Montana PEM Membrane Degradation Study

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Project ID
FCP 13

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FCP 13

Overview

Timeline

- Project start date: 11/30/02
- Project end date: 9/30/06
- Percent complete: 95%

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

Budget

- Total project funding
  - $804,836 DOE
  - $217,685 Match
- Funding expended (DOE):
  FY04 - $134,144
  FY05 - $215,685
  FY05 - $393,243
  Total - $739,072

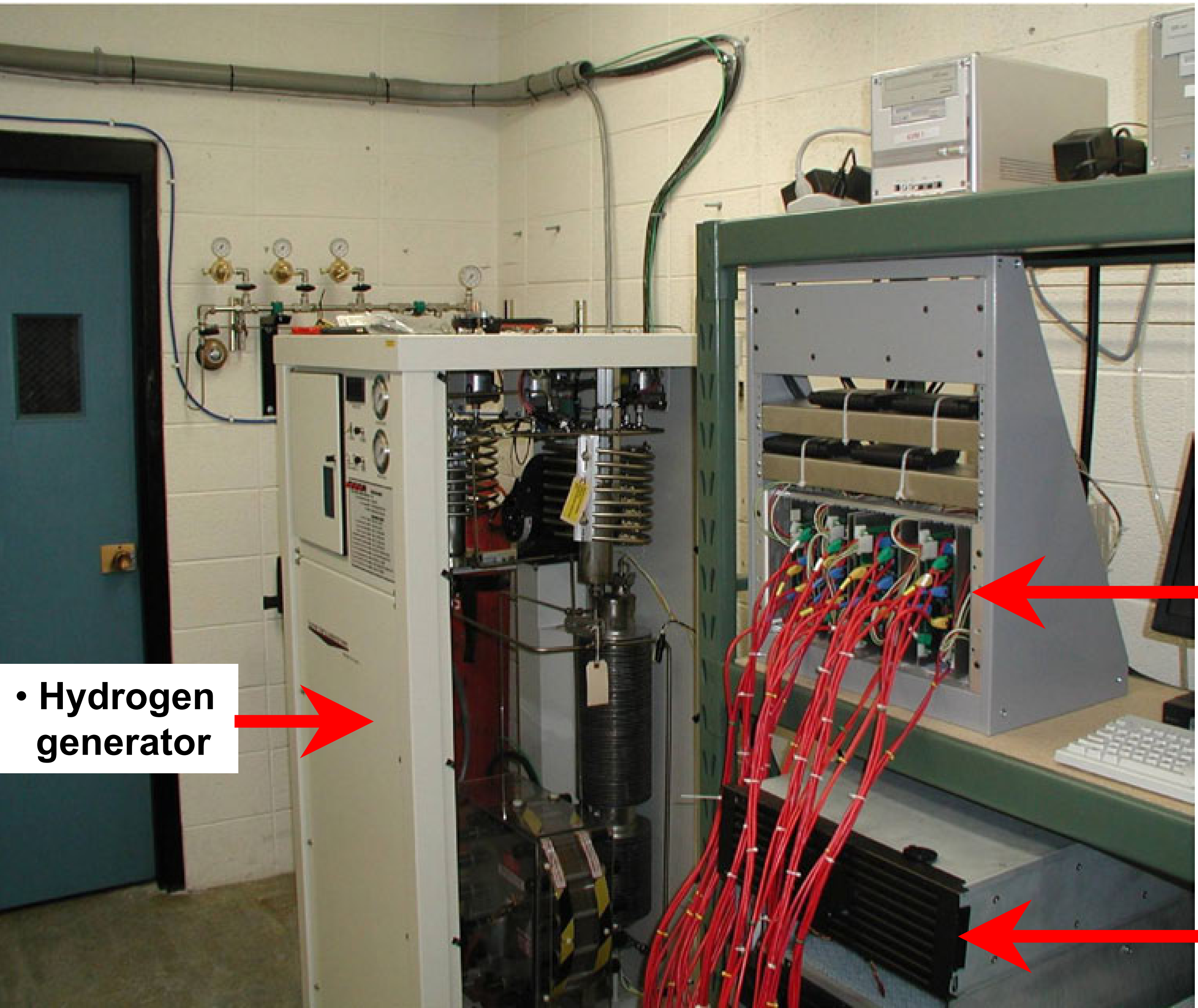
Objectives

- 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

Degradation setup



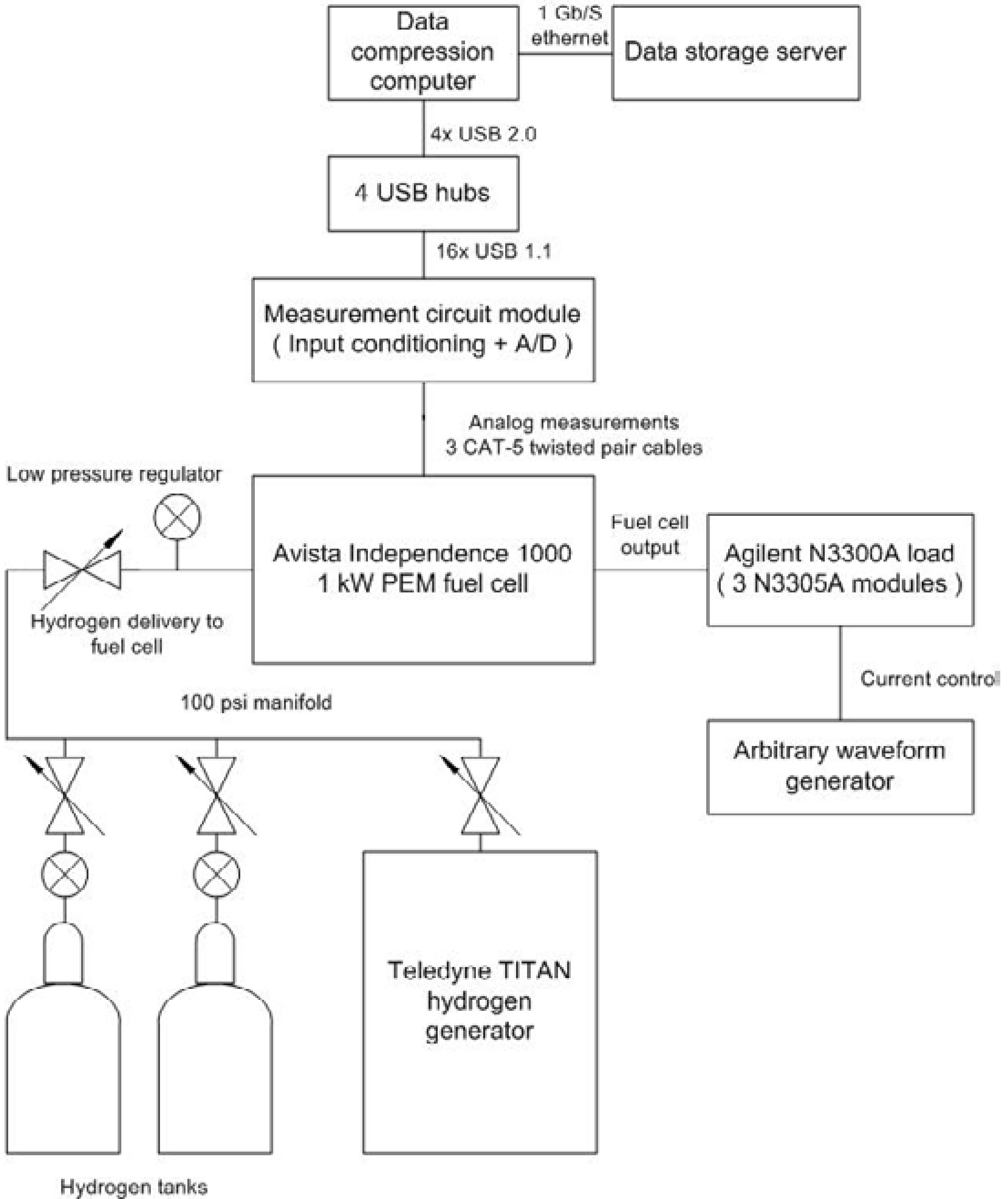
- Hydrogen generator

- Provides a record of performance of each individual membrane over its entire life span.

- Measure voltage, current, and temperature for each membrane.

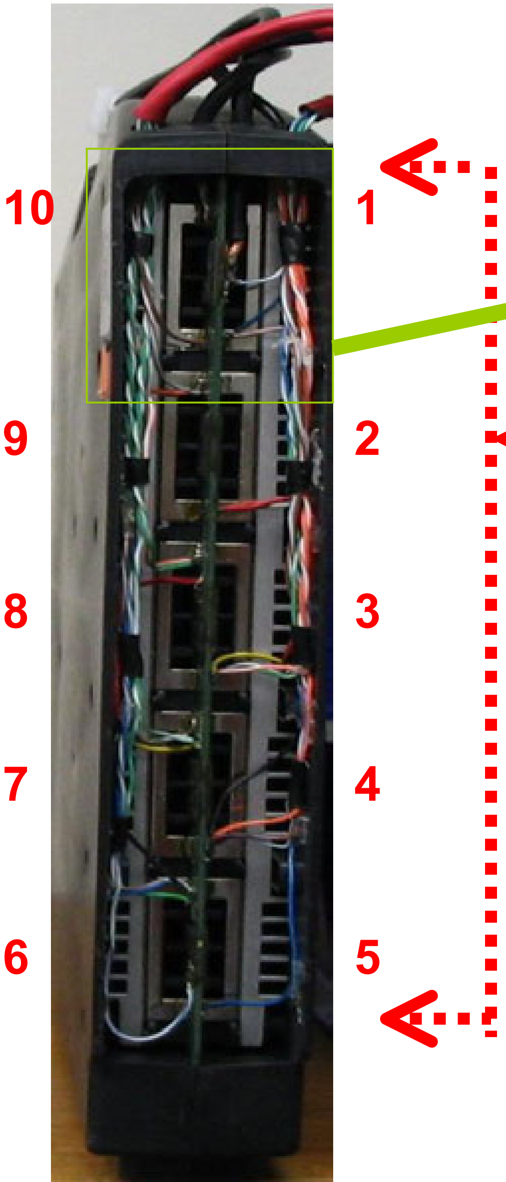
- 80 membranes per test system.

