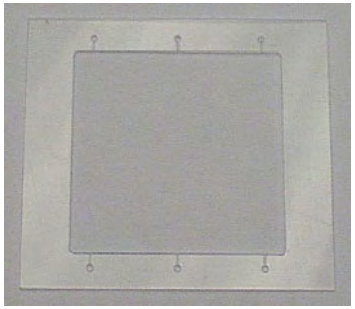
- Demonstrate concept of NGA configuration for HyS electrolyzer
- Determine i-V performance and SO_2 crossover characteristics
- Project suitability of NGA approach for large scale application

Narrow-Gap Anode for HyS Electrolyzer

- Employs a gas diffusion electrode (GDE) in conjunction with an electrolyte gap
- Allows direct gas feed at low pressure
- Obviates need for high pressure electrolysis at utility scale
- Minimizes mass transfer limitations inherent to other types
- Gap provides long diffusion path for dissolved SO_2 – xover
- 25-cm² HW, .031" gap
- Tantalum wire mesh gap support







Narrow-Gap Anode for HyS Electrolyzer
Signficant Milestones Achieved

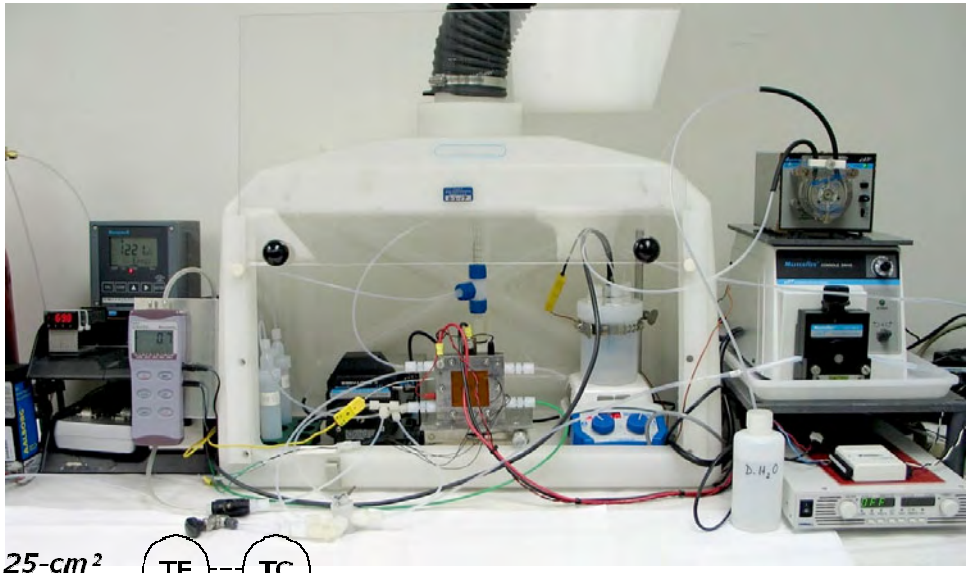
- Demonstrated high GDE/NGA cell conductance in H_2 pump mode
- Developed simple means of SO_2 crossover determination – caustic H_2 scrub/total sulfur
- Demonstrated high performance of GDE/NGA cell in SO_2-electrolysis mode
  - 730-850 mV at 500 mA/cm² depending on PEM
- Demonstrated stable SDE operation performance over 60 hrs

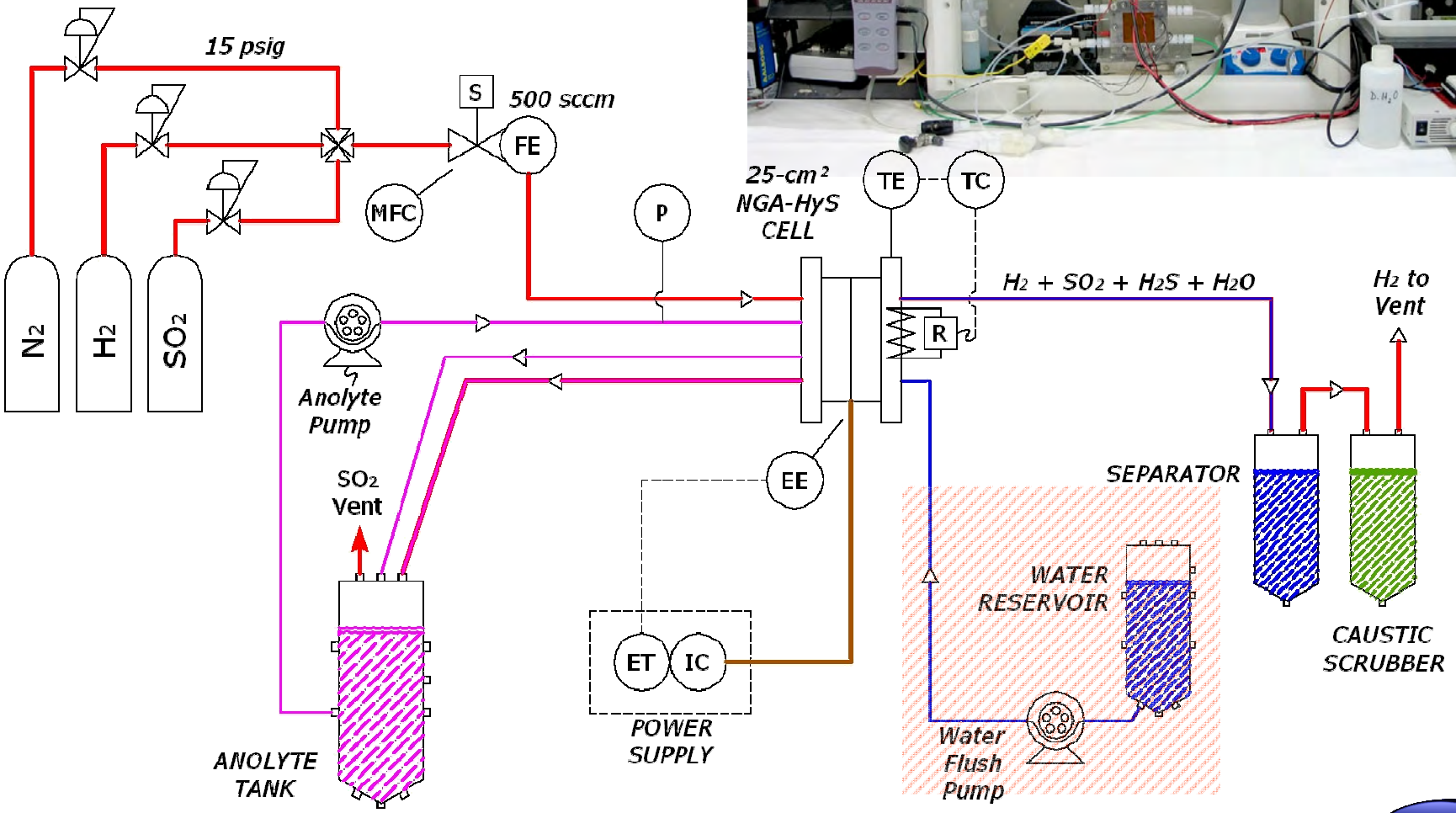
Narrow Gap Anode HyS Status

- Known issues
  - Maintaining [H_2SO_4]
  - Clogging anolyte ports
    - Causes high anolyte inlet pressures
    - Accelerates seepage
      - Reversed by *ex situ* DI water rinse and RT drying
    - Corrosion products (PEEK, others) and/or anode catalyst sloughing are likely clogging agents
- Endurance Testing – 40h to go, 2 rebuilds
- PEM/gap thickness/[H_2SO_4] tradespace

Narrow-Gap Anode

25-cm² Single-Cell Test System





Narrow-Gap Anode

25-cm² Single-Cell Test System – SO_2 Crossover

Caustic Scrubber

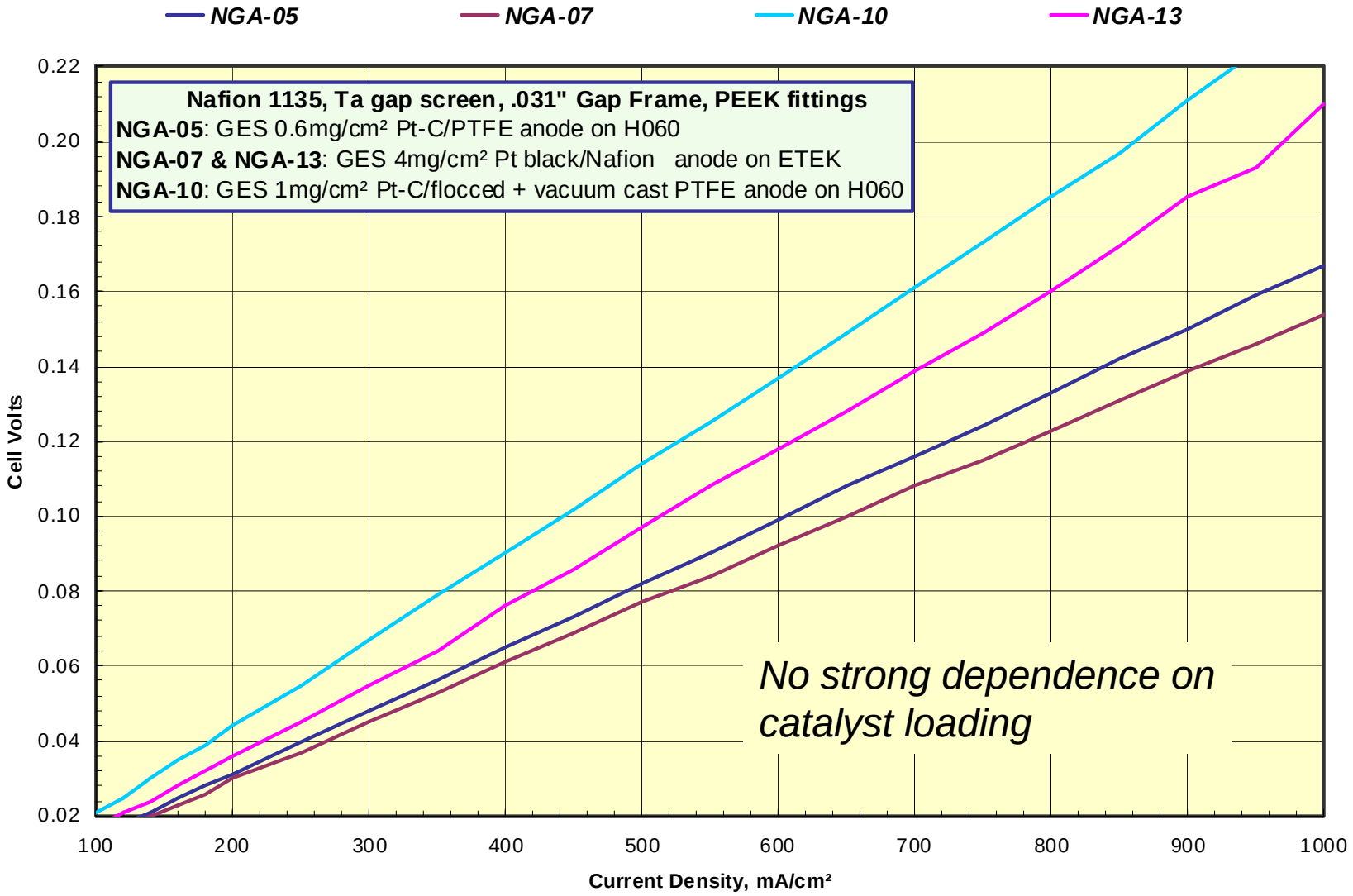
- Circulates 20-40 wt-% NaOH down wetted scrubbing tube
- H_2 product scrubbed and exits top
- Analyze caustic after testing for total sulfur
- ASTM D129-00 (2005)

