

Montana PEM Membrane Degradation Study



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This presentation does not contain any proprietary or
confidential information

- 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

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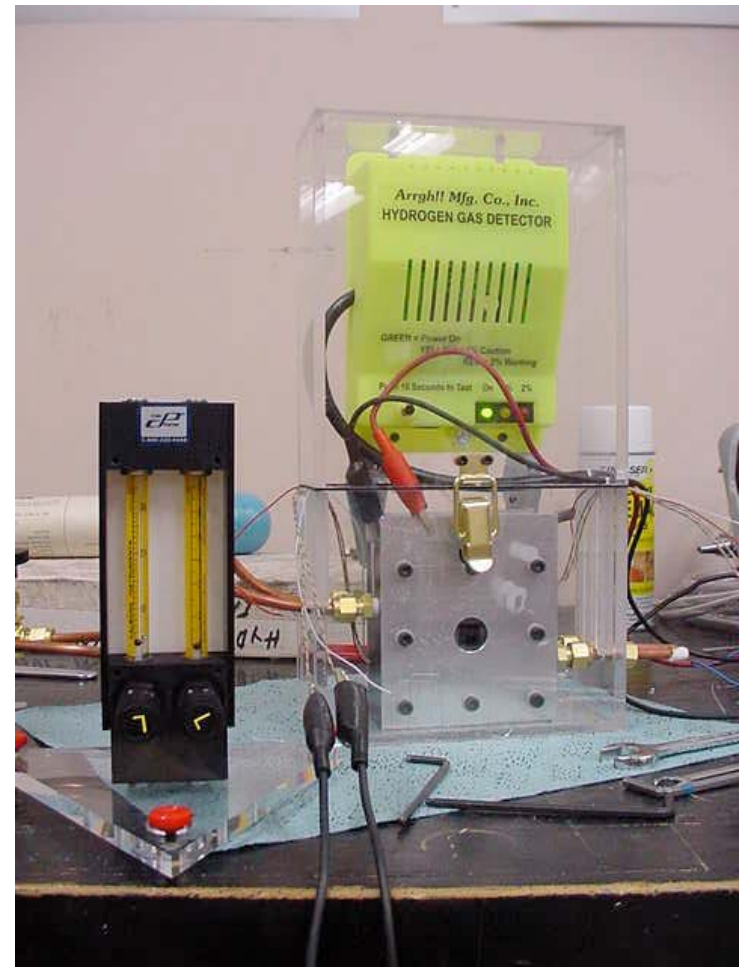
- Total Funding: \$1,022,521
- DOE Share: \$ 804,836
- Match: \$ 217,685
- FY03 Funding: \$ 281,694

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

- 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

Project Safety

- Hydrogen gas monitoring and containment - plexiglass box with a sensitive hydrogen leak detector to identify dangerous concentrations of H₂.



Project Timeline

11/02-11/03

11/03-11/04

11/03-11/04



Year 1:

- Dynamic terminal characteristic models developed for fuel cells
- Data acquisition system designed for fully instrumented fuel cells including development of A/D card that runs under LINUX
- Developed a single cell PEM FC to allow *in situ* synchrotron x-ray measurements of the cell in operation
- First MRI data of PEM's obtained using chemical treatment protocols from literature and replication of bulk NMR data in literature with spatial resolution
- PI Seymour Attended North American Membrane Society Meeting initiating contact with PEM research community
- Ordered high magnetic field gradient coil for measuring small displacements and integration into Electrophoretic NMR probe