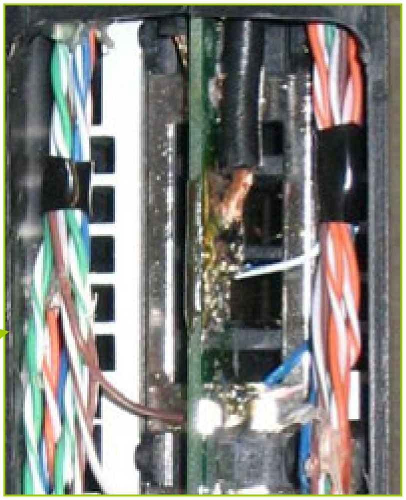
Degradation setup



Degradation setup

- Cartridge modifications

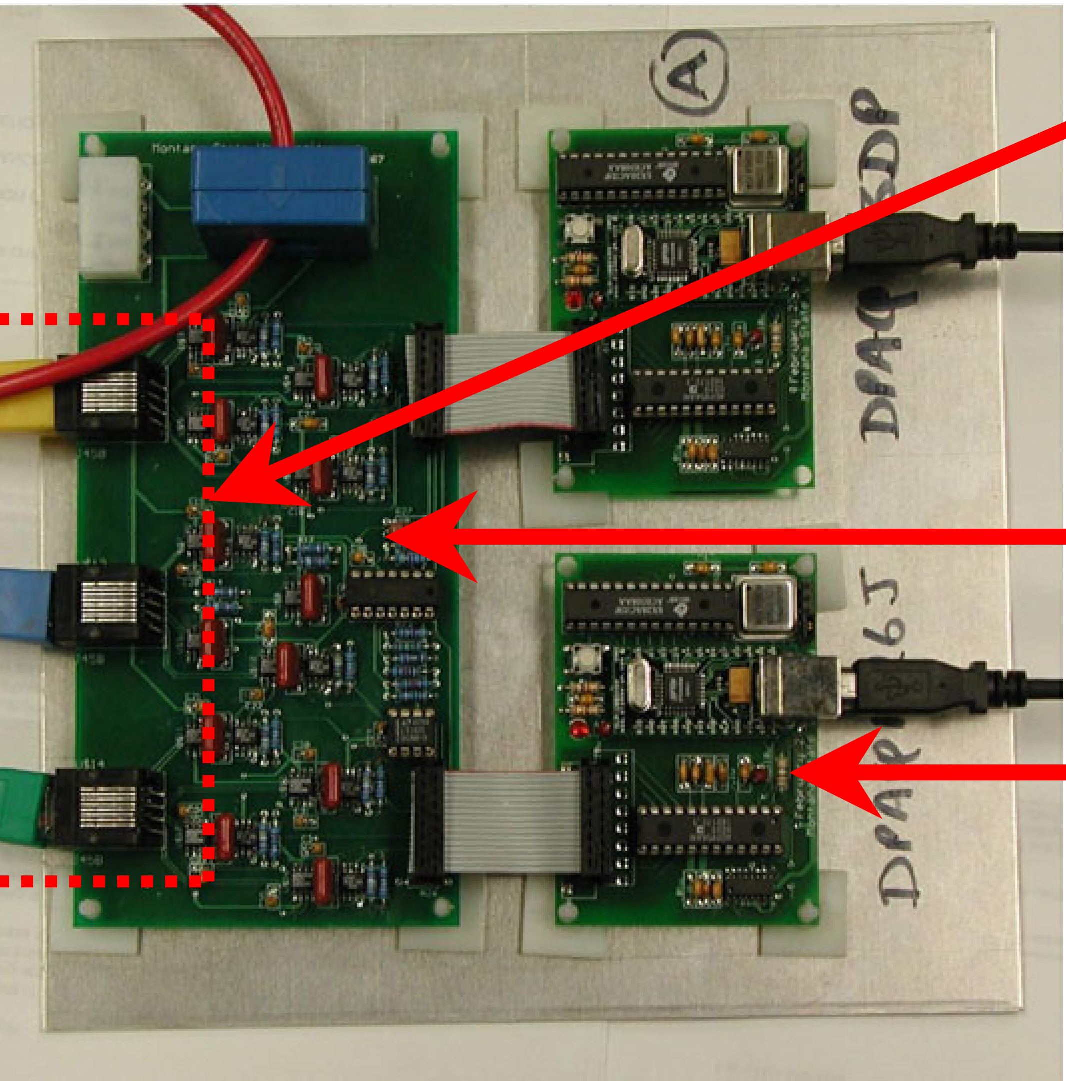




- **Each cartridge contains 10 fuel cells in series, 5 cells in each side.**
- **Required to measure 5 differential voltages, one current, and a heat-sink temperature measurements from each side.**
- **For each cartridge there is corresponding circuit module and 2 A/D boards for cartridge.**

Degradation setup

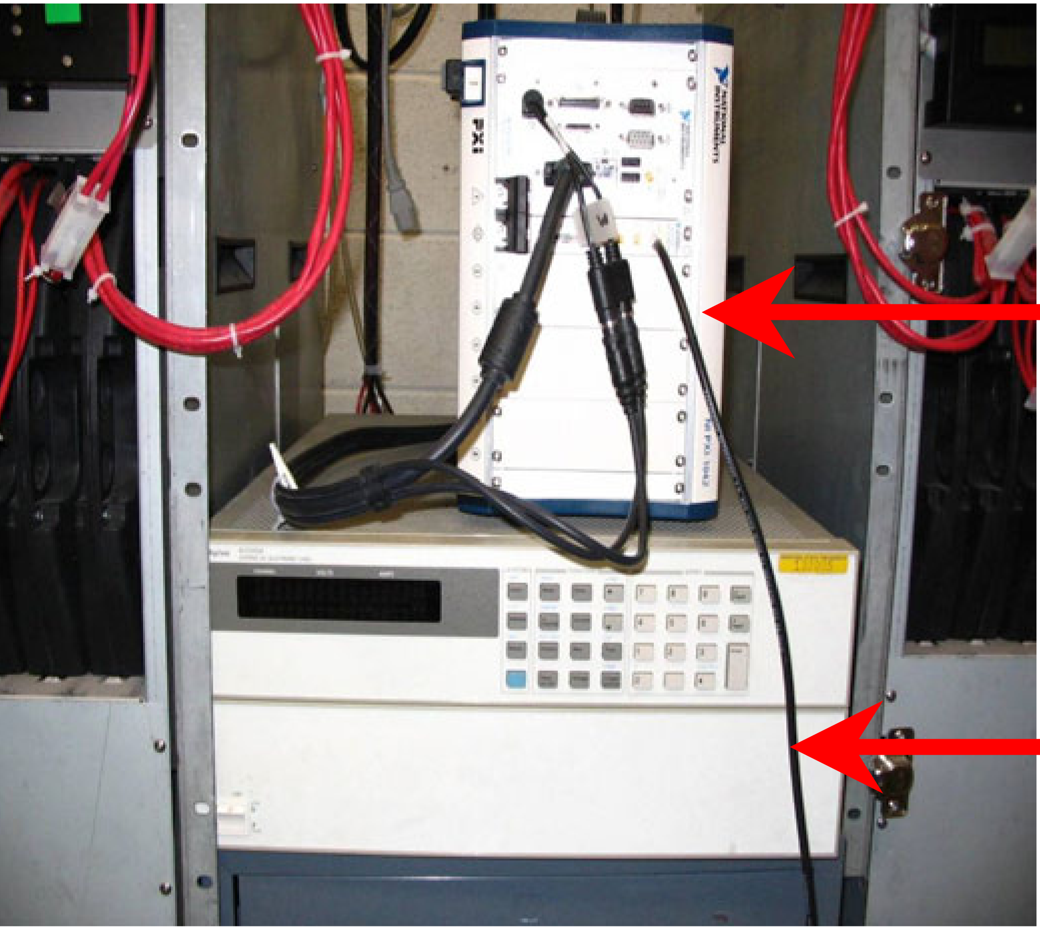
- Analog input conditioning board and two A/D boards

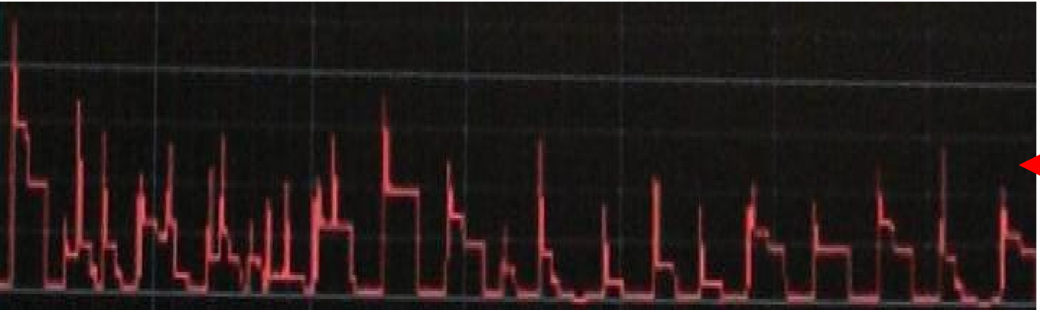


- **Circuit module is connected to the PEM cartridge by a set of 3 CAT-5 twisted pair cables using standard CAT-5 connectors.**
- **The analog processing board on left receives measurements from cartridge.**
- **A/D boards on right digitize the information and send it through USB storage server.**

Degradation setup

- Transient load

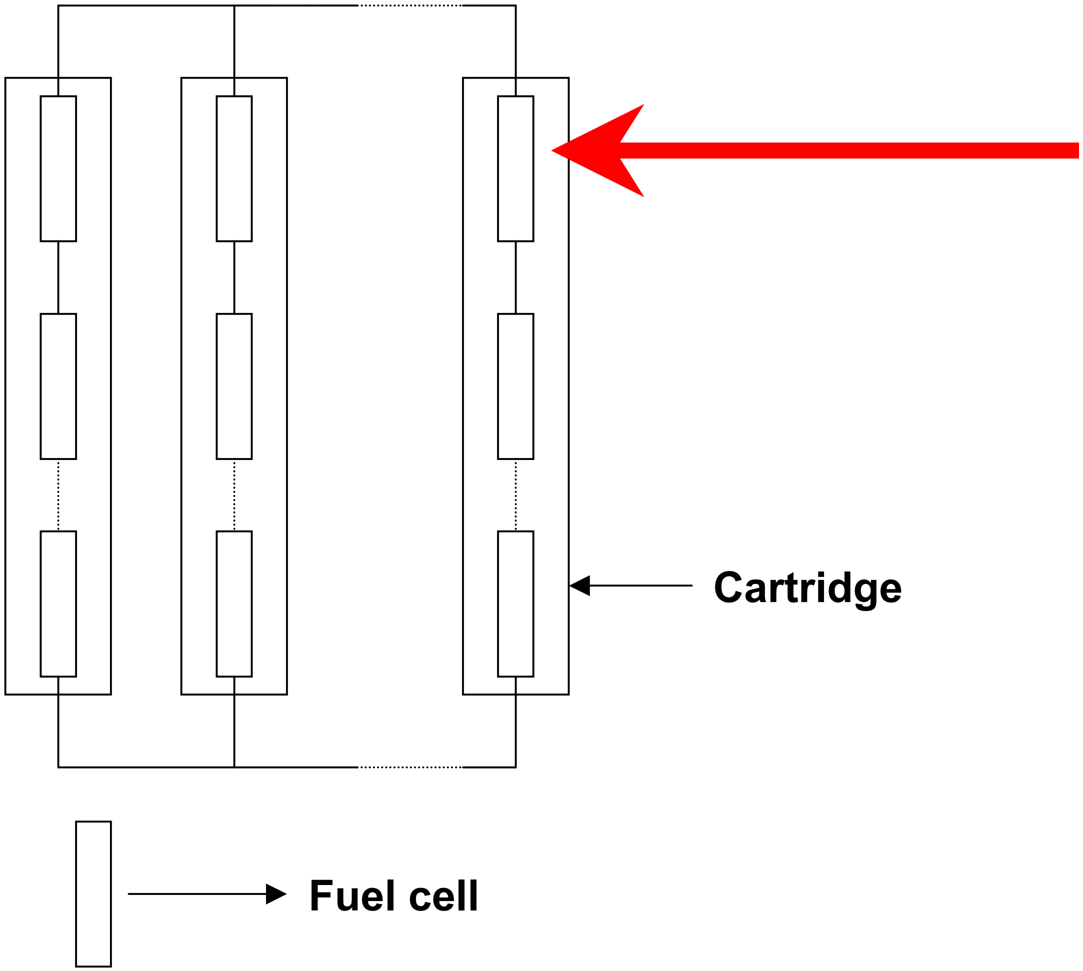




- **An algorithm is developed using Labview software and NI hardware (arbitrary wave generator), for external analog programming provision of the Agilent load.**
- **Independence 1000 is loaded by Agilent active load N3300A**
- **This setup provides transient-rich load waveform.**

Degradation modeling

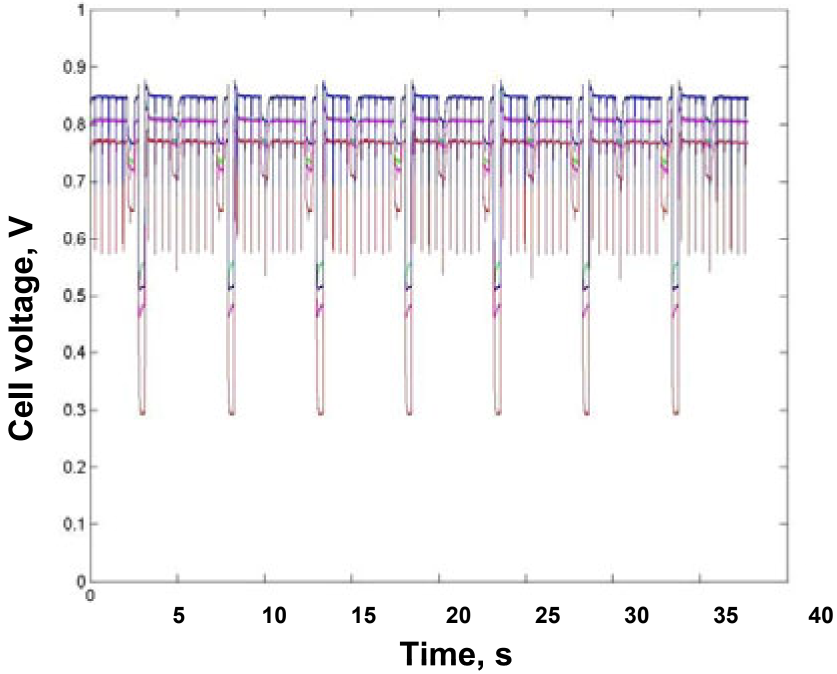
- Choosing degradation model
  - Problem is change in persistence of individual membrane excitation.

