Results from Testing Hybrid Sulfur Single Cell and Three Cell Stack

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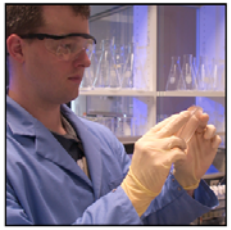
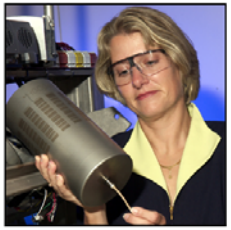
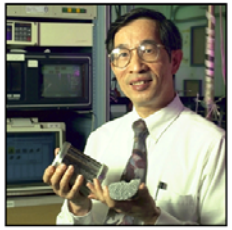
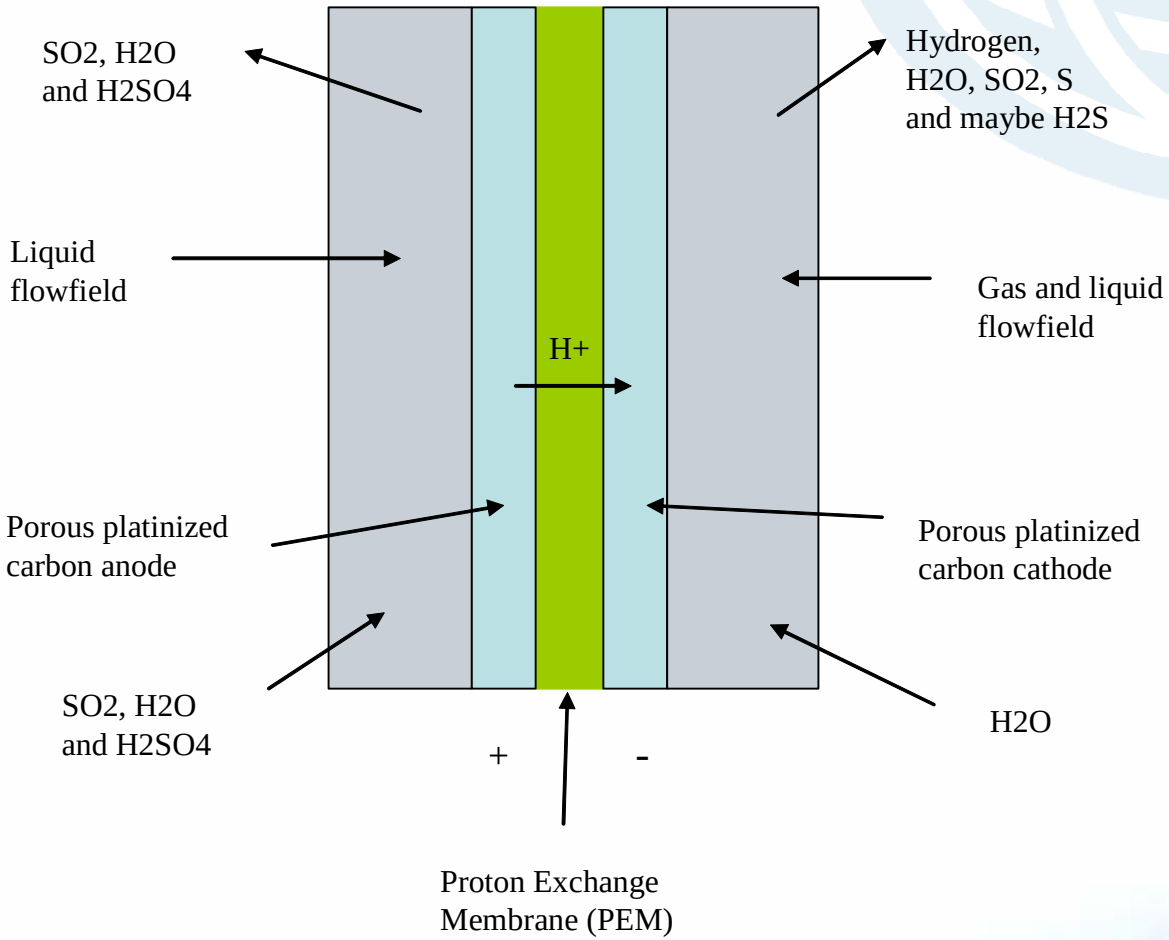




