Montana PEM Membrane Degradation Study

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Montana State University

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Project ID FCP1

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: 11/30/02
- Project end date: 9/30/05
- Percent complete: 85%

Budget

- Total project funding
  - $804,836
  - $217,685
- Funding received in FY04 - $268,278
- Funding for FY05 - $268,278

Barriers

- Barriers addressed
  - DOE Technical Barrier for Fuel Cell Components
    - P. Durability
  - DOE Technical Target for Fuel Cell Stack System for 2010
    - Durability 5000 hours

Partners

- Interactions/ collaborations

Objectives

- The overall objective is to determine membrane degradation mechanisms and how to prevent or mitigate them.
  - Determine changes in membrane materials properties as degradation occurs
  - Determine if any electrical properties can act as a signature of developing degradation.
  - Investigate the potential of advanced control systems to prevent degradation problems

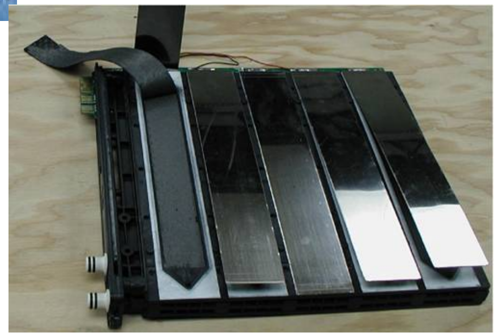
Approach

- Develop a system for monitoring current and voltage output for each individual membrane in a stack.
  - High sampling rate and permanent storage of data
- Develop characterization techniques that can reveal changes in materials properties that occur upon degradation.
  - Magnetic Resonance microimaging
  - Synchrotron based x-ray microimaging

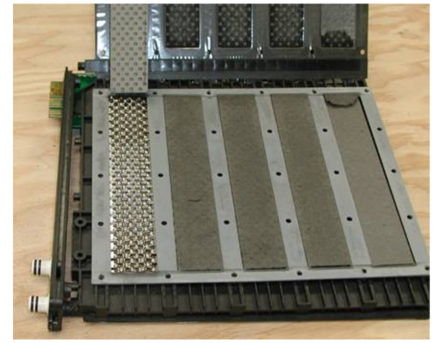
Technical Progress

- 80 membranes/ FC enclosure
- Measure voltage for each individual membrane, current and temperature at 2000 Hz rate.
- Total of 224,000 data points per seconds will be stored.
- Data permanently stored to two 1.4 Tera byte RAID -5 hot-swap arrays.
- Provides a record of performance of each individual membrane over its entire life span.
- Cells run for an extended period