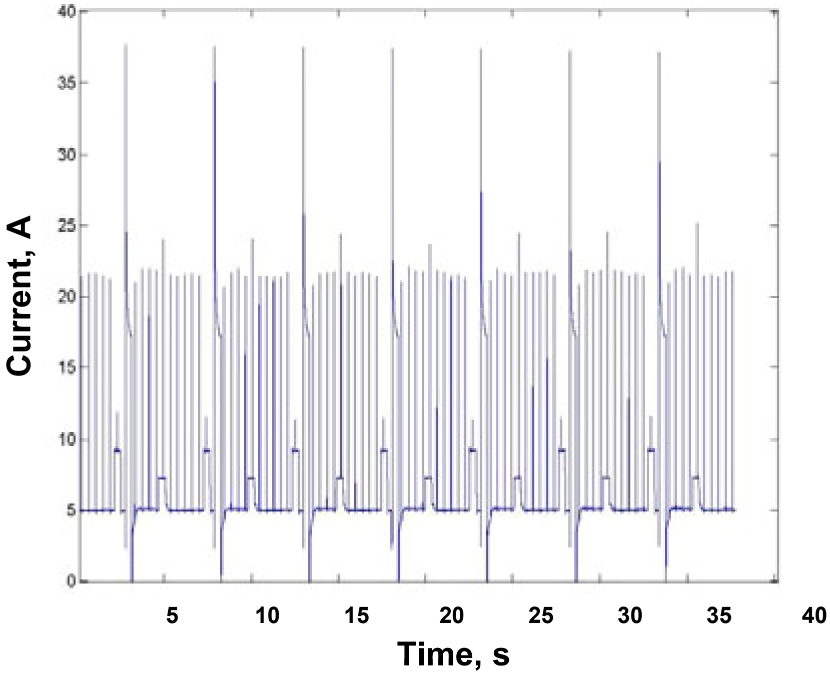


- **In the system fuel cells are arranged in a serial and parallel way.**
- **Fuel cells tend to degrade in different modes and times.**
- **Simple model for the analysis is an optimum choice.**

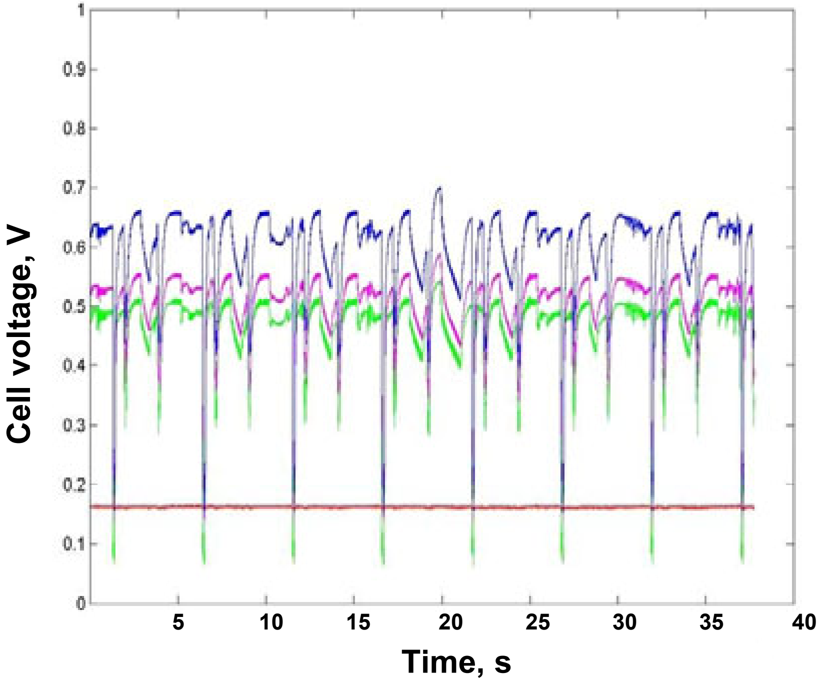
Degradation modeling

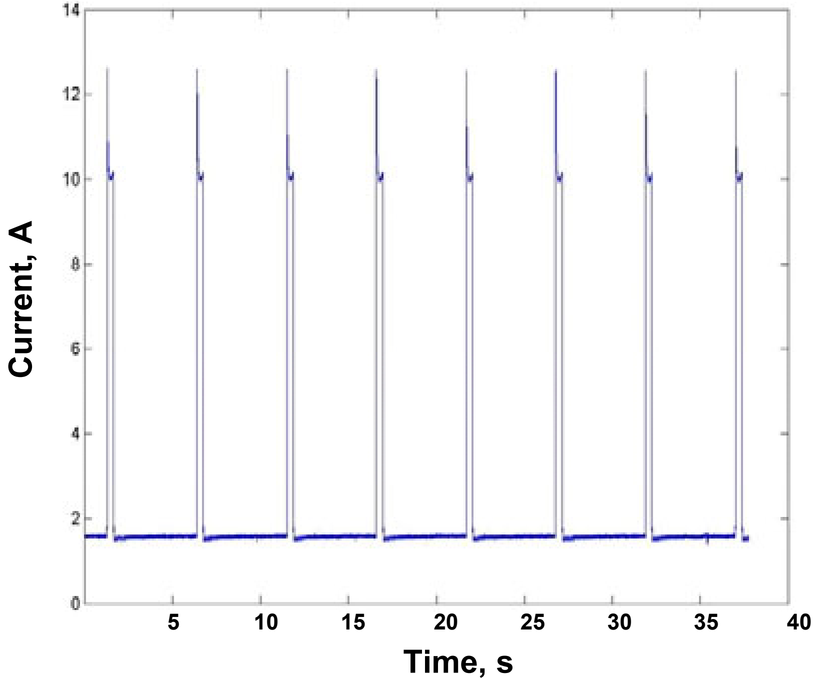
Un-degraded membrane





Degraded membrane





Degradation modeling

- Simple linear resistive model.

$$V_{cell} = \mu_1 - \mu_2 I$$

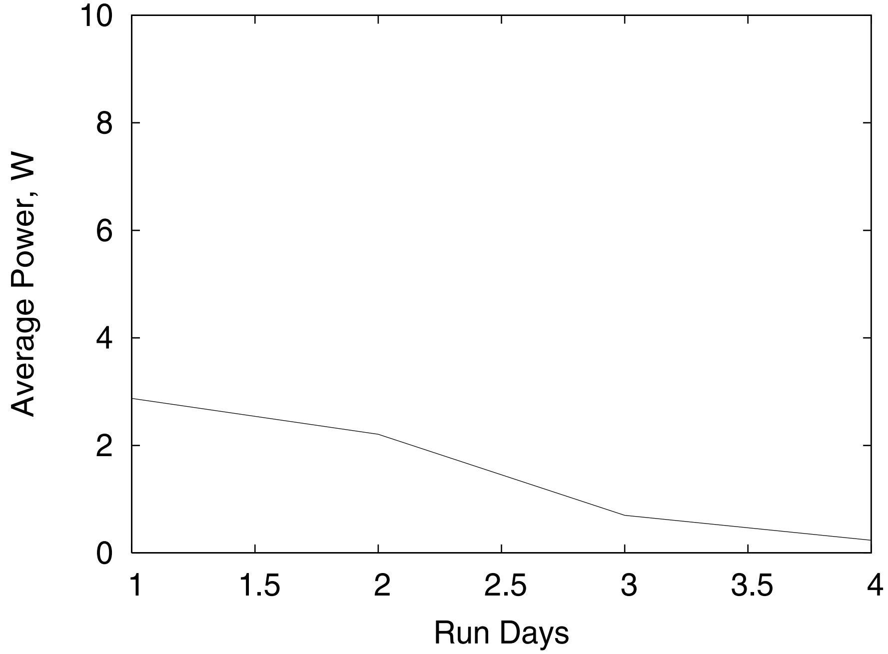
  - $\mu's$ are identification parameters.
  - μ_1 and μ_2 are considered as open circuit voltage and internal resistance for each fuel cell membrane.
  - Can be fit with minimal excitation.

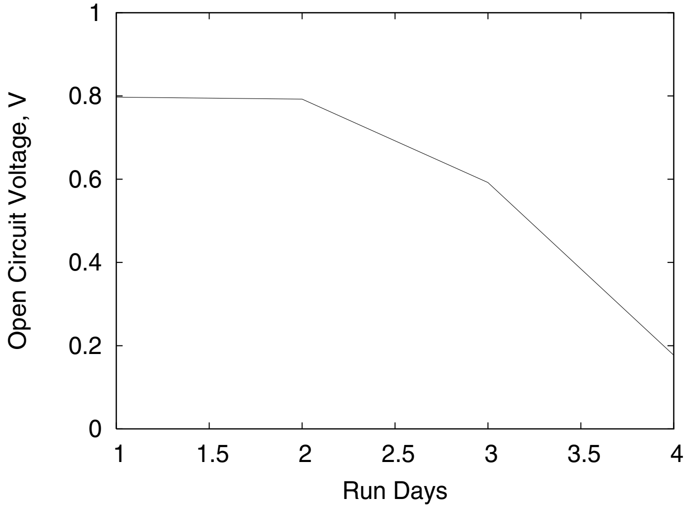
Degradation results

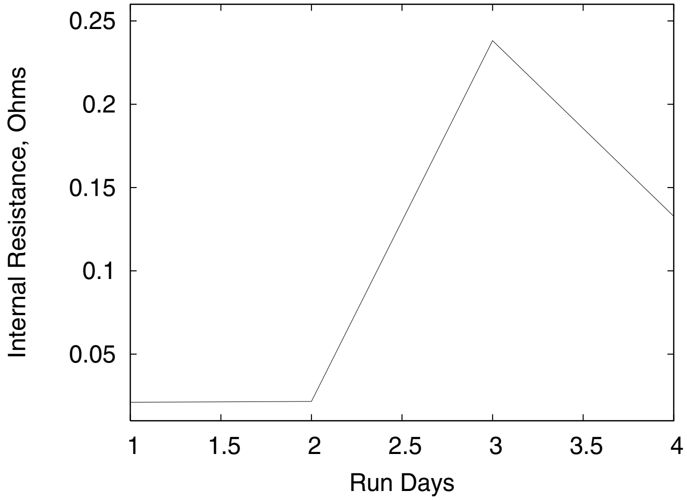
- The performance history of each cartridge is stored.
- The parameters for degradation model were analyzed over a period of time.
- Two membrane degradation or failure modes were identified.
  - Decreasing voltage, increasing resistance failure mode.
  - Increasing resistance failure mode.