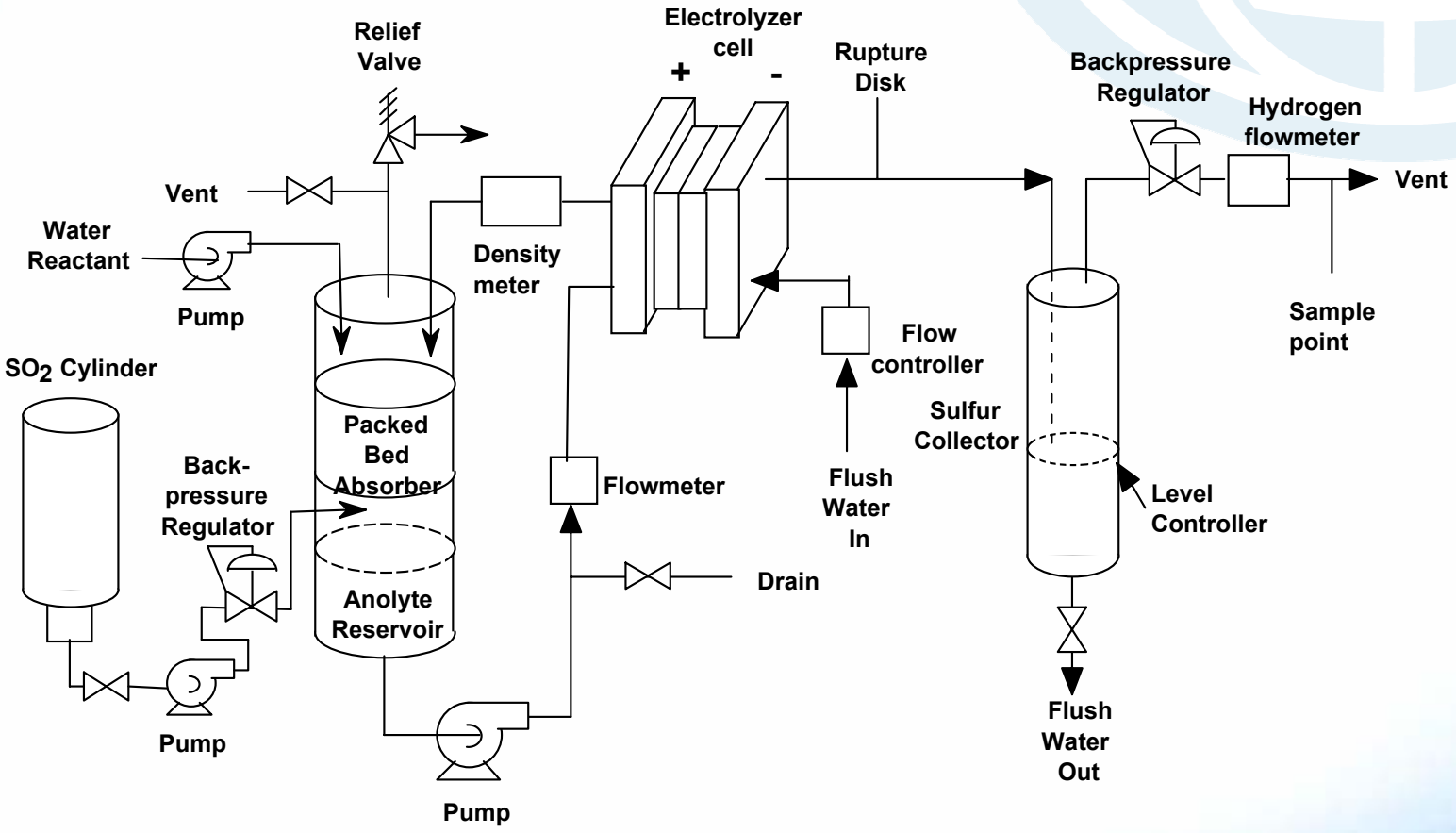
Outline

- **Single cell stack electrolyzer testing**
  - Work to reduce or eliminate sulfur formation
- **Multi-cell stack electrolyzer testing**
- **System upgrades**
- **Future plans**

Electrolyzer Cell Schematic



Schematic of Single Cell Test Facility



Electrolyzer Facility

Single Cell

SO2 Absorber and Anolyte Tank

Goals of Single Cell Testing

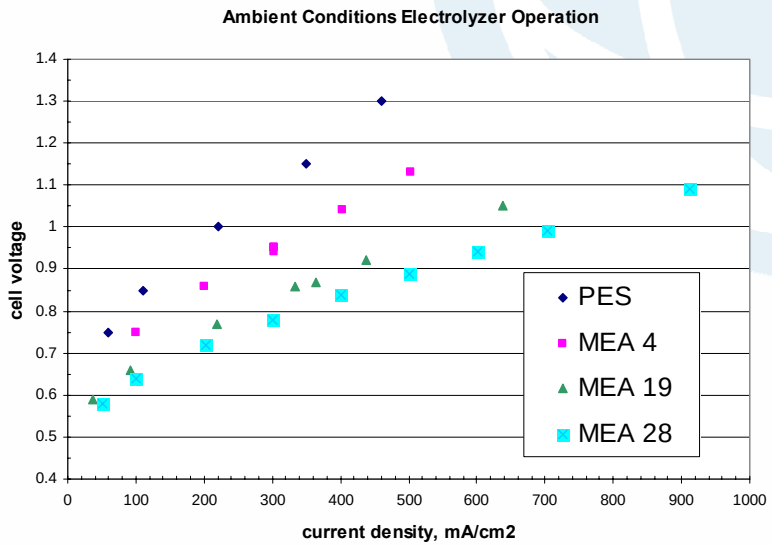
- **Decrease cell voltage, important to overall process efficiency**
- **Increase anolyte acid concentration for balance of plant considerations, decomposition of sulfuric acid**
- **Prevent sulfur formation inside the MEA and reduce H_2S formation at the cathode (parasitic reactions)**
- **Increase lifespan of electrolyzer**

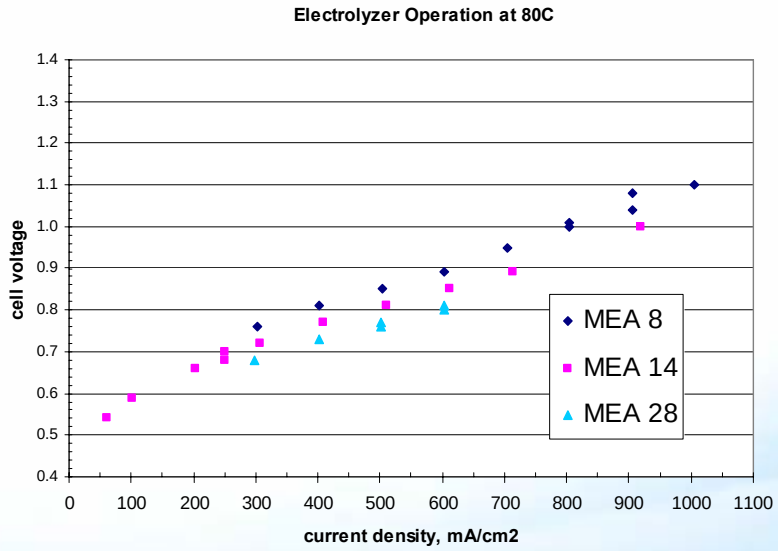
Trends Observed in Single Cell Testing

- **Factors that decrease cell voltage**
  - Increased temperature (increased reaction rate, decreased anolyte viscosity)
  - Increased concentration of SO_2 in anolyte
  - Increased anolyte flowrate
  - Increased catalyst loading
- **Factors that increase cell voltage**
  - Increased acid concentration in anolyte
  - Thicker membrane
  - Increased current density
  - Use of platinum black rather than platinized carbon as catalyst (less surface area per gram)