  Oxygen bomb conversion of all sulfur to sulfate
- ASTM D4327-03

  Ion chromatography for sulfate

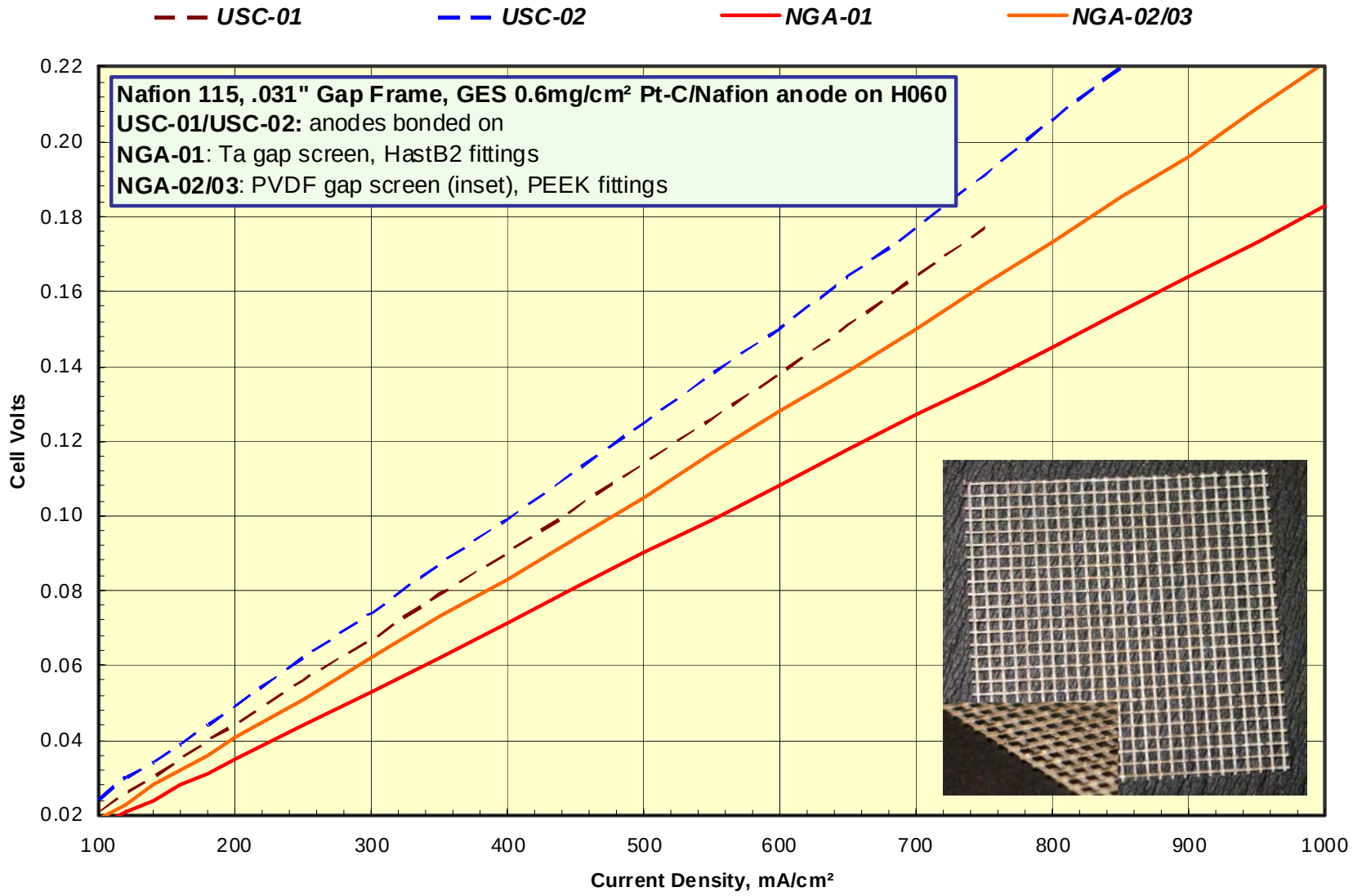
Narrow-Gap Anode (NGA) - **N1135**

Hydrogen Pump Results – 80° C, 1.02-1.05x stoich



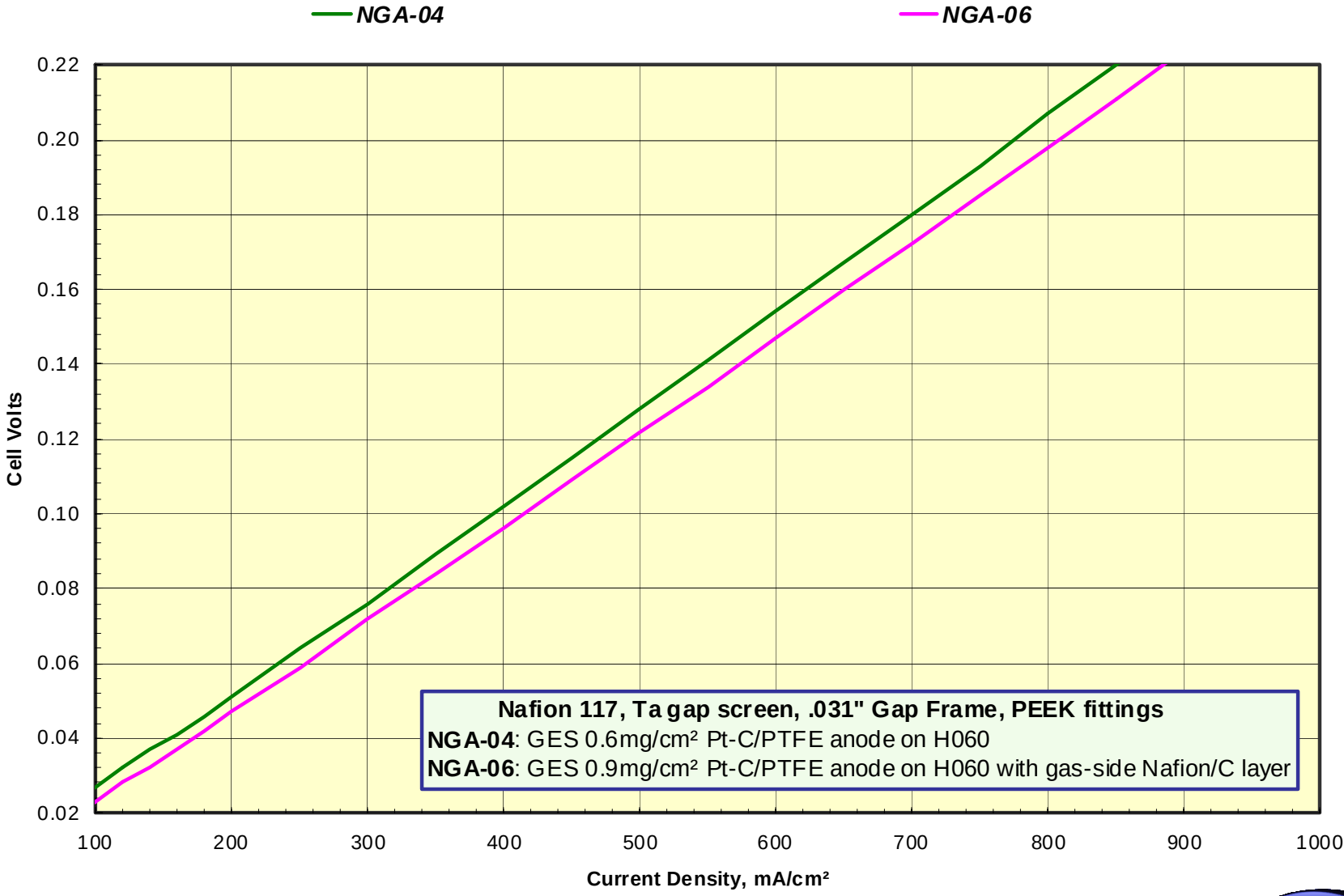
Narrow-Gap Anode (NGA) - **N115**

Hydrogen Pump Results – 80° C, 1.02-1.05x stoich



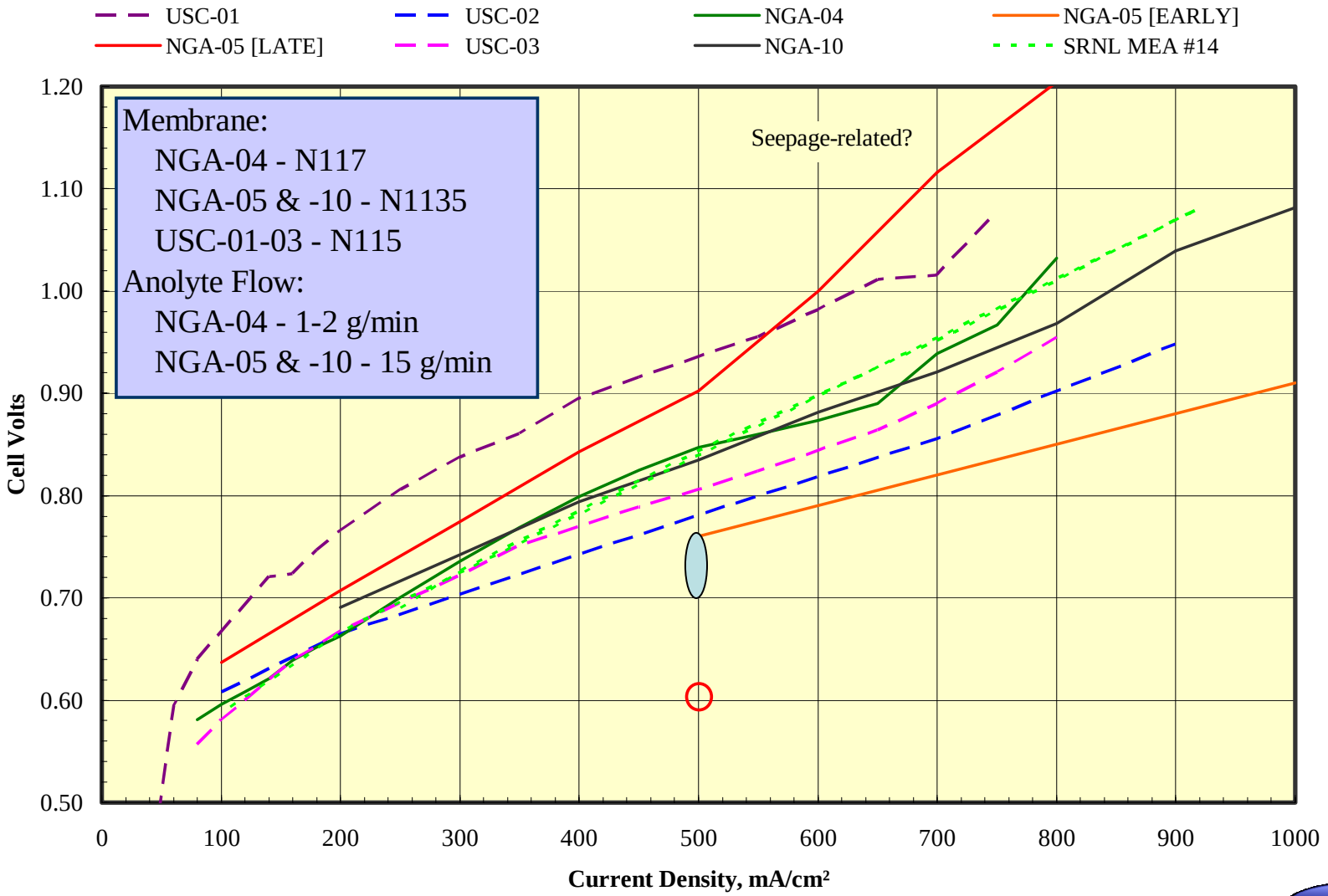
Narrow-Gap Anode (NGA) - **N117**

Hydrogen Pump Results – 80° C, 1.02-1.05x stoich



Narrow-Gap Anode (NGA)

SO_2 Oxidation Results – 80° C, 1.02-1.1x stoich SO_2 flow

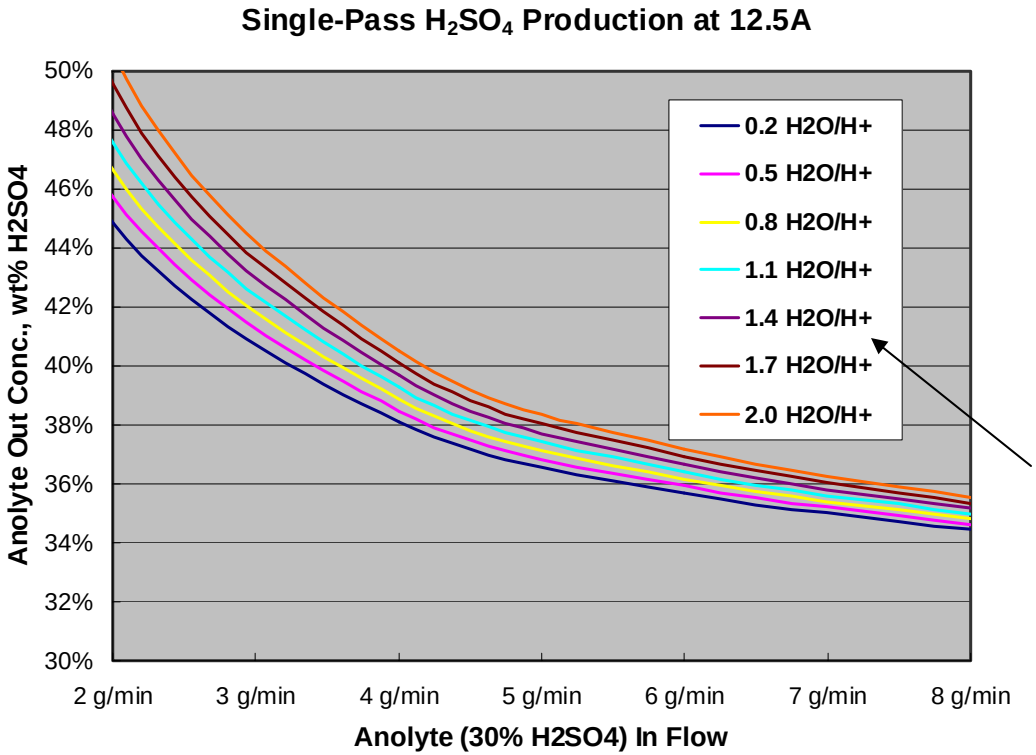


Narrow-Gap Anode (NGA)