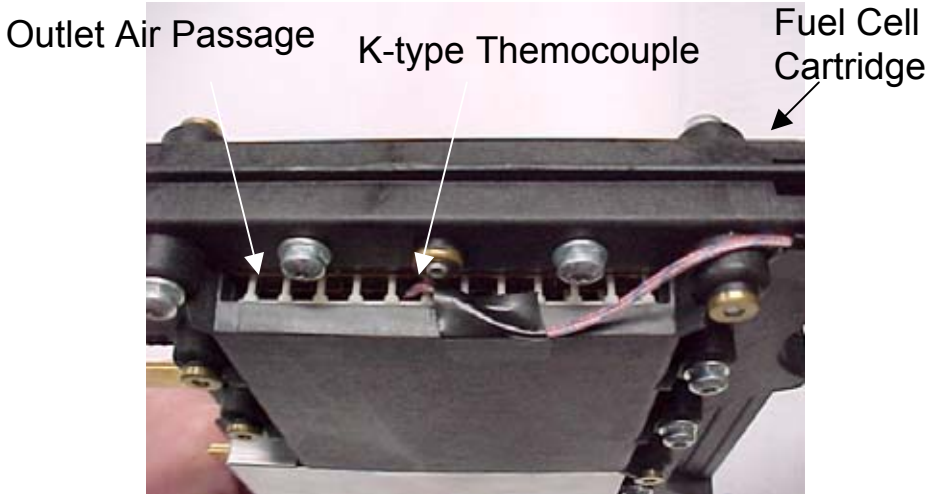
Year 2:

- Fully instrumented 2 separate 80 membrane PEM fuel cells
- Performed initial test runs to debug hardware and software in preparation for long term testing
- Performed initial x-ray analysis on degraded membranes
- Concluding study reproducing bulk NMR study of Nafion 117 solvent mobility dependence on MeOH concentration, manuscript preparation in progress
- Initiating MRI studies of PEM's after failure during Fuel Cell operation by other components of project
- Initiating combined sequential MRI and X-Ray analysis of membranes
- Construction of ENMR probe with M. Holz visiting MSU during summer or fall

Year 3:

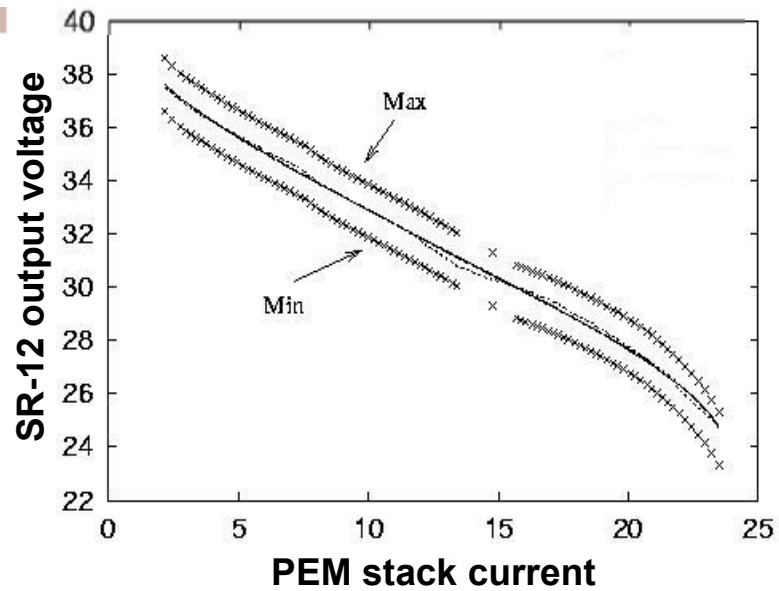
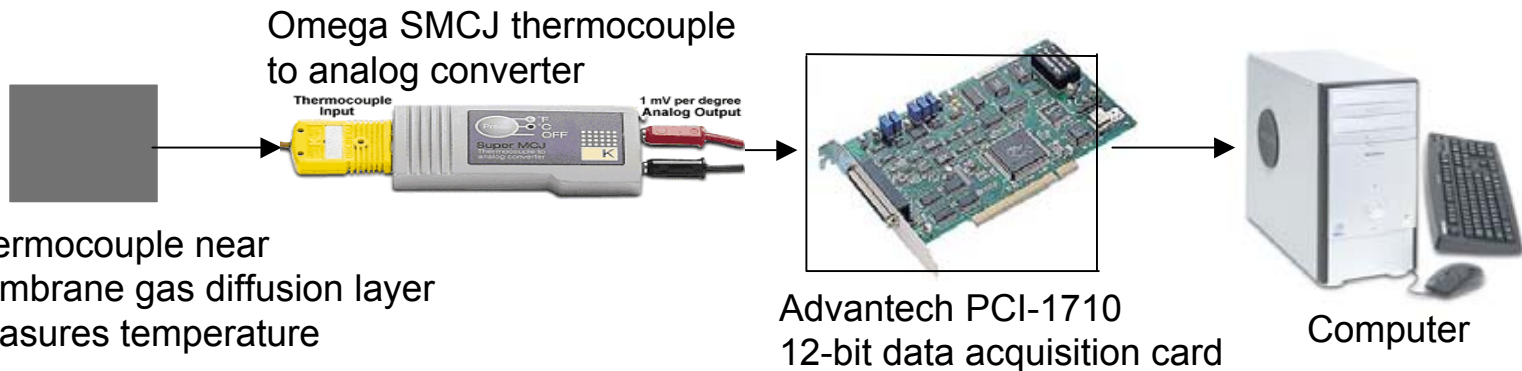
- Run long term degradation by exercising fuel cells with real world load transients
- Integration of MRI and ENMR to attempt spatial resolution of proton transport under load conditions
- Perform spatially resolved x-ray and MRI analysis of membranes at various stages of degradation as identified by electrical characterization
- Investigate control strategies that may help reduce degradation