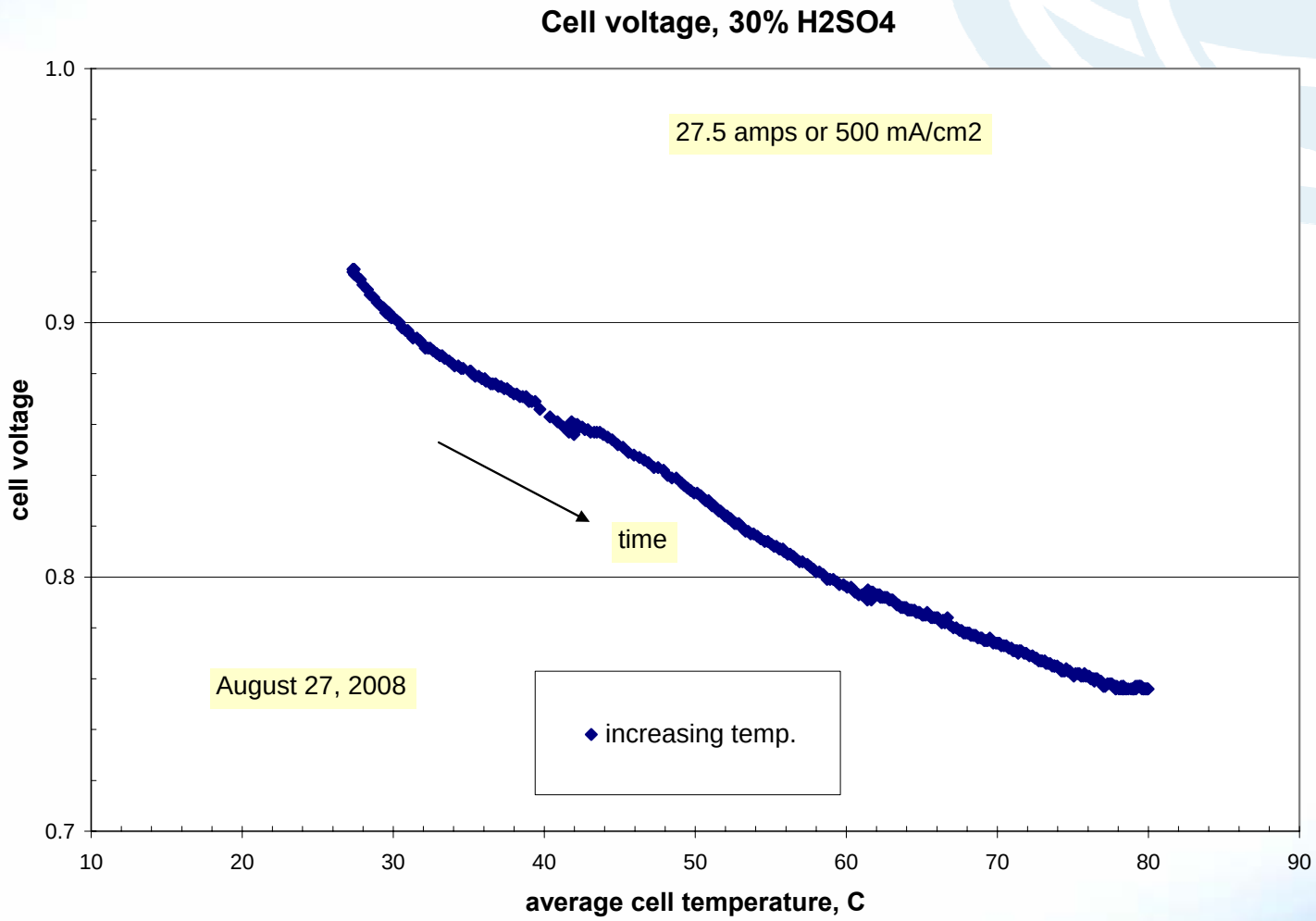
Single Cell Results, Voltage

- Tests conducted at ambient conditions and also 80°C and approximately 5 atm.
- Cell voltages have been generally decreasing over the course of testing.
- Higher temperature and pressure operation results in lower voltages