Decreasing voltage, increasing resistance failure mode

- **For membrane # 4 of 4 in series**



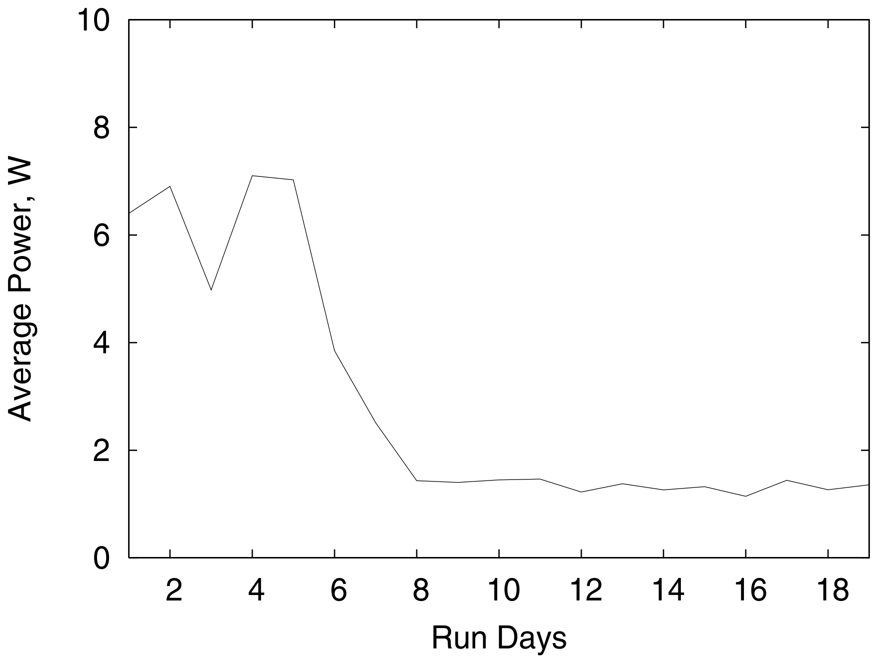


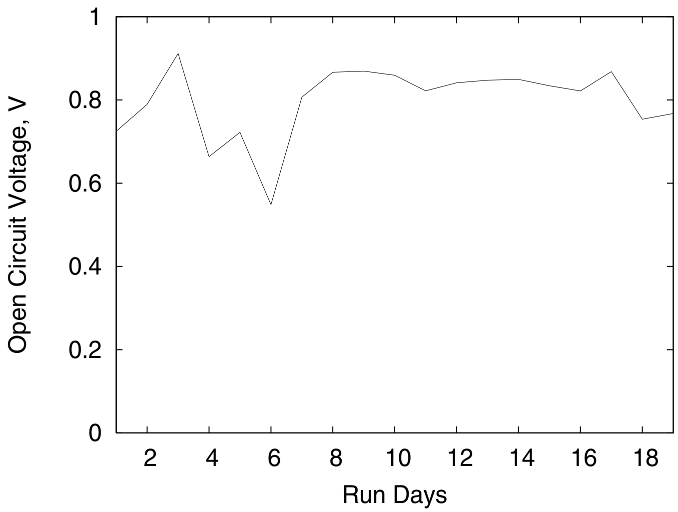


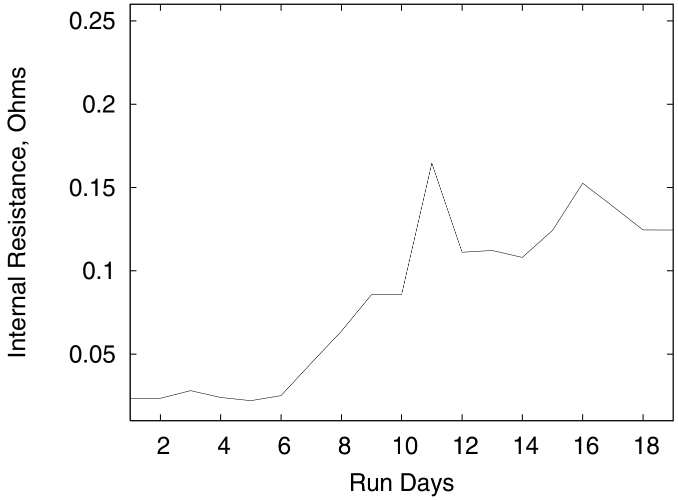
- **Average power, open circuit voltage** (μ_1) **, internal resistance** (μ_2)

Increasing resistance failure mode

- **For membrane # 1 of 4 in series**







- **Average power, open circuit voltage** (μ_1)**, internal resistance** (μ_2)

Discussion

Fuel cell degradation

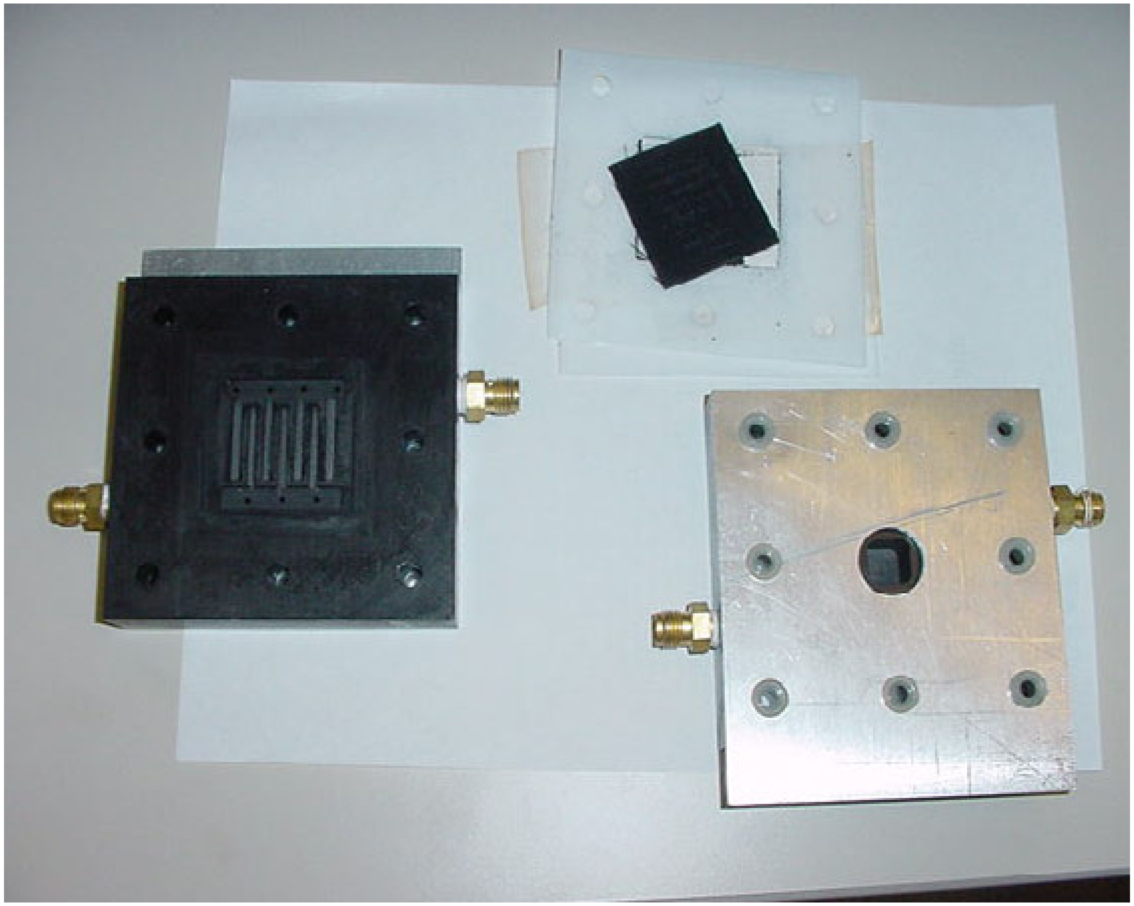
- The amount and complexity of the data has been a challenge. Tens of thousands of data files per membrane exist.
- Change in persistence of individual membrane excitation is an issue. The degradation of the cartridge modifies the extent to which the cartridge participates in the system and changes the excitation.
- Two modes of membrane degradation/failure were identified.
  1) Decreasing voltage, increasing resistance failure mode.
  2)Increasing resistance failure mode.
- Still need connection of electrical failure modes to fuel cell materials/physical aspects.

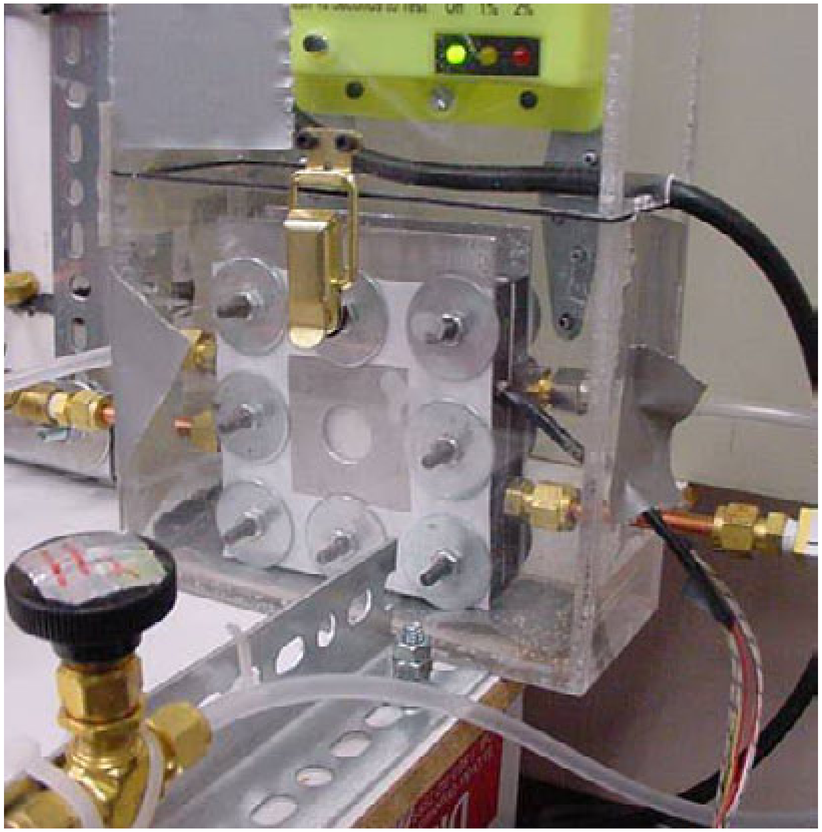
X-Ray Characterization Approach

- Monitor current and voltage output for an X-ray compatible single fuel cell as a function of temperature, humidity, and drying/humidification cycling.
- Characterize membrane thickness and density (porosity) variation using synchrotron based X-ray small angle scattering before and after degradation.

Technical Progress

X-ray compatible PEM Fuel Cell





Technical Progress

MAJOR CONCLUSIONS

- Significant decrease in PEM fuel cell performance from spatially localized membrane densification resulting in reduced proton diffusion.

- Although the membranes are initially uniform in thickness, they are not uniform in porosity. Densification occurs mainly in regions that initially showed lower porosity.

Technical Progress

- Time-dependent I-V response curves of abrupt loading of the fuel cell suggest that PEM performance degradation is due, in part, to reduced hydrogen diffusion through the membranes.

