2007 DOE Hydrogen Program Review

Test of High Temperature Electrolysis ILS Half Module

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Project ID # PDP 26

Overview

Timeline

- Half-ILS Module
  - Test start date: 6/28/2006
  - Test end date: 9/22/2006
  - Time on stream: 2055 hours
  - Production rate: 1.25 Nm^3/hr

Barriers

- H_2 generation by water electrolysis
  - G – Capital Cost
  - H – System Efficiency
  - I – Grid Electricity Emissions
  - J – Renewable Integration

Budget

- Total project funding
  - DOE NHI Program
  - Ceramatec sub to INL
- Ceramatec FY06 Funding
  - ~ $450k
- Ceramatec FY07 Funding
  - TBD

Partners

- INL: Lead Laboratory
- Ceramatec: Fabrication/Testing
- ANL: Post Test Examination

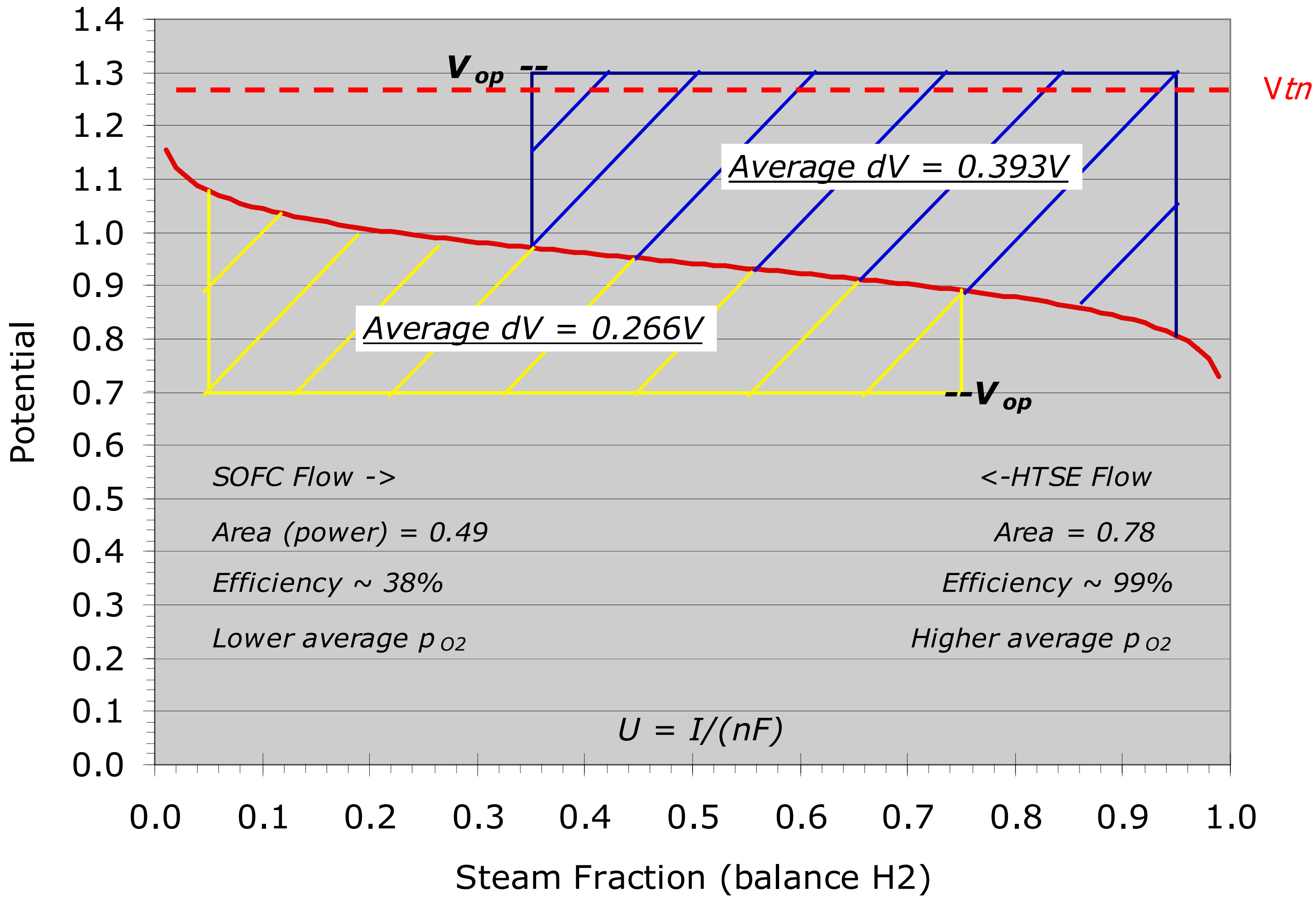
Objectives

- 2006 Preparations For INL CY07 Test
  - Integrated Laboratory Scale (ILS) Hydrogen Production
- Test “Half-ILS Module” at Ceramatec
  - 2x60 cell stacks in similar configuration to full module
  - Show performance scales with stack height
  - Assess system issues with tall stacks
  - Exercise component production capacity
    - 100 cells/month
  - Deliver first full ILS module to INL

Approach

- SOEC Leveraged By SOFC Background
- Influenced by Ceramatec 20 years of SOFC R&D
  - Cell & stack foundation R&D: EPRI, GRI, DOE
  - System view developed from larger demo projects
    - NorCell 1993, 1.5kW system on natural gas
    - DARPA 1996, 1.2kW system on JP-8
    - DOE Advanced Manufacturing … (AMPS)
    - DOE SECA team
  - Back to foundation R&D, SECA CTP, SBIR, etc.
- Ceramatec now has only ~ 4 years in SOEC R&D
  - INL, SBIR, DOE EERE H_2 Production

SOFC-SOEC
Contrasts in (Potential:Composion) Space



Implications Drawn From Thermodynamics

- SOEC relative to SOFC has
  - Higher average p_{O2}
    - More severe corrosion conditions from steam & O_2
    - Less potential for undesirable mixed conductivity, e.g.
      - Ceria electrolyte
      - Perovskite icons
  - Higher performance (current, power, efficiency)
  - More uniform stack temperature
  - Potential system heat deficiency

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SOFC vs. SOEC Design Differences

- Cells are virtually identical
  - Same electrolyte, electrodes, pattern, etc.
  - Oxygen evolution creates asymmetry in oxygen electrode supported SOEC
  - Opposite effect exhibited in hydrogen electrode supported SOFC
- SOEC seals more challenging
  - Higher back pressure on seals due to product collection vs. burner
  - Low molecular weight stream vs. reformate
    - Diffusion mechanism more active relative to hydrodynamic
    - Hydrogen permeation in metal icon destabilizes air side scale
- SOEC is more corrosive environment
  - High steam content
  - High oxygen concentration
  - <u>Coating changes and seal compatibility study (glass fluxes scale)</u>
- Potential icon design differences due to
  - Design air channels for heat rejection or injection (channel size)
  - <u>SOEC has potential for very large cell areas</u>

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SOFC-SOEC System Differences

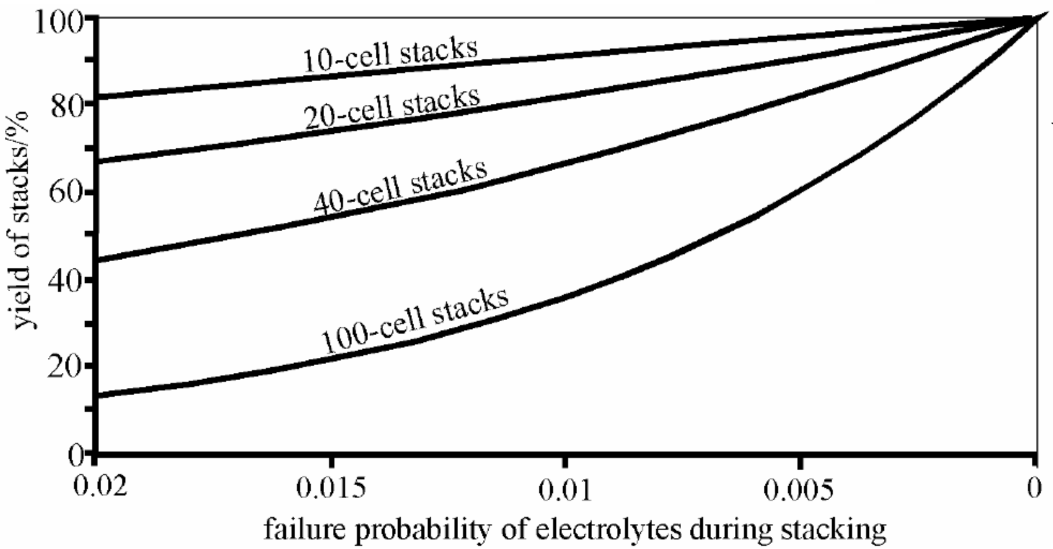
- SOFC spent fuel burner
- SOFC heat rejection to enclosure
- Steam generator vs. reformer heat loads
  - SOFC reformer is a chemical recuperator
  - SOEC stack is a chemical recuperator
- Air flow & preheat requirements
  - SOFC 6-12 air stoichs relative to current
  - SOEC 0-2 air stoichs relative to current

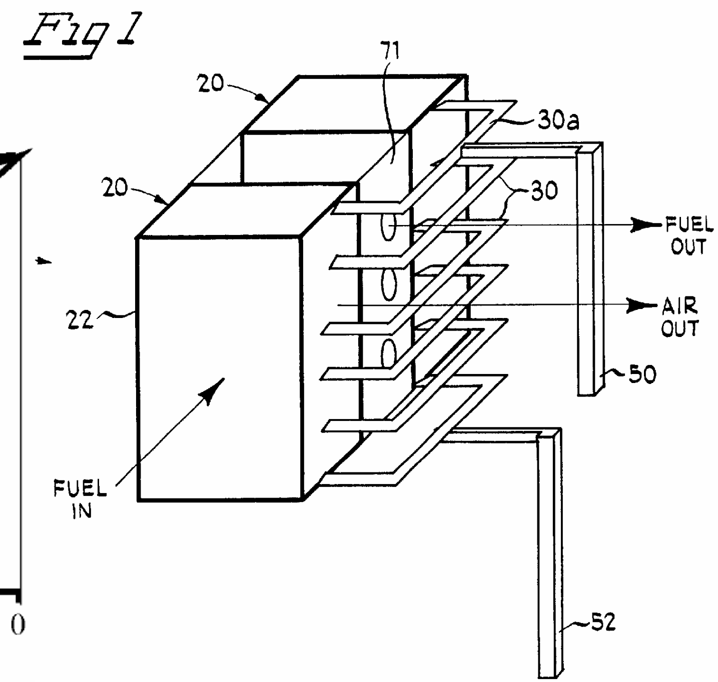
SOFC-SOEC Operational Differences

- Power source/sink
  - Power supply simpler than SOFC power cond.
  - Fast voltage slew rate, little risk of thermal shock
- Potential difference in migration/transport
  - Cr poisoning?
    - Oxygen concentration gradients and flux reversal
  - Other electrode electro-migration issues
    - SiO_2 transport reported by Risø
- Additional undiscovered issues?