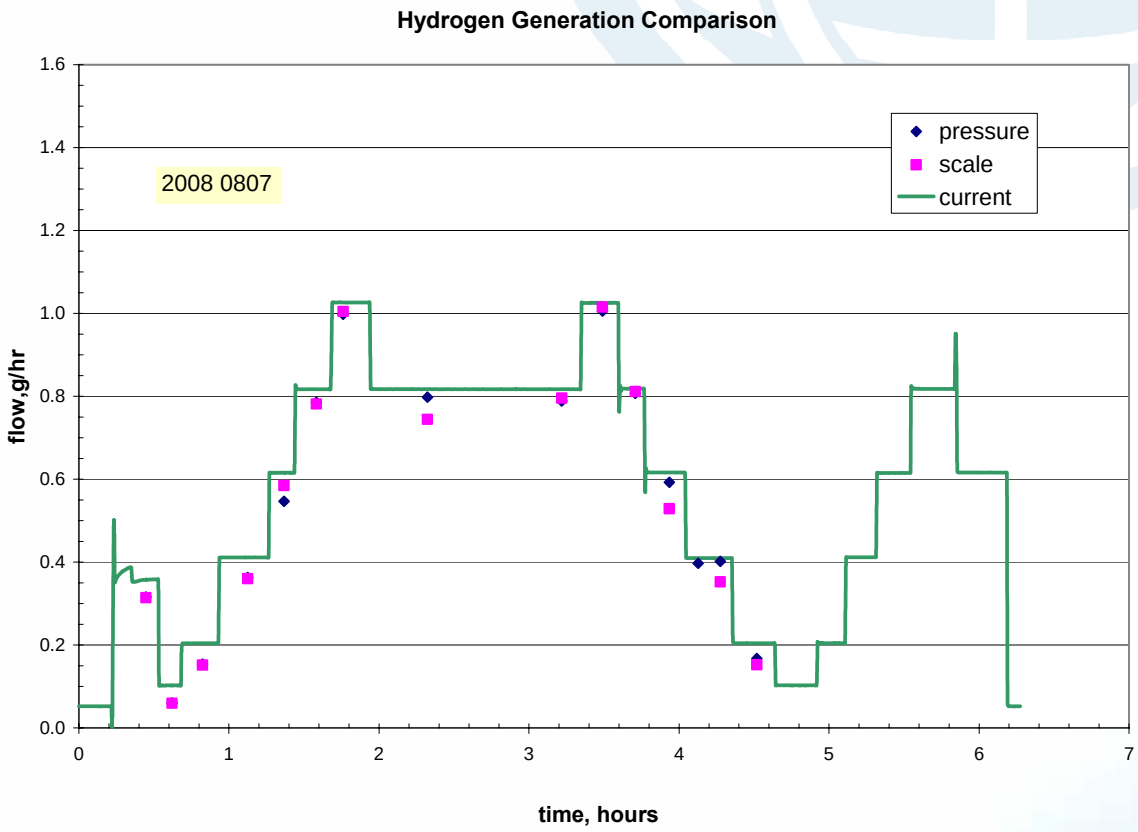


Single Cell Test, Effect of Temperature, MEA 28



Single Cell Results

Measured hydrogen production rate has agreed well with theoretical rate

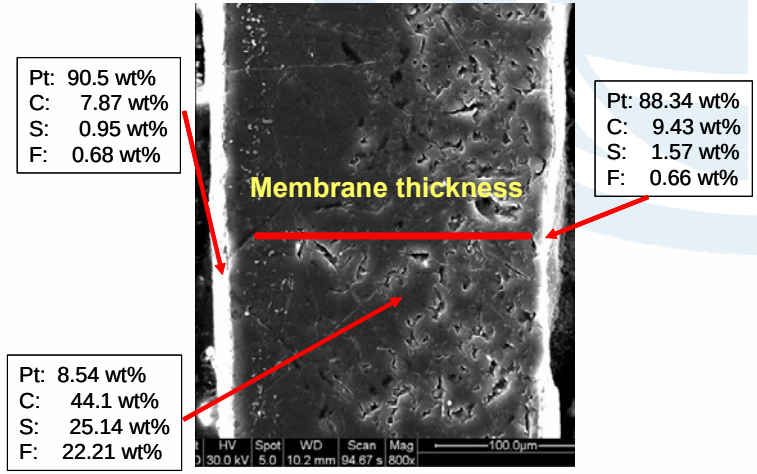


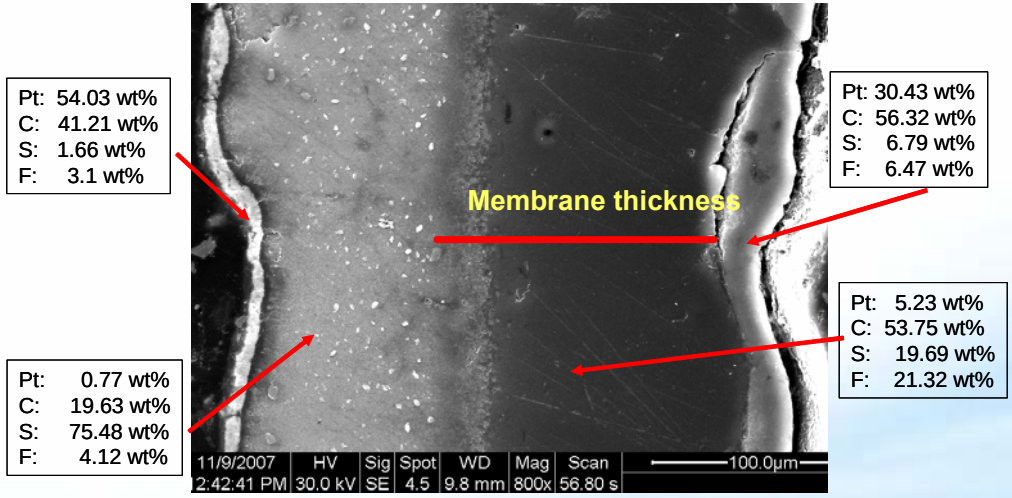
Sulfur and Hydrogen Sulfide Formation

- **Scanning Electron Micrographs (SEM) have been made of some of the MEAs tested in the Single Cell Electrolyzer**
- **Prior to November 2008 most MEAs formed a sulfur layer between the membrane and cathode**
  - Sulfur layer increases cell voltage and increased MEA thickness can cause crush damage to platinized carbon and carbon paper flowfield
  - SRNL Button Cell MEAs did not form sulfur layers.
- **Water flowing out of cathode has strong hydrogen sulfide odor**
- **Sometimes colloidal sulfur is observed flowing from cathode**
  - We add a low flow of flush water to the cathode to help hydrate the membrane, usually Nafion.

SEMs Showing Sulfur Formation

- **Top MEA 9 did not form sulfur, bottom MEA 20 did form sulfur**
- **SO_2 dissolves in water, electro-osmotic drag of water and diffusion of SO_2 transports water from anode to cathode.**
- **First place that SO_2 can be reduced by hydrogen gas is interface between membrane and cathode.**