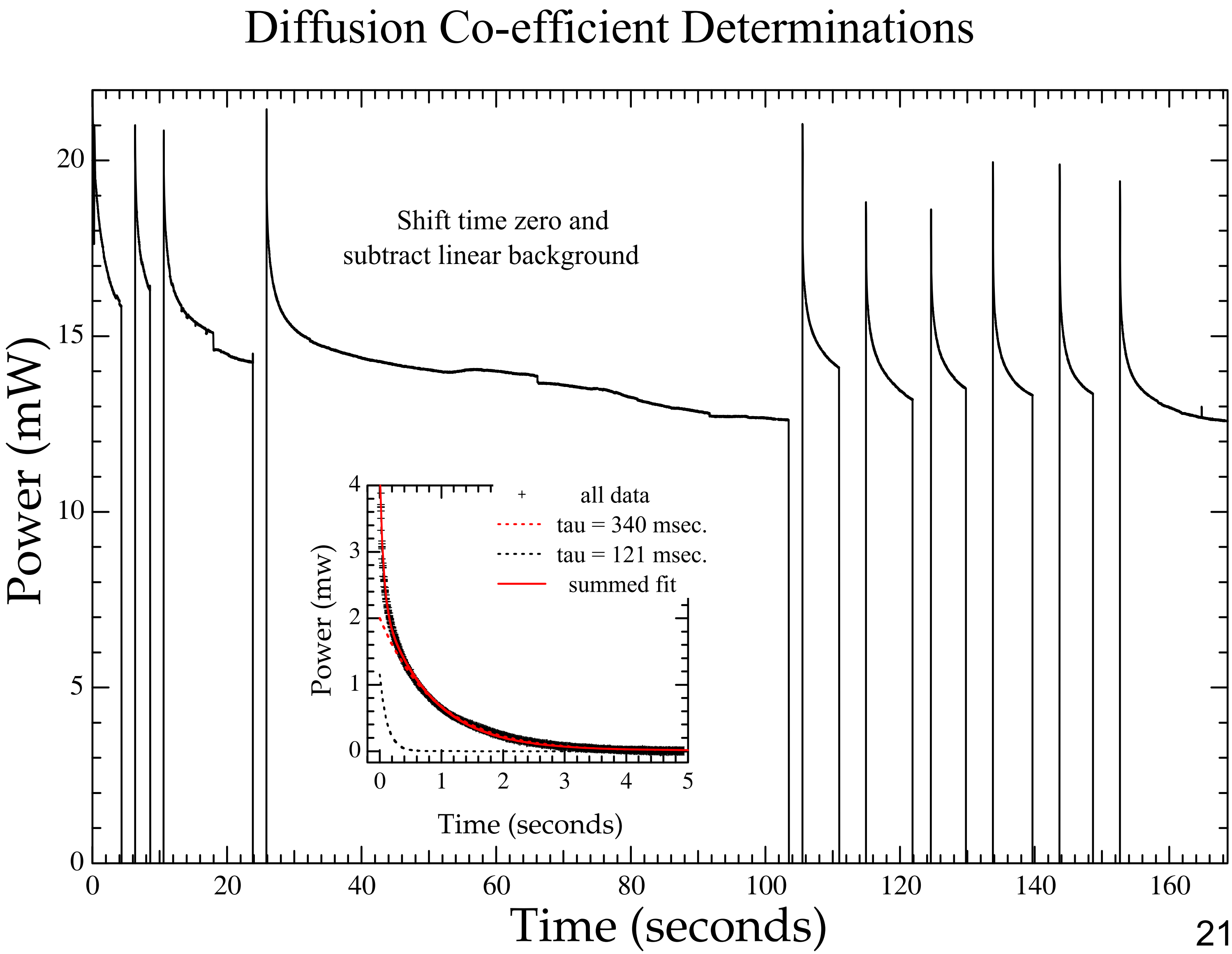
- Spatially resolved X-ray characterization of the before and after membranes (5 membranes after 200-500 hours and 10-30 drying cycles), show no change in chemical make-up, but show a densification of the membrane.

- Strong correlation between initial density variation of membrane and the changes in membrane density with repeated hydration/drying cycles.

Technical Progress

Power curves at room temperature and no humidification

Inset shows double exponential extraction.



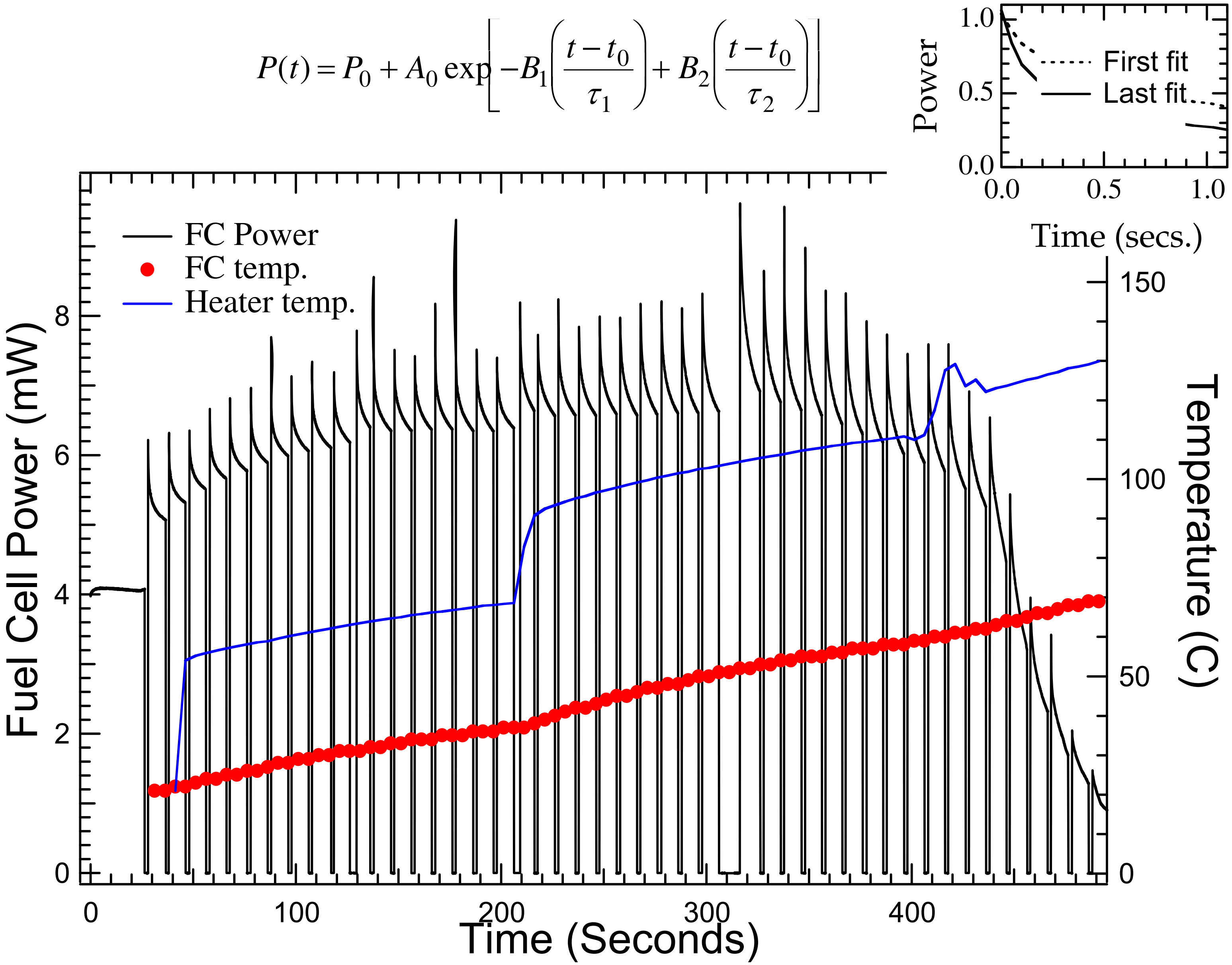
Technical Progress

- Determined temperature dependence of the two extracted exponential lifetimes.
- Determine exponential lifetime variation with drying cycles,
- Unable to extract humidity dependence
  - Measure intake and outlet gas humidity
  - NOT a good measure of membrane humidity.

Technical Progress

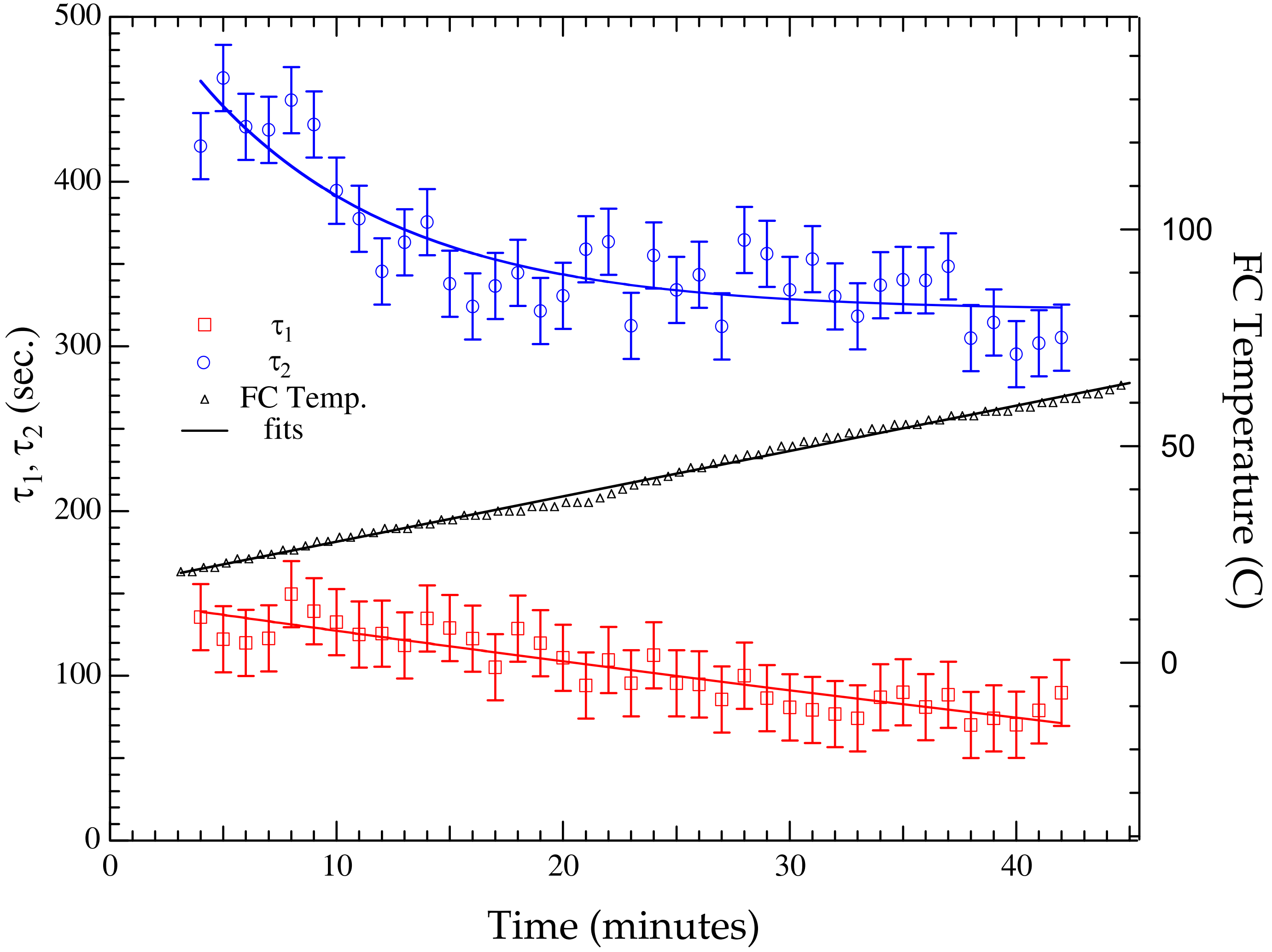
PEM Fuel Cell Time Constants

$$P(t) = P_0 + A_0 \exp\left[-B_1\left(\frac{t-t_0}{\tau_1}\right) + B_2\left(\frac{t-t_0}{\tau_2}\right)\right]$$