Addressing Tall Stack Failure Probabilities

U.S. Patent Apr. 9, 2002 Sheet 1 of 3 US 6,368,739 B1



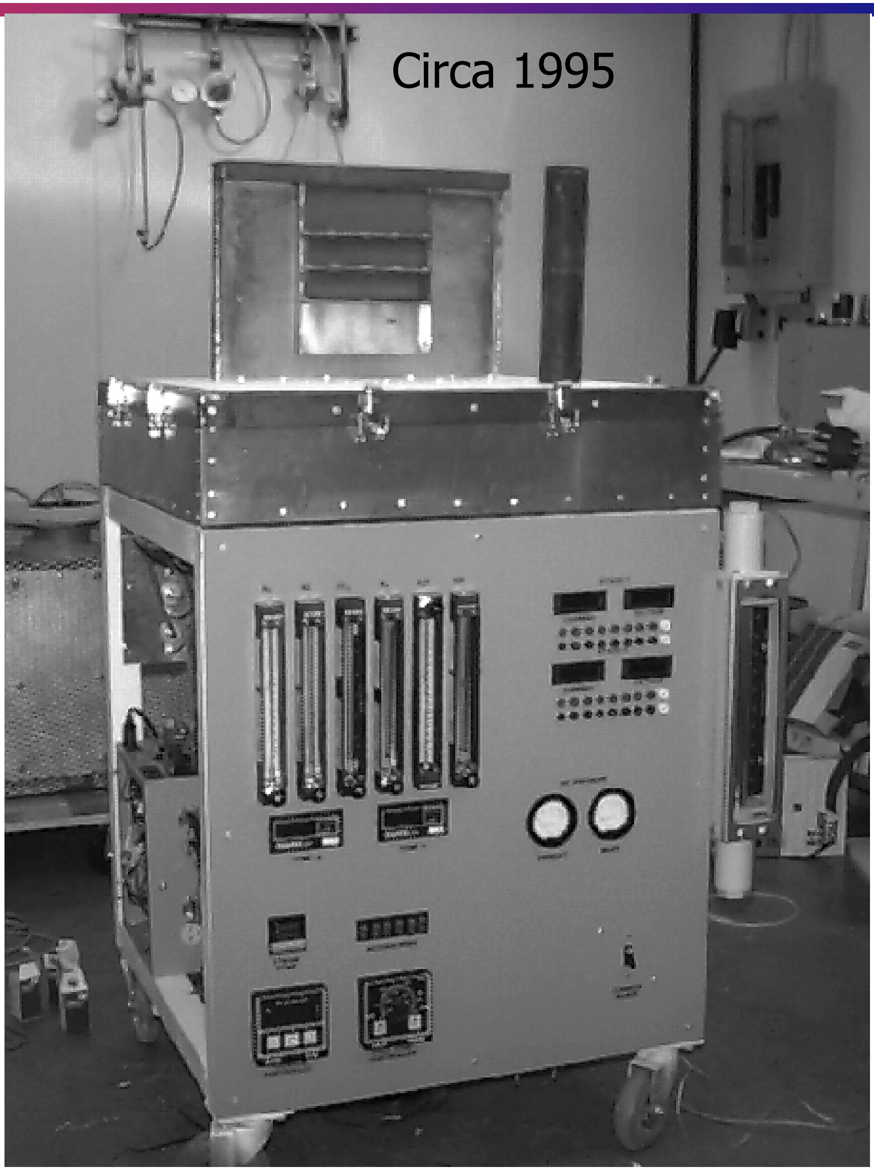


From Detlef Stolten
High Temperature Electrolysis IEA Meeting
05 November 2004, San Antonio, TX

Ceramatec approach to mitigate risk in tall stacks

SOFC Test Stand Used In Half-ILS Test

- Test stand features
  - SOFC thermally self sustaining (TSS) unit
  - Air recuperator
  - Reformer/Steam Generator
  - Process instrumentaion and controls
  - Space to accommodate desired stack pair
  - Electric heater w/trim natural gas burners
  - Custom LabView Data System



Facility Safety Features

- Outside bulk storage of H_2 & N_2
  - Pressure relief vents outside with regulator failure
  - Reduced cylinder handling
  - Outside emergency shutoff
  - Solenoid valve shutoff by hydrogen sensor or power failure
- Flow restriction orifice for each test station
- Fusible link, release to close flammable gas valves
- Air flow sensing ΔP switch hardwired to DC supply
- Alarm auto-dialer triggered by data range windows in data acquisition software

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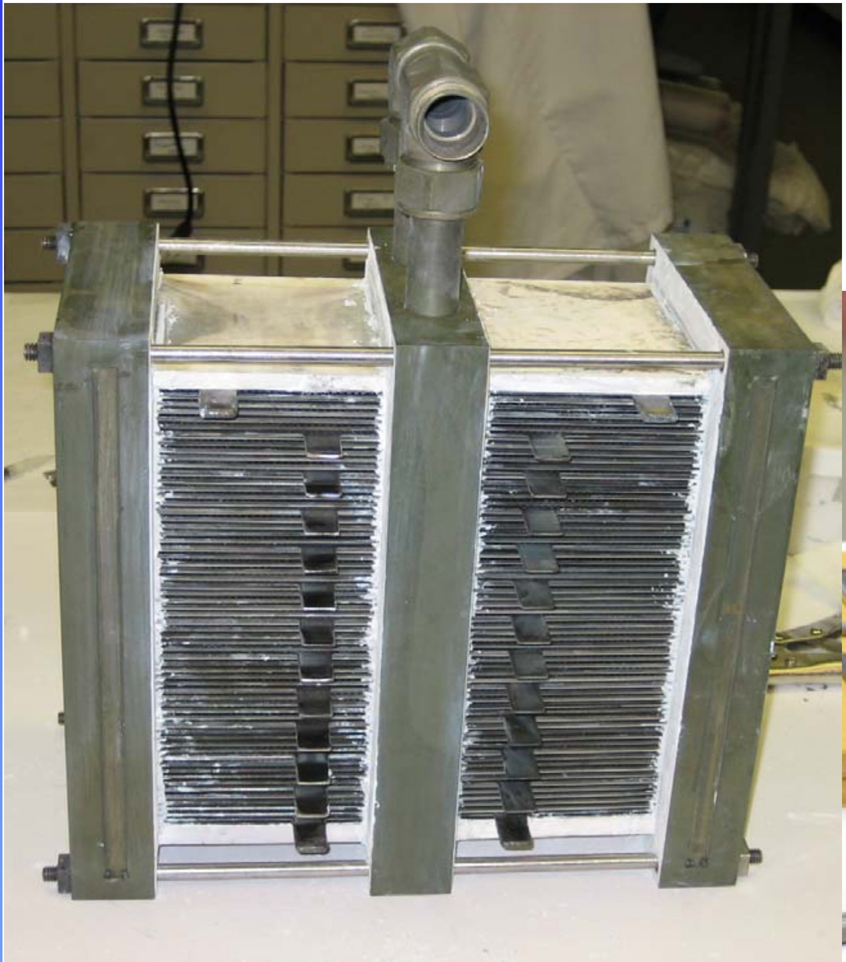
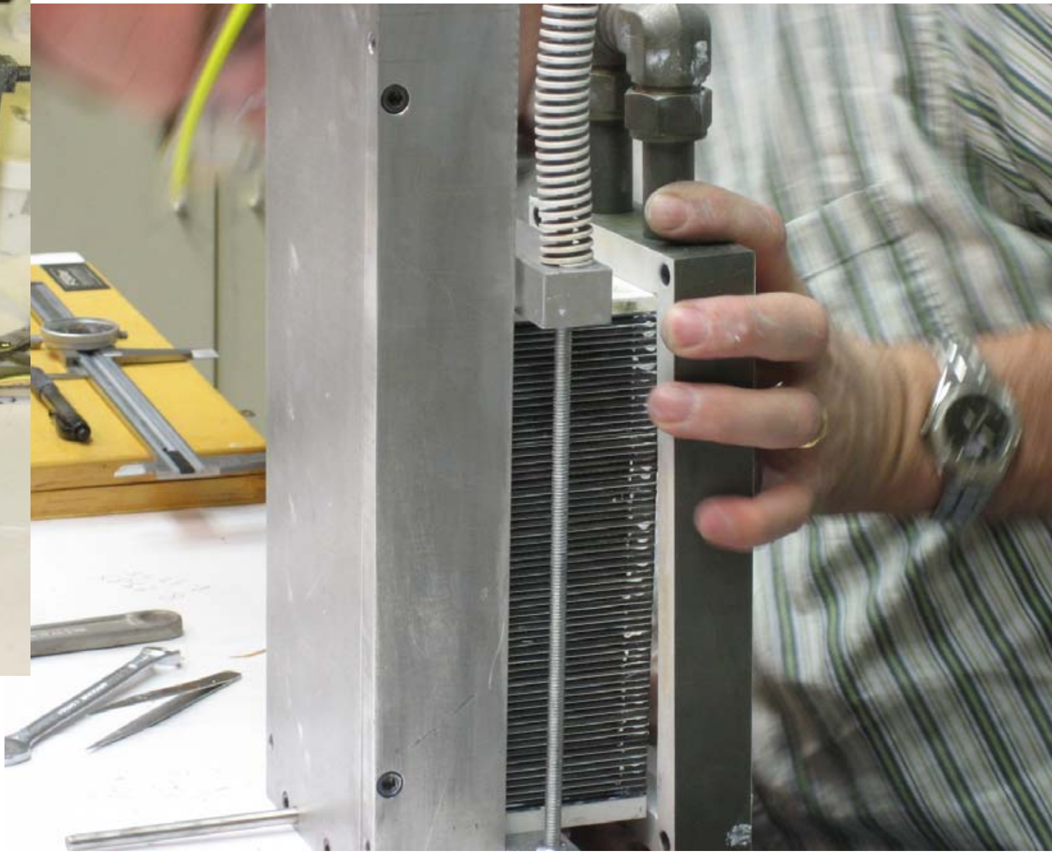
Half ILS Module 60 Cell Stack Pair