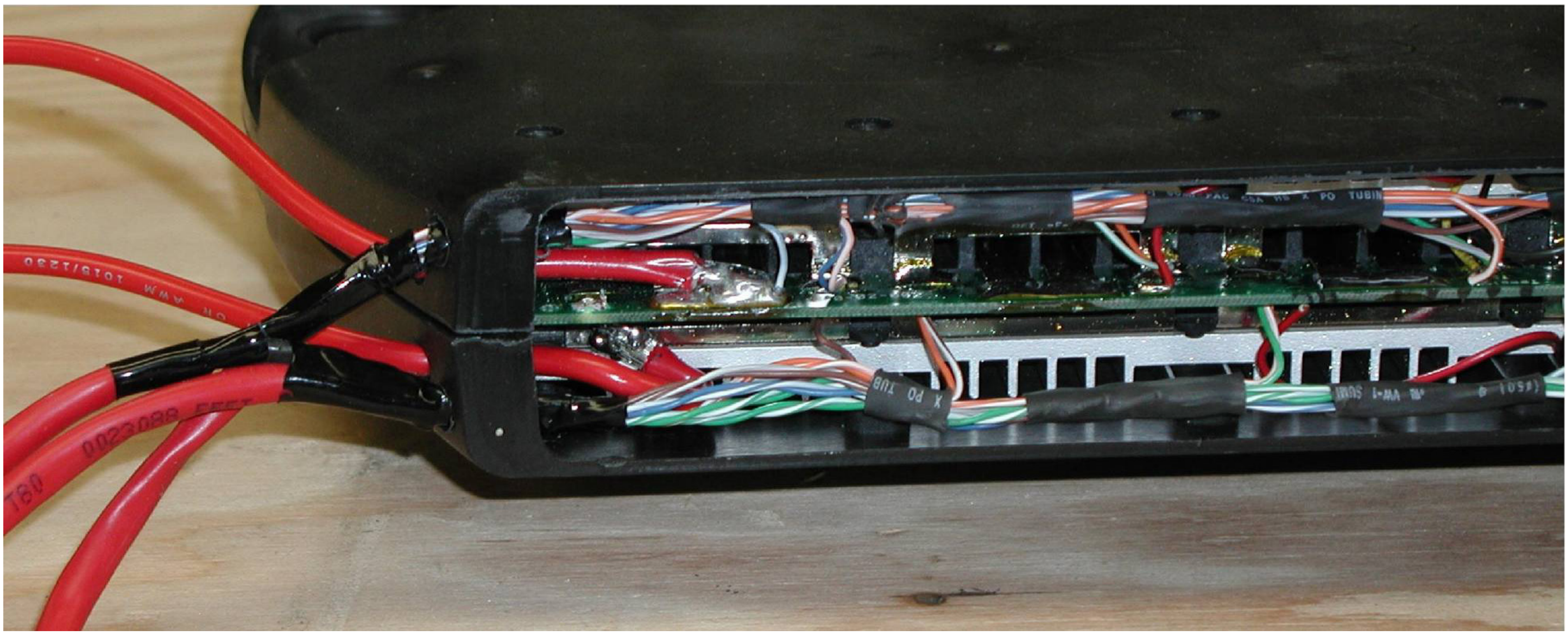
Technical Progress



Anode (H2 side) Current Collectors

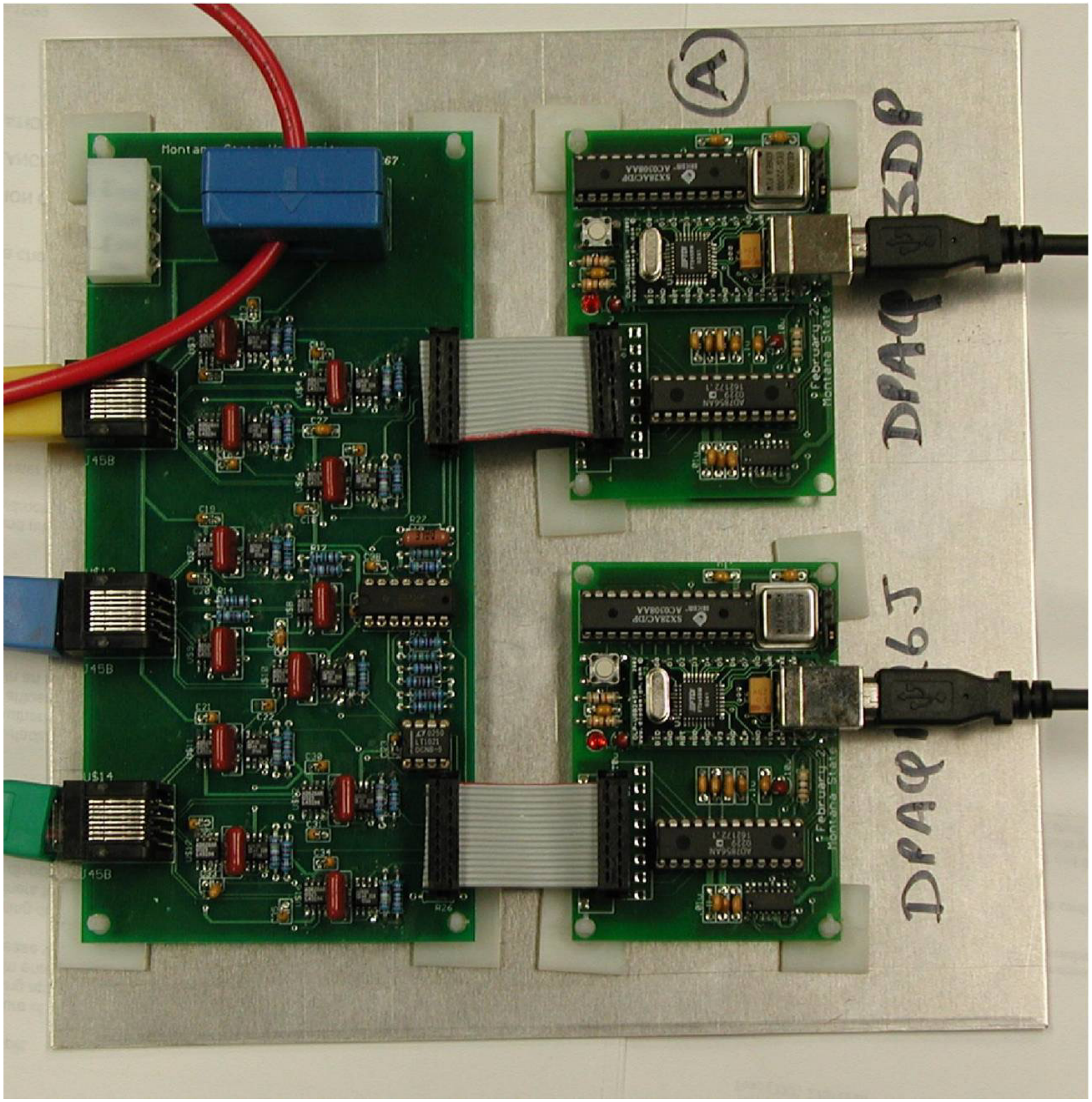


Cathode (Air Side)



Cartridge Modifications made to accommodate current and voltage sensors for each cell, temperature for each half cartridge.

