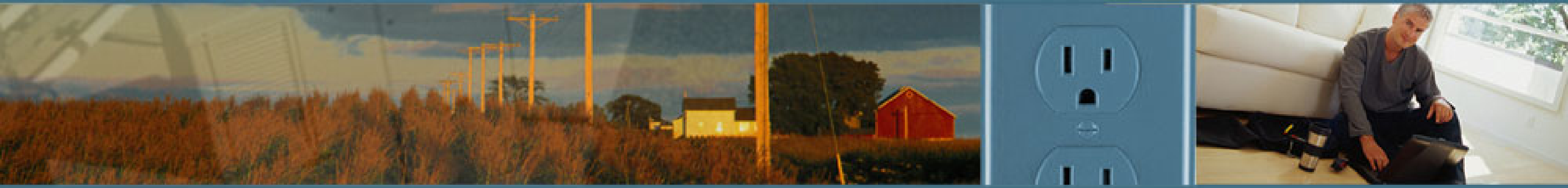


2004 DOE Hydrogen, Fuel Cells, & Infrastructure Technologies Program Review

Development of Polybenzimidazole-based, High Temperature Membrane and Electrode Assemblies for Stationary and Automotive Applications

Rhonda Staudt and Jeffrey Boyer

May 24, 2004

PROJECT OVERVIEW AND OBJECTIVES TO DATE

To identify and demonstrate an MEA based on a high-temperature polybenzimidazole (PBI) membrane that can achieve the performance, durability, and cost targets required for both stationary and automotive fuel cell applications.

- Complete initial screening of potential PBI-based chemistries and structures and downselect top 5 - 10 candidate materials based on chemical and physical properties.
- Initiate rapid screening of candidate PBI materials in 50 cm2 MEAs.
- Initiate detailed electrochemical characterization of MEAs made with selected PBI polymers.
- Initiate evaluation of low cost acid-absorbing materials for phosphoric acid management within the system.
- Initiate design and development of bipolar plates with PBI-specific flow fields.
- Initiate development of a PBI membrane-based MEA with advanced electrode structures providing high catalyst utilization and performance exceeding that of Nafion.

DOE TECHNICAL BARRIERS

- O. Stack Material and Manufacturing Cost
- P. Durability

DOE TECHNICAL TARGETS

- Applicable to both automotive and stationary fuel cell systems
- Operating temperature > 120^{o}C
- Operating pressure from 1 – 3 atm (abs)
- Membrane area specific resistance < 0.1 Ω-cm^2
- Gas crossover < 1%
- MEA manufacturing process scalable from 50 to at least 250 cm^2
- Automotive MEA cost target of < $10/kW at a volume of 500,000 fuel cell stacks per year
- Stationary system cost target of < $1500/kW at 1,000 fuel cell stacks per year
- Projected design lifetime > 40,000 hours

TEAM

- Plug Power Inc.
  - Prime contractor
  - Membrane and membrane electrode assembly (MEA) characterization
  - PBI-specific hardware development
- Rensselaer Polytechnic Institute
  - Membrane formulation, evaluation, and selection
  - Membrane processing parameter optimization
- Albany NanoTech, University at Albany, SUNY
  - Nanofabricated electrodes
- Celanese Ventures GmbH
  - Membrane and MEA production
  - MEA cost modeling

PROGRAM BUDGET

CY	Total $	DOE $	Contractor $
2003 Actual	$ 509,578	$ 407,662	$ 101,916
2004	$ 3,352,106	$ 2,681,685	$ 670,421
2005	$ 2,268,780	$ 1,815,024	$ 453,756
2006	$ 1,163,799	$ 931,039	$ 232,760
Total	$ 7,294,263	$ 5,835,410	$ 1,458,853

CY 2003 shortfall of $600K moved to 2004 - 06.