Sulfur Formation

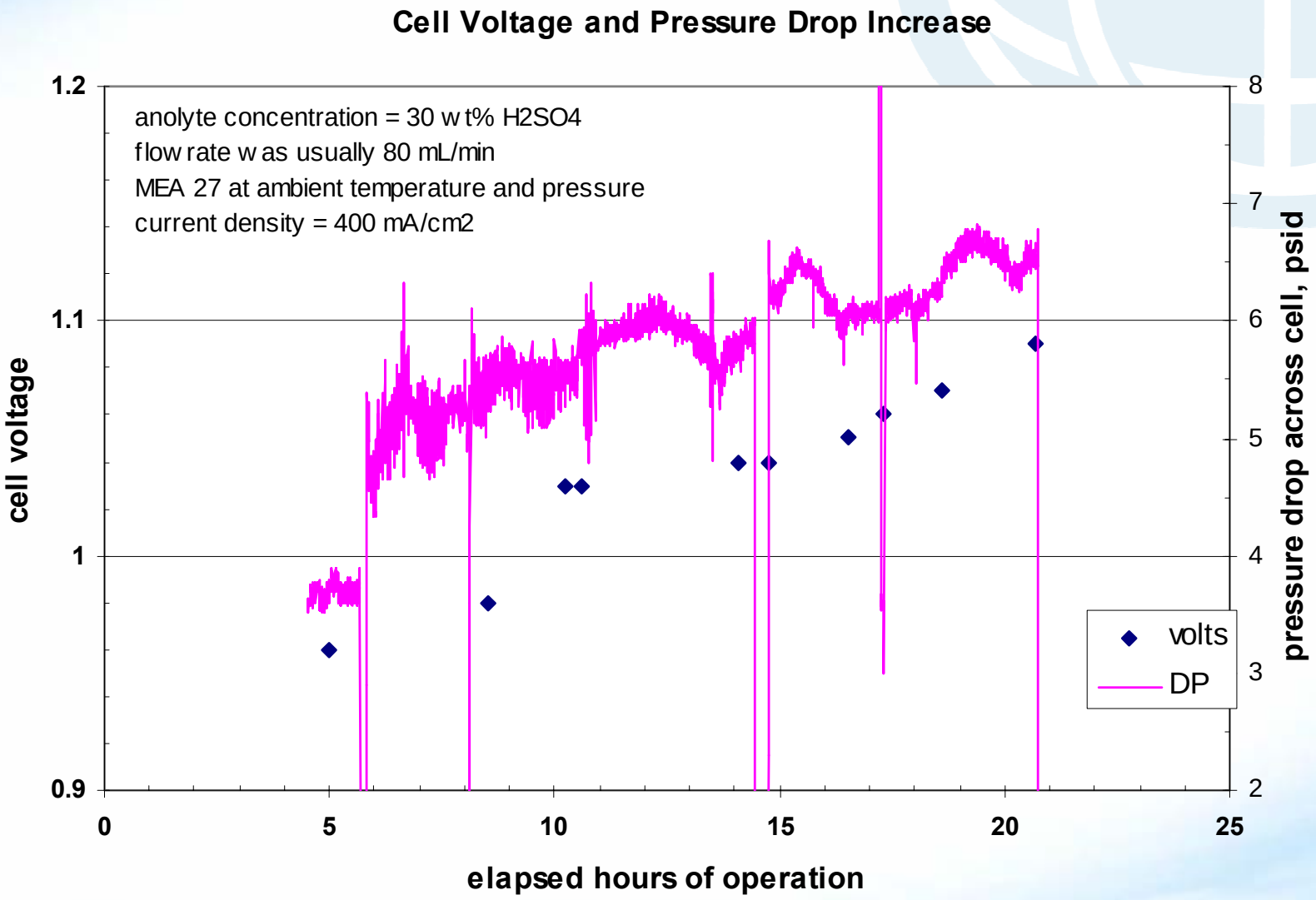
- **Sulfur forming reactions**

$SO_2 + 3H_2 = H_2S + 2H_2O \quad \Delta H_0 = -70.5$ kcal/mole S

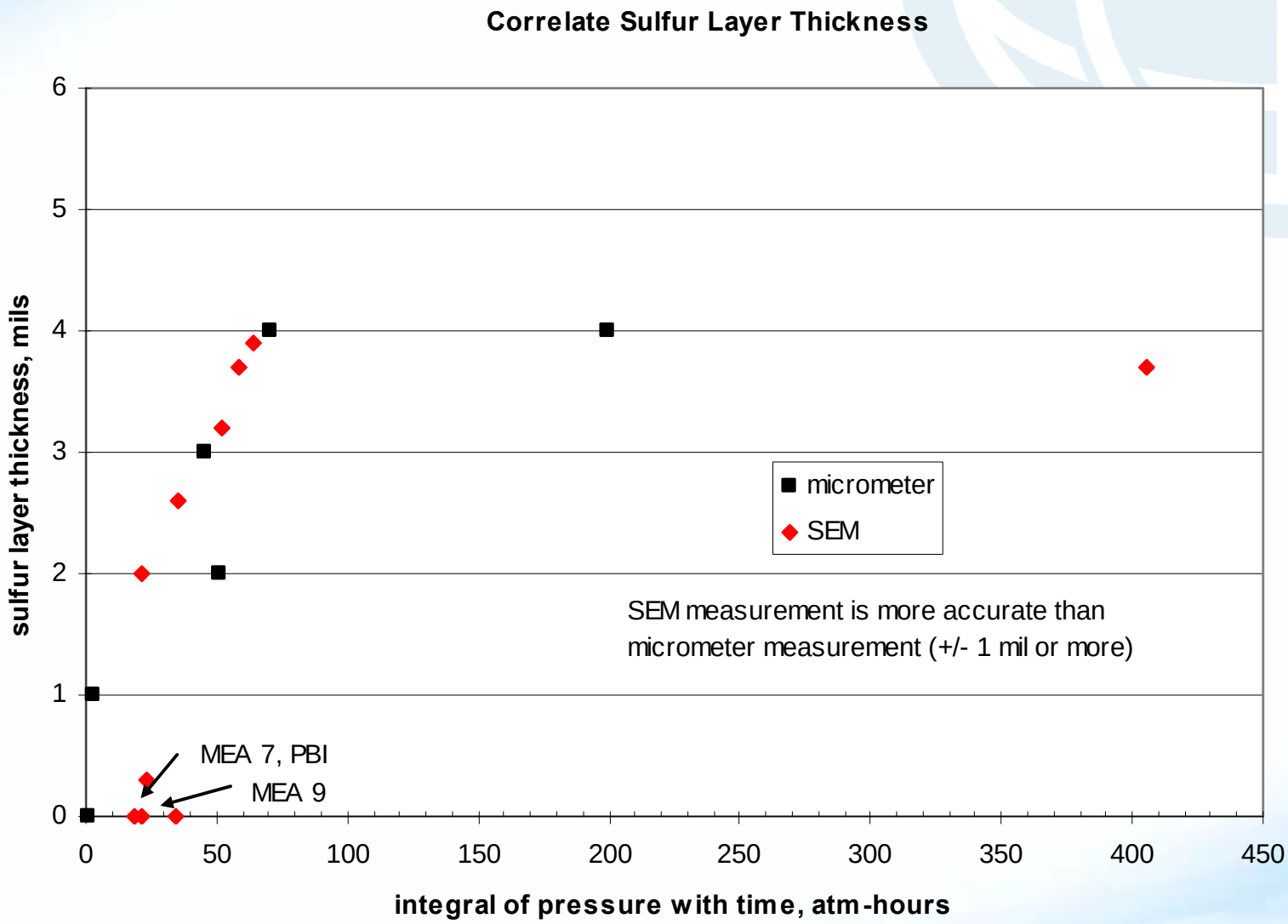
$2H_2S + SO_2 = 3S + 2H_2O \quad \Delta H_0 = -18.7$ kcal/mole S

- **We have been exploring two methods for greatly reducing or eliminating sulfur formation**
  - Altering operating conditions to reduce concentration of SO2 in anolyte.
  - Using membranes in the MEA with much less permeability for SO_2.