Technical Progress

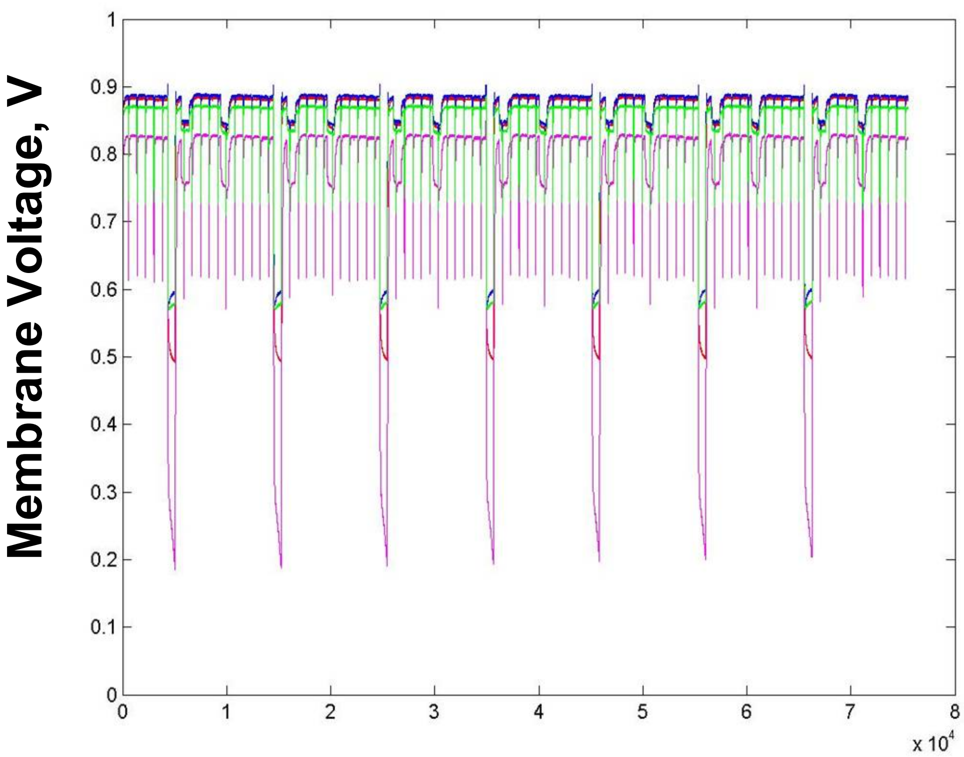


Digital to analog converter designed specifically for this project. Buying a commercially available DAC would have been cost prohibitive because of the large number of MEAs to be monitored.