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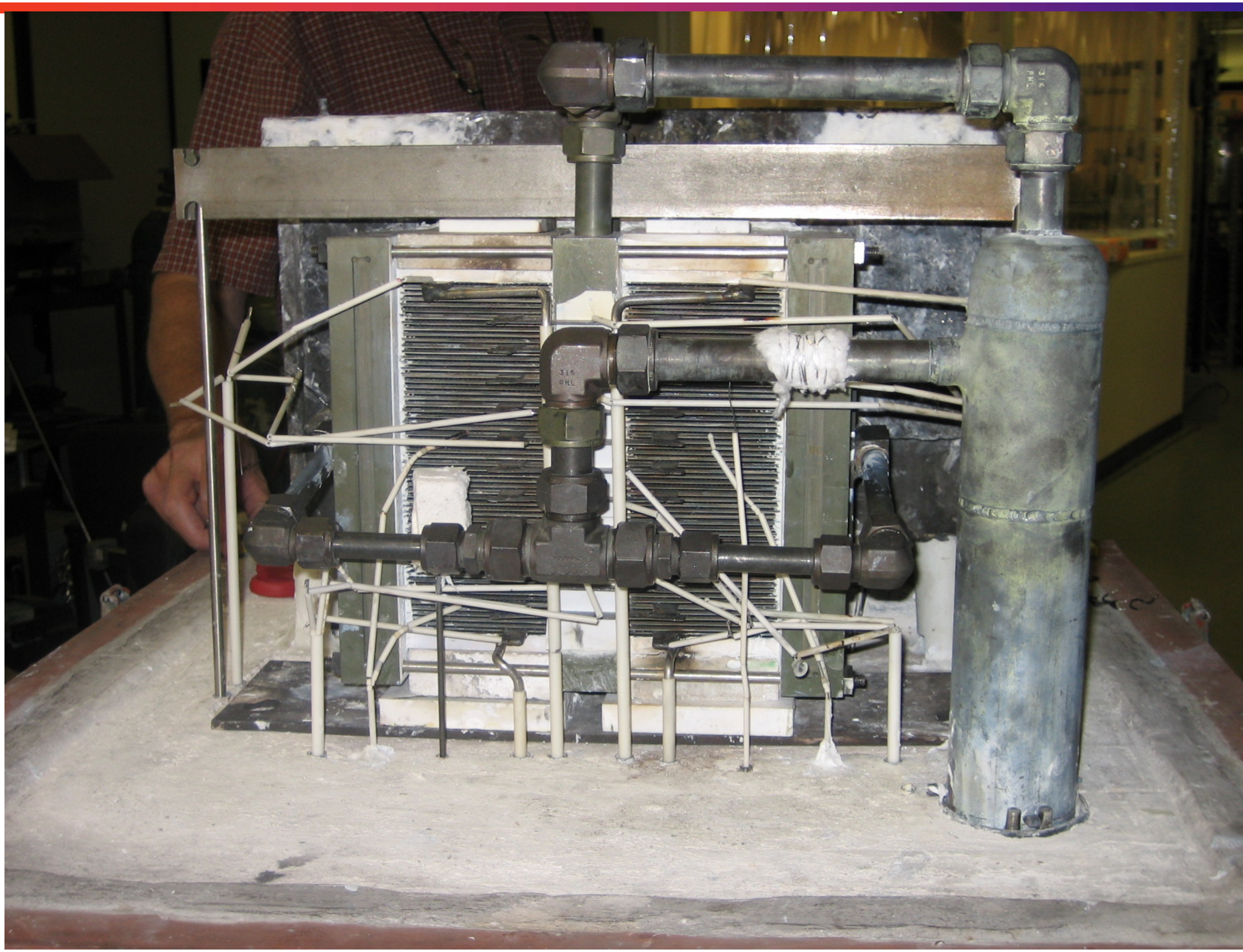
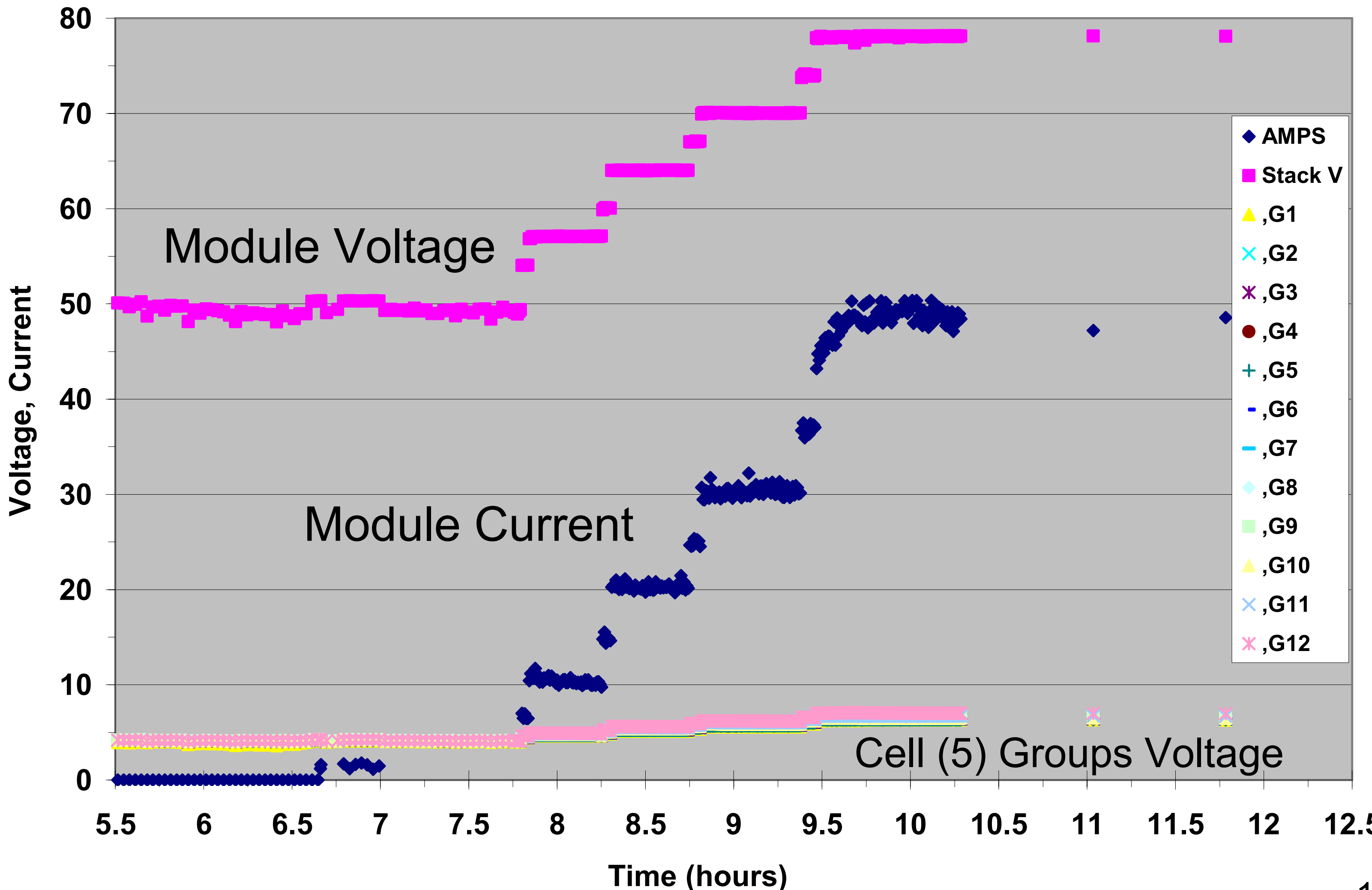
Installed Half-ILS 2x60 Cell Stack Module