Evidence that Sulfur Layer Grows Continuously



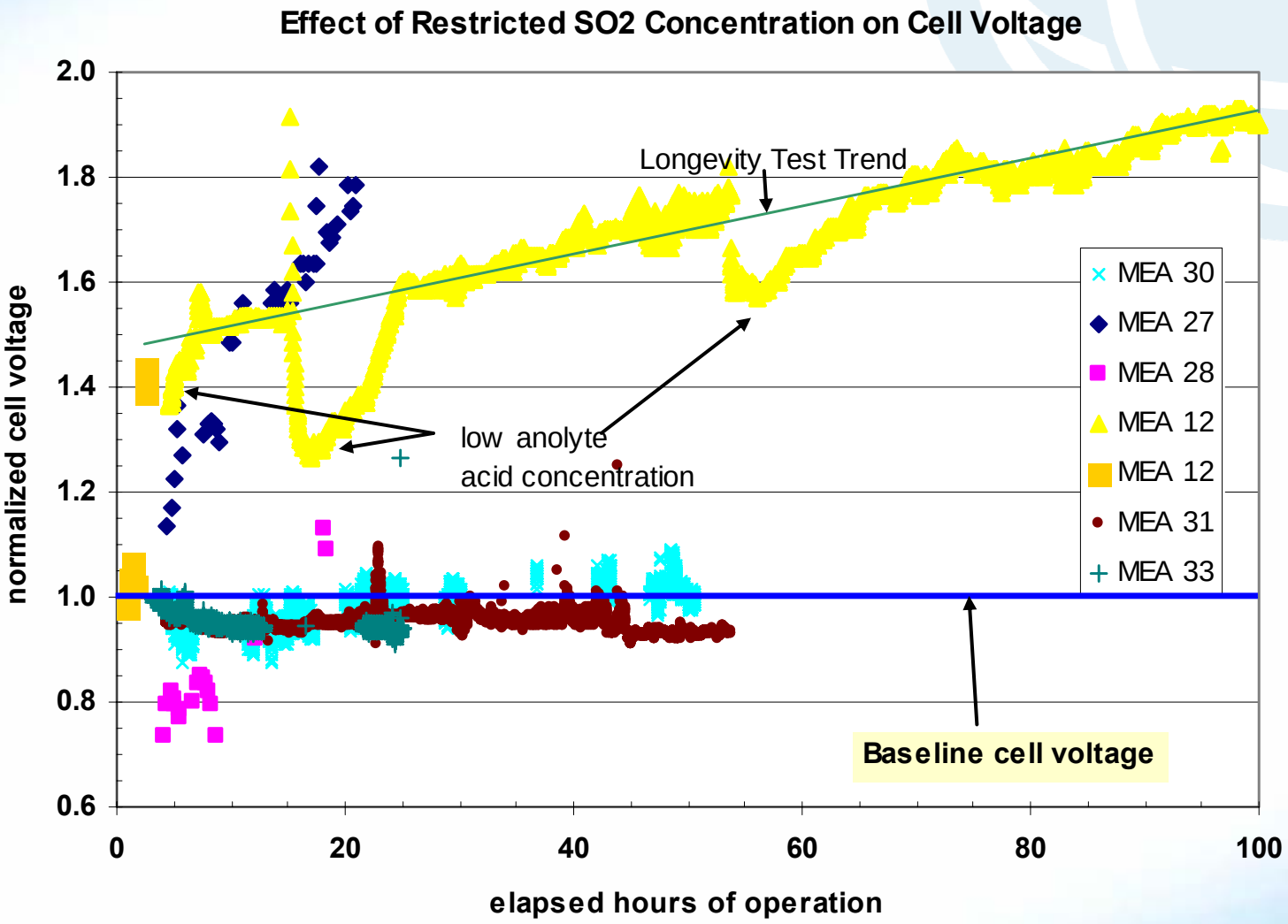
Sulfur Layer Thickness



Changing Operating Conditions to Reduce Sulfur

- **SRNL Button Cell did not form sulfur layer and was operated at ambient pressure and 80°C, so low SO_2 concentration in anolyte**
- **Single Cell was usually operated at four to six atm and 80°C and frequently formed sulfur layers.**
- **When current to Single Cell was abruptly stopped and consumption of SO_2 ceased, a cloud of elemental sulfur was observed at the cathode outlet.**
- **Decided to try testing with lower concentration of SO_2 in anolyte, but sufficient for anode reaction**
- **Tests of idea are very promising**
  - Little or no increase in cell voltage
  - Much less H_2S out of cathode.

Tests of Restricted SO_2 Concentration



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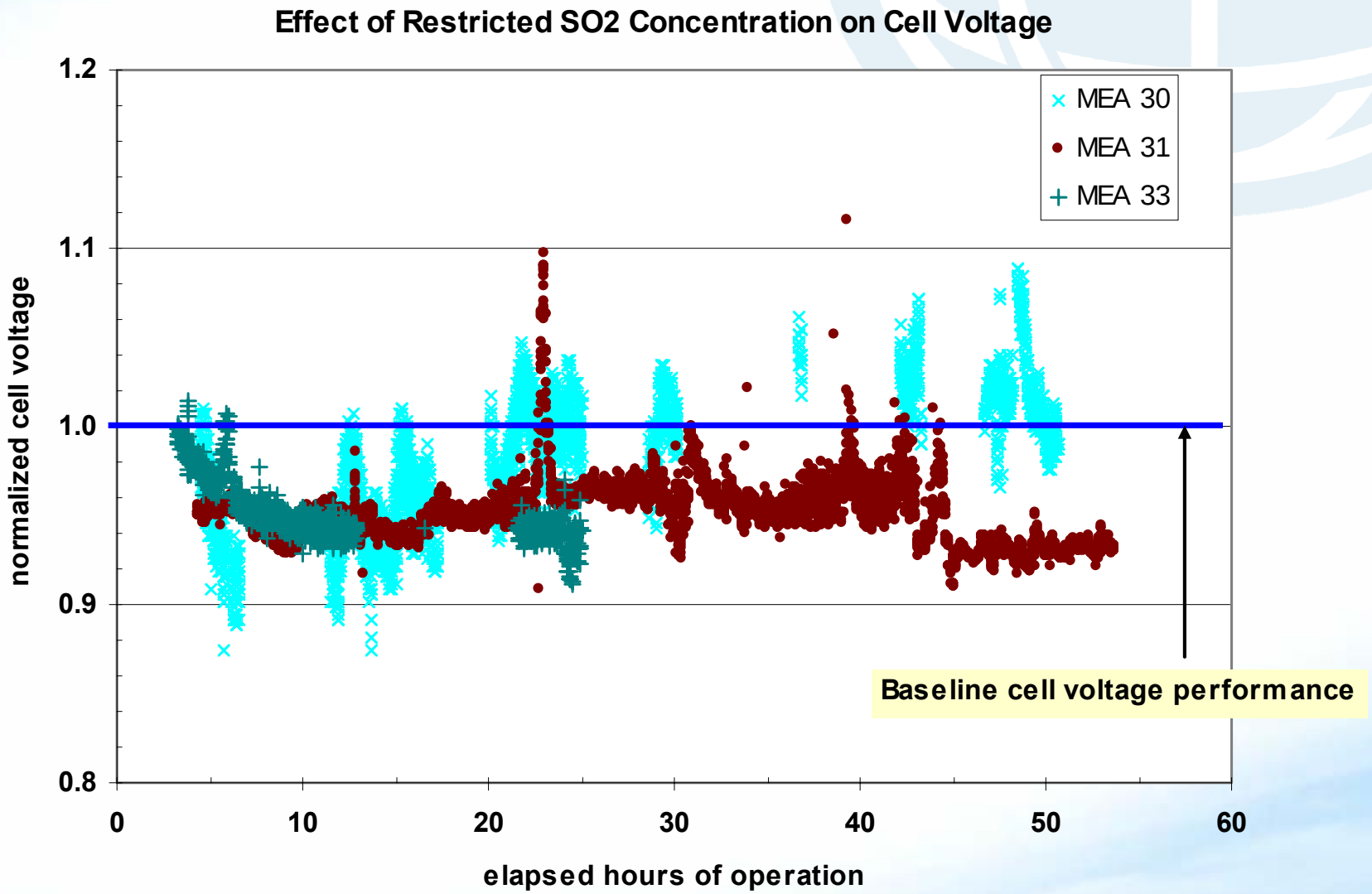