APPROACH - Focus 1

Screening of candidate polymers and membrane fabrication processes

- Task 1: Polymer screening and preliminary evaluation
  - Identify and standardize chemical, physical, and mechanical test methods
  - Identify potential PBI-based polymers for evaluation
  - Characterize polymers by molecular weight, phosphoric acid content, proton conductivity, and film mechanical strength
  - Identify 5 - 10 lead candidate materials for further evaluation
- Task 2: Detailed polymer characterization
  - Characterize the structure and properties of polymer films
  - Determine the relationships between polymer structure and membrane properties
  - Develop processes to produce larger quantities of material (~1 L)
  - Identify 1 - 3 candidates for continued evaluation
- Task 3: Low-cost membrane formation techniques
  - Identify the key parameters for membrane formation
  - Define the optimum processing conditions for membrane formation (e.g., polymer concentration, temperature, casting speed, humidity levels)
- Task 4: Membrane scale-up
  - Demonstrate ability to produce membranes in sufficient quantities to meet program needs.

APPROACH - Focus 2

MEA Characterization

- Task 5: 10-50 cm^2 MEA screening
  - Fabricate MEAs from membranes made from candidate and standard gas diffusion layers
  - Test at limited conditions - 120°C and 160°C, reformate with 50 ppm CO and 10,000 ppm CO
  - Operate for 10 hours
  - Combine MEA screening performance with Task 1 property screening data for downselection

- Task 6: 50 cm^2 MEA evaluation
  - Conducted detailed parametric studies of MEAs made with membranes with acceptable physical and electrochemical properties
  - Operate cells at multiple temperatures between 100 and 200°C, pressures between 1 and 3 atm (abs), hydrogen/air and reformate/air, multiple CO concentrations in reformate.
  - Combine MEA performance data with property data obtained in Task 2 for selection of final candidate materials.

- Task 7: 440 cm^2 MEA test in short stack
  - Evaluate the final membrane material(s) in short stack

- Task 8: Long-term MEA performance characterization
  - Fabricate MEAs for testing in a 50 cm^2 single cell, in a 440 cm^2 single cell, and in a 440 cm^2 short stack
  - Operate cells/stack for at least 1,000 hours under expected operating conditions
  - Determine cell degradation rate and degradation mechanism

APPROACH - Focus 3

Hardware Development and Demonstration

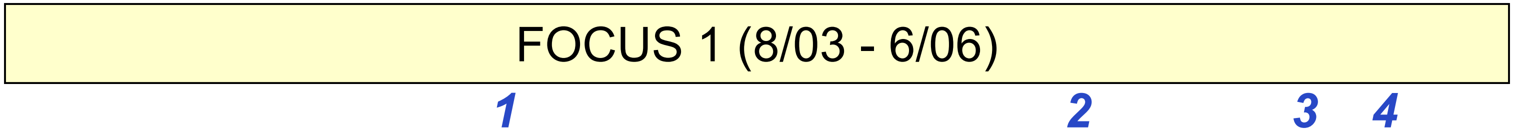
- Task 9: Acid management
  - Characterize the acid-absorbing capacity of several candidate materials under different temperature and pressure conditions.
  - Select the optimum material and design an enclosure with at least two-years of acid-absorbing capacity.

- Task 10: PBI-specific flow field design
  - Conduct CFD simulations to determine the optimum flow field geometry for PBI membranes
  - Confirm simulation results with 50 cm^2 cells
  - Design prototypical sized plates incorporating lessons learned
  - Design sealing mechanism that provides adequate sealing with minimal compression.

- Task 11: Electrode development and performance improvement
  - Develop a model of phosphoric acid electrodes to determine optimum electrode properties
  - Characterize the effects of electrode structure on performance.
  - Develop a nanostructured electrode that maximizes catalyst utilization.

- Task 12: Cost assessment
  - Build a cost projection model that incorporates data obtained during this program - membrane composition, membrane and MEA manufacturing processes, MEA performance, degradation rates, etc.
  - Project MEA costs based on anticipated market demand