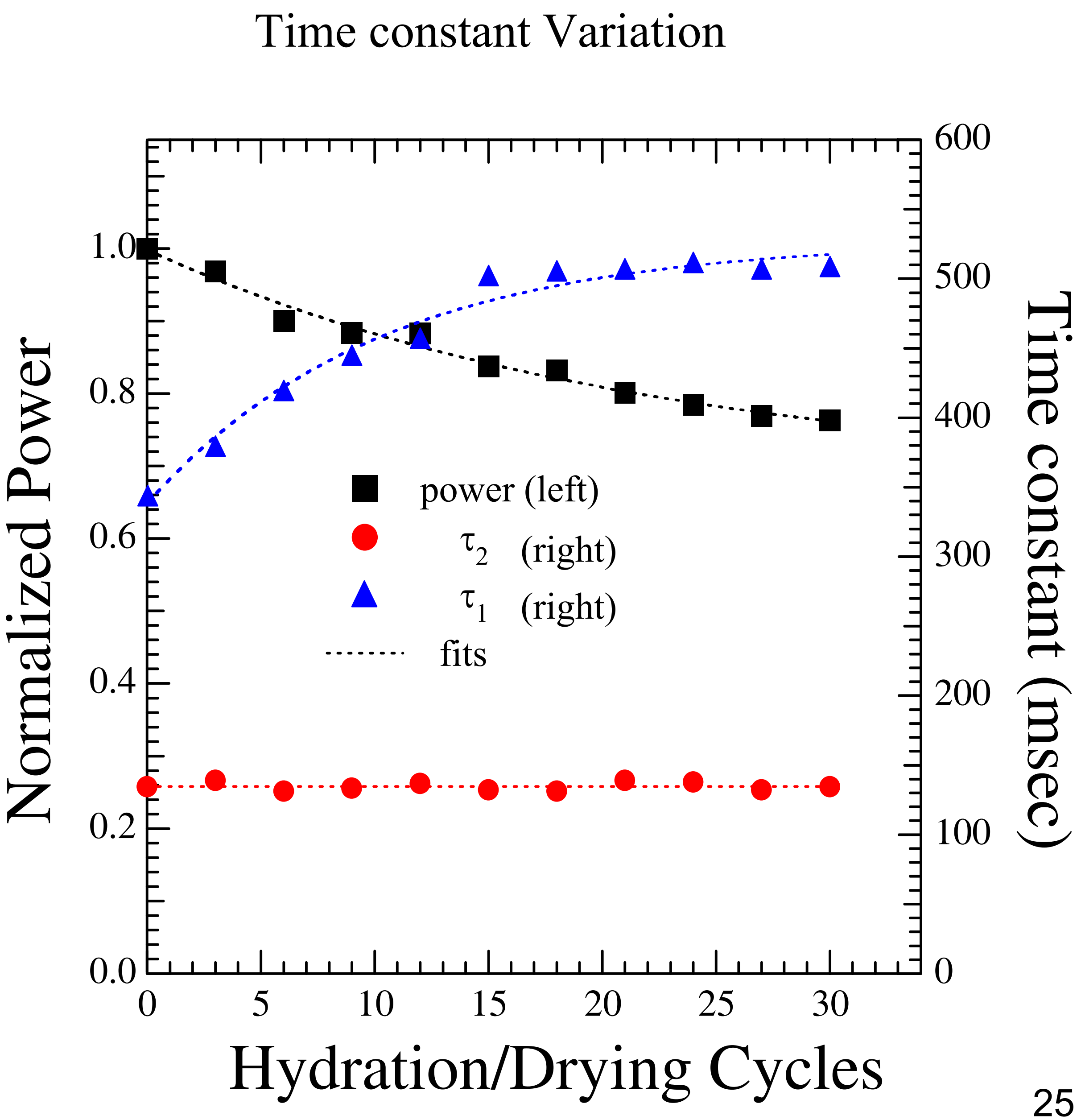
Technical Progress

Extracted time constants variation with temperature



Technical Progress

Extracted time constant variation with repeated drying cycles.



Technical Progress

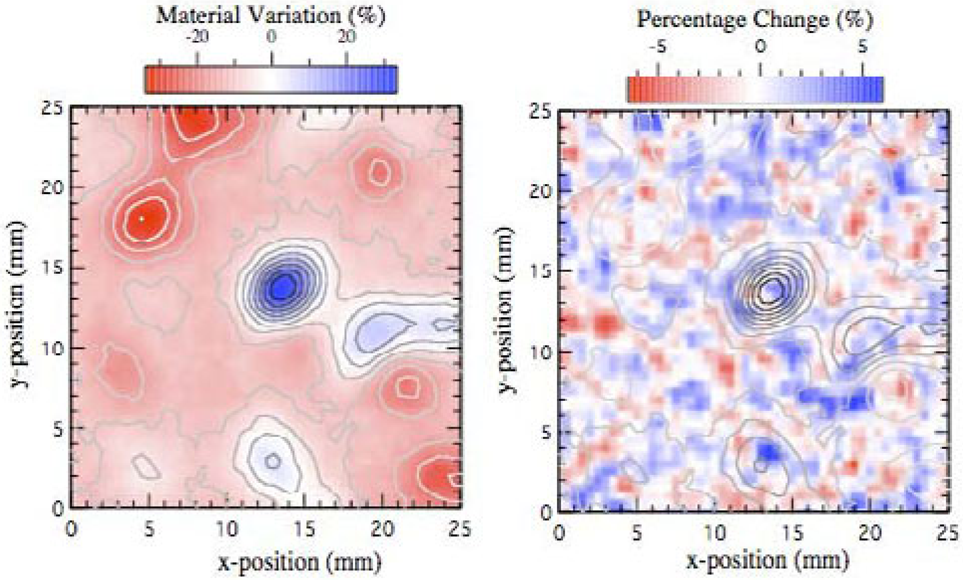
- Determined spatially resolved (0.25 mm^2) changes in membrane density and thickness as a function after significant (35%) increase in one exponential lifetime (associated with the proton diffusion).
- Determined the correlation between density changes and initial porosity.

Technical Progress

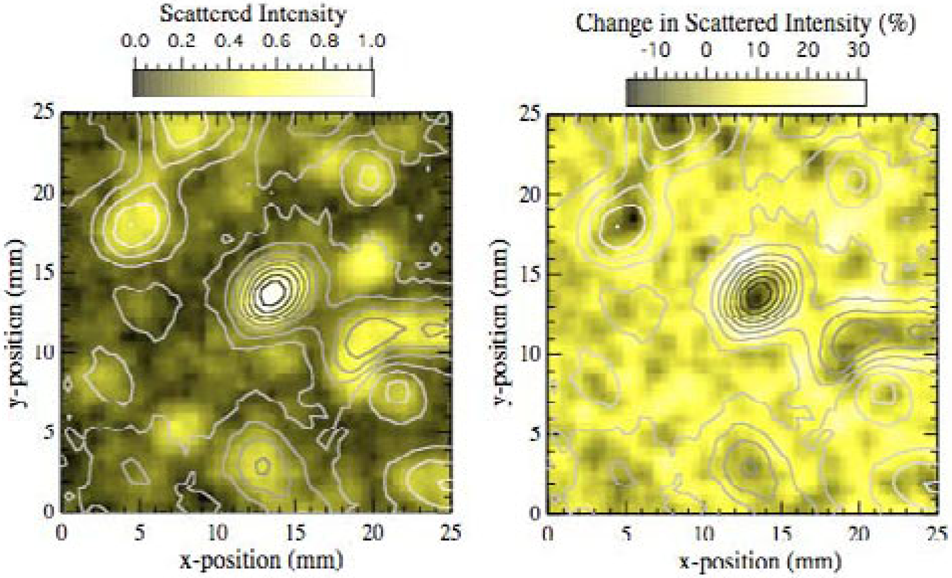
- Small angle X-ray scattering used to determine amount of material (intensity of transmitted direct, or specular, X-ray beam) and density (intensity of small angle scattered X-ray beam).
- Membranes were of uniform thickness, but non-uniform density (50% variation).
- After repeated drying cycles, membranes showed significant increase in density in regions previously identified as being less dense.

Technical Progress

Transmitted X-ray Intensity showing total material variation before use (left) and percentage change (right) after PEM performance decrease.

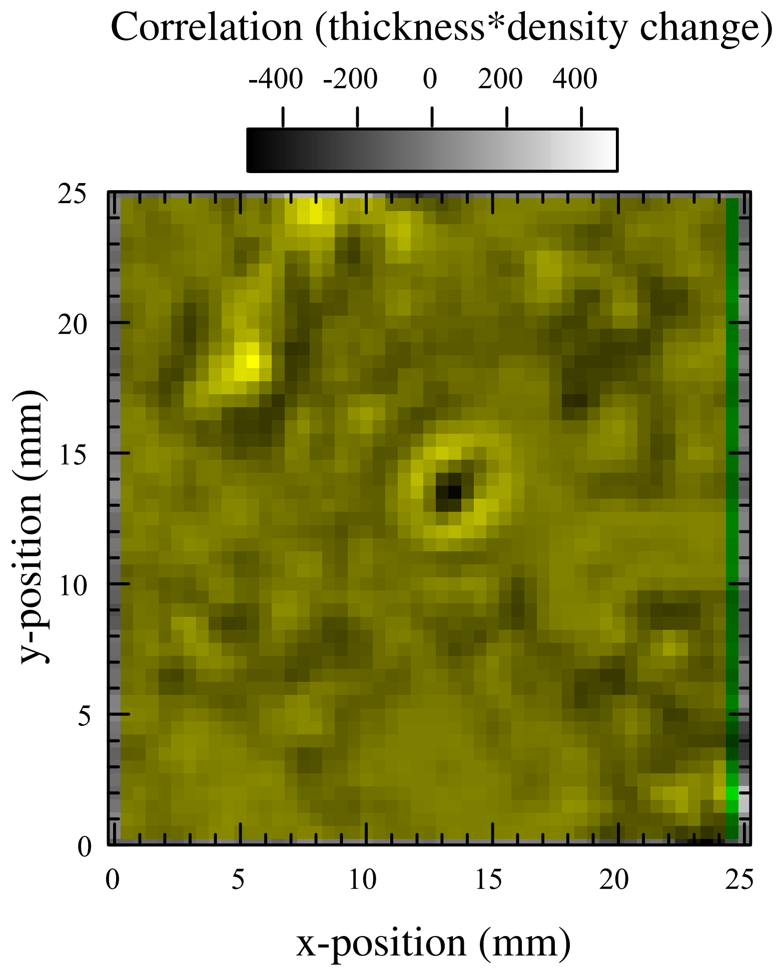


Scattered X-ray Intensity showing density variation before use (left) and density change (right) after PEM performance decrease.



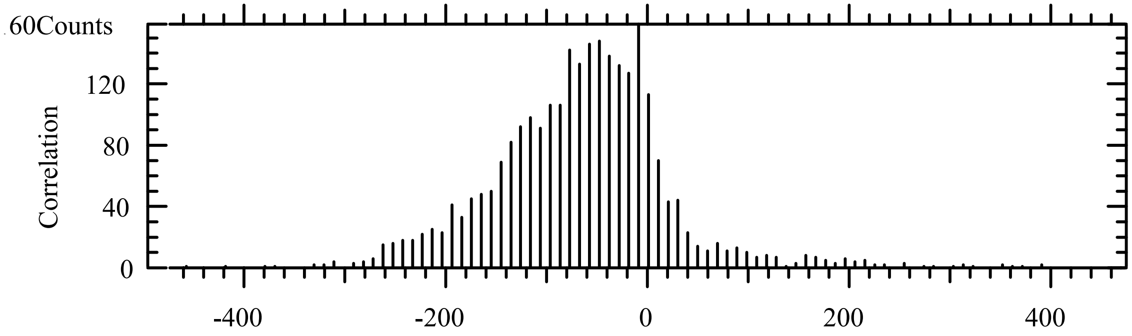
Technical Progress

Correlation of density change and original porosity for one membrane



Line plot correlation for 5 membranes

No correlation would be centered about 0.