SO_2 Oxidation Testing:

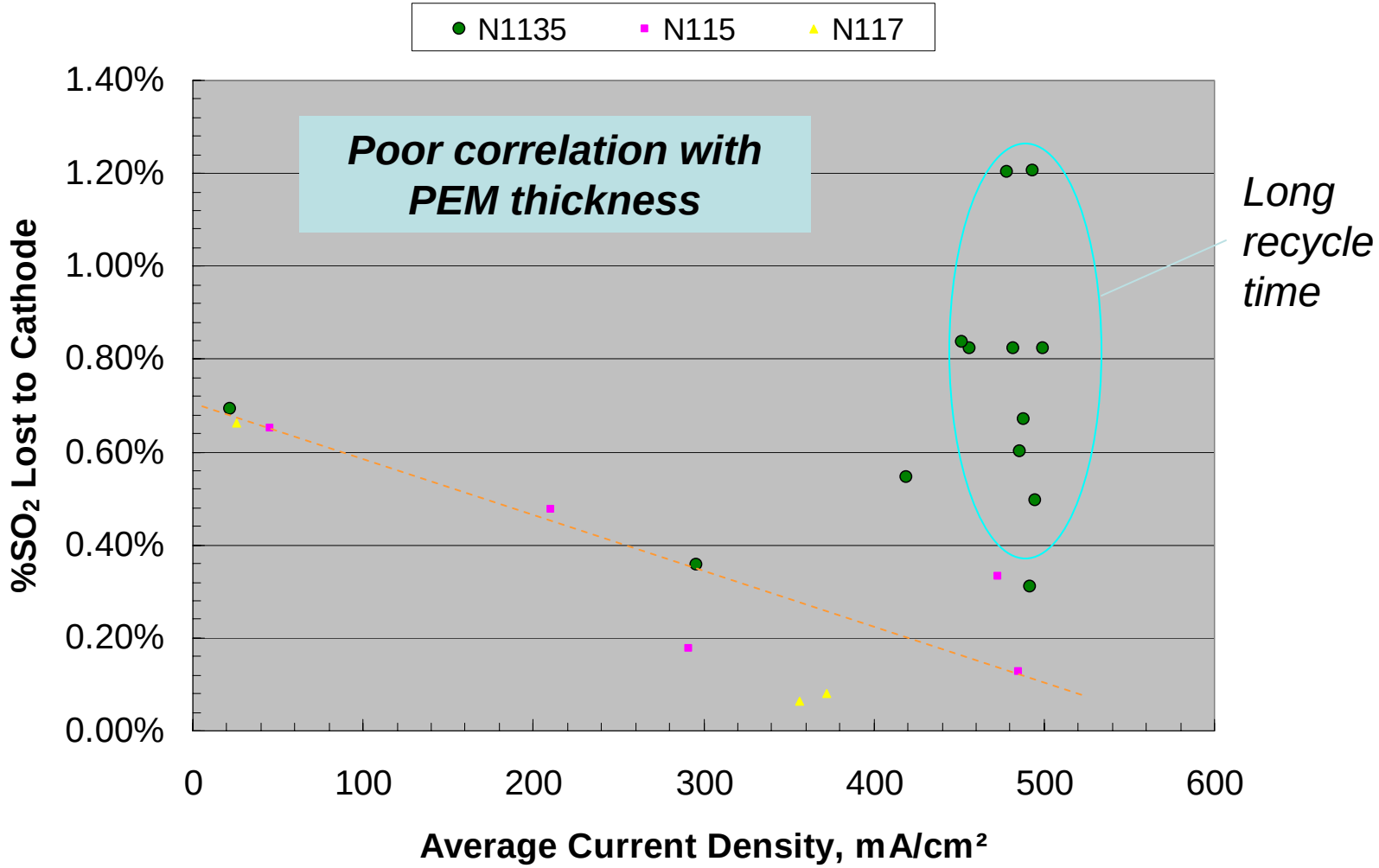
- *13 NGA Builds tested*
- *3 Direct Feed controls tested*

- ***Cell performance not sensitive to SO2 stoichiometry down to ~1.02x***
- ***Performance very sensitive to anolyte flow***



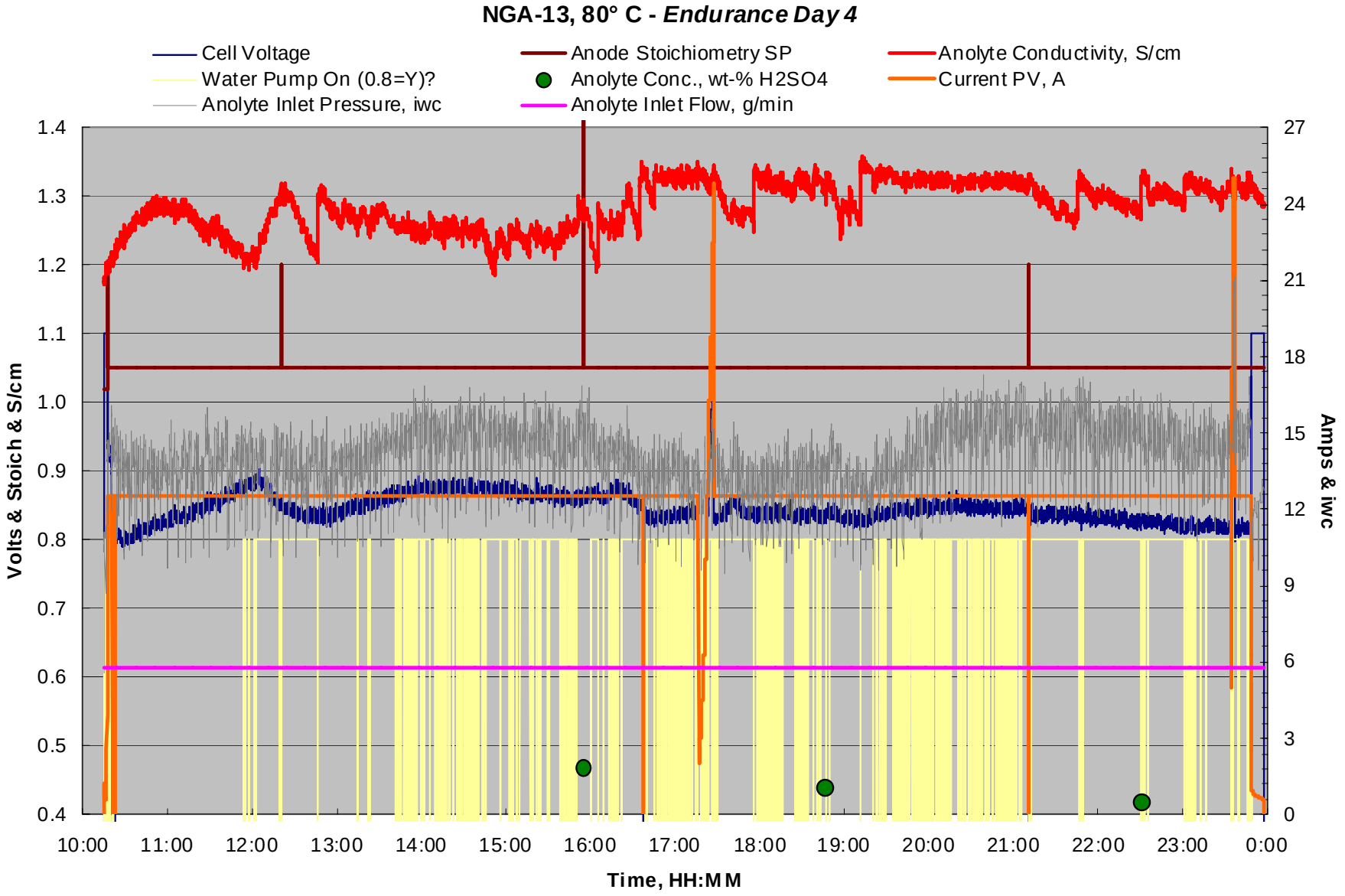
What is net water transport?

Narrow-Gap Anode – SO_2 Crossover

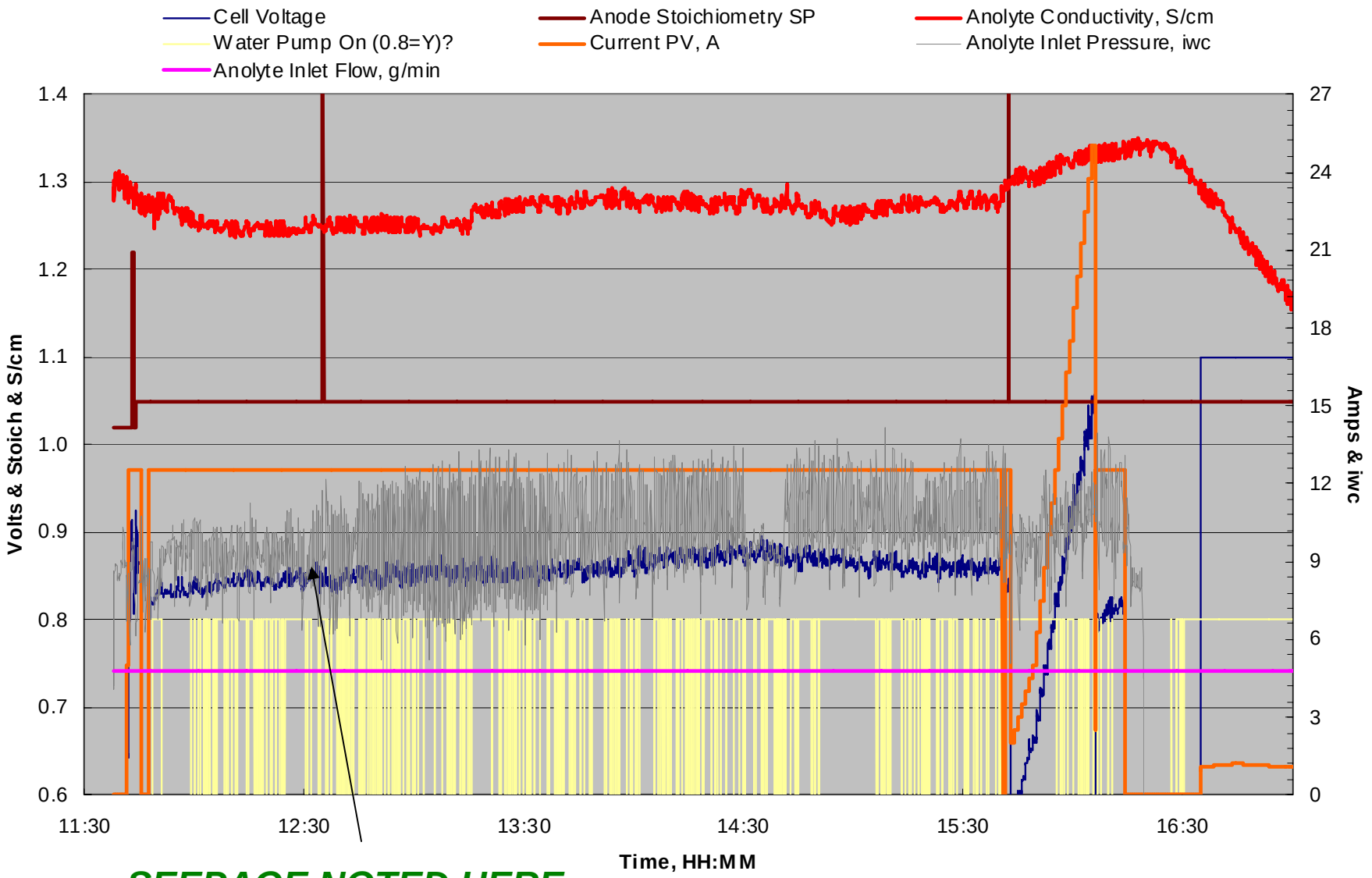


Crossover results to be complemented by microscopy to reveal extent of sulfur layer formation on cathode