Technical Progress



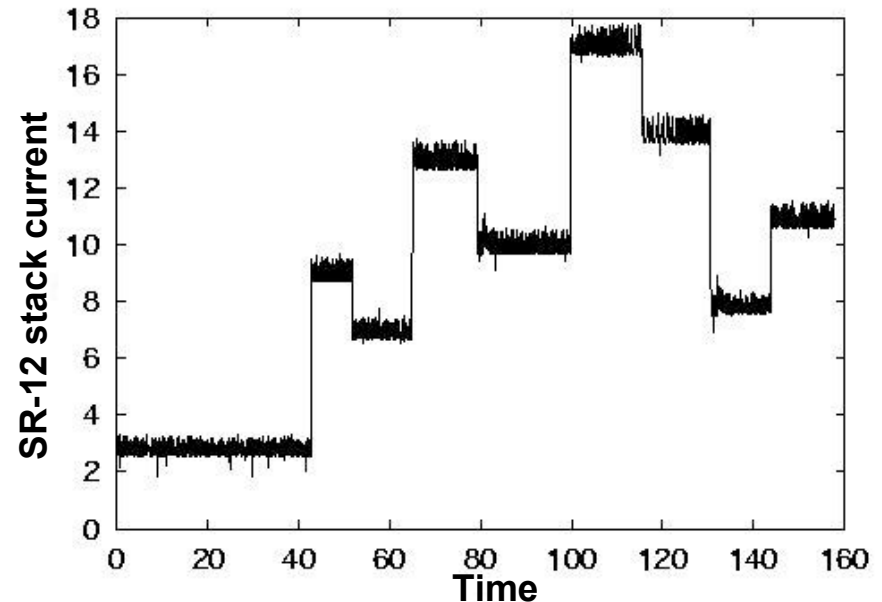
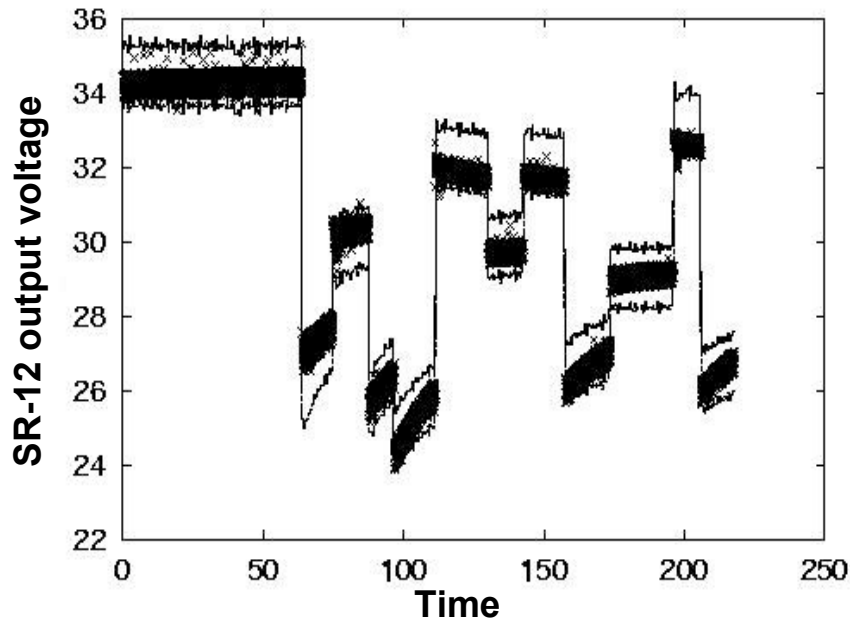
Location of K-type thermocouple in SR-12 fuel cell stack