Technical Progress

SUGGESTIONS

- Improved density uniformity may extend PEM fuel cell performance.
- Repeated drying cycles were shown to be one cause of this densification and should therefore be minimized.

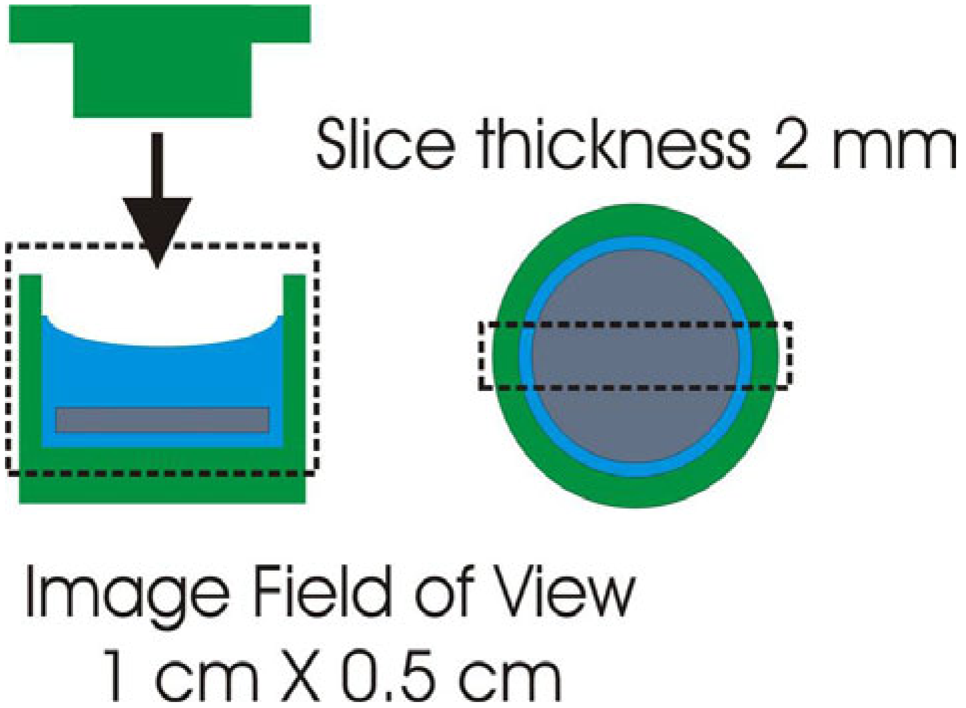
PEM Experimental Details

Nafion® 117: 177 μm dry thickness

B. MacMillan, A. R. Sharp and R. L. Armstrong
Polymer **40** 2471 (1999)

- Soak in 80°C 2 M HCl for 2 hours
- Wash in 100°C distilled H_2O
- Soak in 0.01 M EDTA 24 hours
- Boil and rinse in distilled H_2O

Cut out 10 mm disk of PEM

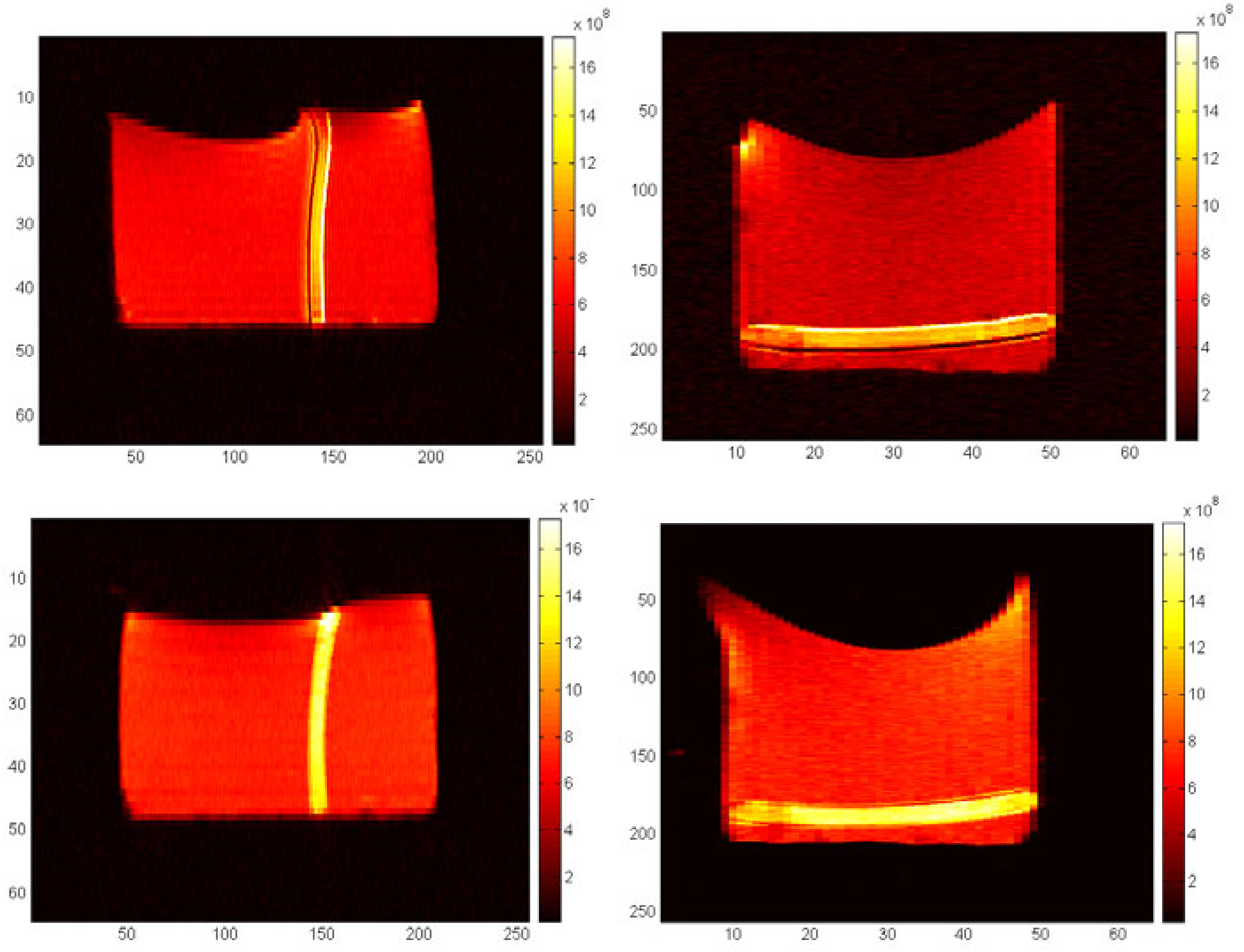


Imaging Artifacts

[Codd et al. *Appl. Mag. Res.* In press (2006).]

B_o parallel to membrane surface

B_o perpendicular to membrane surface

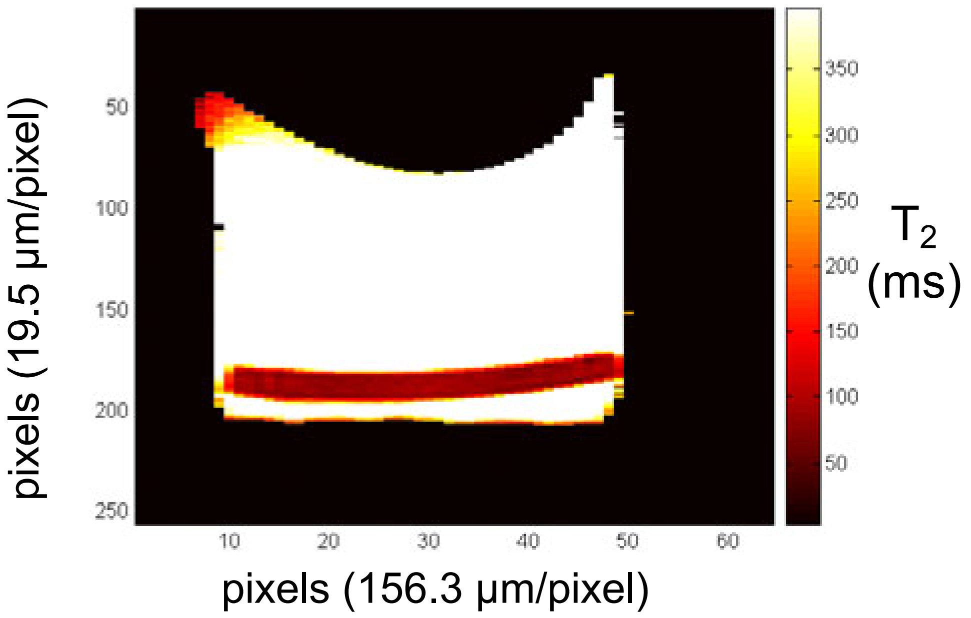


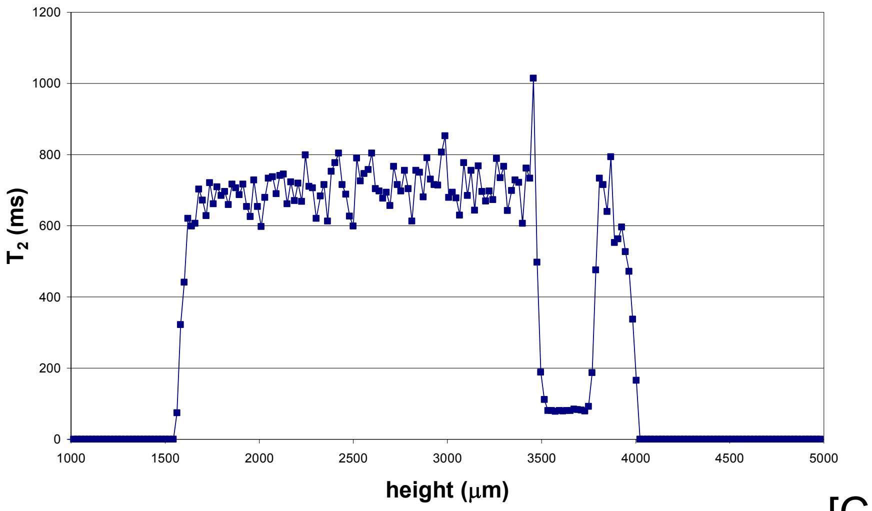
Spatial read encode gradient perpendicular to membrane surface generates chemical shift and susceptibility artifacts

Spatial phase encode gradient parallel to membrane surface artifact free. A susceptibility artifact with Bo perpendicular is just detectable.