Endurance Testing – NGA-13 – **Day 4 (14 hrs)**

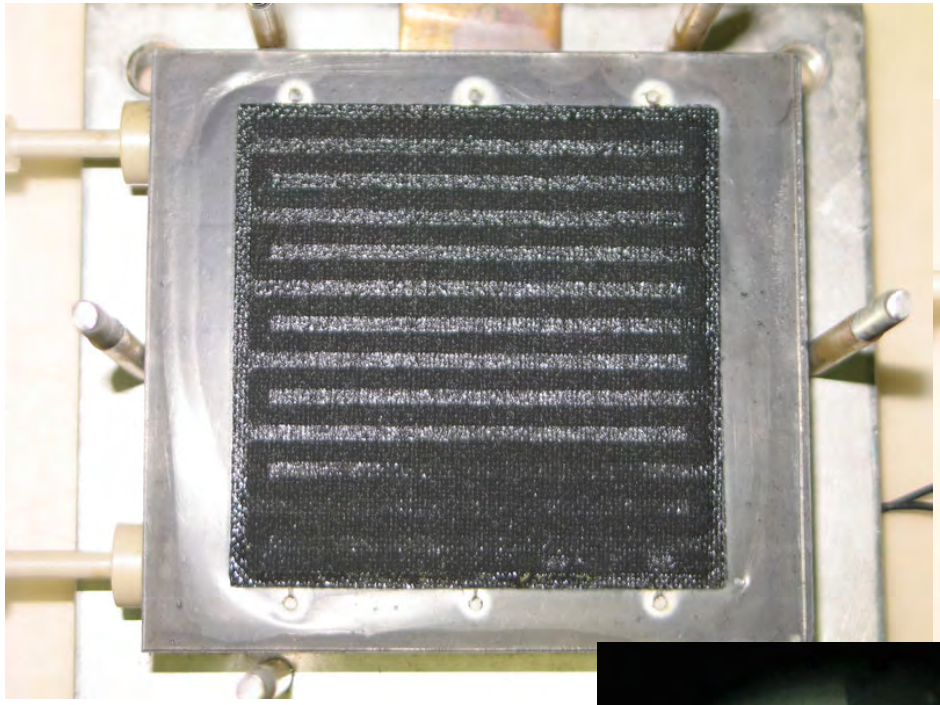


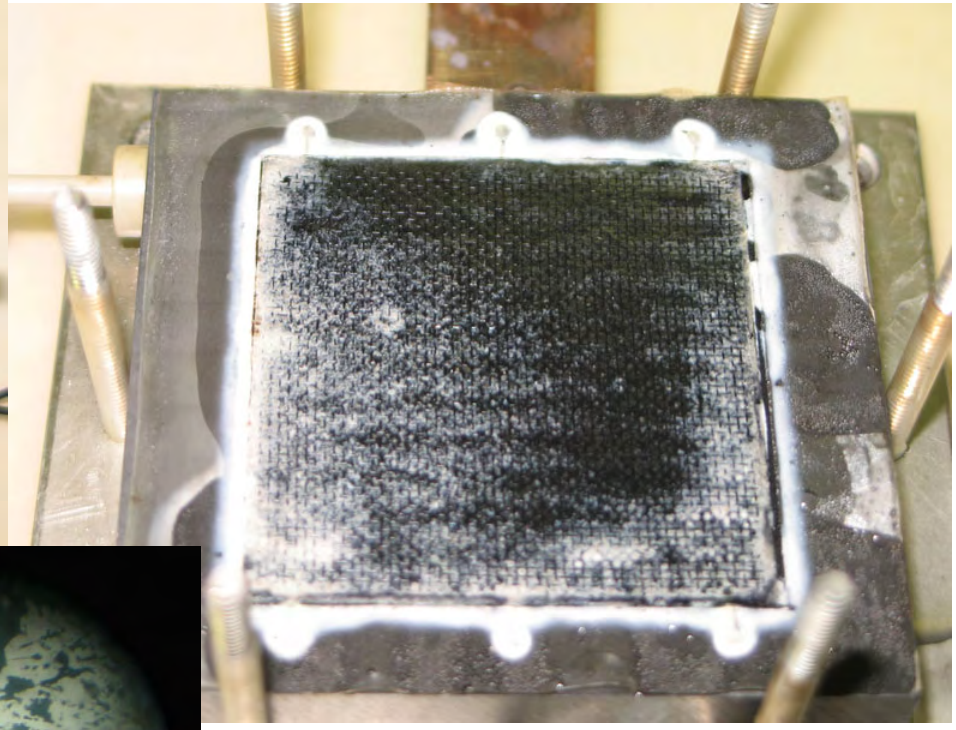
Endurance Testing – NGA-13 – Day 7

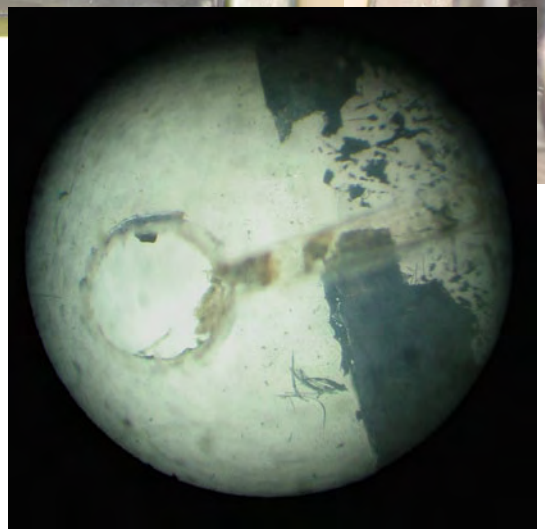


SEEPAGE NOTED HERE

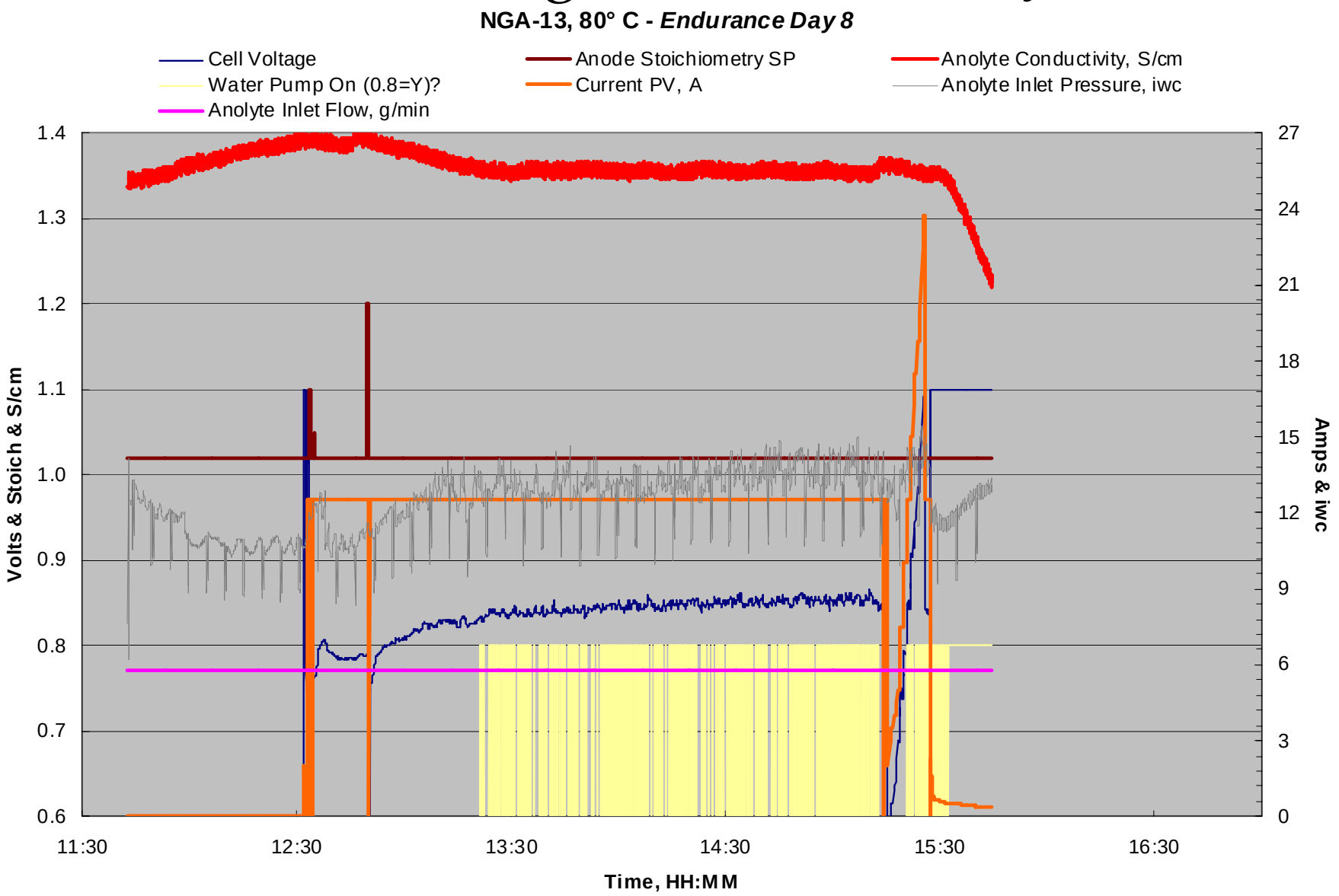
Endurance Testing – NGA-13 – 1st Disass'y