SCHEDULE / MILESTONES



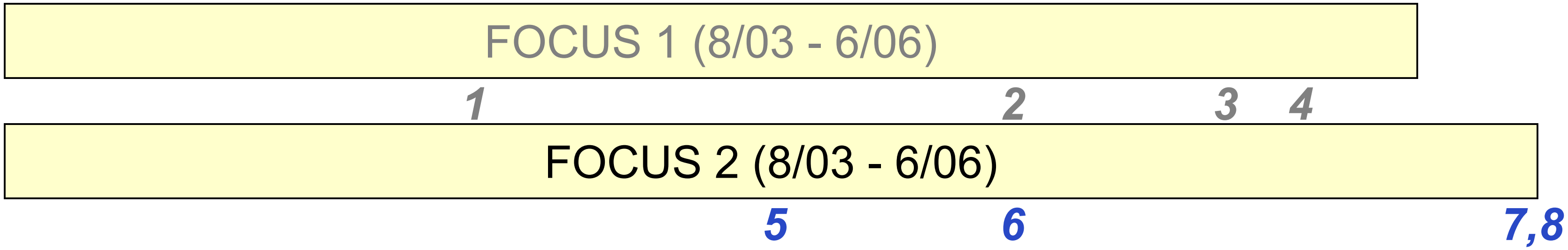
FOCUS 1 (8/03 - 6/06)

1 **2** **3** **4**

<u>Focus 1 - Polymer and membrane screening and fabrication</u>

1 *Initial list of 5 - 10 candidate materials*
2 *List of ~3 final candidate materials*
3 *Membrane fabrication process parameters defined*
4 *Full-size MEAs from scaled up process delivered for testing*

SCHEDULE / MILESTONES



FOCUS 1 (8/03 - 6/06)

1 2 3 4

FOCUS 2 (8/03 - 6/06)

5 6 7,8

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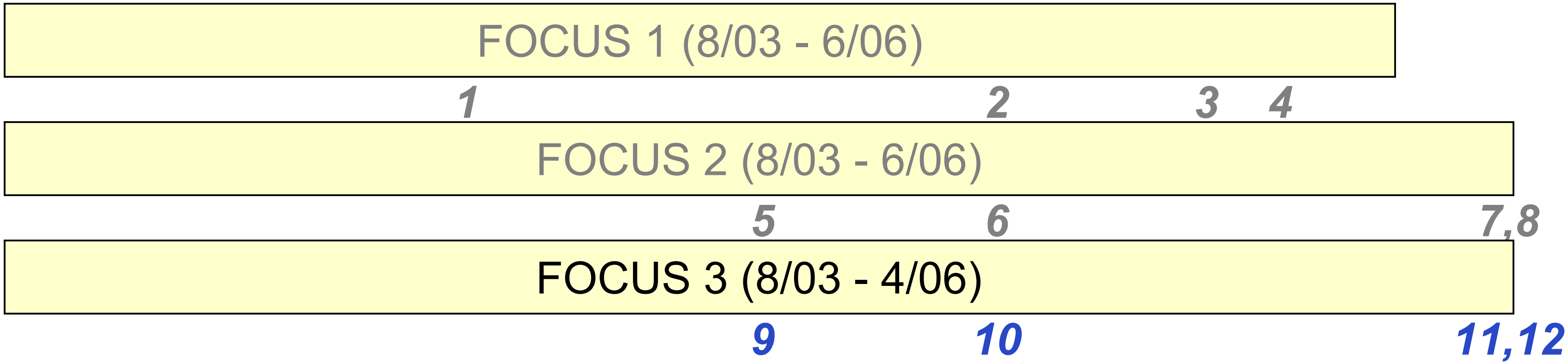
Focus 2 - MEA characterization

5 *Initial MEA screening complete*
6 *MEA electrochemical property data*
7 *Full-sized MEA testing in short stack completed*
8 *MEA degradation mechanism(s) and rate identified*

SCHEDULE / MILESTONES



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Focus 3 - Hardware development and demonstration

9 *Absorbent material and enclosure for acid management verified*
10 *Optimized flow field designed and verified*
11 *Improved electrodes demonstrated*
12 *MEA cost model and cost projections completed*

PROJECT SAFETY

- Full-time EHS manager provides oversight, training, and guidance.
- Annual laboratory safety training of all personnel and new employees.
- Laboratories designed to meet OSHA/NFPA Class I, Div. 2 requirements.
- Standard operating procedures prepared and maintained for all test and laboratory equipment.
- Safety reviews of all test systems and laboratories prior to operation.
- Chemical inventory and storage records audited annually.
- Use of an Open Safety Items tracking system to schedule and ensure closure of any identified safety issue.
- All products subjected to industry certifications as appropriate (e.g., UL, CSA, NEBS, and CE).