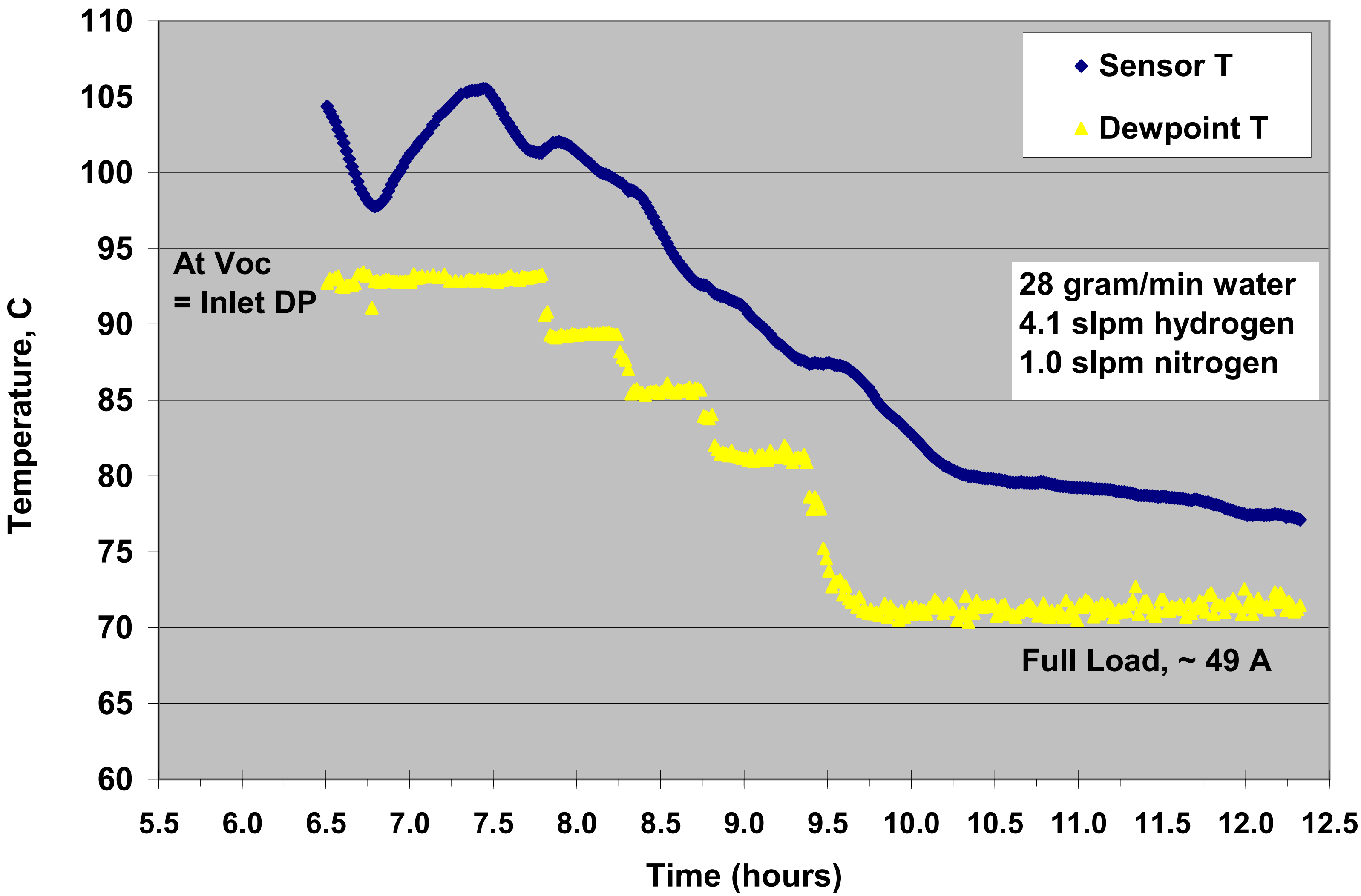
Technical Progress & Results

Half-ILS Steam Electrolysis Module in Operation

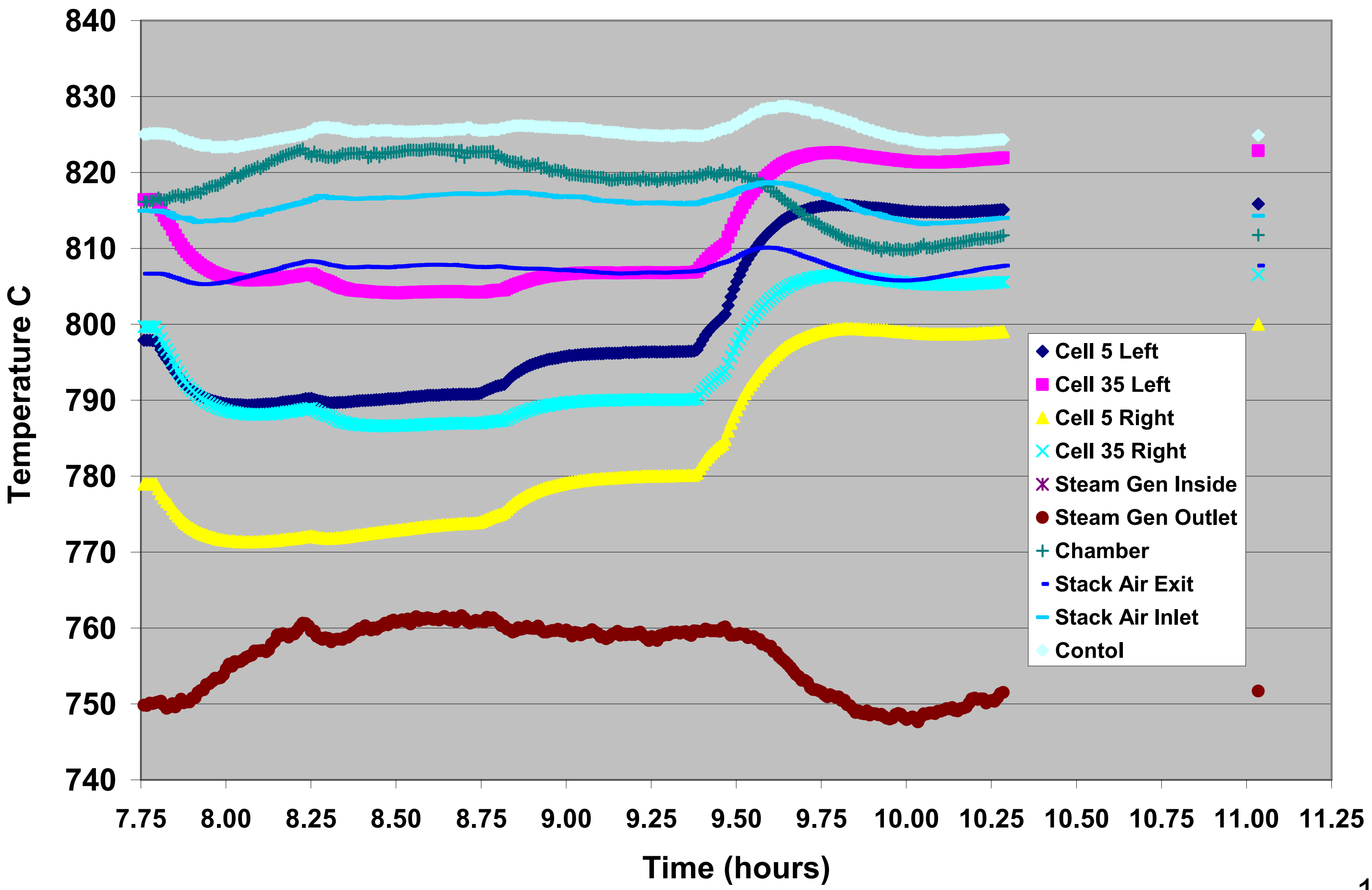
Initial Load Steps of Half ILS Module



Outlet Dewpoint Response To Initial Loading



Temperature Response To Initial Load Steps



Predictions Reconciled to Average Initial 18 Hour Data

HTE GAS FLOW WORKSHEET
Half ILS Module Qual Stacks

June 29, 2006

2	Stacks						
60	Cells/Stack		9.65E+04	Faraday's Constant			
120	Total Cells		82.06	R, cm^3-atm/g-mol K			
64	cm^2 active		815	T, C			
20.0%	Nitrogen% of H2+N2		1088.15	T, K			
92.0	Inlet Dewpoint	197.5	273.15	Tstd, K		YSZ thickness	0.02
58.3%	Steam Utilization					rhoel ohm-cm	22.28
2.4	Sweep Air Stoichs					k S/cm	0.045
1.045	ASR ž-cm2					YSZ ohm-cm^2	0.446
1.301	Vop V/cell					OP ohm-cm^2	0.614
						cell ohm-cm^2	1.060

78.06	Stack Vop		48.63	total current
0.872	Inlet Steam fraction			
0.364	Outlet Steam fraction			
0.833	V/cell $E_n(U)$	Reversible potential at steam inlet		
49.98	Stack Voc			
0.958	V/cell $E_n(U)$	Reversible potential of hydrogen product		
0.904	V	E_{nbar}		
-0.380	A/cm ^{2} j_i	current density	1.23	Apparent ASR
-0.652	A/cm ^{2} j_f	100% steam utilization current density		
-24.31	Amps/stack	Stack Current		
-41.71	Amps	100% steam utilization current		
-3795.8	Watts	Total Power		

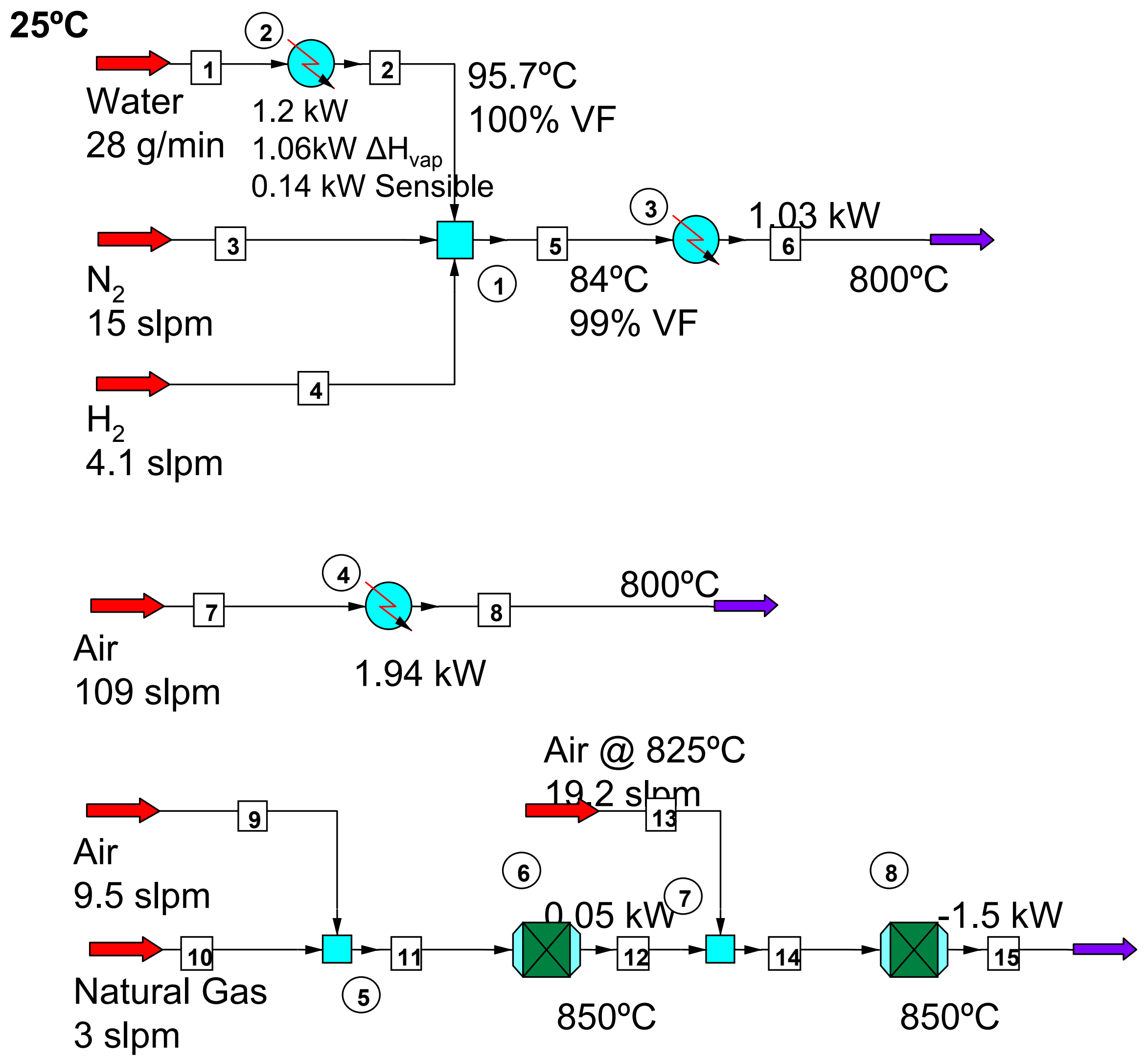
	Air Flow Rate	H2O Feed Rate	H2 Feed Rate	N2 Rate	H2 Exit Rate	H2O Exit Rate	H2 Production
g-mol/sec	8.64E-02	2.59E-02	3.05E-03	7.63E-04	1.82E-02	1.08E-02	1.512E-02
g/sec	2.51E+00	4.67E-01	6.15E-03	2.14E-02	3.66E-02	1.95E-01	3.05E-02
normal liters/min	116.2	28.0	4.1	1.0	24.437	11.69	20.335
		liquid cm ^{3}/min ^^^				liquid cm ^{3}/min ^^^	

Air Rotameter 16%

	Inlet	Outlet	Dry	GC
N2	0.026	0.026	0.040	3.46
H2	0.103	0.611	0.960	96.55
H2O	0.872	0.364		100.01
	1.000	1.000		