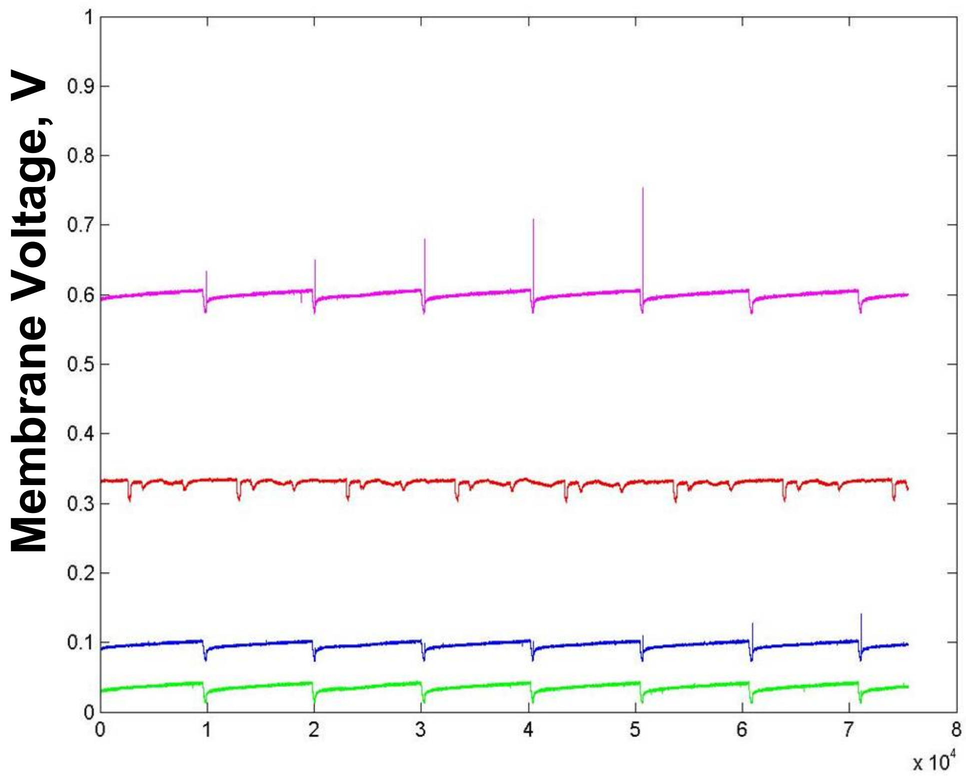
Technical Progress

PEM Degradation

Example #1: Four membranes (from Cartridge 1) under observation



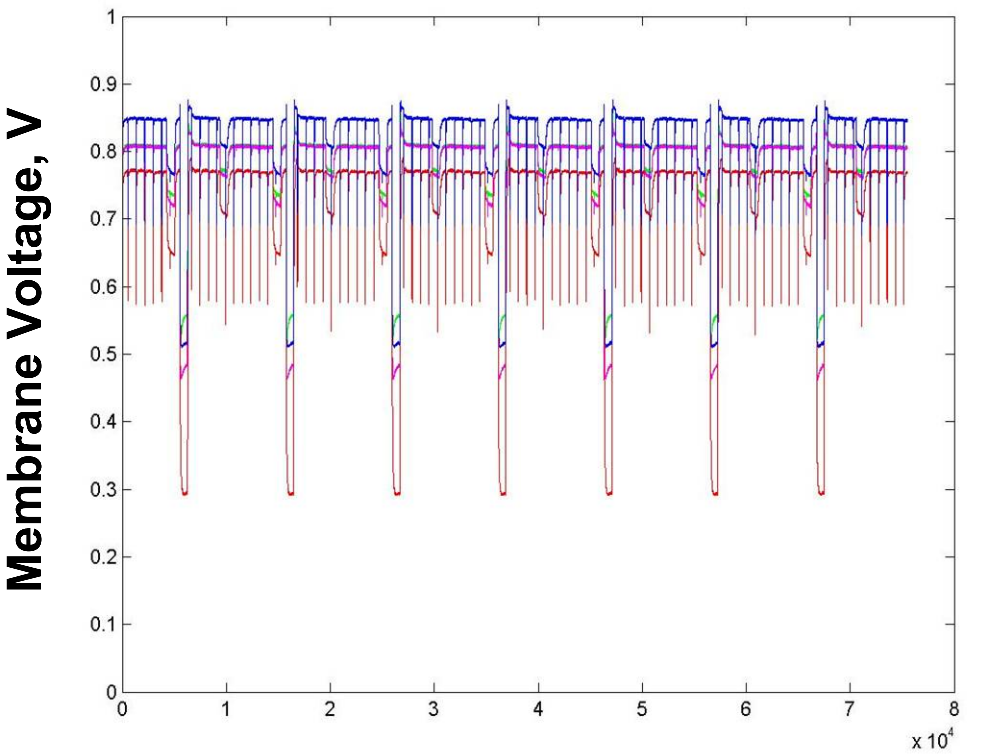
Un-degraded membranes, Aug 24, 2004



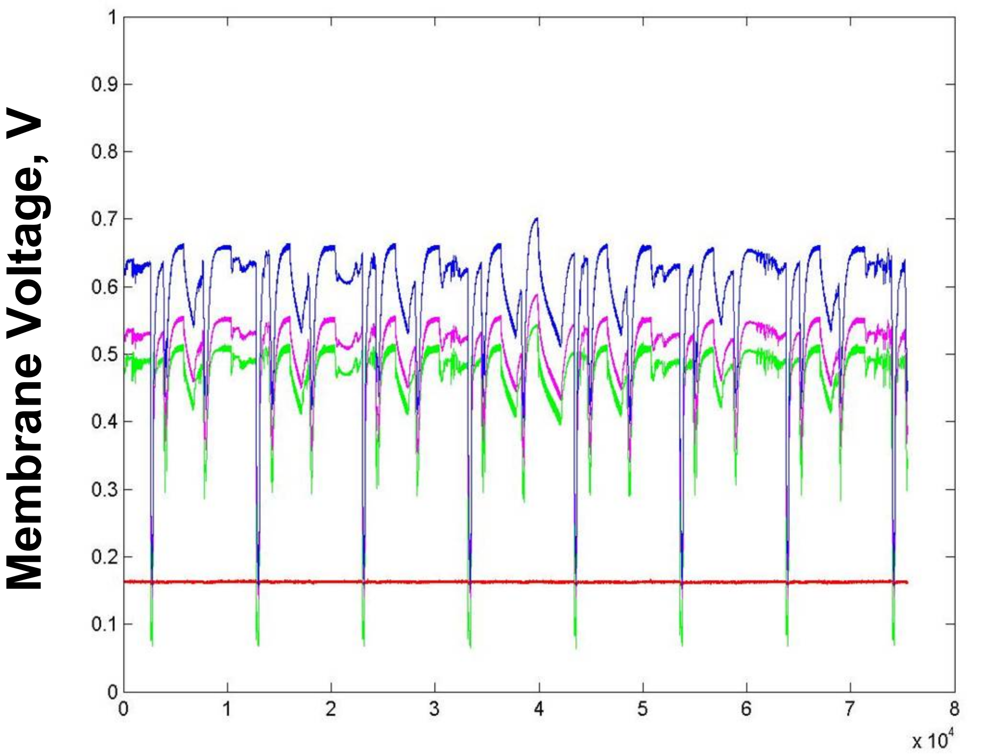
Degraded membranes, Nov 1, 2004

PEM Degradation

Example #2: Four membranes (from Cartridge 2) under observation



Un-degraded membranes, Aug 24, 2004



Degraded membranes, Nov 1, 2004

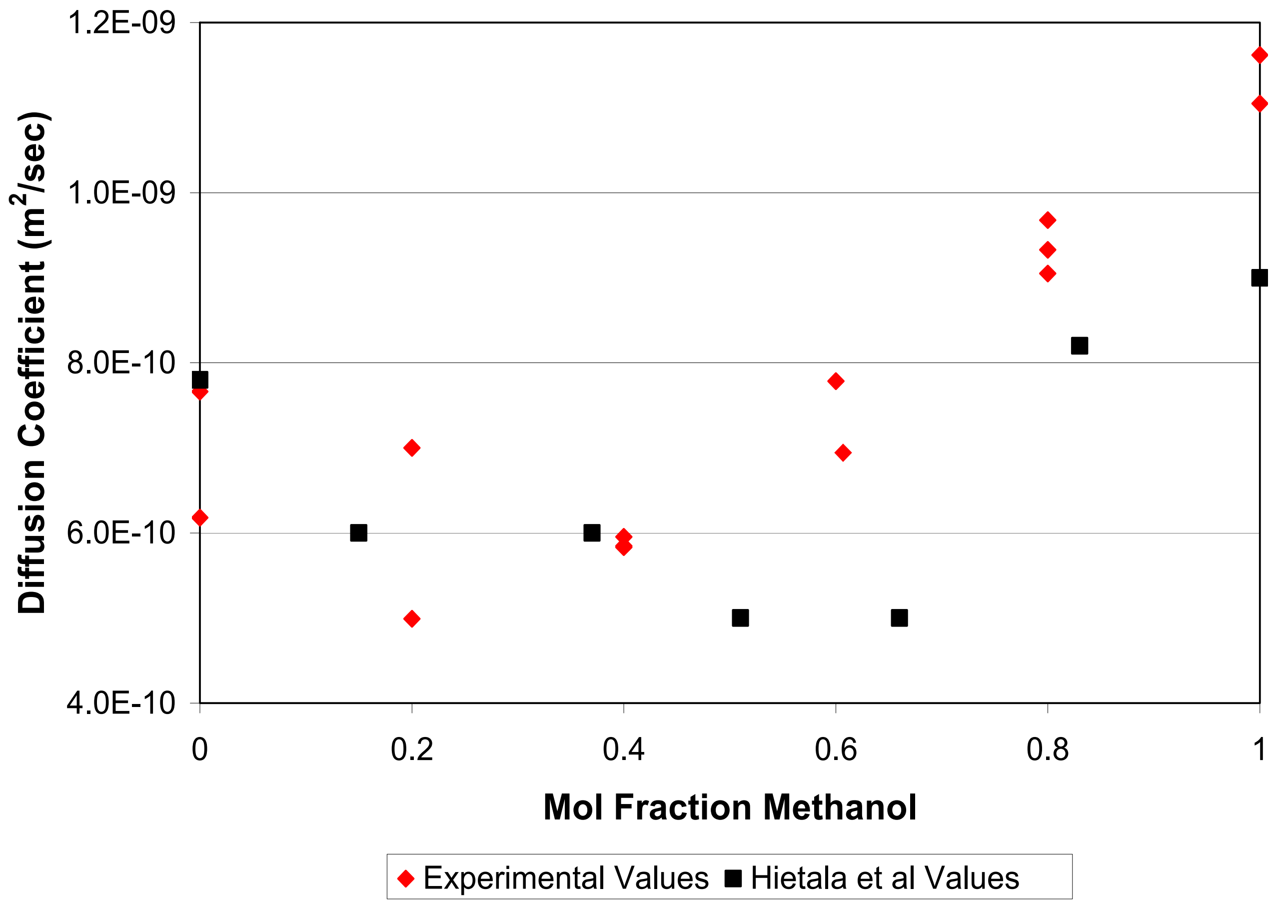
Technical Progress

- There is some variation in initial performance of cells.
- There does not seem to be a correlation between initial performance and longer term degradation.
- We are in the process of analyzing the initiation to degraded performance data to look for "signatures" of degradation / failure. Since the sampling rate is 2000 points/sec, this generates over 5 billion data points per cell per month. We are looking into efficient ways to analyze the data.