TECHNICAL ACCOMPLISHMENTS

Polymer Screening (Task 1)

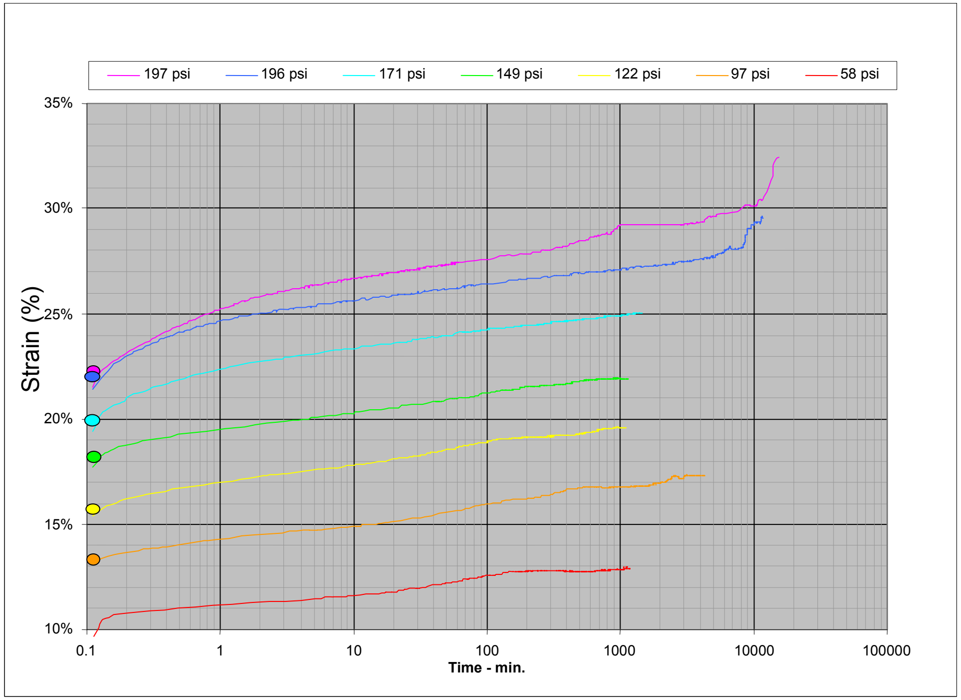
Composition	IV (dL/g)	Polymer Content (wt%)	Acid Content (wt%)	Water Content (wt%)	$n(H_3PO_4)/n(PBI)$	Conductivity (S/cm) at 160° C
1	2.9	6	65	30	38	0.18
2	4.1	4	72	24	49	0.18
3	0.8	15	60	25	46	0.2 (*)
4	1.7	6	80	14	42	0.2 (*)
5	1.2	21	63	16	10	0.1

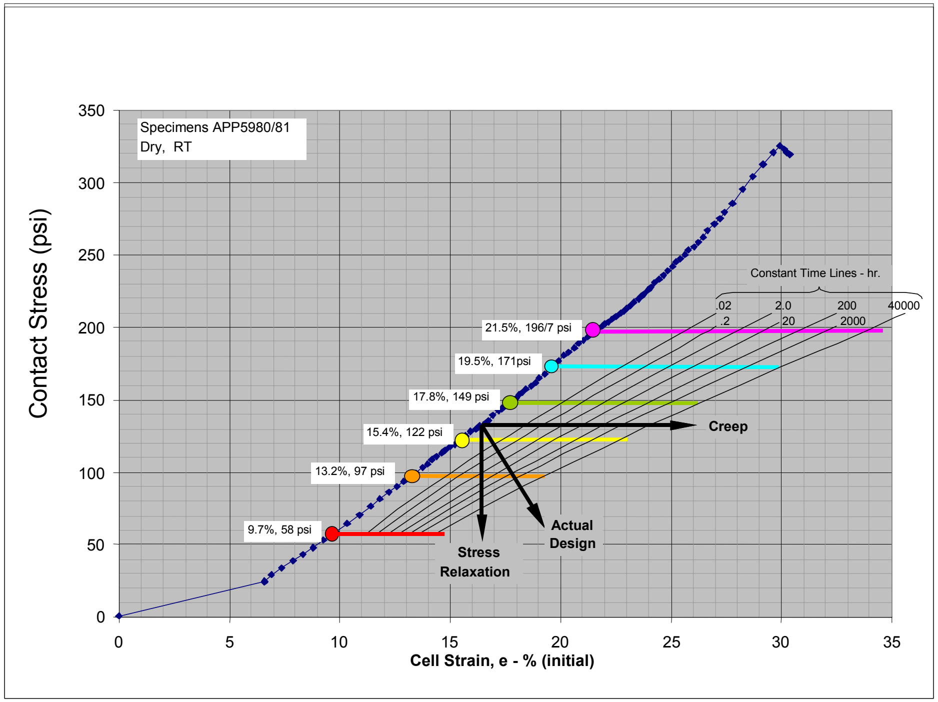
(*) Measured at 140°C; membrane melted at 160°C.