Temperature Measurement For Dynamic Thermal Model



- # An accurate and simple physically motivated electrical terminal model for PEM fuel cell.
- # Accurate prediction of steady-state SR-12 stack voltage as a function of stack current.

Cross validation predicted SR-12 output voltage (dark line is the predicted response). Dynamic models are needed for design of multi-source and distributed power systems that incorporate fuel cells to ensure good system performance and prevent degradation.



Publications

S. Pasricha, M. Keppler and S. R. Shaw, "A Dynamic PEM Fuel Cell Model".

Technical Progress

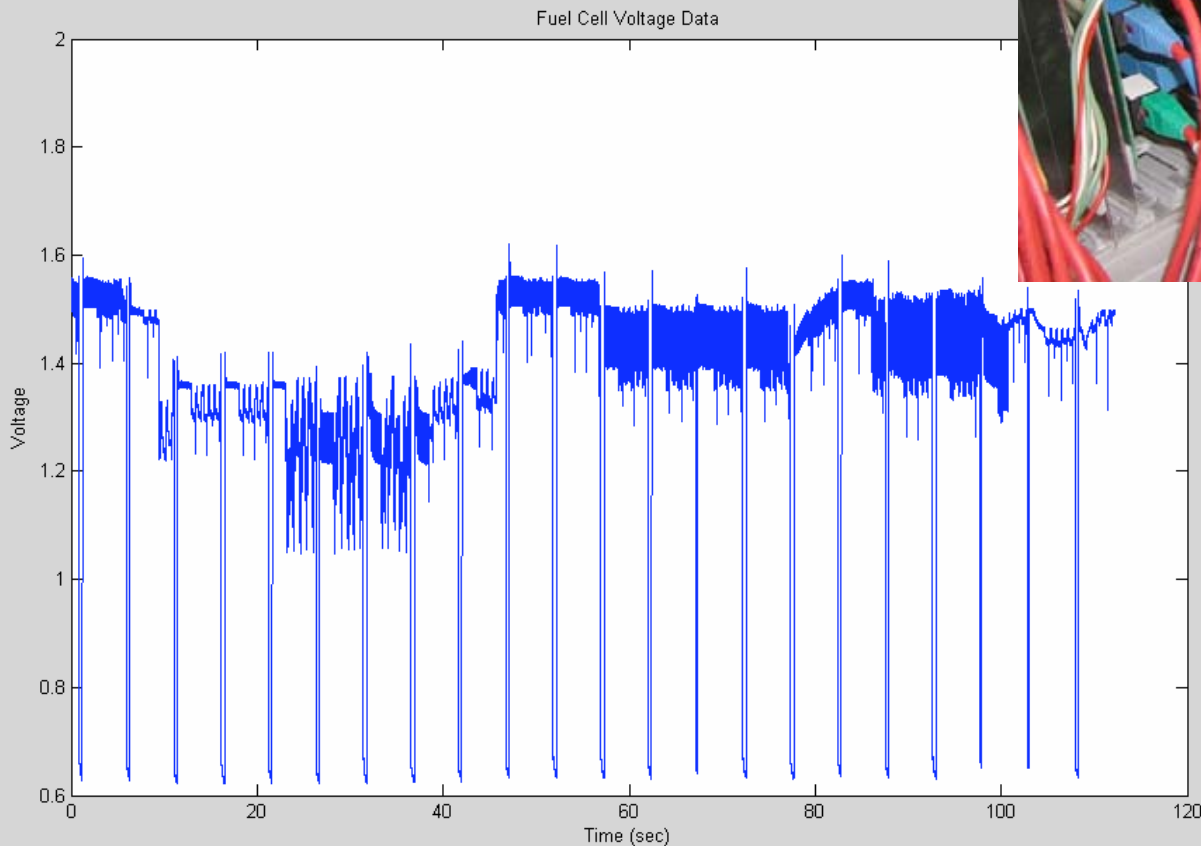
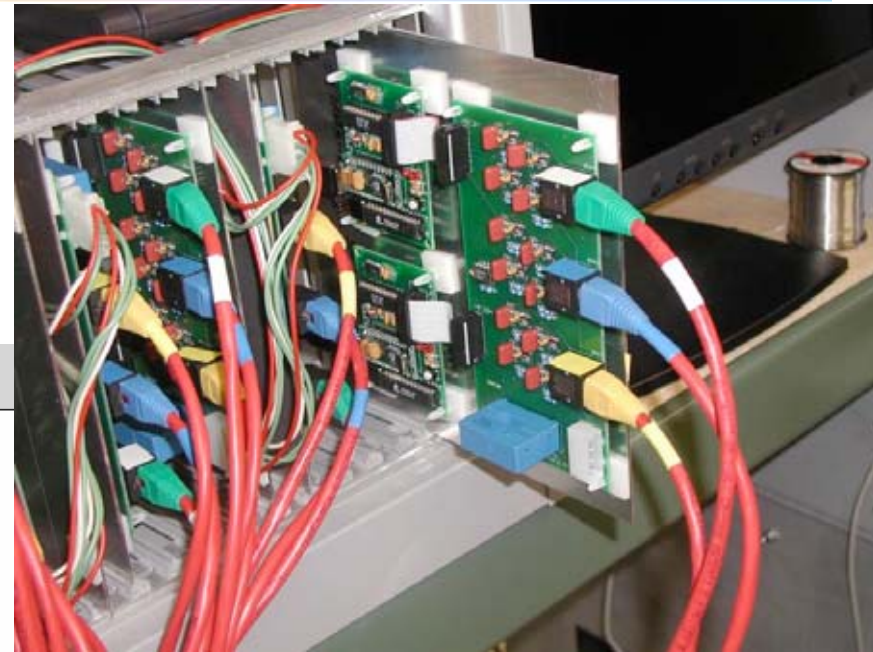
Ongoing Experiments