1220.1	nlph H2 production
2.633	kg/day
3.659	RT kW H2
96.4%	Efficiency

ChemCad Preheat Duty Worksheet

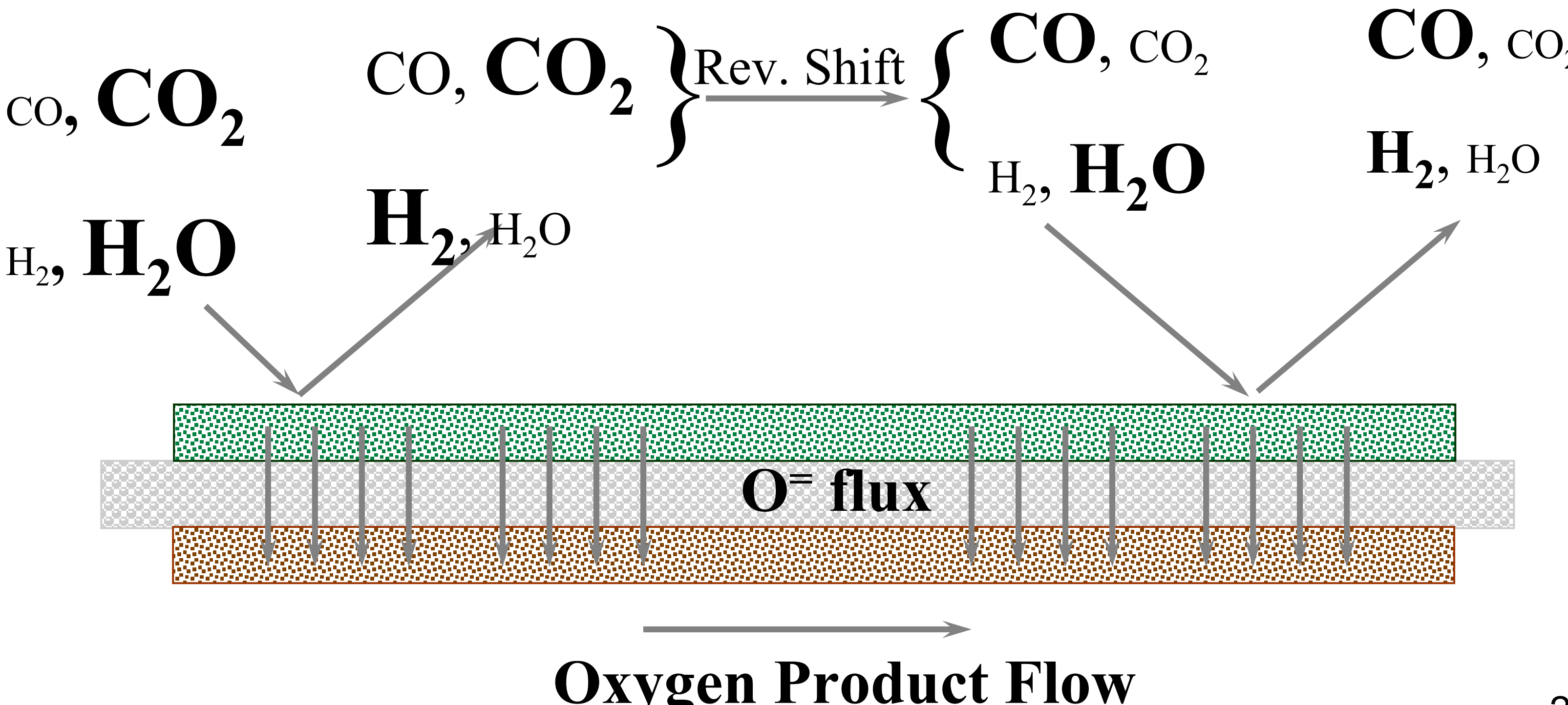


Reverse Shift & Electrolysis Of CO_2

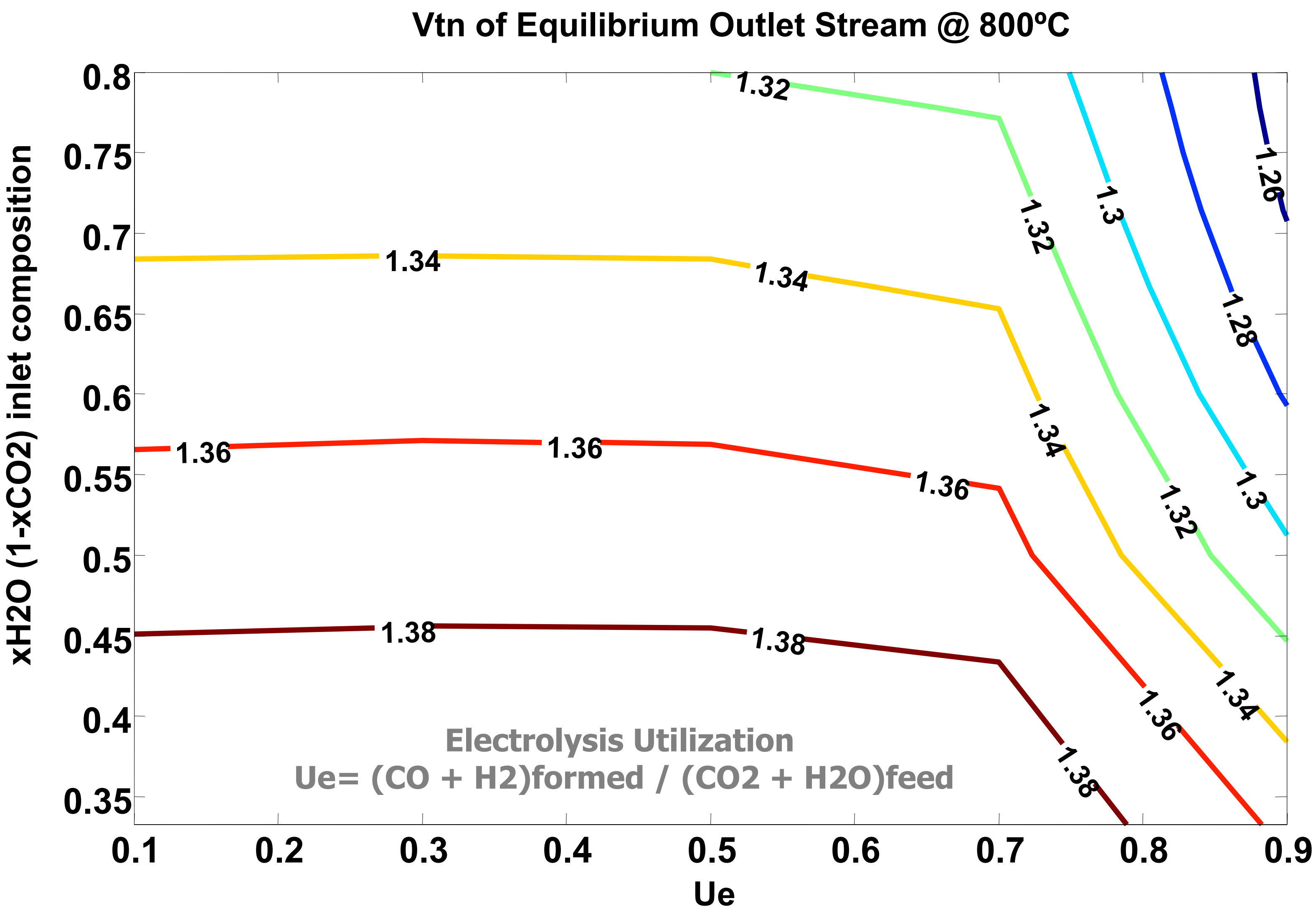
Feed: H_2O, CO_2, (minor H_2, CO)

Reverse Shift Reaction: $CO_2 + \Uparrow H_2 \Longleftrightarrow CO + \Downarrow H_2O$

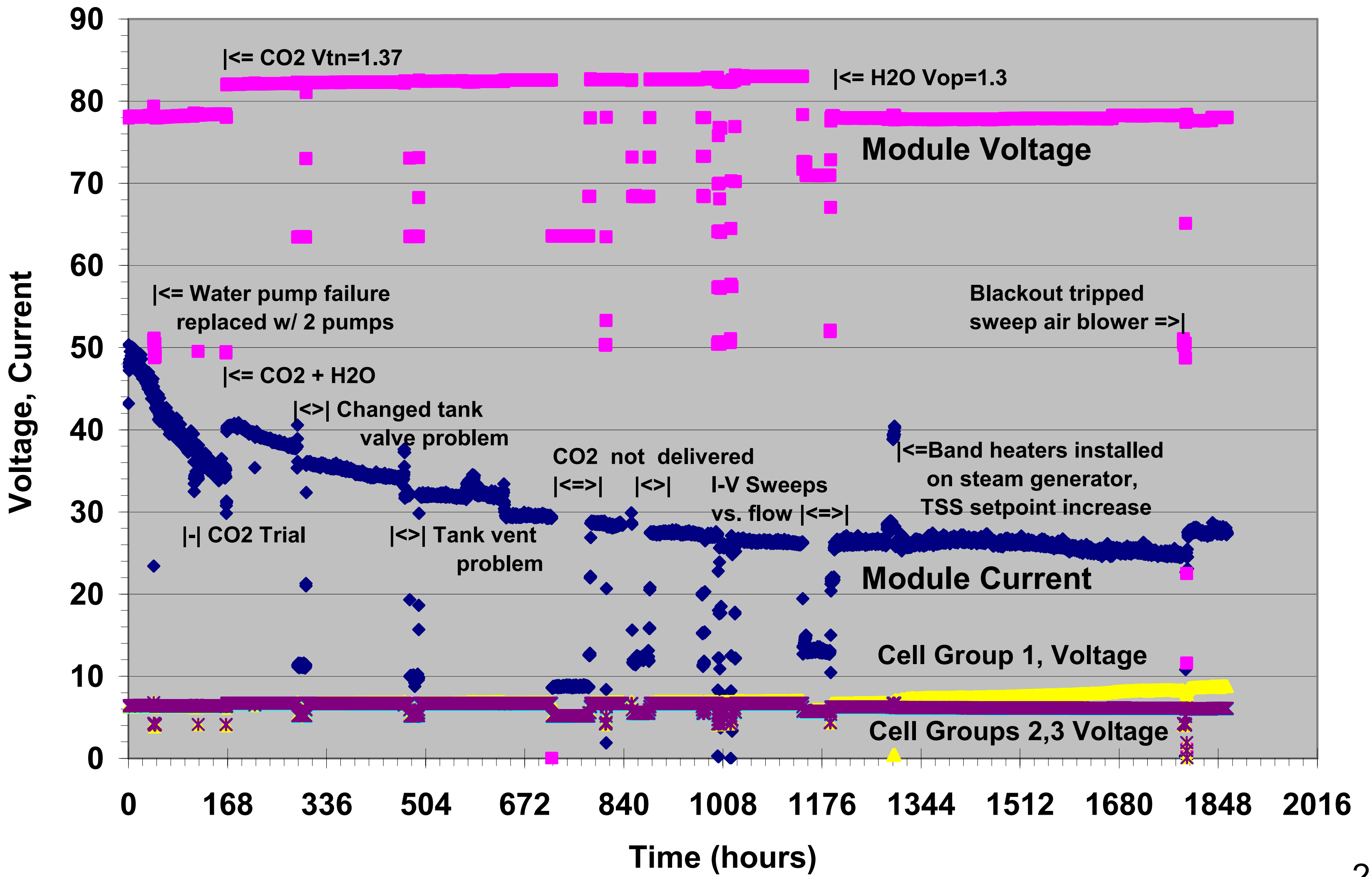
As steam is consumed and H2 produced the RSR proceeds to the right