- First 5 PBI compositions identified, each with a unique chemical structure.
- Membranes were made from each of the first 5 polymers.
- High molecular weight polymers were obtained (typical plant-grade PBI inherent viscosity is 0.8 - 1.0 dL/g).
- All of the phosphoric acid contents obtained were greater than previously reported for PBI materials.

TECHNICAL ACCOMPLISHMENTS

Membrane Characterization (Task 2)

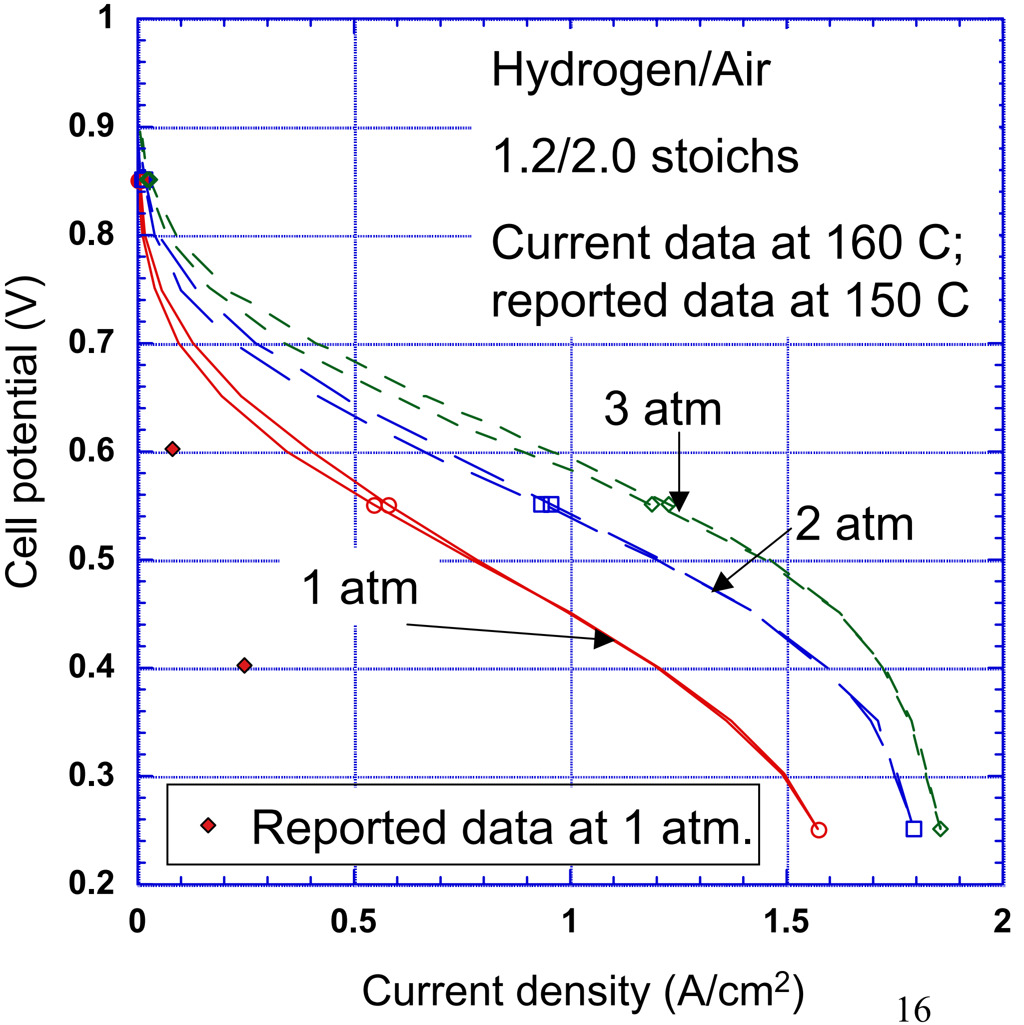




- Membranes exhibit a high initial rate of creep under constant load.
- This behavior has significant ramifications for stack design.
- Membrane behavior will affect the design of stack seals, end hardware, and plates.