- 80 membranes/ FC enclosure
- Measure voltage for each individual membrane, current and temperature at a 2000 Hz rate.
- Total of **224,000 data points per second** will be stored to provide a permanent
- Data permanently stored to two 1.4 Terabyte RAID-5 hot-swap arrays.
- Provides a record of performance of each individual membrane over its entire life span.

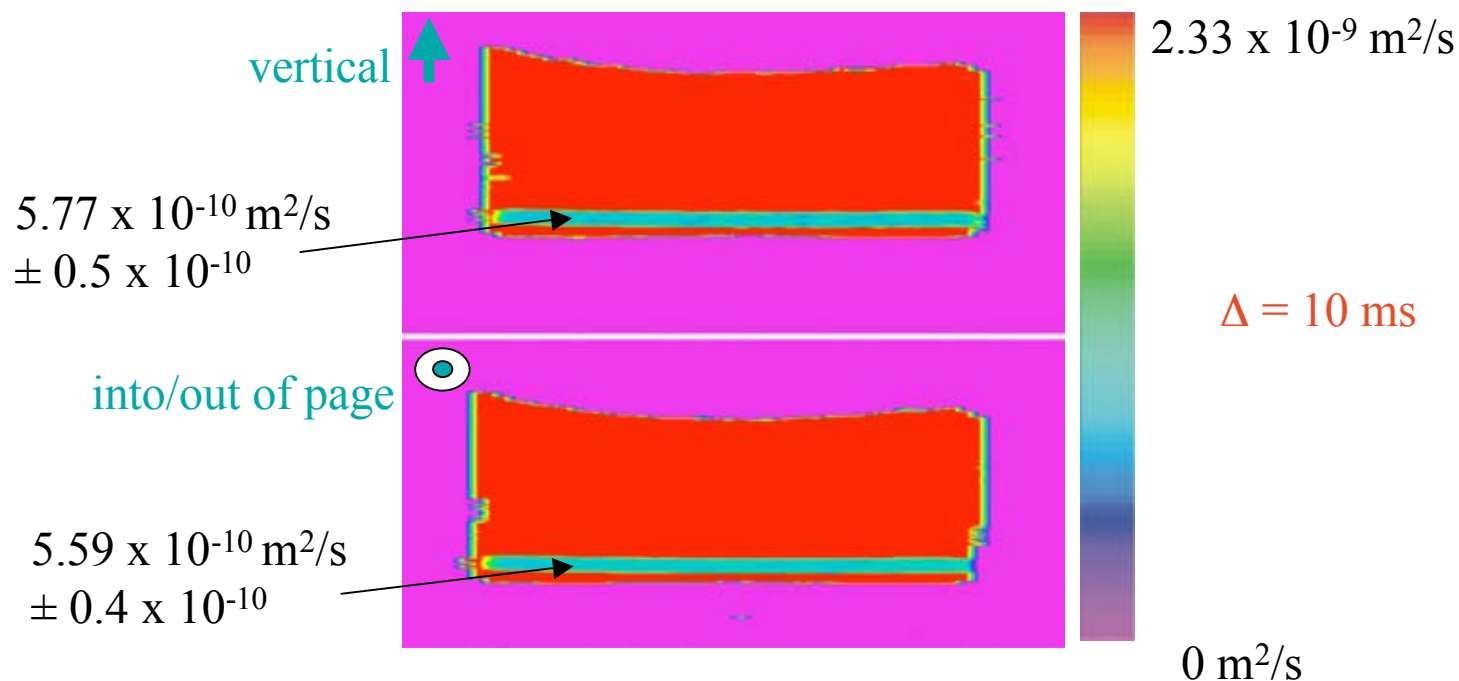
Results

Example of high resolution temporal data acquired from system. Spikes are due to FC system switching membranes on & off.