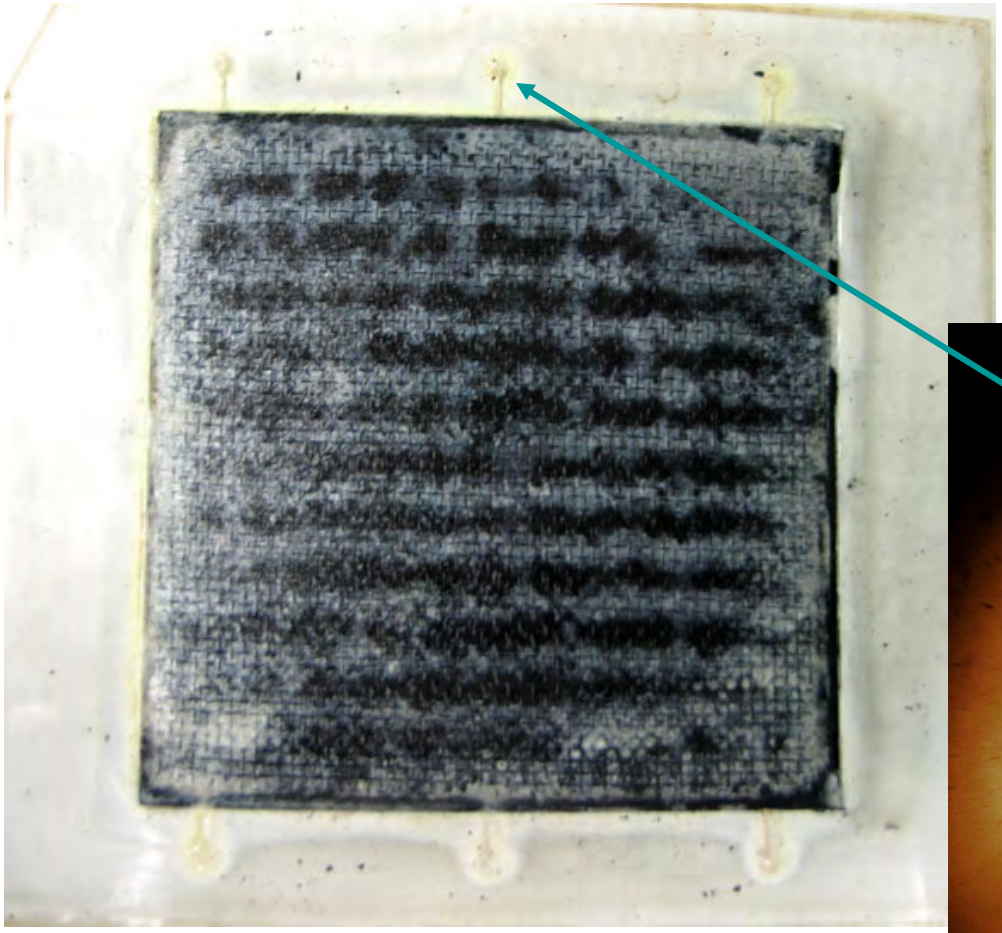


Endurance Testing – NGA-13 – Day 8 (*rebuilt)*

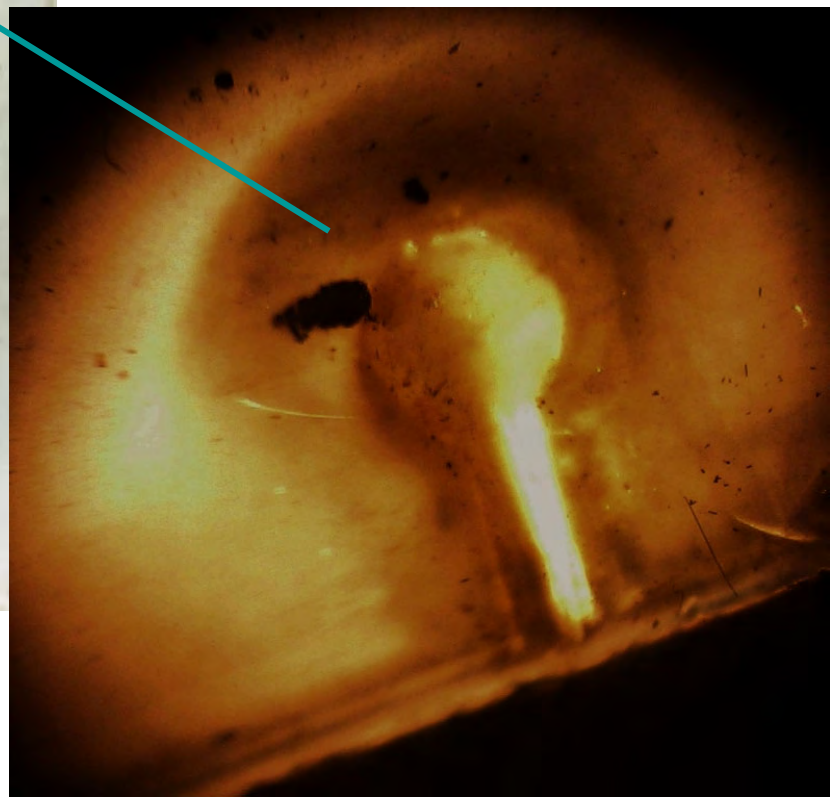


Endurance Testing – NGA-13 – 2nd Disass'y

Day 10



Swelling height of membrane 1-4 mils

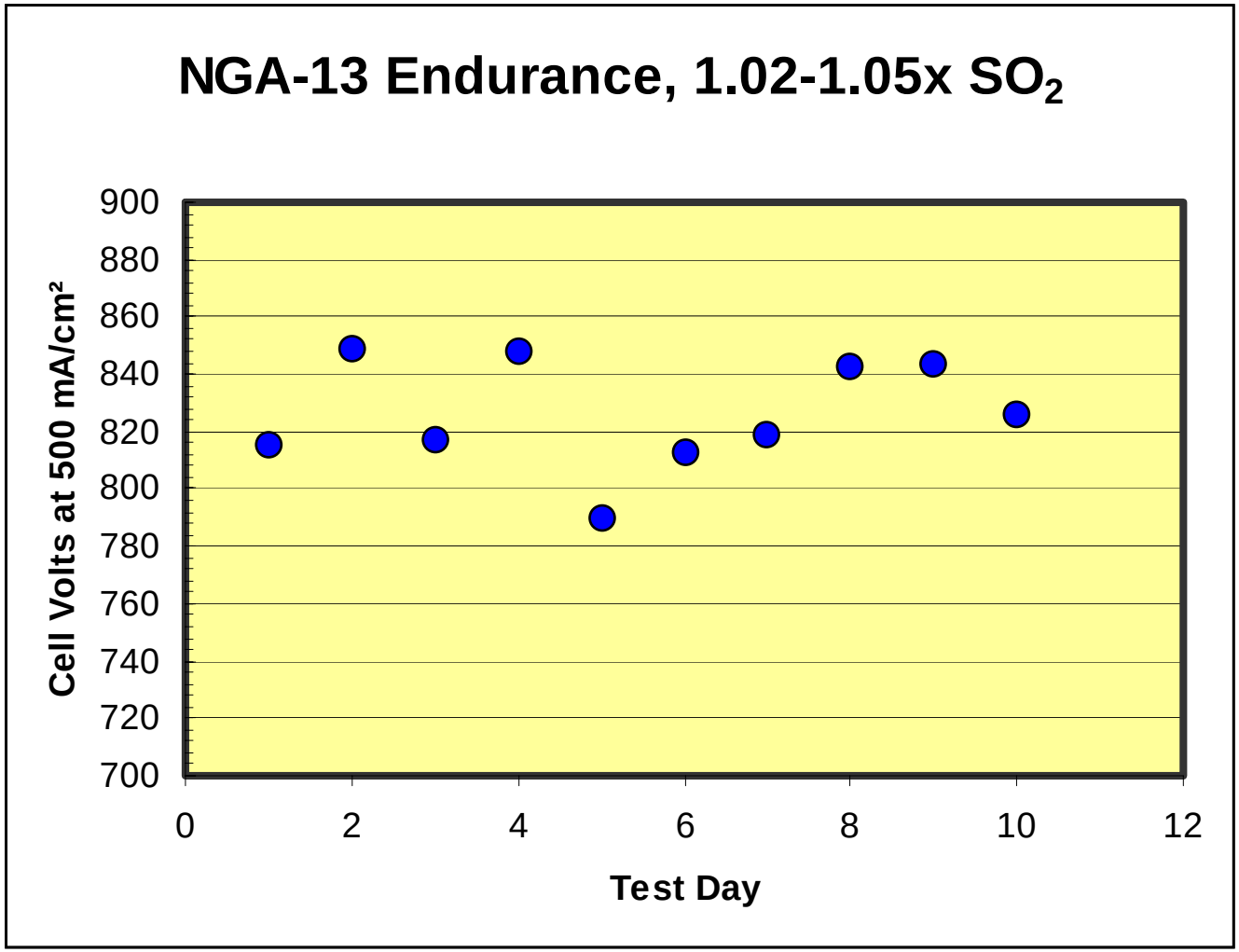


Membrane swollen in area of port vias

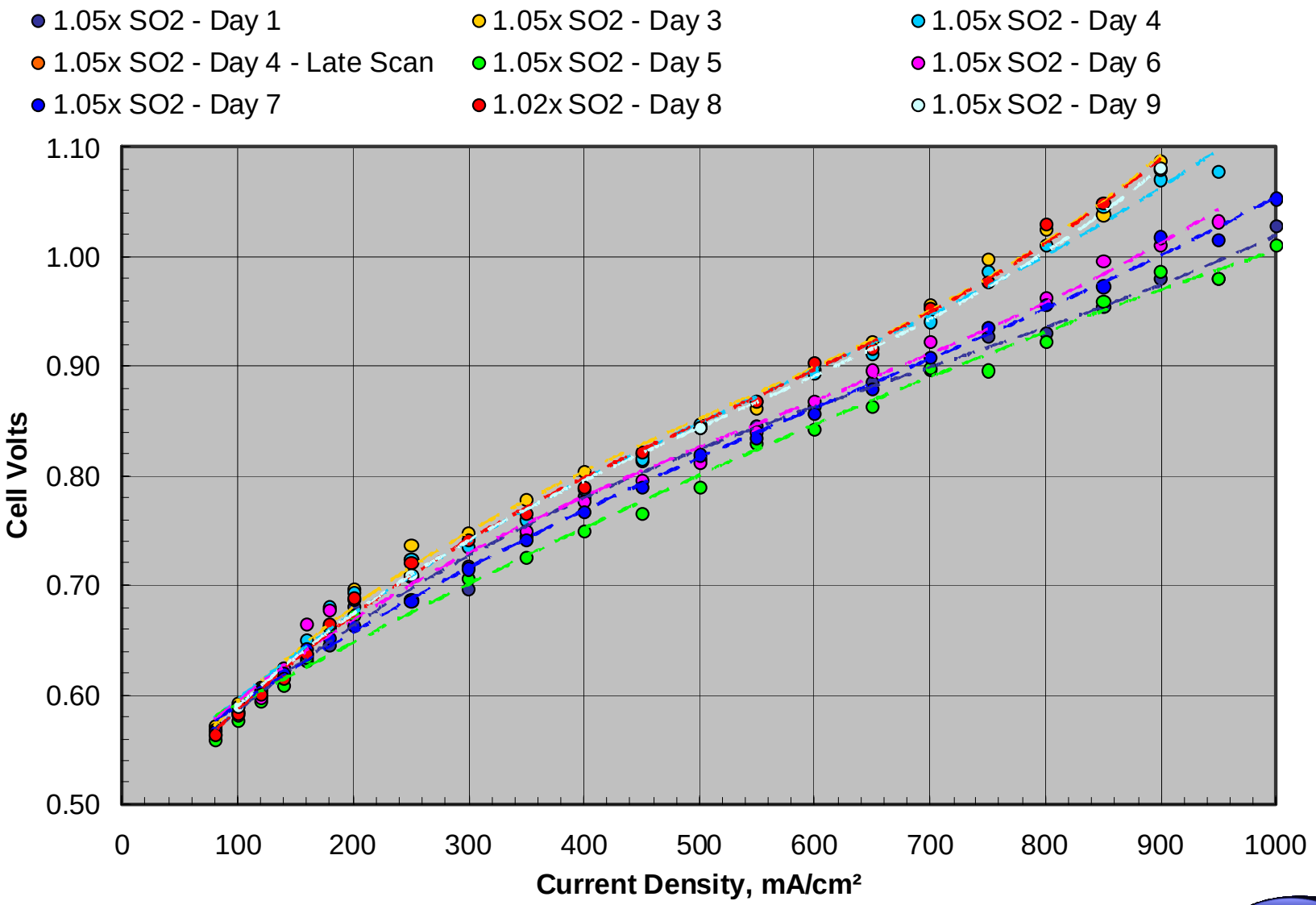
- Sulfur swelling?
- Membrane creep?