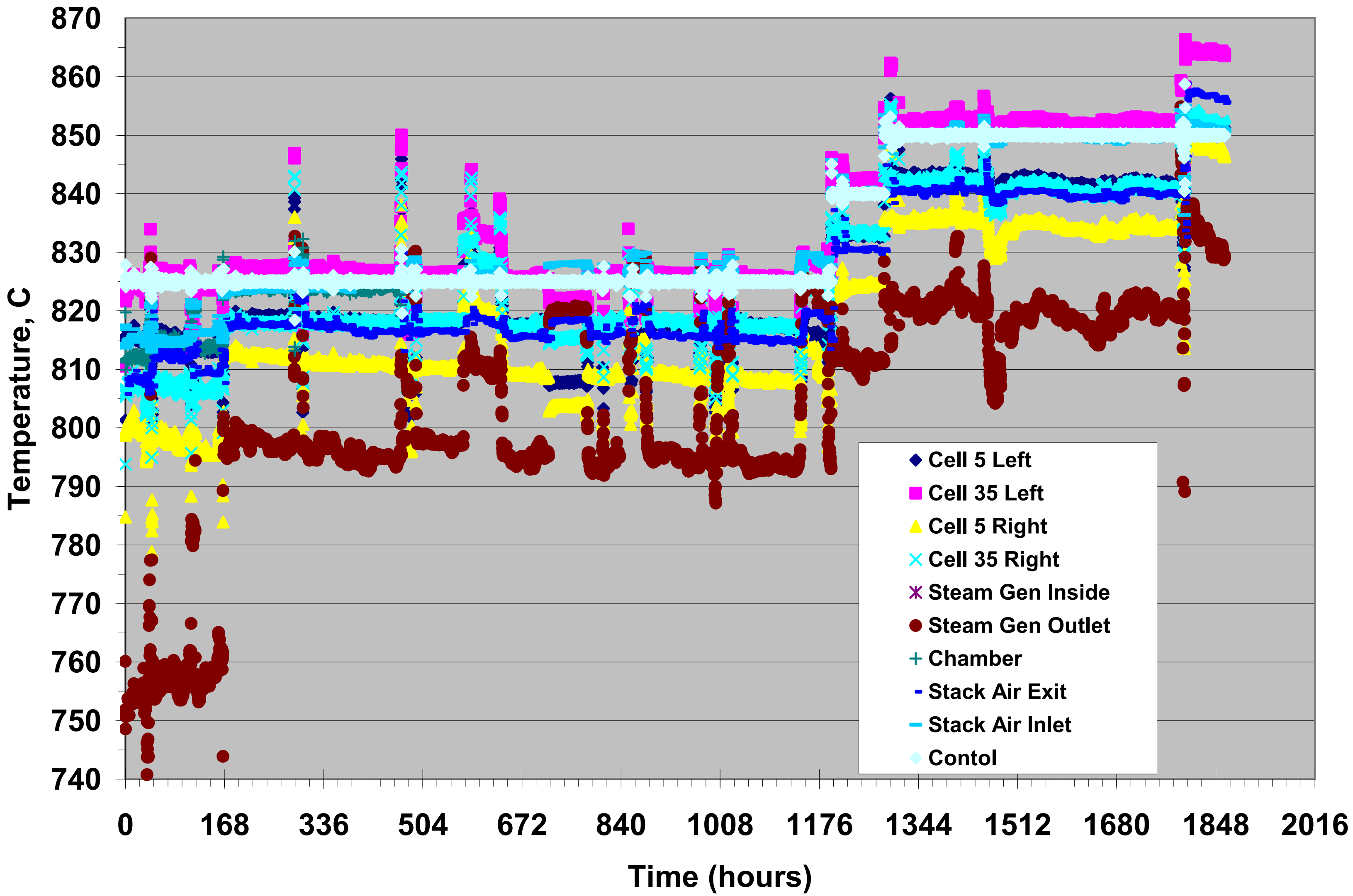
CO_2 Co-Electrolysis Thermal Neutral Voltage Map



Half ILS Module Load History



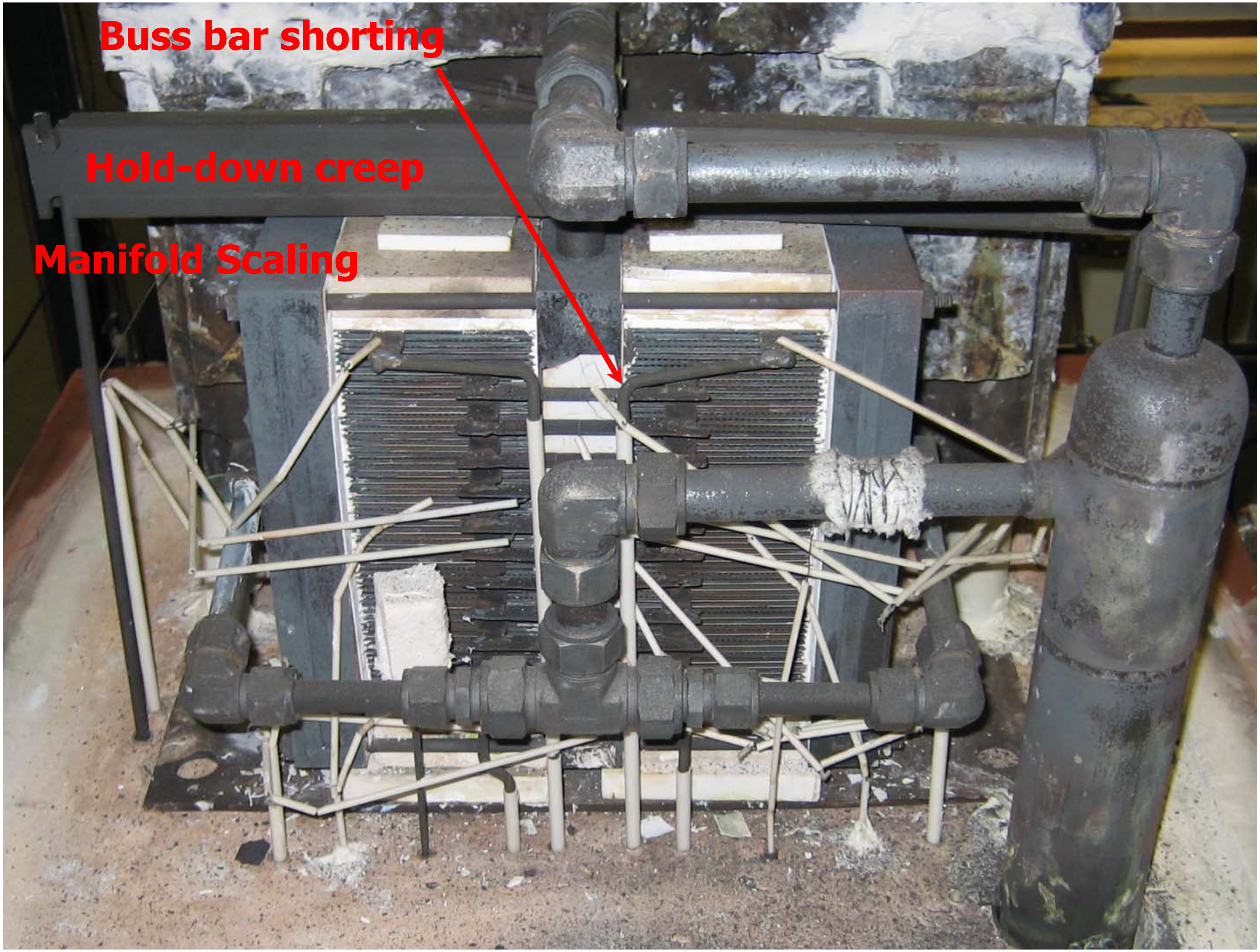
Half ILS Module Temperature History



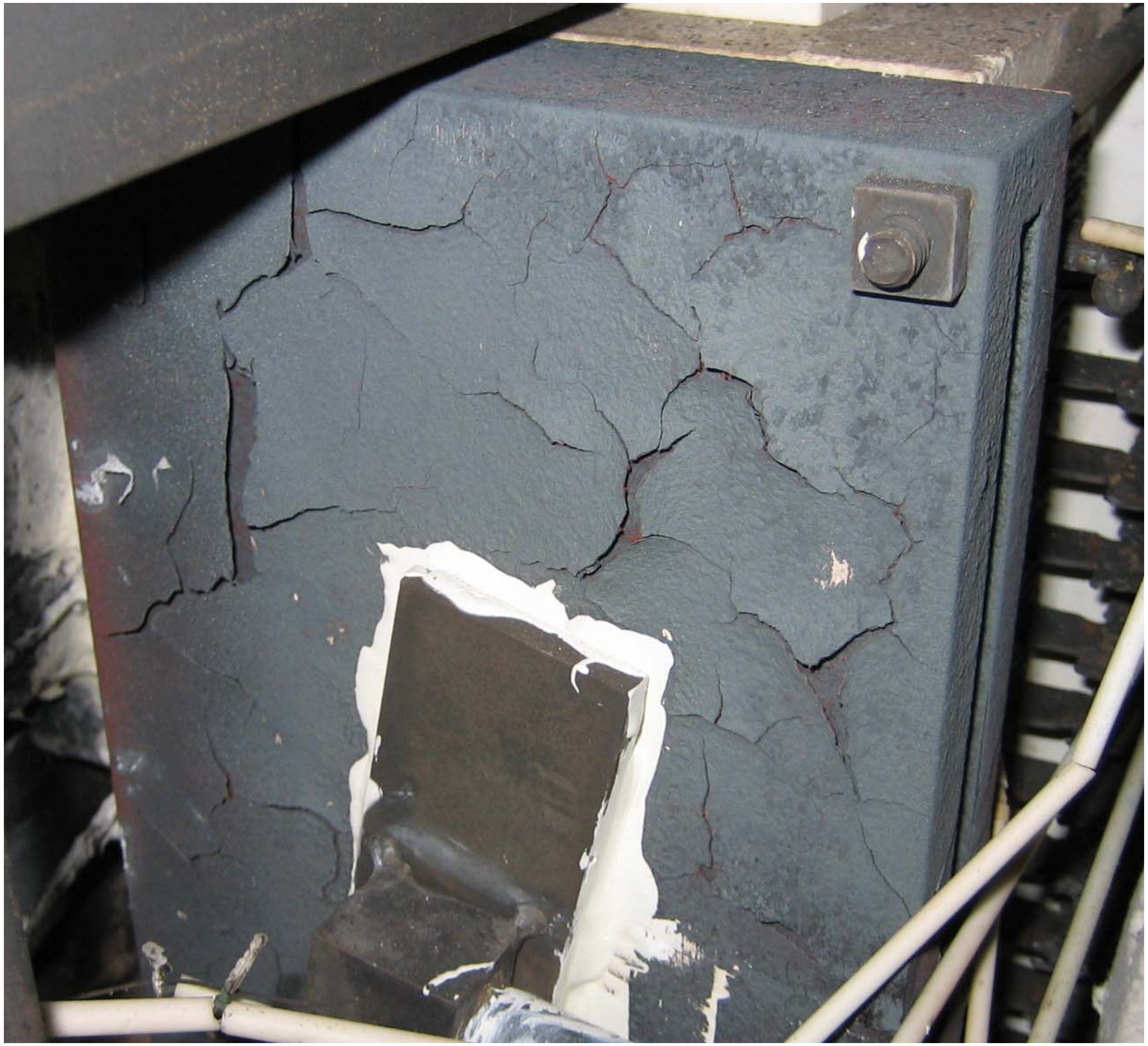
Operational Issues

- Water
  - Metering pump failures
  - DI line shutoff anticipated (check valve & bladder pressure tank)
  - Steam generator
    - Higher than anticipated duty
    - Band heater failures
- CO2
  - Delivery, tanks, etc.
- Intense thunderstorm blew rain in vents, shutoff DC power
- Blower Trip (variable speed control reset after blackout)
- Furnace heating, initially appeared underpowered heaters
- DAQ System lockup
- Equipment scavenged for new tests
- …as the history charts show, reality isn't always pretty.