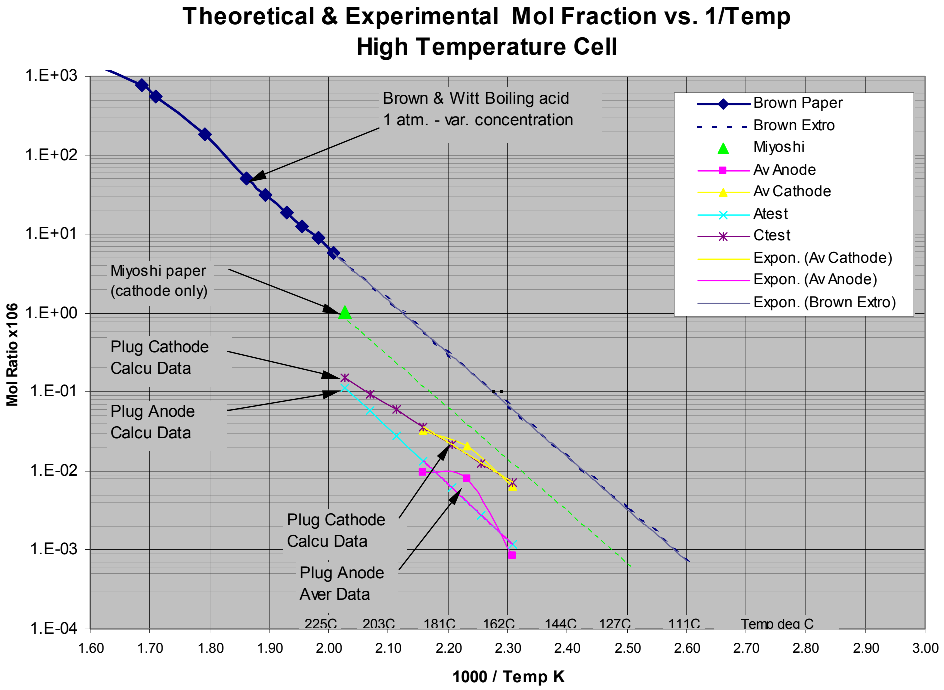
TECHNICAL ACCOMPLISHMENTS
MEA Screening (Task 5)

- MEA performance exceeds previously reported polarization data.
- Measured pressure effect: $\Delta V\ (\text{mV}) = 75 \log(P_2/P_1)$
- PAFC theoretical value: $\Delta V\ (\text{mV}) = 146 \log(P_2/P_1)$



TECHNICAL ACCOMPLISHMENTS
Acid Management (Task 9)

- Identified the mechanisms for acid transport in and from a cell:
  - Diffusion
  - Capillary transport
  - Compression
  - Evaporation
- Steady state phosphoric acid evaporation losses were studied on the current membrane and found to be less than theoretical.
- Isolating a cell from test station prevents phosphoric acid loss during startup and shutdown .