Facility Improvements

- **Over-voltage protection**
  - Cell voltage in excess of 1.3 volts can generate enough oxygen to damage carbon components in cell
  - So Data Acquisition System turns off current to cell when cell voltage exceeds 1.2 volts
- **Warning of pressure imbalance across MEA to prevent mechanical damage**
- **Warnings of temperatures, pressures and anolyte volume out of range**
- **Warning of cessation of hood ventilation flow**
- **Installed on-line anolyte density measurement, cell voltage is affected by acid concentration (density)**

Facility Improvements

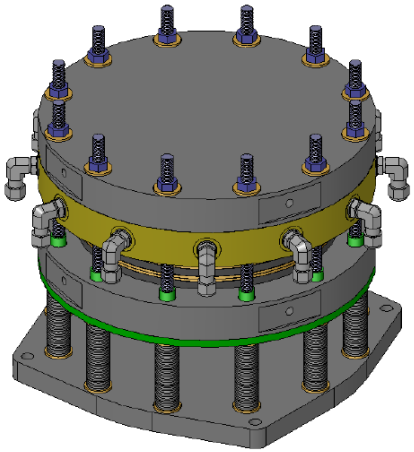
- Computer controls flowrate of SO_2 to the Anolyte Tank to control pressure.
- Controls flowrate of water to Anolyte Tank to control anolyte density.
- Controls volume of anolyte by draining excess. Lasers sense anolyte volume.
- Refills water and SO_2 syringe pumps when they empty.
- Added hydrogen mass flowmeter.
- Added isolation amplifiers for more accurate voltage measurements.
- Increased facility temperature limit from 80°C to 95°C.
- Control panel may now be read off-site.

Current Test

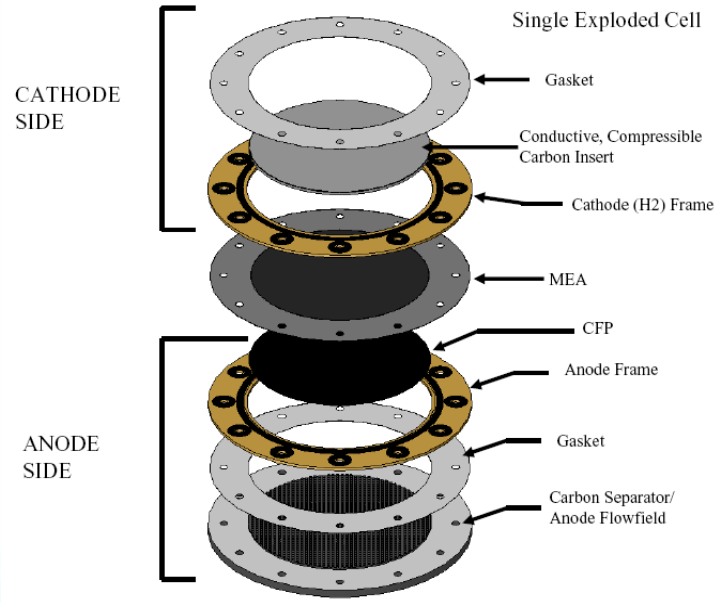
- **Test of MEA 33 began April 16 under computer control and SO_2 restricted operation.**
- **For first 24 hours everything ran smoothly.**
- **Then problems**
  - Automatic valve first stuck open, then stuck closed.
  - Large pressure oscillations
  - A computer restart caused a pressure surge that damaged the carbon paper inside the cell.
- **Will have to rebuild cell and correct problems, then restart 200 Hour Run.**

Multi-cell Stack Development

- Established partnership with Giner Electrochemical Systems
- Leverages existing PEM water electrolyzer technology
- Maximizes use of existing components and hardware
- Incorporates SRNL experience with PEM-type SO_2 electrolysis
- Bi-polar 3-cell stack using round plates with 160 cm^2 active area per cell
- Rated capacity is 100 L/h of hydrogen production under SO_2-depolarized conditions