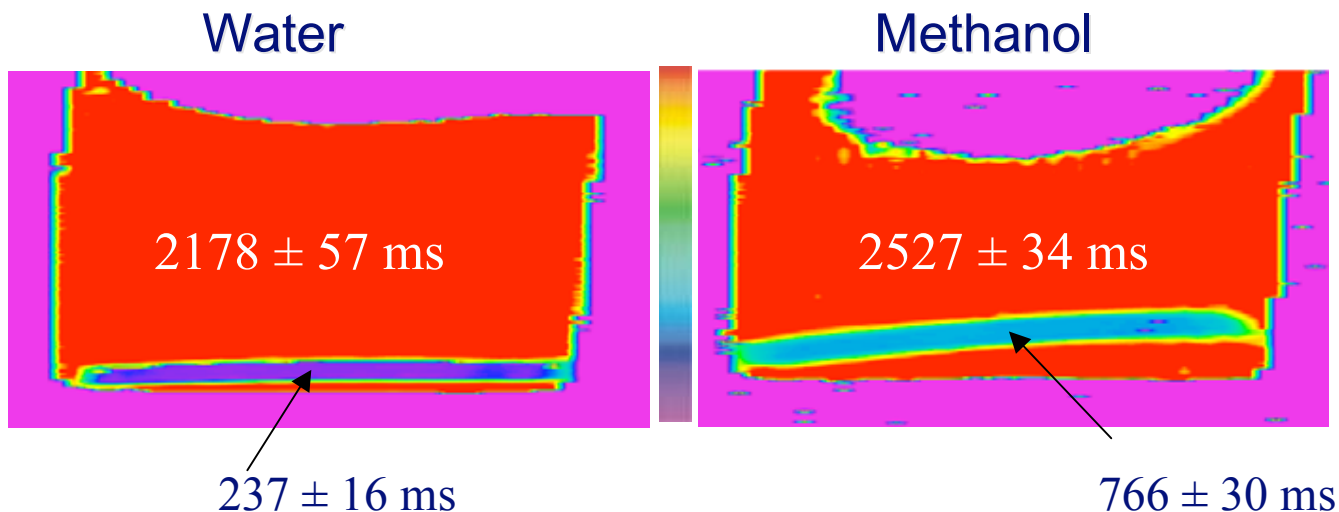
Spatially resolved data on proton mobility using T_1 and T_2 magnetic relaxation and molecular self-diffusion as a function of membrane depth have been reproduced bulk NMR measurements from literature with spatial resolution under liquid saturated conditions and as a function of MeOH concentration [S. Hietala, S. L. Maunu and F. Sundholm, *J. Polym. Sci. B Polym. Phys.* **38** 3277 (2000); B. MacMillan, A.R. Sharp and R.L. Armstrong, *Polymer* **40** 2471 (1999).]