Technical Progress

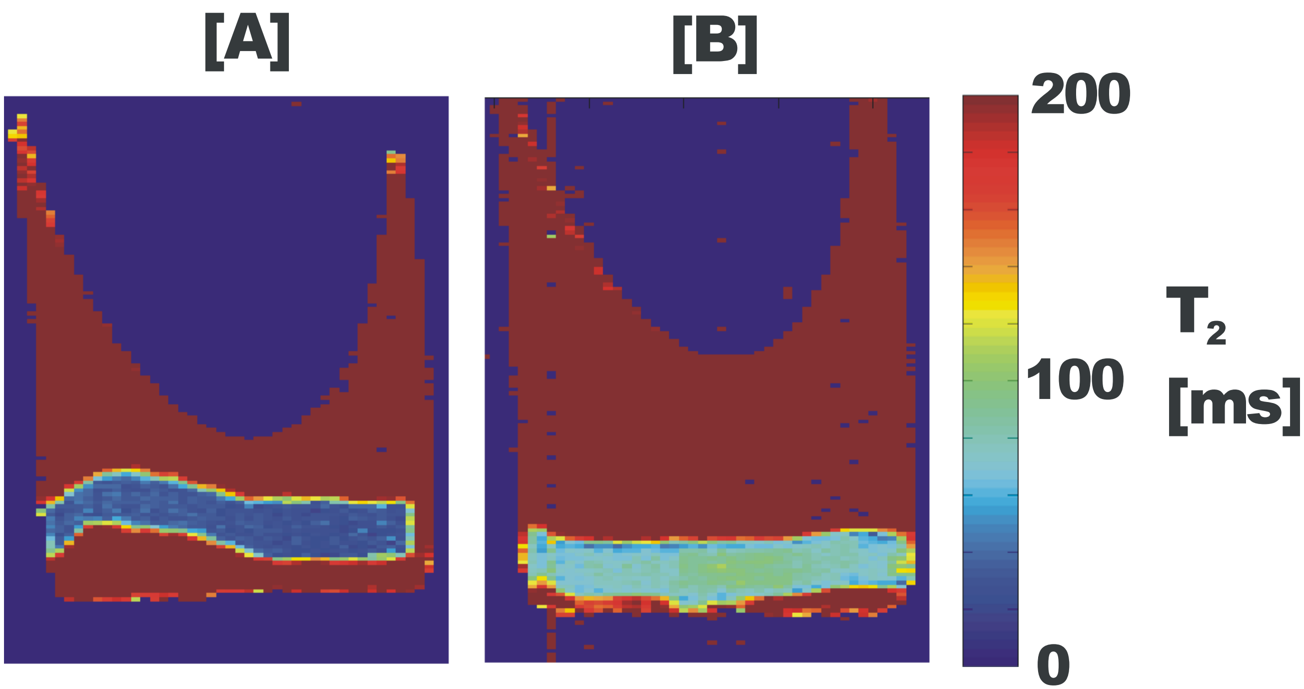
- Spatially resolved experimental solvent molecular self-diffusion as a function of MeOH concentration compared to bulk measurements of [S. Hietala, S. L. Maunu and F. Sundholm, *J. Polym. Sci. B Polym. Phys.* **38** 3277 (2000).]
- Bulk measurement on 2 cm rolled up sample, spatially resolved on single PEM.
- Variation in individual 10 mm disks of PEM's is significant.
- MeOH generates an initial decrease in solvent mobility within the polymer network, mirroring the pure solvent decrease in diffusion at mole fractions below ~0.5 and then generates increased mobility