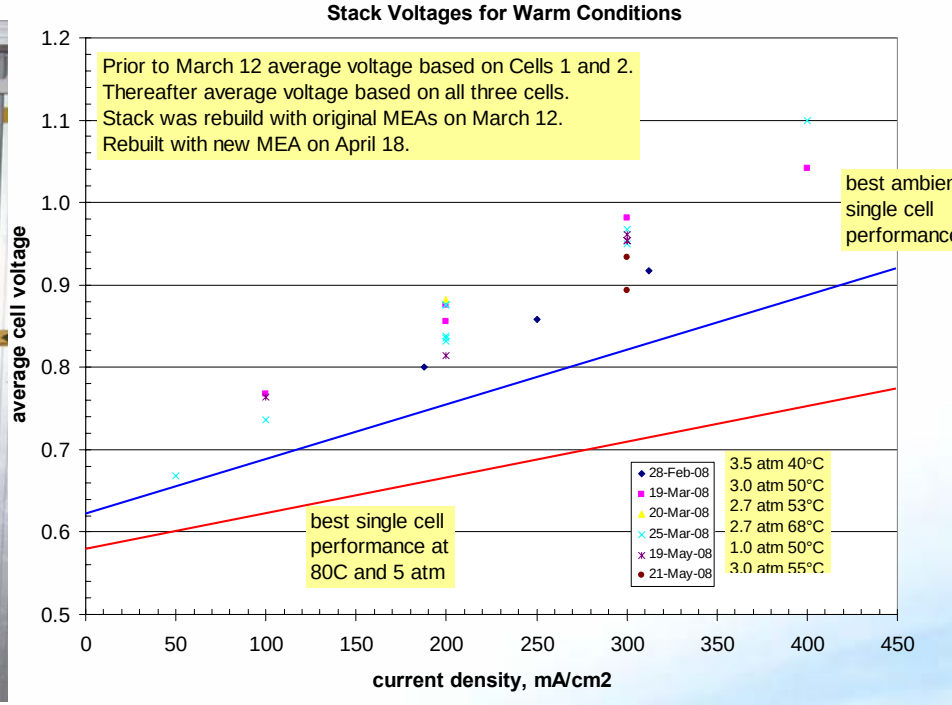
3-cell SDE



Multi-Cell Stack Testing Completed

- Level 1 Milestone Completed on 3/26/08 (ahead of schedule)
- Demonstrates 8x scale-up and multi-cell stack capability (86 L/h H2)
- Voltage higher than best single cell performance due to restrictive anolyte flow passages in stack and insufficient SO_2 Absorber capacity
- Key step leading to larger scale demonstration plant

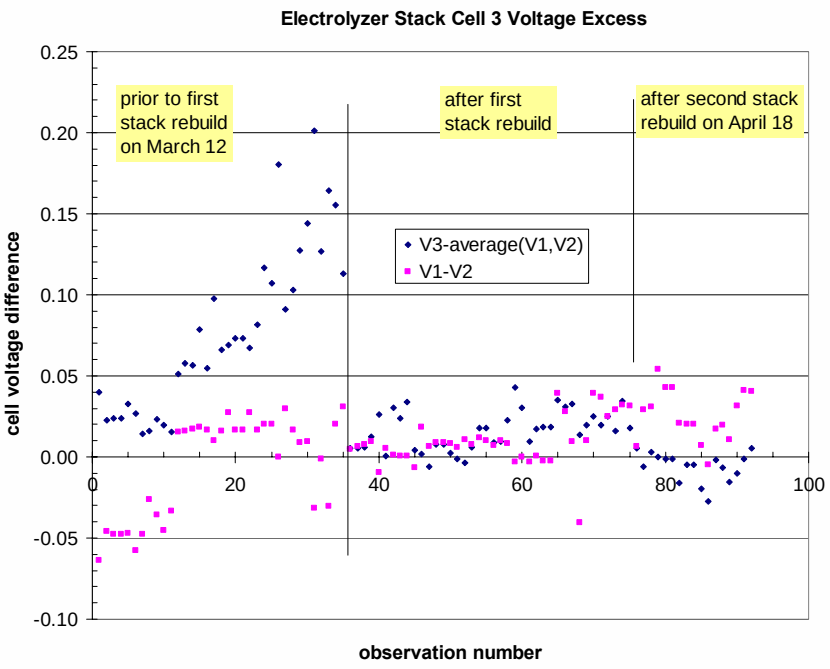
Stack installed in test facility

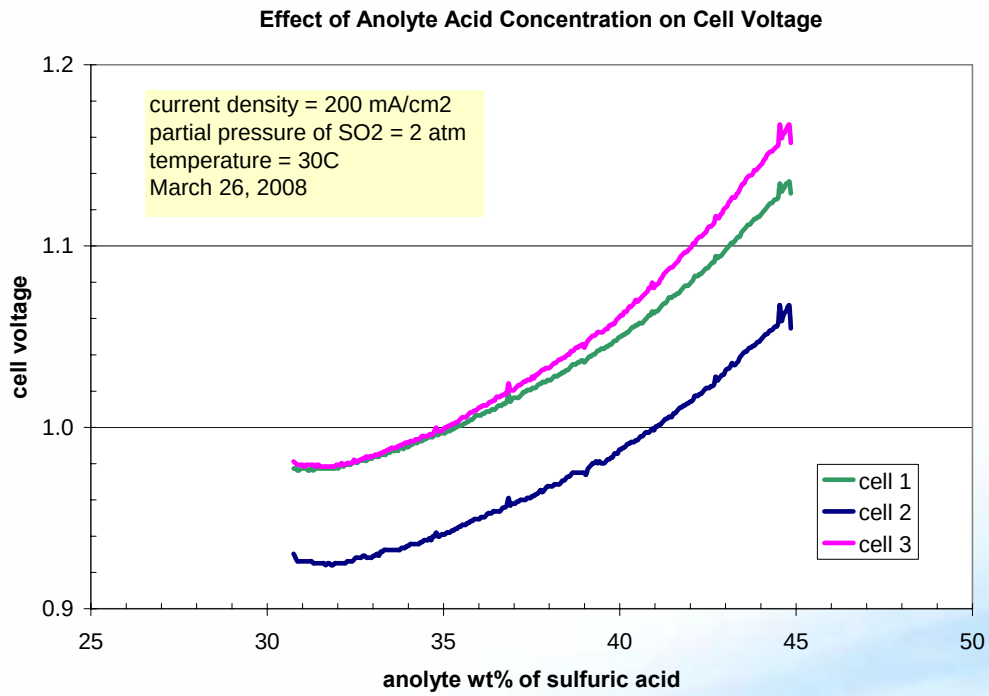


Multi-cell Stack Polarization Curve

Multi-cell stack results

- **Cell voltages were about the same, except when Cell 3 flow was partially blocked**
- **Cell voltage increased with increasing sulfuric acid concentration in anolyte**





Future Test Facility Upgrades

- **Before testing electrolyzer stack again, enlarge anolyte flow passages.**
- **Increase capacity of SO_2 Absorber before future stack testing.**
- **Increase temperature capability above 100°C. Teflon lined tubing.**
- **Add gas chromatograph.**

Electrolyzer Testing Conclusions

- **Test facility operates well**
- **Flexibility of facility design allows for quickly changing MEA and operating conditions**
- **Have tested 33 MEAs and also three cell stack**
- **Have very promising operational technique for greatly reducing, if not eliminating sulfur**
- **Present SO_2 Absorber has insufficient capacity for multi-cell stack testing.**