Water Translational Self-Diffusion



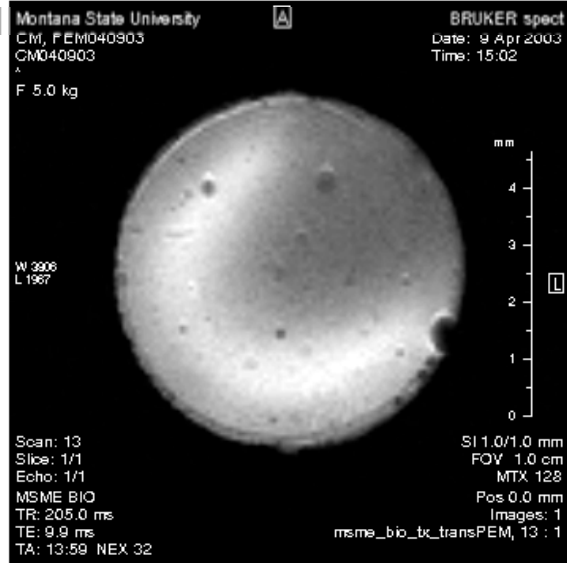
- T_1 relaxation maps showing depth distribution of mobility-high T_1 high molecular mobility; Note PEM swelling and increased mobility of MeOH relative to H₂O

T_1 maps of Nafion® 117

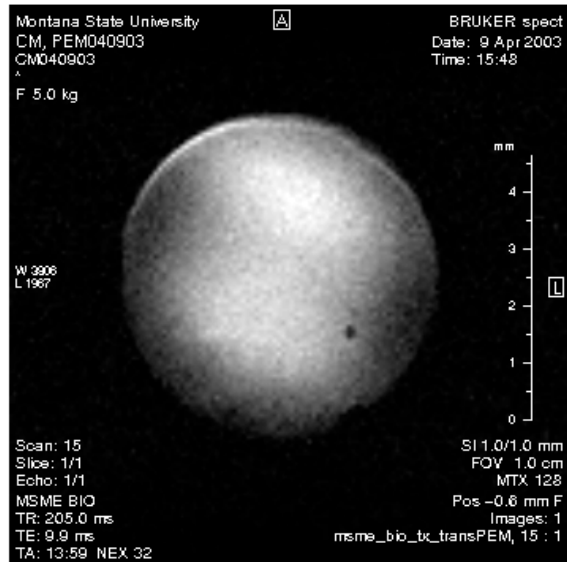


- Students Supported: James C. Mabry, Daniel Howe MS ChE
- Publications / Presentations:
 - J.D. Seymour, Sarah L. Codd, James C. Mabry, Scott C. Busse and Eric S. Peterson. "NMR microscopy of water and methanol distribution and dynamics in polymer electrolyte membranes." North American Membrane Society, 14th Annual Meeting, Jackson Hole, WY, May 17-21, 2003.
 - J.C. Mabry, S.L. Codd, S.C Busse, and J.D. Seymour, "MR microscopy of water distribution and dynamics in Polymer Electrolyte Membranes (PEMs)", 7th International Conference on Magnetic Resonance Microscopy, Snowbird, UT, Sept. 21-25, 2003. Poster P12.
- Related proposals funded: None