Solvent Diffusion in Nafion® 117



Technical Progress

T_2 maps of Nafion® 117 Hetrogeneity

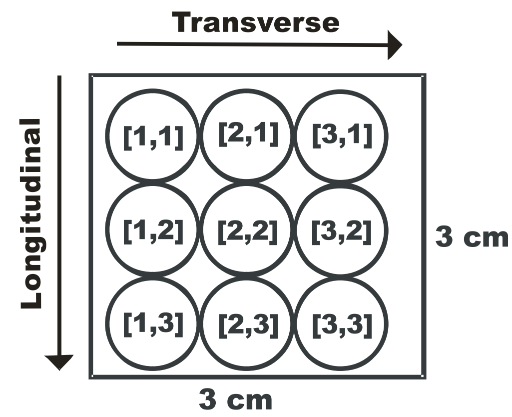


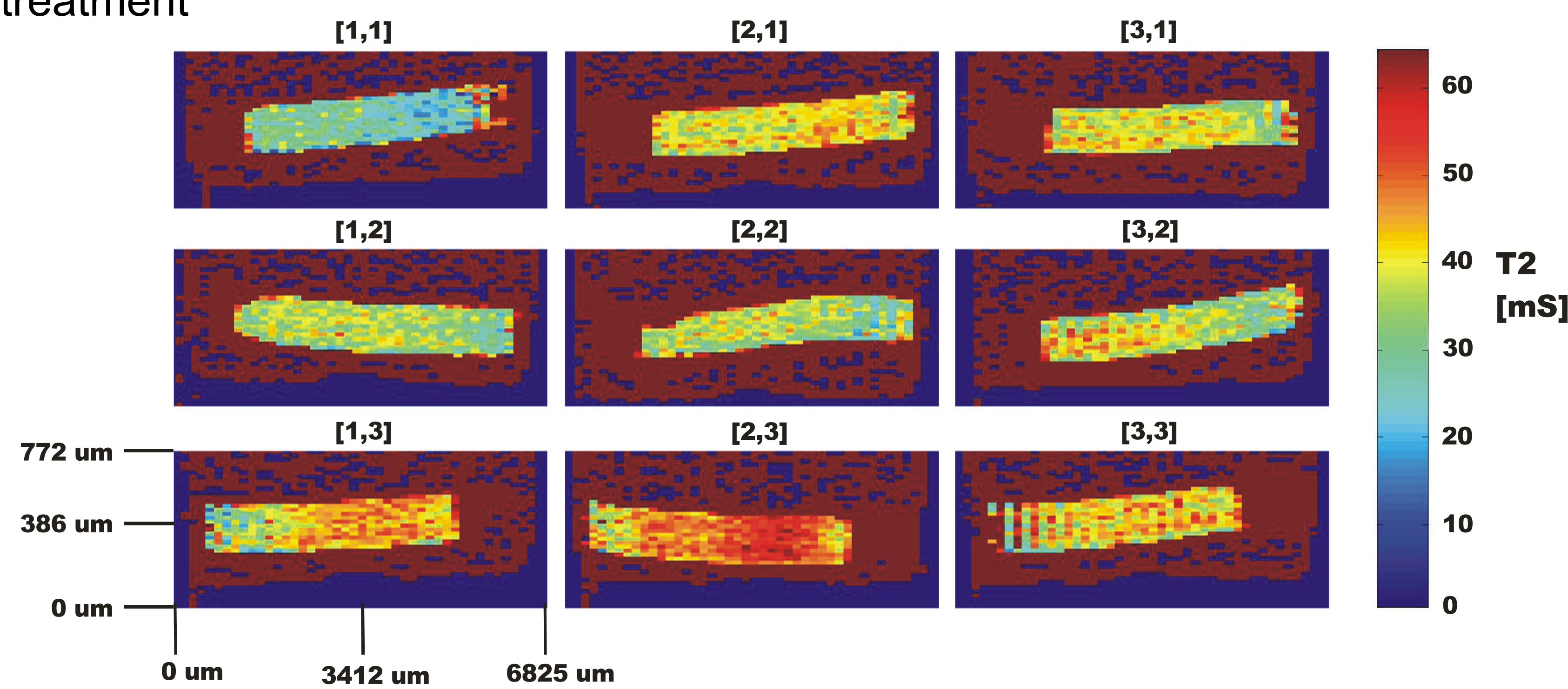
PEM's prepared identically in X_{MeOH} = 0.6 show very different solvent mobility, in [B] T_2 = 68 ms and in [A] T_2 = 22 ms indicating more molecular restriction in [A]

Technical Progress

- Significant heterogeneity in solvent
molecular mobility is evident on the scale of the image resolution 19.5 μm/pixel in the vertical and 156 μm/pixel horizontal as well as on scales of 10 mm from disk to disk cut from the 3 cm sample prepared in a single chemical treatment