Half ILS Module Post Test



Manifold Scaling and Buss-bar Shorting

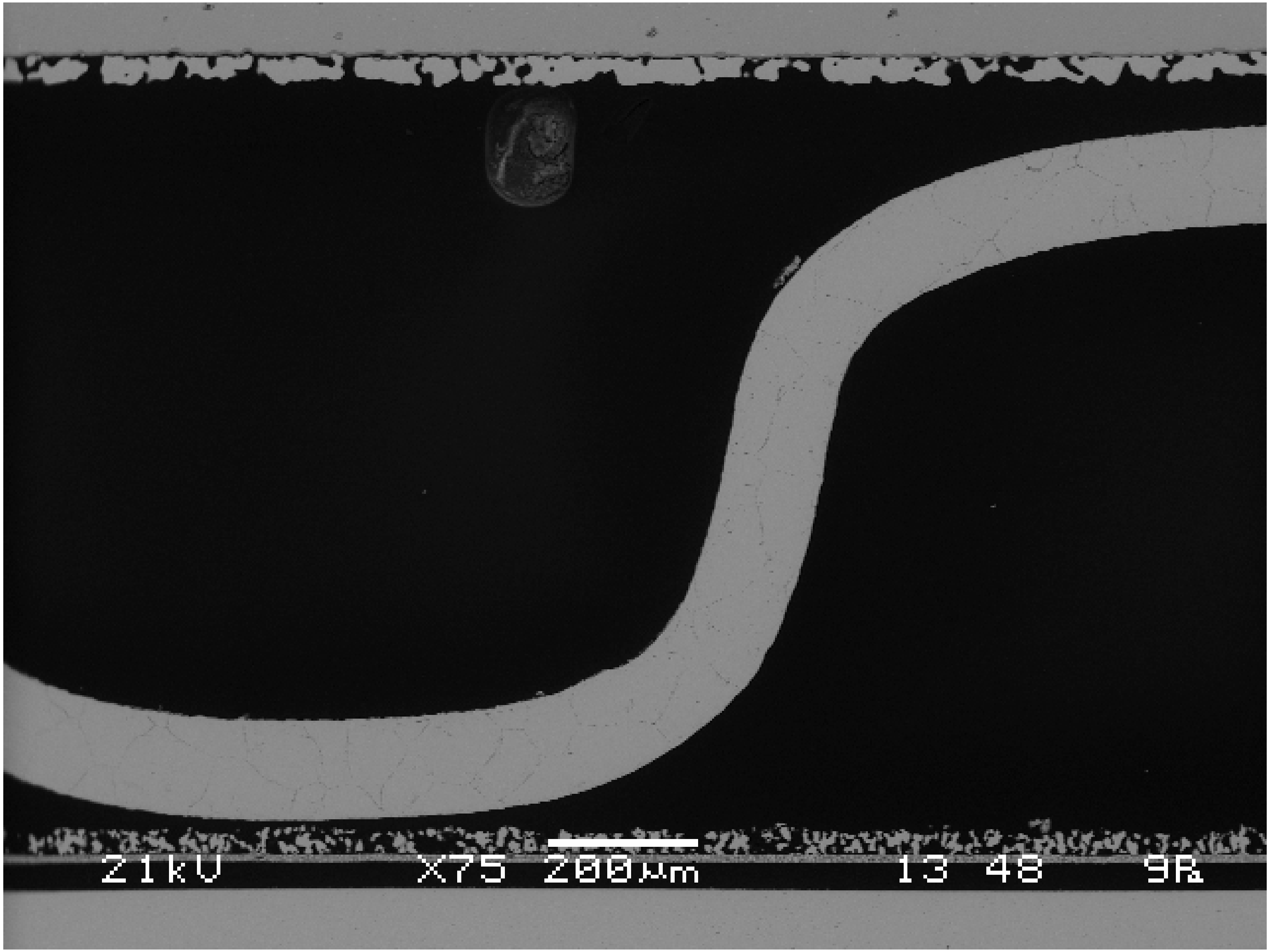


Half-ILS Manifold Corrosion

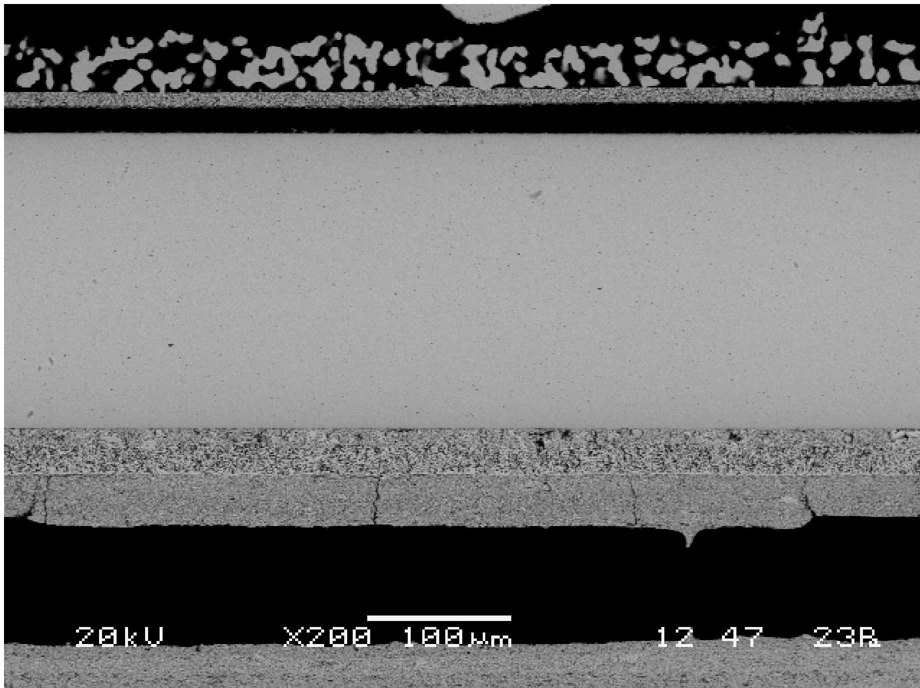
Top-Right-Outside Face of Center Frame

Manifold Corrosion Shorting of Cell Group #1

Cross Section of Repeat Unit From Half-ILS Stack

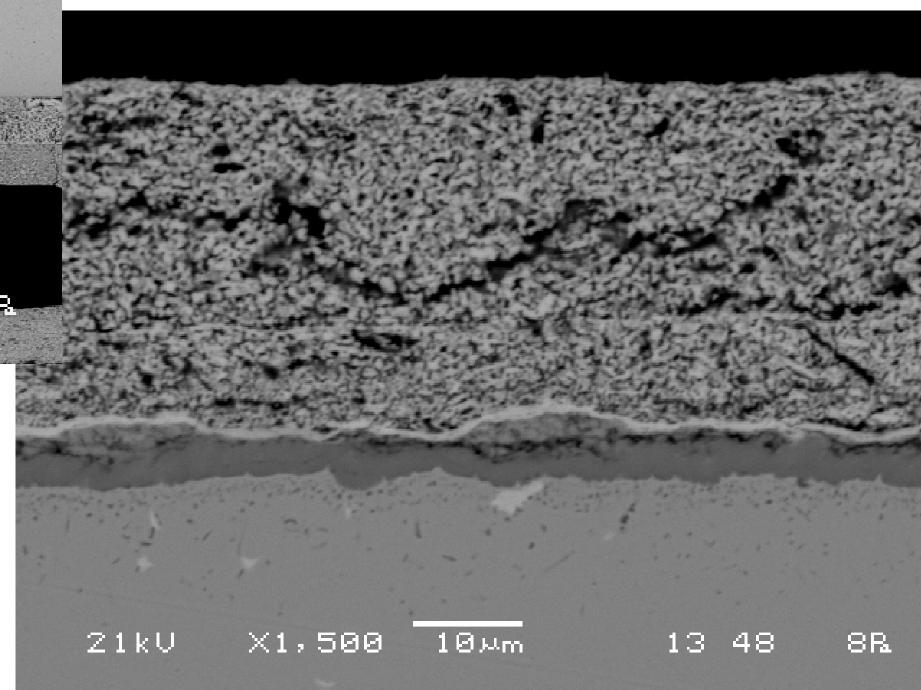


Cell and Interconnect SEM Examination



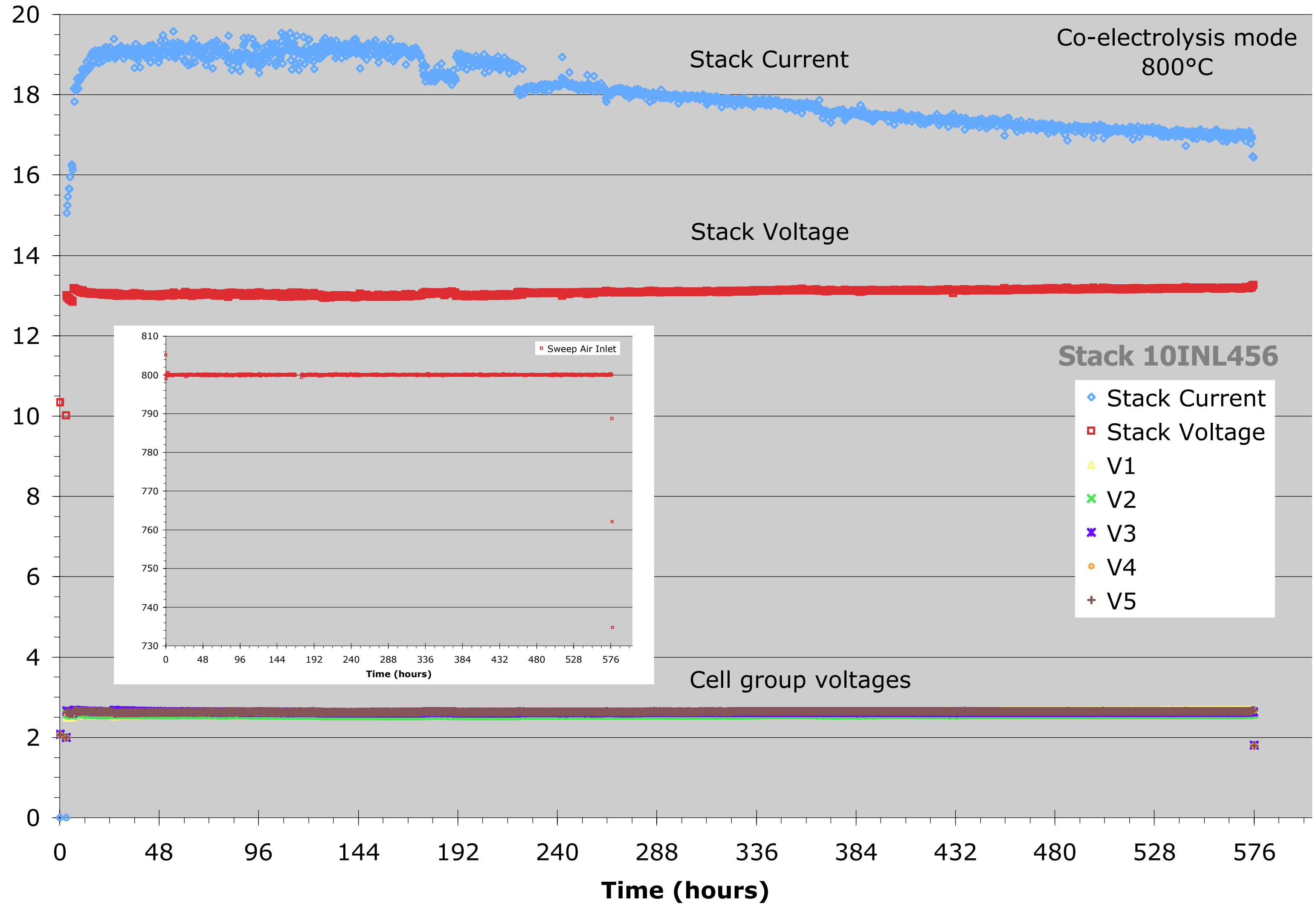
Hydrogen electrode

Electrolyte

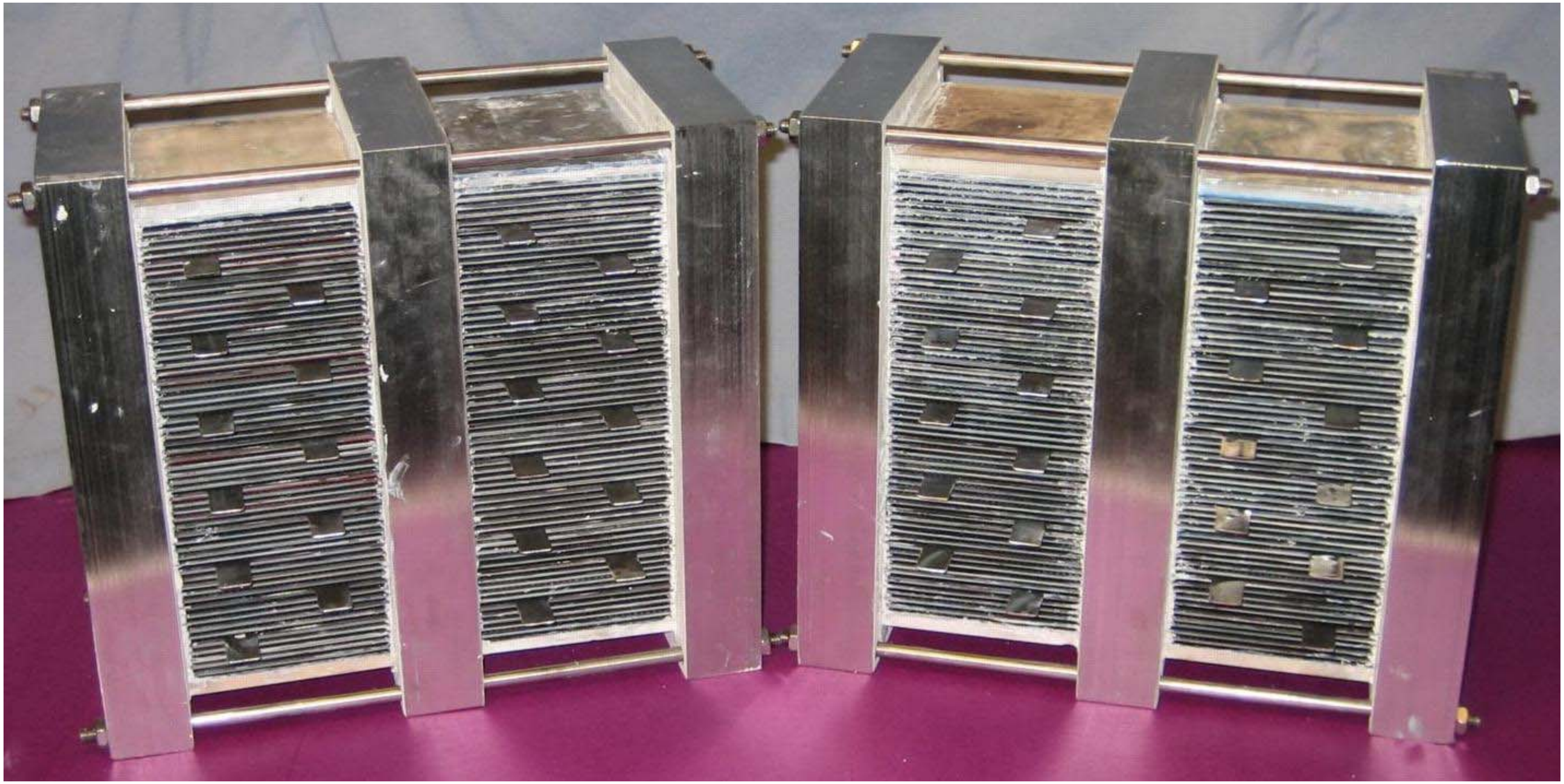


Metal separator plate,
oxygen evolution side

Improved Stacking Process (Post Half-ILS)

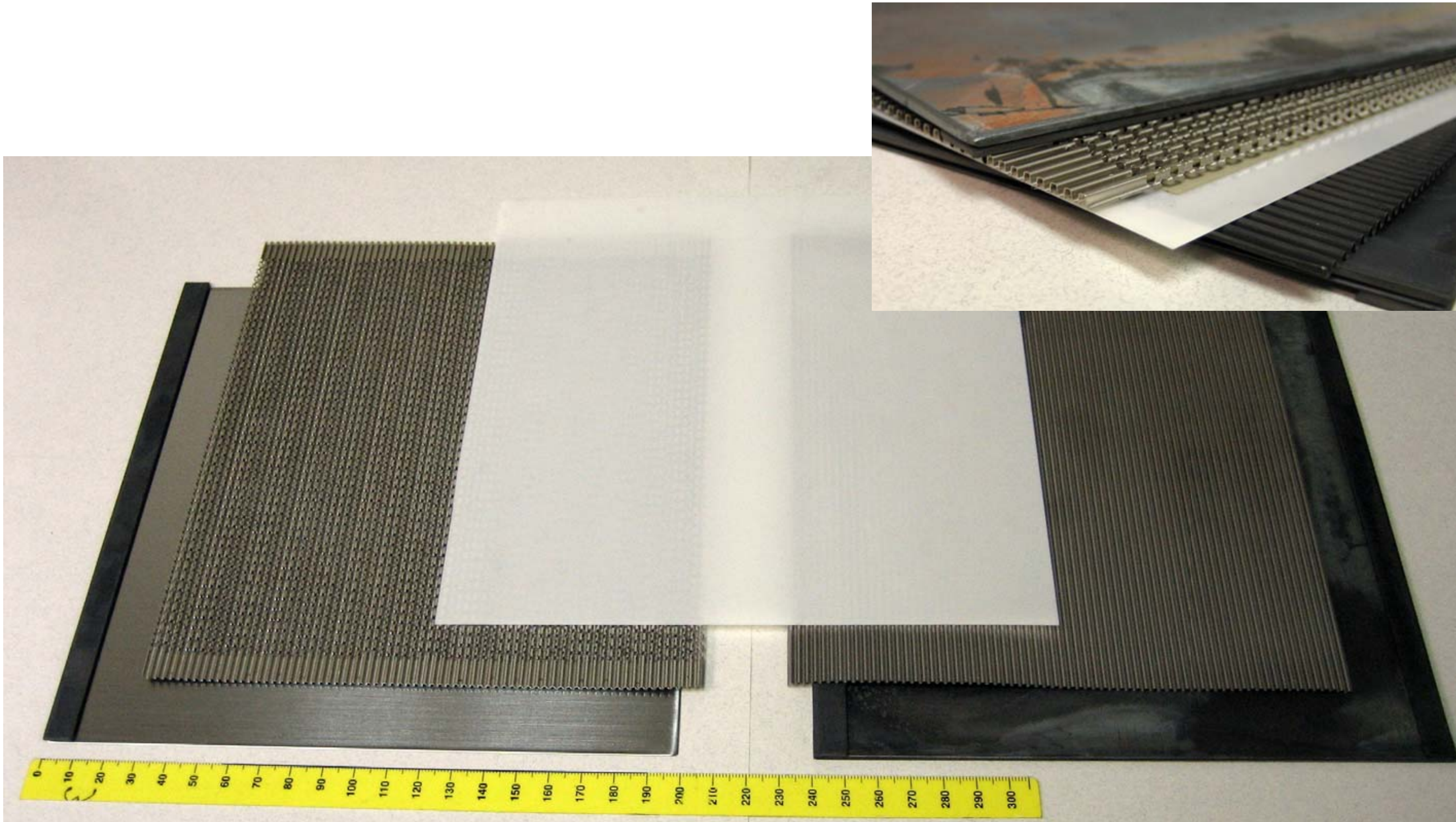


ILS Full-Module Delivered to INL



First 240 Cell Steam Electrolysis Stack Module Delivery

Future Plans



20cm Electrolysis Stack Components

20cm Stack Component Production

- Flowfields complete
  - 1.5mm height vs. 1.0mm for 10cm parts
- Edge rails & separator plate coatings
  - Testing Crofer 22 APU alloy (available in needed form)
- Manifolds
  - Fabrication drawings done
  - Replacement for 440C alloy required custom hot rolling
- Cells
  - Sample electrolyte produced
  - Electrode printing screens order in Nov.
- Short stack test fixture/furnace insert

Summary

- Half ILS test at Ceramatec successful in
  - Narrowing gap from cell to stack
  - Showing tall stack ASR matching 10 cell stack
  - Proving co-electrolysis in stacks
  - Showing extended operation, but deg. high