Cell rebuilt with .003" Zr shim over vias

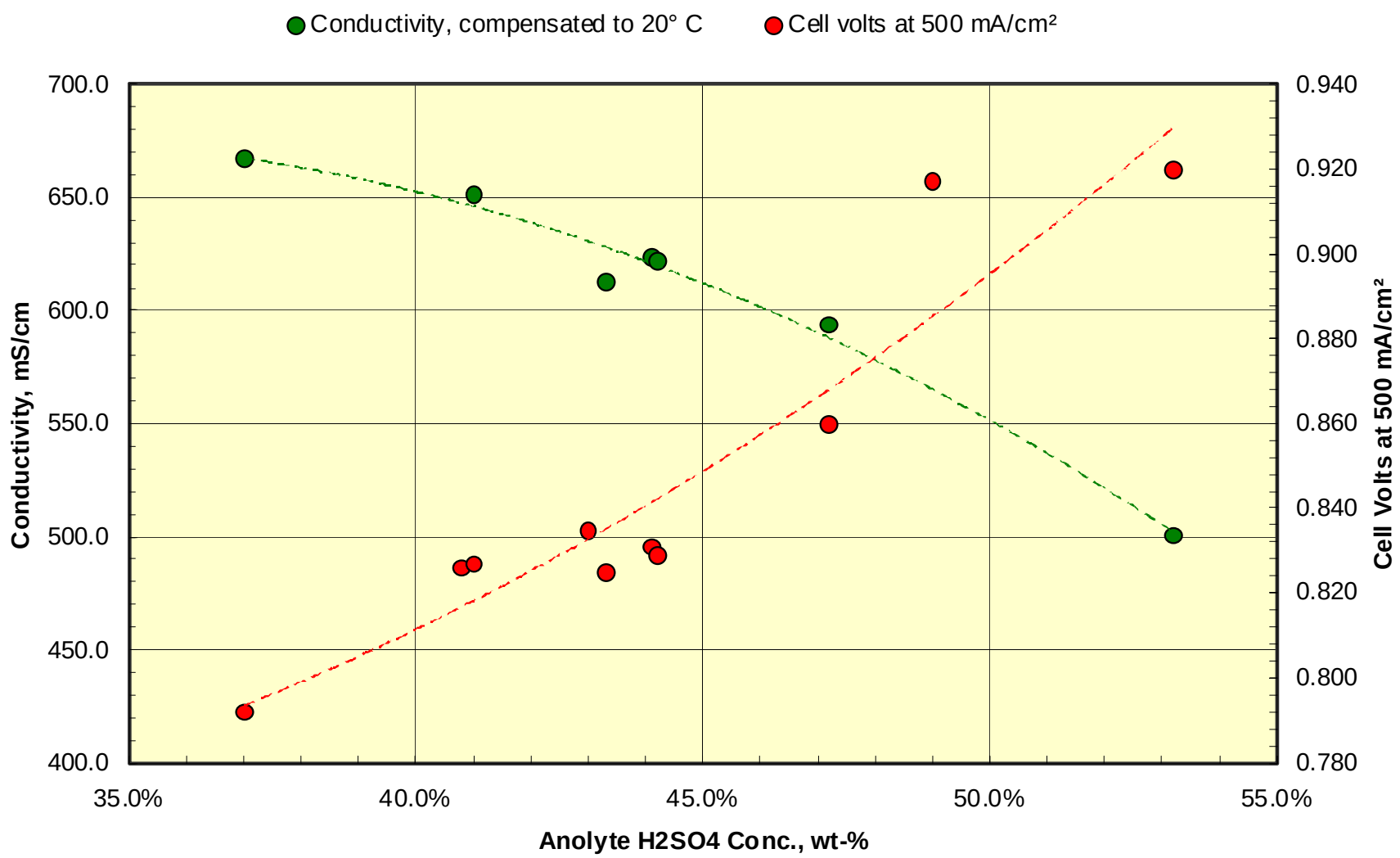
Endurance Testing – NGA-13



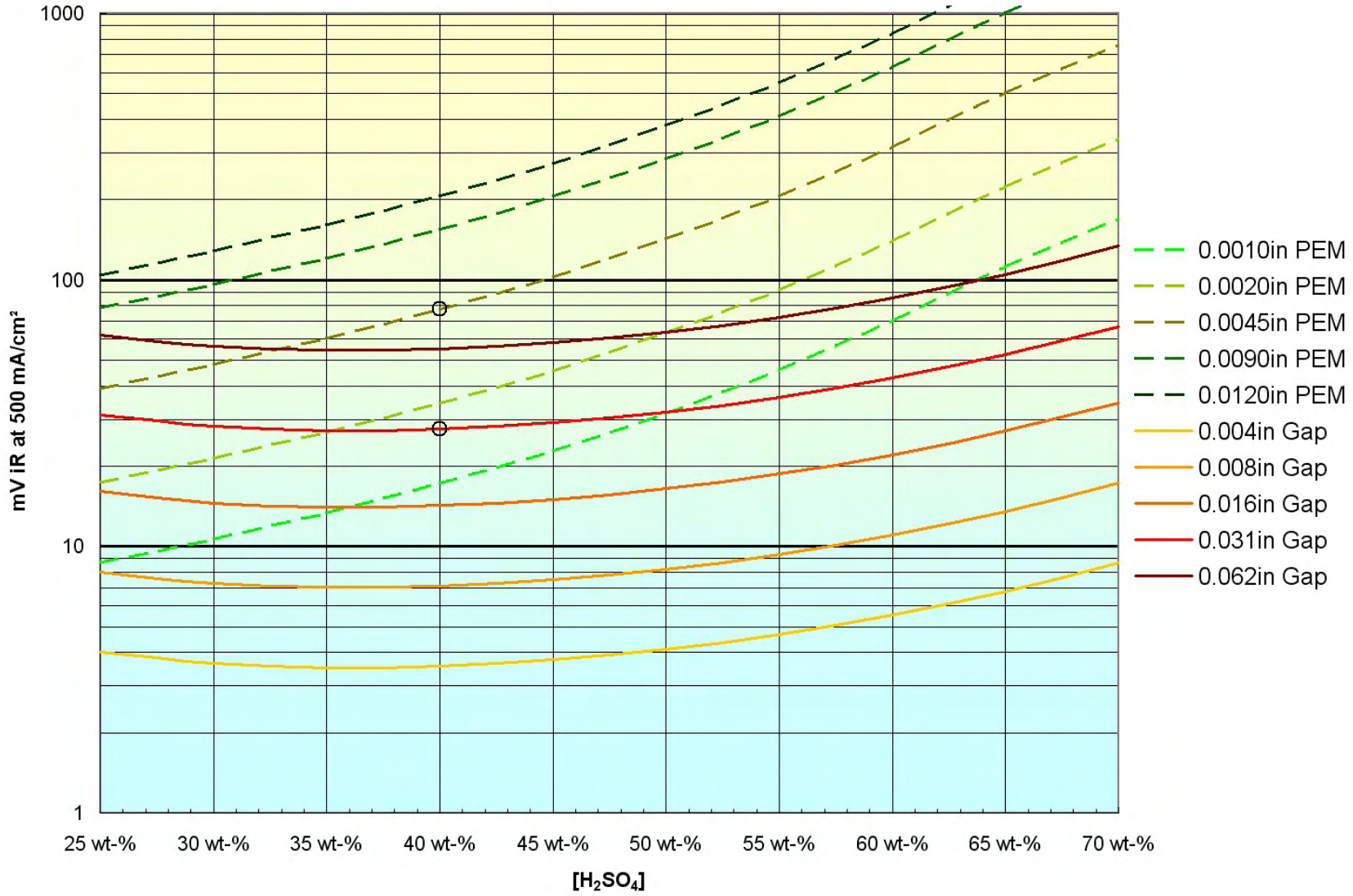
Endurance Testing – NGA-13



Endurance Testing – NGA-13



NGA – PEM/Gap Thickness Tradespace



Conclusions

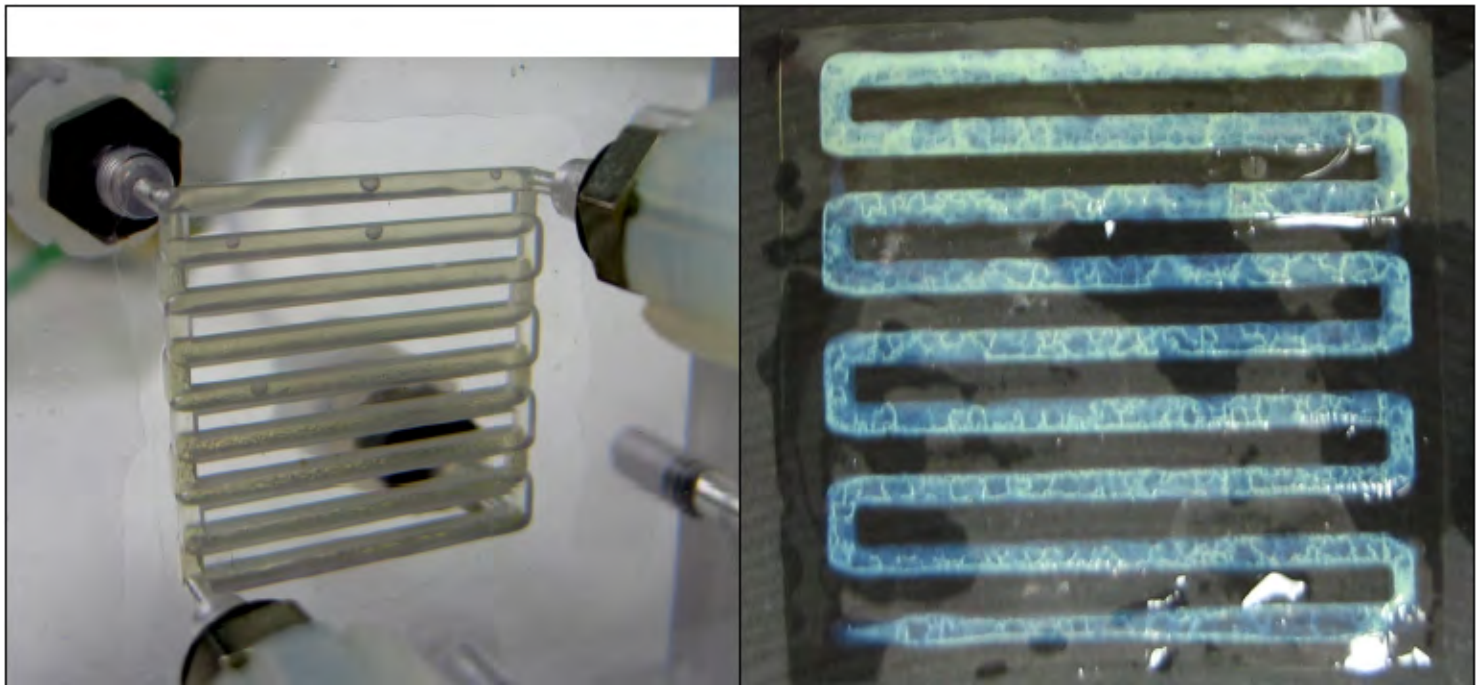
- NGA SDE performance
  - *Successfully decouples mass transfer limitations from pSO2 and PEM water transport*
  - Membrane resistance dominant
  - Episodes of high overpotential are reversible – H_2O
  - Need to control spikes in anolyte pressure to prevent seepage
- Crossover method partially developed
  - Sulfur deposits visible on cathode
    - Not apparently significant to cell performance
  - SO_2 loss not reduced vs. direct feed SDE
  - Continue testing without anolyte recirculation
- Cell performance endures, 40 hrs to go

Membrane Sulfurization Experiment

Nafion 1135, no catalyst on either side, fully hydrated

Test 1: SO_2-saturated DI water (RT) flowing on one side, hydrogen gas flowing on other
- No reaction visible over 3 hrs

Test 2: SO2-saturated DI water (RT) on one side, H_2S-laden N_2 gas on other
- Immediate sulfur formation ***in and on*** membrane, with ***water generation***



→ H_2S and SO_2 react readily to form sulfur

$$16\ H_2S + 8\ SO_2 \rightarrow 3\ S_8 + 16\ H_2O \text{ (Claus Reaction)}$$

Narrow-Gap Anode (NGA) for HyS Electrolysis

Items pending:

- Complete endurance testing to 100 hrs
- Retest anode formulations under controlled [H_2SO_4]
- Correlation of SEM/optical microscopy with SO_2 xover
- Projections for utility scale HyS application

Items for Follow-On Work:

- Optimize gap for low pressure drop and high conductivity
- NGA electrolyzer at high temperature/[H_2SO_4]

Anode Concepts for the HyS Electrolyzer

DOE Phase I SBIR Program

Grant #DE-FG02-08ER85113

April 20, 2009

Giner Electrochemical Systems, LLC

Anode Concepts for the HyS Electrolyzer

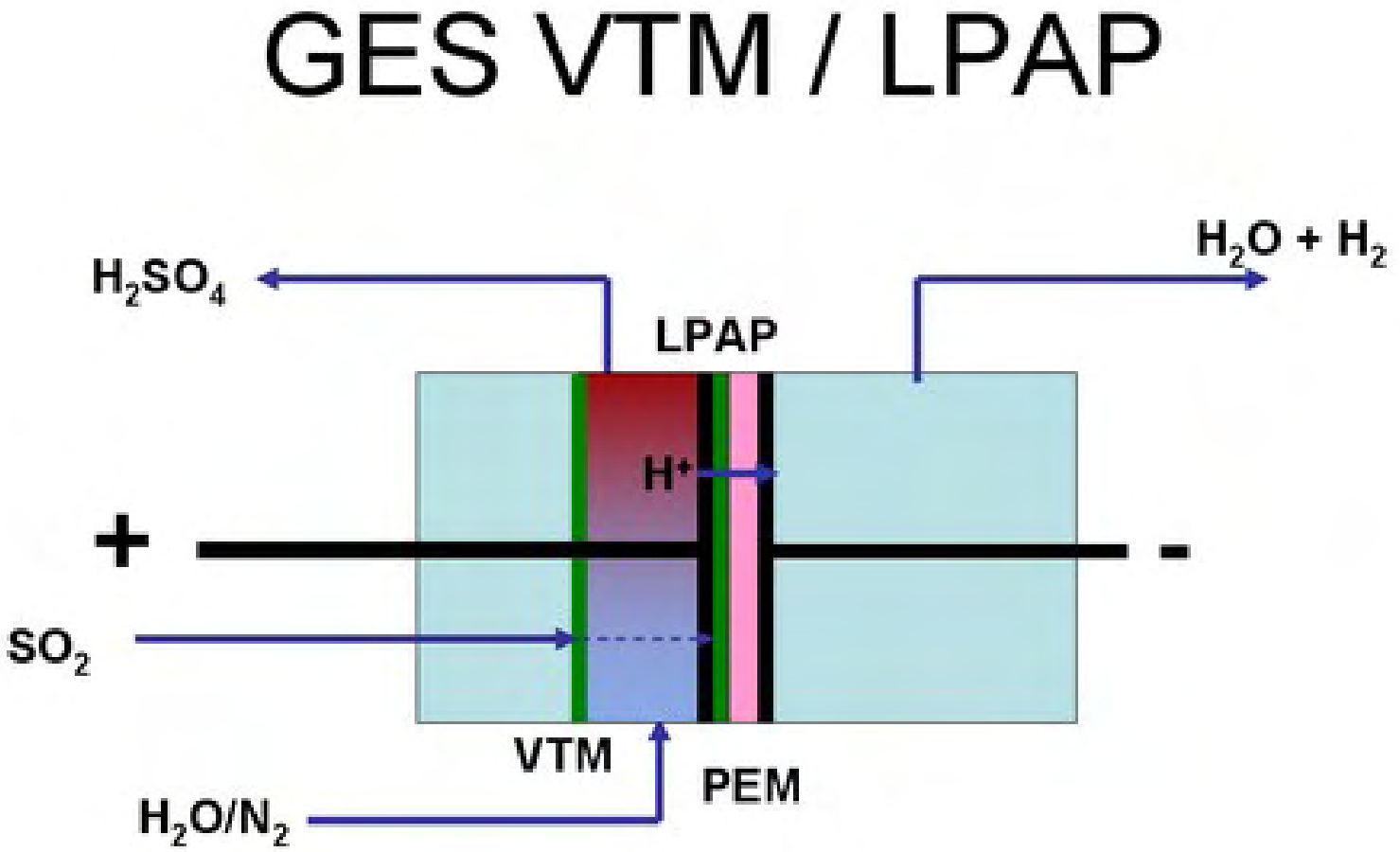
Objectives:

- Develop alternative anode formulations targeted to minimize SO_2 crossover through PEM
- Demonstrate nominal performance and reduced sulfur crossover vs. controls

<u>Two approaches:</u> vapor transport membrane (VTM) and low-permeability anode prelayer (LPAP)

University of South Carolina (Prof. John Weidner) as subcontractor for electrolyzer and analytical testing