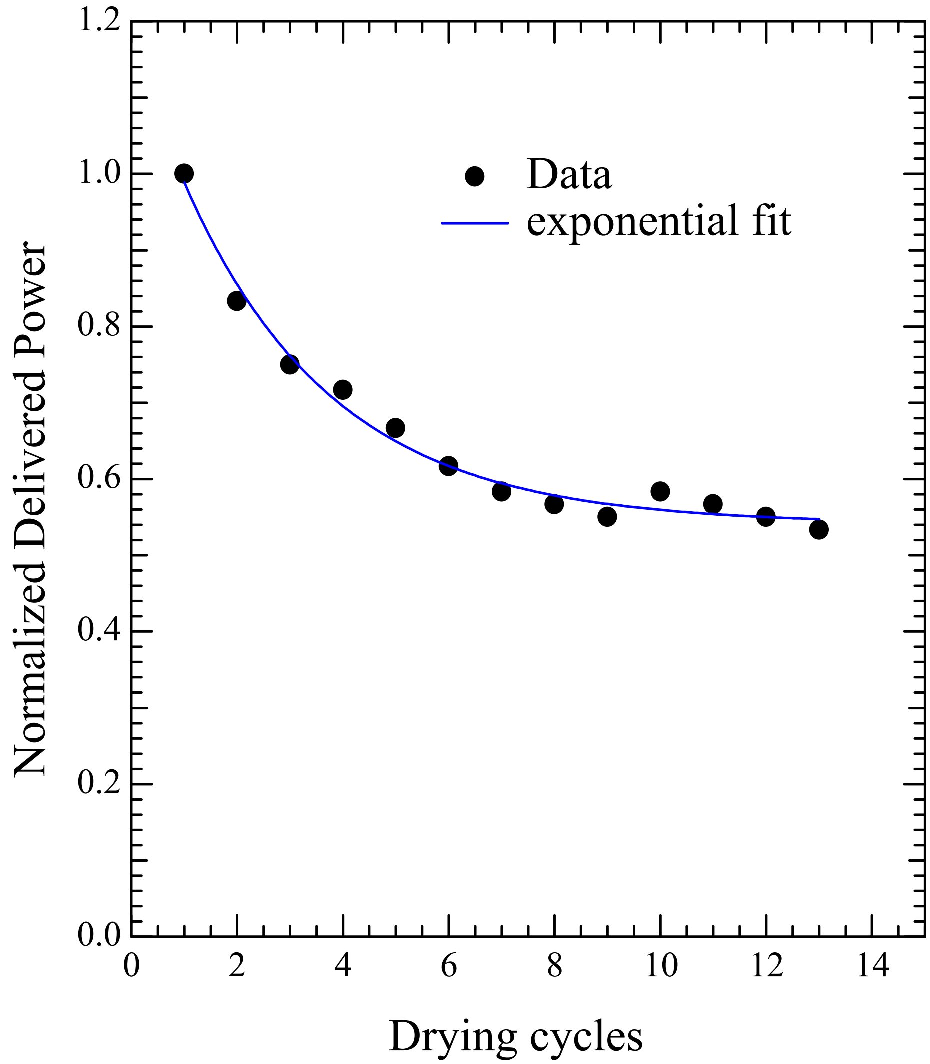
T_2maps of Nafion® 117 Hetrogeneity





Technical Progress

Membrane performance degradation with repeated severe hydration/drying cycles showing a nearly 50% reduction in maximum deliverable power.



Technical Progress

- In some single-cell experiments time-dependent I-V response curves of abrupt loading of the fuel cell suggest that degradation is due to reduced hydrogen diffusion through the membranes.
- Spatially resolved X-ray characterization of the before and after membranes, show no change in chemical make-up, although a small sulfur peak with nearly uniform spatial distribution was found.

Future Work

- Compare spatially resolved x-ray studies with spatially resolved MRI data for new and degraded (by thermal, humidity, and load cycling) membranes to determine hydrogen diffusion variability.
- Analyze I-V data to look for electrical “signitures” of failure.

Responses to Previous Year Reviewers' Comments

- No reviewer comments were provided.

(See Notes page for further information)

Supplemental Slides

The following three slides are for the purposes of the reviewers only – they are not to be presented as part of your oral or poster presentation. They will be included in the hardcopies of your presentation that might be made for review purposes.

Publications and Presentations

- C. Chen, R. Baker, D. Resnick, E. Negusse, and Y.U. Idzerda; “Identification of Mechanisms for PEM Membranes by Power Utilization Curve Analysis” (2004 - in preparation).
- A. Lussier, D. Larsen, and Y.U. Idzerda; “Performance of an X-ray Compatible cell for Fuel Cell Material Characterization” (2004 – submitted).
- C. Chen, D. Resnick, E. Negusse, and Y.U. Idzerda; “Identification of Mechanisms for PEM Membranes by Power Utilization Curve Analysis” Hydrogen, Fuel Cells & Infrastructure Technologies Review, Bozeman, MT (2004).
- R. Baker, C. Chen, D. Resnick, E. Negusse, and Y.U. Idzerda; “Solid Oxide PEM Fuel Cells” MAP Program Review Bozeman, MT (2004).
- Invited Lecture: J.D. Seymour "Magnetic resonance microscopy of scale dependent transport phenomena in bioreactors and polymer electrolyte membranes," 1st International Symposium on Micro & Nano-Scale Sensing Techniques for Energy and Bio System. Keio University, Yokohama, Japan, September 14, 2004.
- D.T. Howe, J.D. Seymour, S.L. Codd, S.C. Busse and E.S. Peterson, “NMR Microscopy of Material Inhomogeneity in Polymer Electrolyte Membranes (PEMs)”, accepted poster 8th International Conference on Magnetic Resonance Microscopy, Utsunomiya, Japan. August 22-25, 2005.
- Steven R. Shaw “Instrumentation for PEM Fuel Cell transient Degradation Monitoring” Proceeding of the IEEE PES General Meeting, Denver 2004.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

The most significant hazard is that a student drop the pressurized hydrogen gas bottle during bottle exchange and the top of the pressurized bottle is broken off, resulting in both physical damage due to the high pressure gas emission from the bottle and the possibility of the gas igniting.

Please be specific in your description. (*The most significant hazard is one that you believe is credible and could pose the greatest potential impact to personnel, and/or destruction or loss of equipment or facilities.)*

Limit your description to one slide.

Bullet comments are fine to use.

Hydrogen Safety

Our approach to deal with this hazard is:

Hydrogen gas bottles are secured to the wall at all times with protective caps on the valve in place if not in use. Any hydrogen gas bottle exchanges are performed by me and not by the students. During bottle transfers, bottles have protective caps and are always chained to the wall or the transfer dolly. For the electrical monitoring study which requires large amounts of hydrogen, an electrolyzer was purchased to eliminate the need to handle large numbers of cylinders.

Please list pertinent safety measures you are implementing and/or plan to implement. (*Cite specific standards, special measures, special operating procedures focused on this hazard, limits on personnel access, etc. that you are using to mitigate the potential impact posed by the specific hazard.)*

Limit to one slide.

Project Safety

- Hydrogen gas monitoring and containment - plexiglass box with a sensitive hydrogen leak detector to identify dangerous concentrations of H_2.