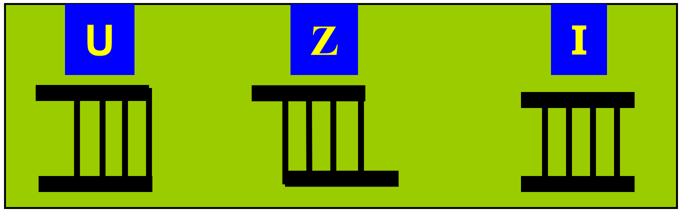


Theoretical & Experimental Mol Fraction vs. 1/Temp
High Temperature Cell

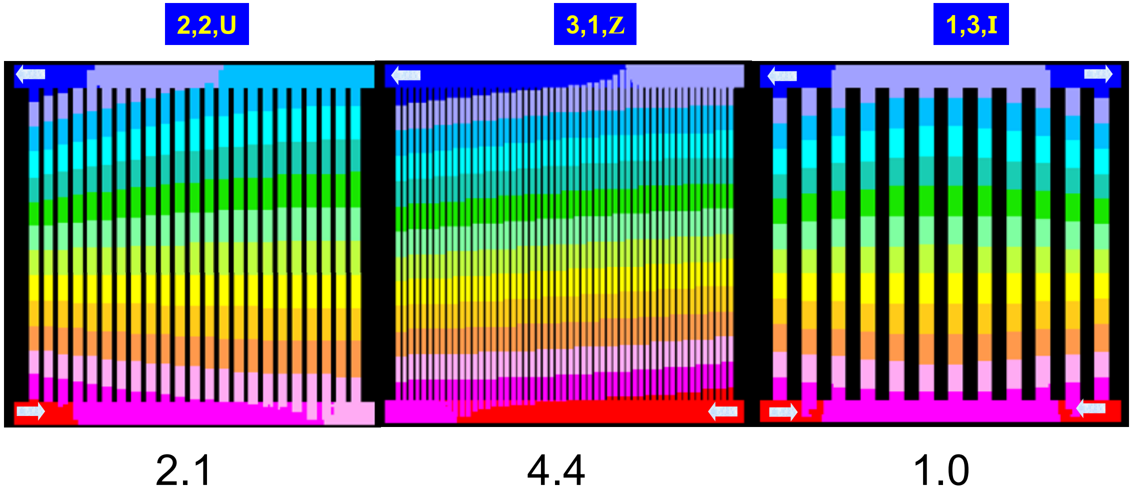
Projected cell life is 40,000 hours with these loss rates.

TECHNICAL ACCOMPLISHMENTS
Flow Field Optimization (Task 10)

Experiment number	Channel/land ratio	Relative channel width	Relative flow area	Manifold configuration
1	1.0	1.0	1.0	U
2	1.0	2.0	2.0	Z
3	1.0	3.0	3.0	I
4	2.0	1.0	2.0	I
5	2.0	2.0	3.0	U
6	2.0	3.0	1.0	Z
7	3.0	1.0	3.0	Z
8	3.0	2.0	1.0	I
9	3.0	3.0	2.0	U



Pressure distribution - Relative flow area = 3.0



Relative ΔP between inlet and outlet

- Flow uniformity decreases as flow area increases.
- Channel width does not impact flow distribution.
- Channel-to-land ratio does not impact flow distribution.
- Manifold size and configuration strongly impact flow uniformity and pressure distribution.

KNOWLEDGE AND TECHNOLOGY TRANSFER ACTIVITIES

- Elter, John, “IPHE as Facilitator of Hydrogen and Fuel Cell Markets for Stationary Applications,” Presentation to the International Partnership for a Hydrogen Economy, Washington, DC, November 2003.

- “NextGenCell - The next generation of stationary fuel cells,” Expression of Interest submitted to the European Commission, Plug Power Inc., Vaillant GmbH, and Celanese Ventures GmbH, March 2004.

- Benicewicz, Brian, “PBI Membranes and MEAs for Stationary and Automotive Applications,” Presentation to Los Alamos National Laboratory, Los Alamos, New Mexico, March 2004.

- Benicewicz, Brian, “PBI Membranes and MEAs for Stationary and Automotive Applications,” Presentation to University of New Mexico, Albuquerque, New Mexico, March 2004.

FUTURE WORK

- Remainder of 2004:
  - Prepare additional polymers and membrane materials for testing.
  - Test and evaluate lead candidate materials in 50 cm^2 single cells.
  - Characterize the physical and mechanical properties of the lead candidate materials.
  - Develop a concept to manage acid loss.
  - Design a prototypical size PBI-specific flow field.

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- 2005 - 2006:
  - Downselect to the 1 - 3 polymers that show highest likelihood of achieving the program performance, reliability, and cost goals.
  - Complete an in-depth parametric characterization of final candidate materials.
  - Complete and verify an optimized flow field design in a short stack.
  - Complete and demonstrate appropriate acid management hardware.
  - Determine and understand the MEA degradation rate in a short stack.
  - Demonstrate a PBI-based MEA that meets or exceeds program goals in a short stack.
  - Develop and exercise a model to project MEA cost at high volumes.

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