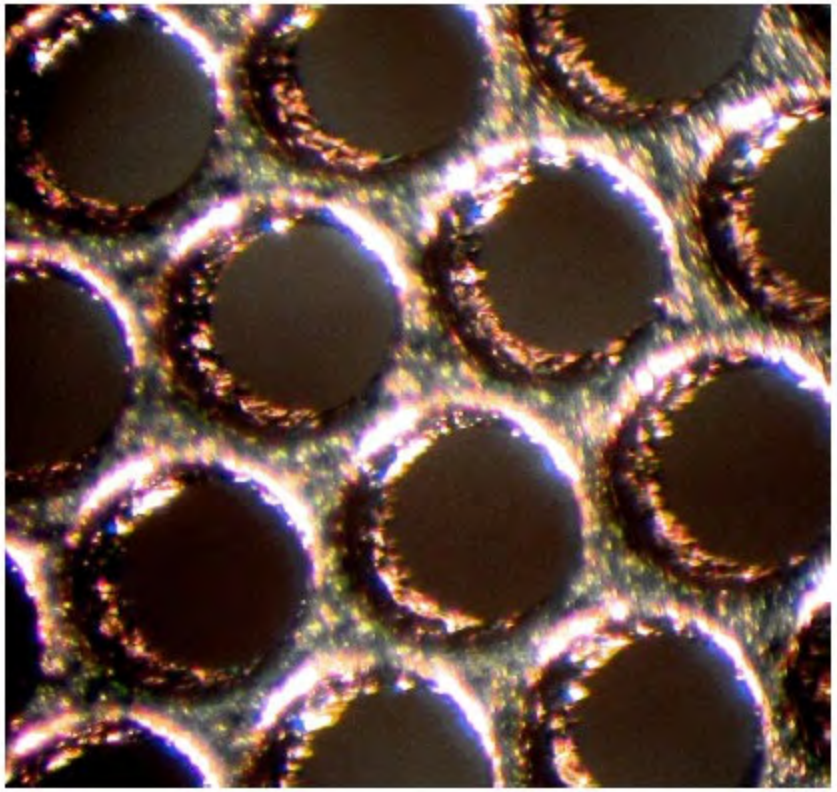
Anode Concepts for the HyS Electrolyzer



Anode Concepts for the HyS Electrolyzer

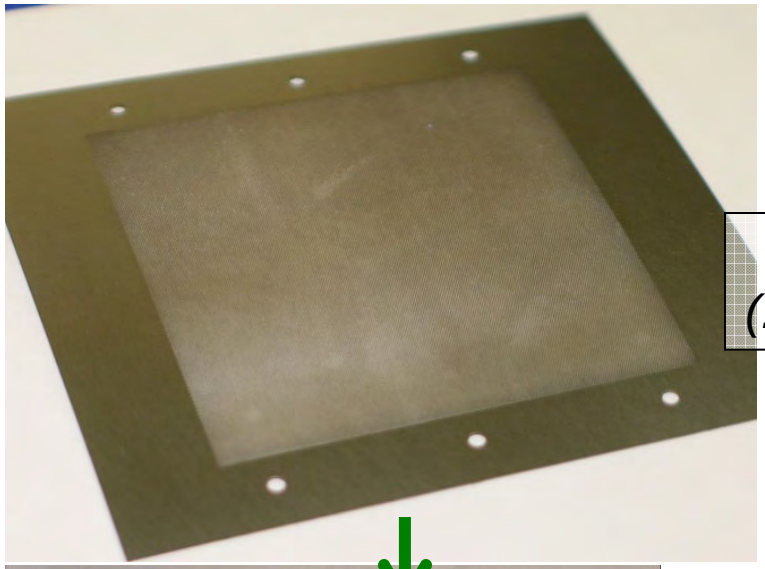
Vapor Transport Membrane (VTM)

- Builds off of GES VTM IP in DMFCs and RFCs
  - Patents issued and pending
- Permeable to SO_2 and electrically conductive
- Fill holes with carbon/ionomer ink
- Configuration allows significant $[O_2]$ in SO_2 stream, which may simplify HyS process

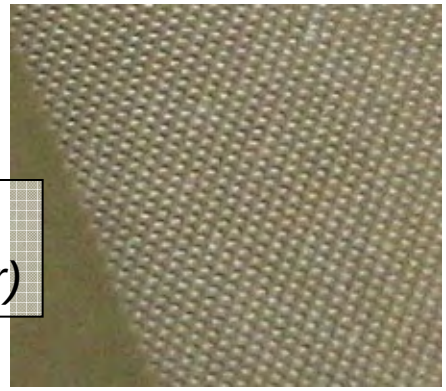


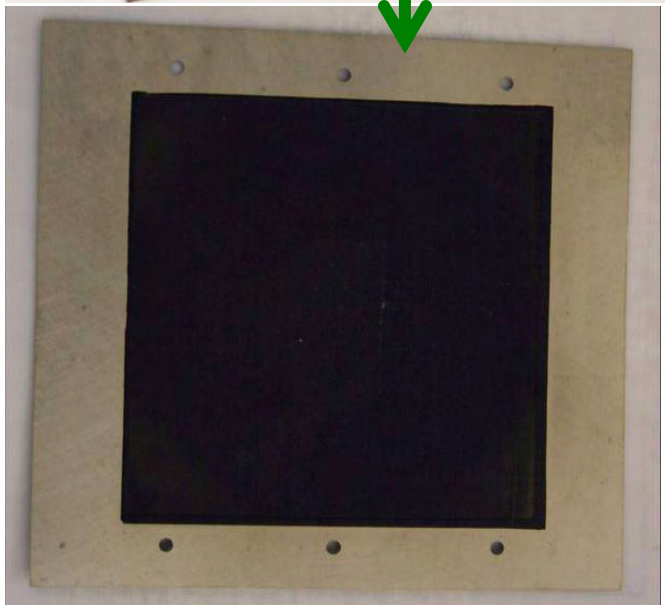
Ti foil with 125μm holes

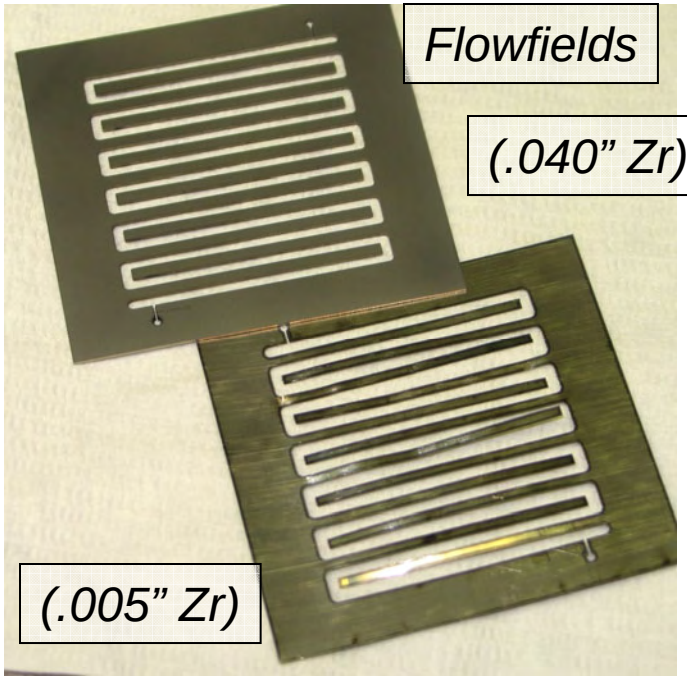
VTM Cell Components



VTM (.005" Zr)





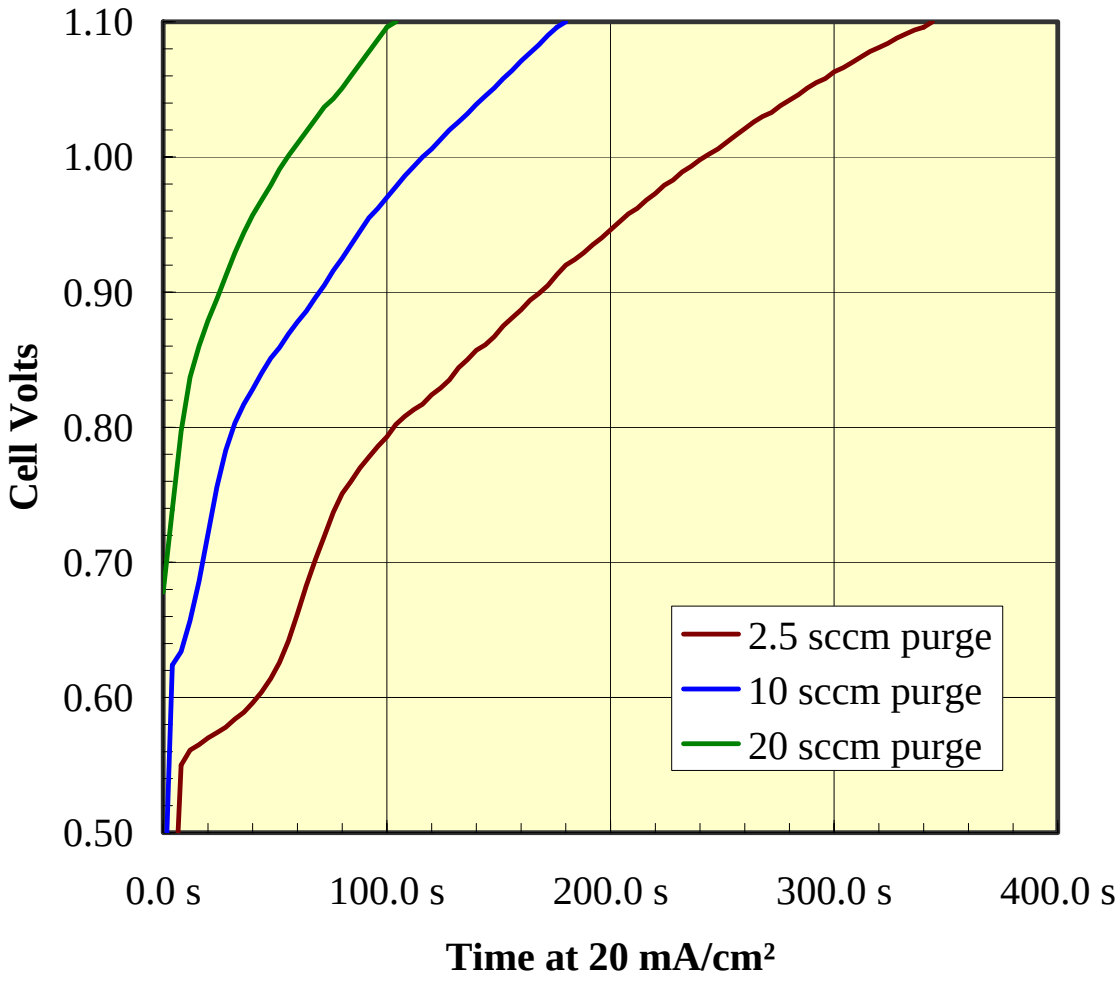


Flowfields

(.040" Zr)

(.005" Zr)

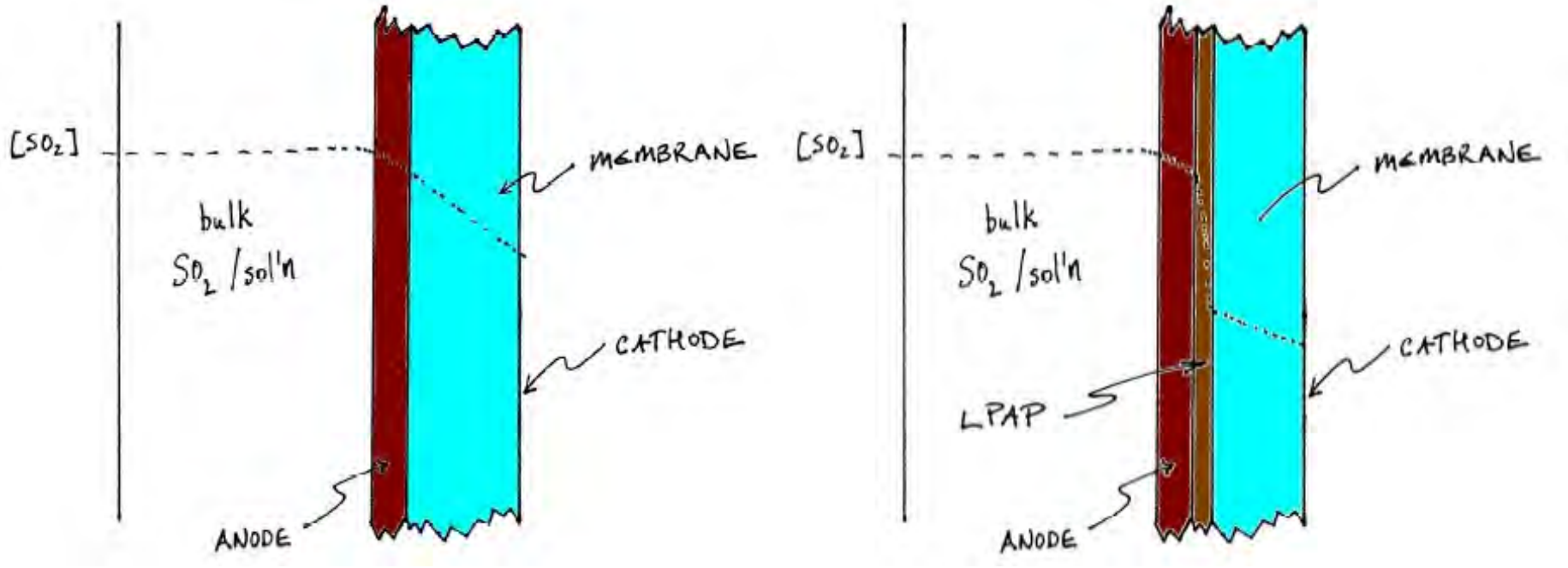
VTM Performance - .040” flowfield



- Current density is SO_2-flux limited to ~20 mA/cm²
- Decreasing flowfield thickness to .005” increases steady state current limit to only 30 mA/cm²
- VTM, not gap thickness, is limiting factor
- Xover not evaluated due to low CD
- Further work may address thinner VTM, higher pSO_2