T₁ Weighted ¹H Intensity Images Nafion®



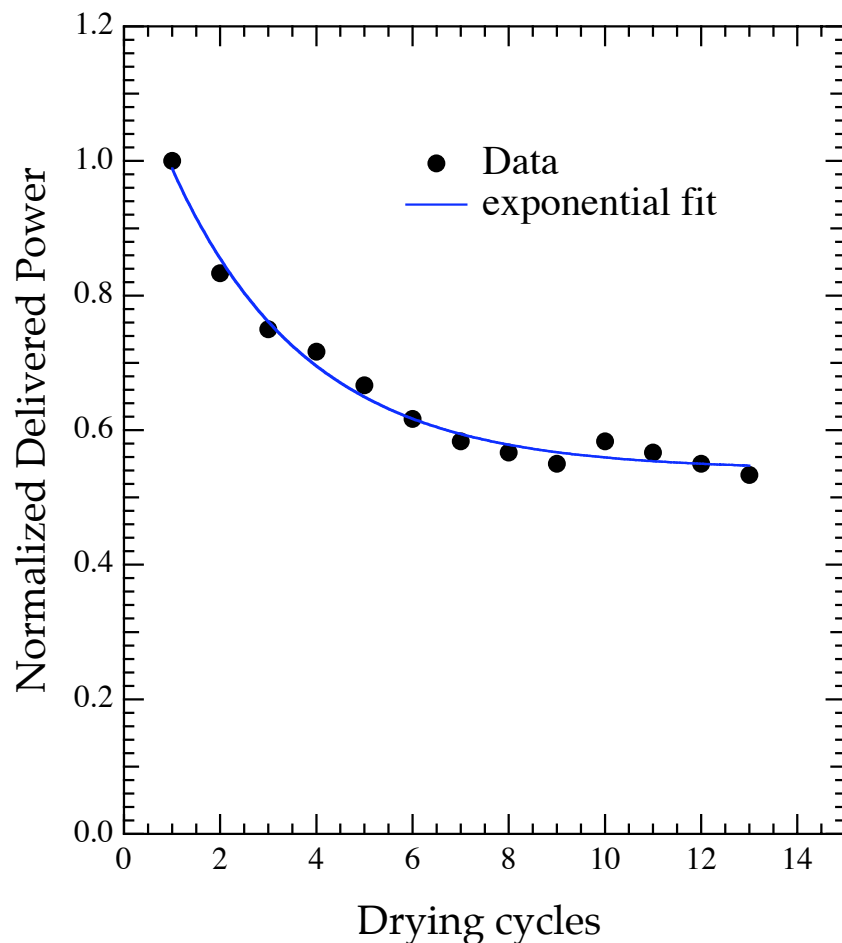
in supernatant
H₂O



in air

- Students Supported
 - Two masters candidates, a PhD candidate, and two undergraduates have been supported in this work
- Publications / Presentations
 - The paper "Instrumentation for PEM Fuel Cell Degradation Monitoring was written, submitted, and accepted.
 - **NMR microscopy of water and methanol distribution and dynamics in polymer electrolyte membranes**, North American Membrane Society, 14th Annual Meeting, Jackson Hole, WY, May 17-21, 2003, Joseph D. Seymour, Sarah L. Codd, James C. Mabry, Scott C. Busse and Eric S. Peterson
 - M. Keiderov, A. Lussier, and Y.U. Idzerda; "Identification of Thermal Failure Modes of PEM Membranes by Finite Element Modeling" (2003 - in preparation).
 - A. Lussier, D. Larsen, and Y.U. Idzerda; "Performance of an X-ray Compatible cell for Fuel Cell Material Characterization" (2003 – in preparation).

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



- 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.

- This program supported a graduate student and two REU (research experience for undergraduates)
- Publications M. Keiderov, A. Lussier, and Y.U. Idzerda; “Identification of Thermal Failure Modes of PEM Membranes by Finite Element Modeling” (2003 - in preparation).
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- 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.