  - Convincing that system factors are important
- Full module tests planned in CY07
  - Delivered full 4 stack module in March 2007
- 20x20cm parts in process for testing in CY07
- Need to develop industrial scale cells

Energy Policy Options Enabled by HT Electrolysis

- Produce
  - Hydrogen for heavy crude, tar sands and oil shale upgrading
  - FT liquids &,methane motor fuel for liquid fuel and CNG vehicles
    - Energy density and delivery compatible with current equipment
  - Byproduct oxygen for coal/biomass gasifiers
  - Be ready for Hydrogen Economy when distribution and storage issues solved
- Synfuel production (FT liquids & Methane) exothermic
  - Integrate CPV, wind, and nuclear power
  - Both secondary processes exothermic (process integration)
    - Integrate process heat from synfuel (FT or methanation) exotherm
- Switch between hydrogen or syngas production as needed.
- Leverage DOE Fossil Energy developed SOFC technology
- Utilize some CO2 captured from baseload coal plants to capture energy in intermittent RE sources

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High Temperature Electrolysis Research Needs

- More testing
  - "Milestone Event" vs. routine development test modes
  - Exercise production capacity
- More test stations
  - Evaluate materials and process improvements
  - Statistical performance distributions
  - Extended lifetime testing
- Cell area scale up
- Stack size scale up
- System BOP development