Anode Concepts for the HyS Electrolyzer

Low-Permeability Anode Prelayer (LPAP)



- ***LPAP film is anodically electrocatalytic***
- ***High vol% of binder in film reduces porosity***
- ***Combined properties allow scavenging of SO_2***

LPAP Films

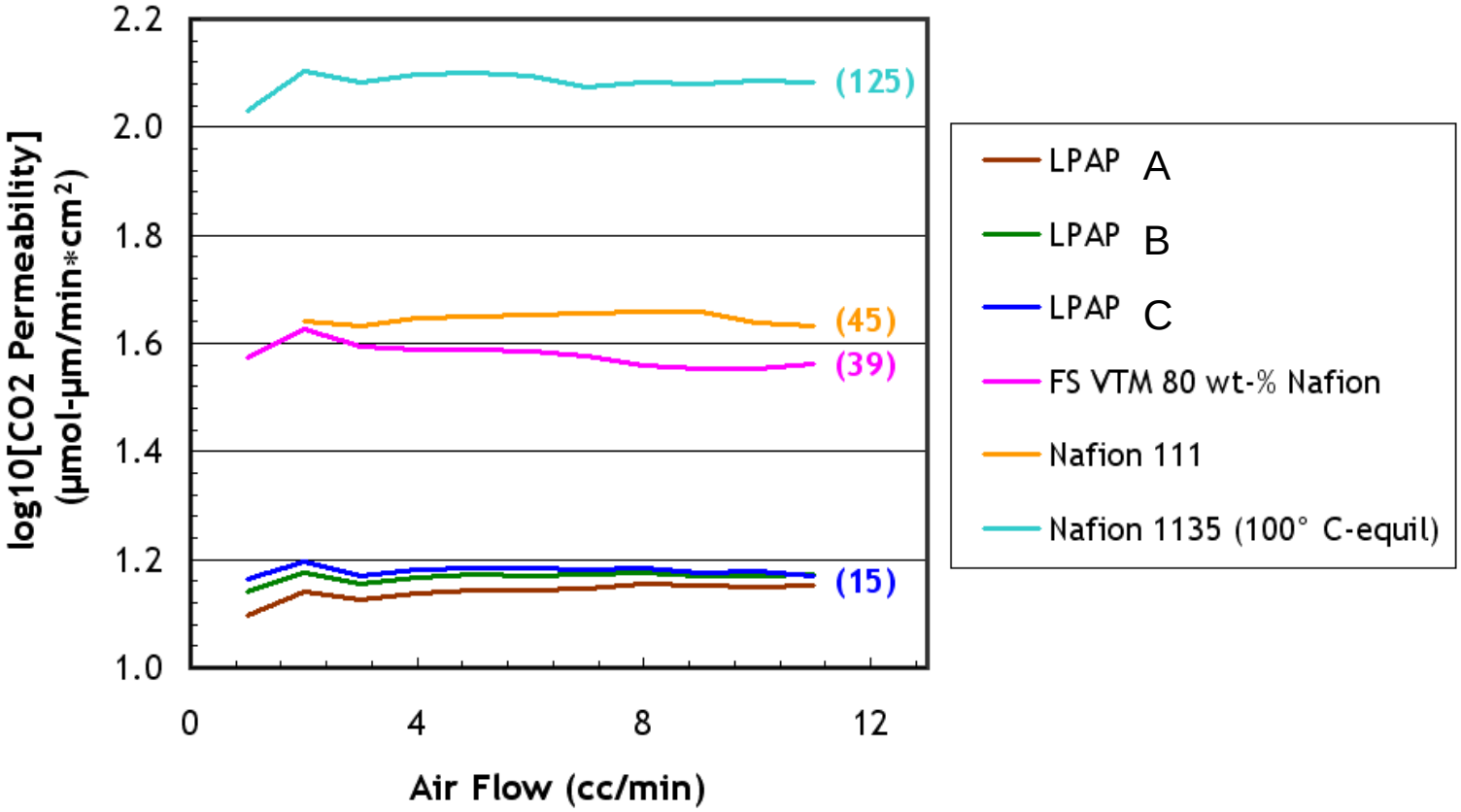
(3) Films Each	Thickness Range
• 20% Pt/C with 80% binder:	0.0008-0.0014"
• 45% Pt/C with 55% binder:	0.0006-0.0012"
• 67% Pt/C with 33% binder:	0.0006-0.0009"

Experimental approach:

1. Determine conductivity of LPAP films by in-plane AC/DC conductivity
2. Measure permeabilities of films using CO_2 as surrogate for SO_2
3. Evaluate films in unitized MEA constructions in direct feed SDE

Anode Concepts for the HyS Electrolyzer

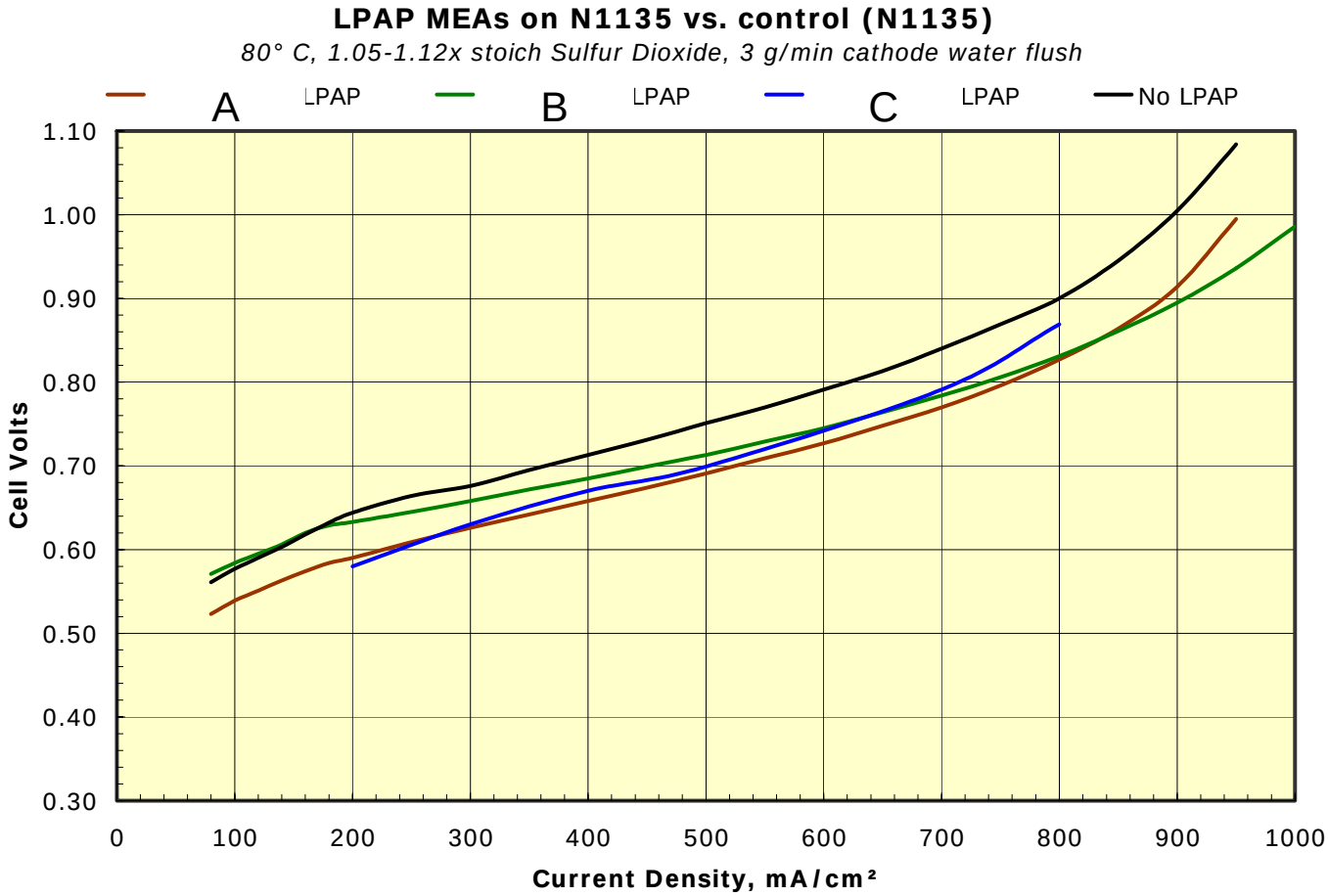
LPAP – CO_2 Permeability (21° C)



- *Films have very low permeability*
- *Little dependence on binder/catalyst ratio*

Anode Concepts for the HyS Electrolyzer

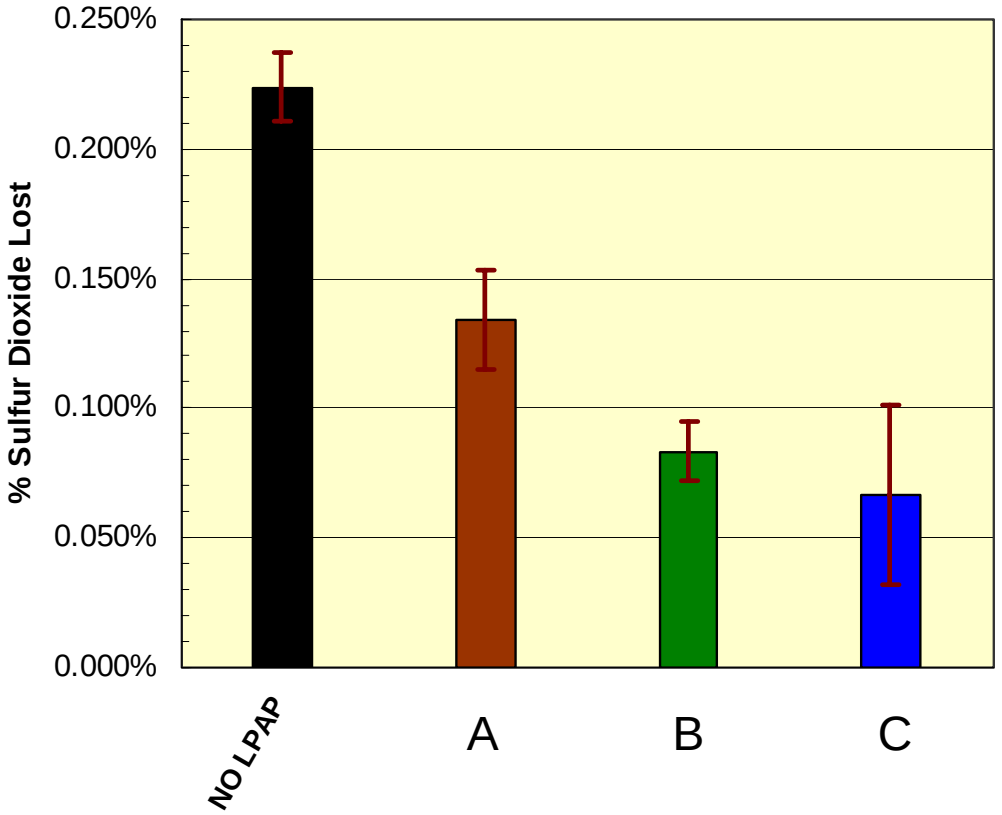
LPAP – SDE Performance



- *Performance generally improved with LPAP – Pt loading*
- *i-V behavior verified in USC testing*

Anode Concepts for the HyS Electrolyzer

LPAP – SO_2 Crossover During SDE Testing



- ***Up to 70% reduction in SO2 crossover losses***
- ***Sulfur layer formation to be examined***

Acknowledgements

NGA

- Steve McCatty – GES
  - Test stand development, cell testing
- Dave Herman – SRNL
  - Program support and coordination

PhI

- Steve McCatty, Will Braff – GES
  - Sample preparation & characterization
- John Weidner, John Staser – USC
  - MEA testing