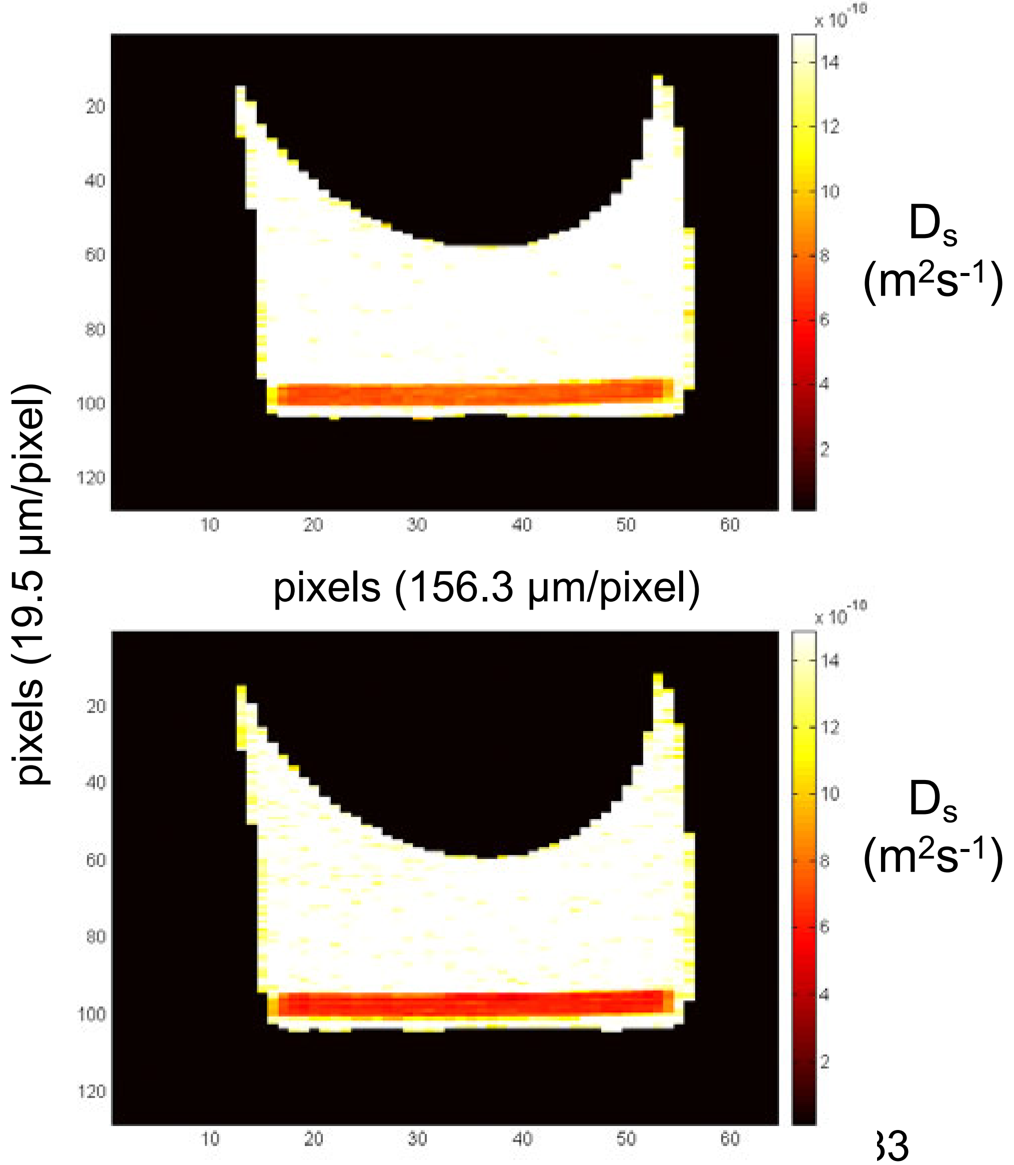
T_2 and Diffusion Maps

T_2 spatial distribution map and 5 pixel wide average of T_2





D_s spatial distribution maps motion sensitivity vertical and into page



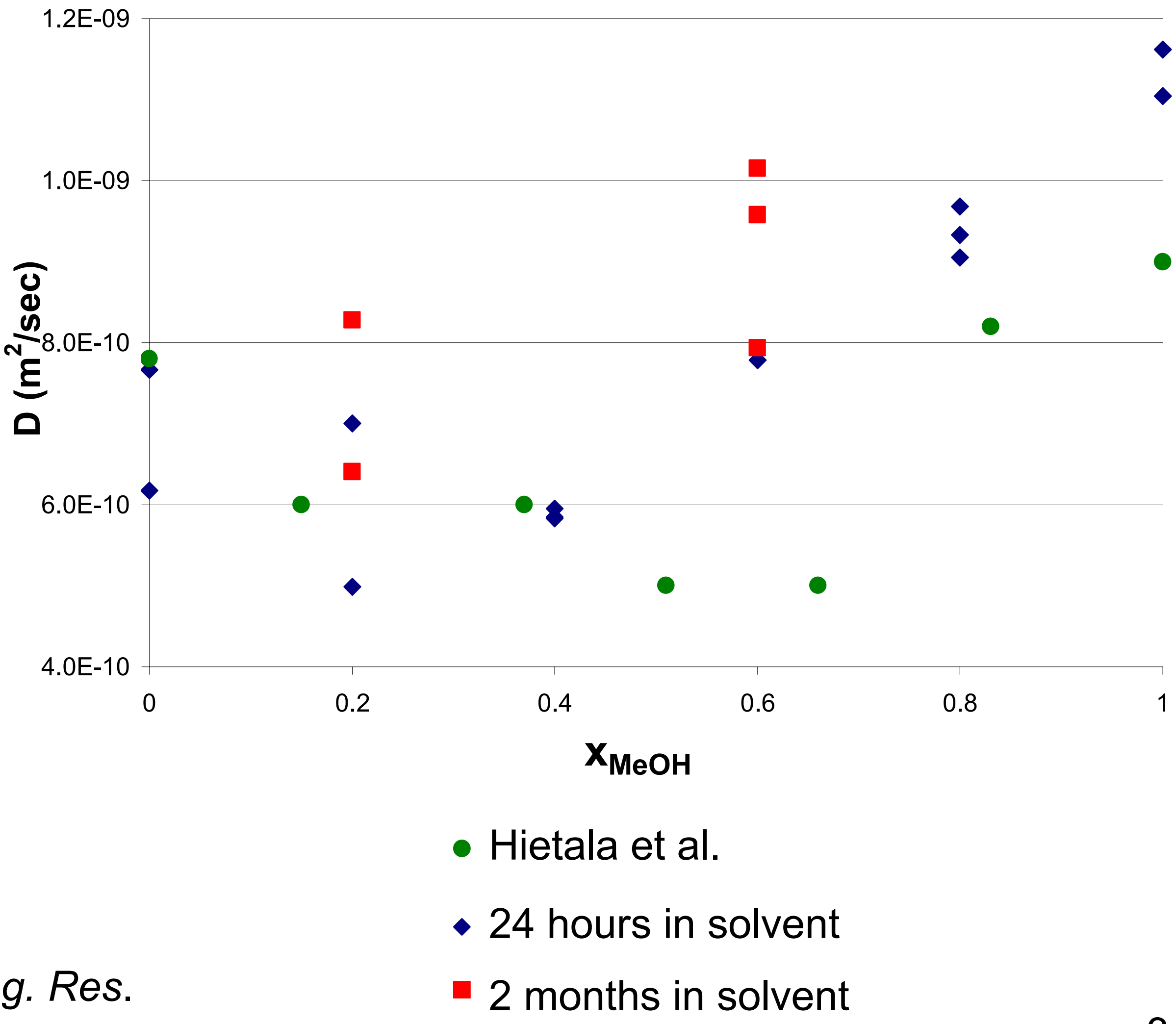
[Codd et al. *Appl. Mag. Res*. In press (2006).]

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

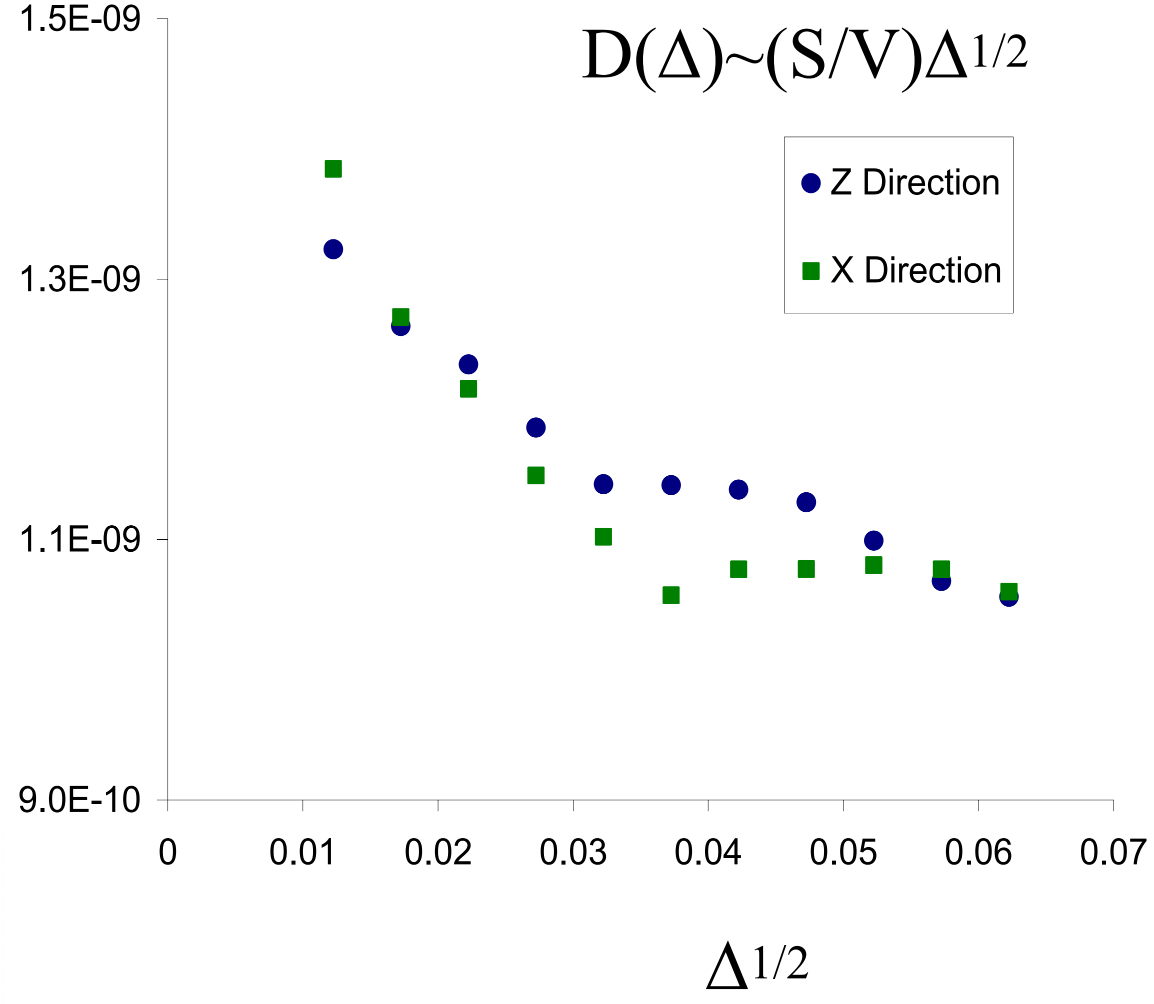
[Codd et al. *Appl. Mag. Res.* In press (2006).]

Solvent Diffusion in Nafion® 117



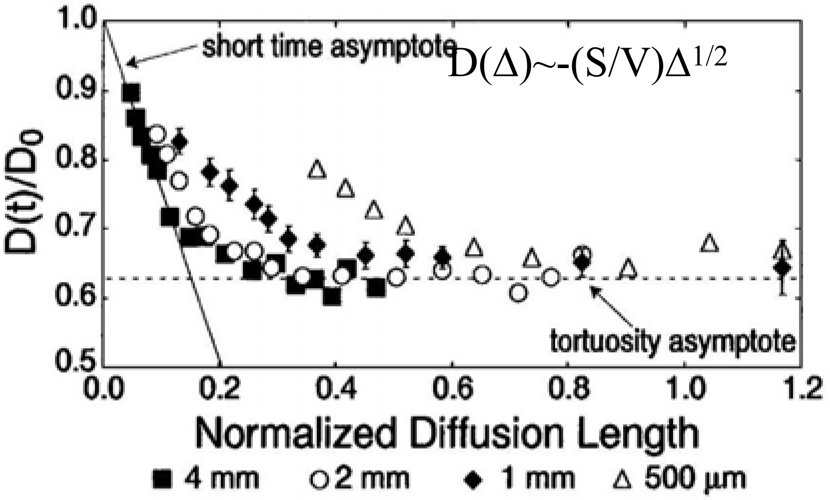
Time Dependent Diffusion

Restricted solvent motion of 0.2. mole fraction MeOH in Nafion 117 indicates the surface to volume ratio (S/V) is different in the membrane depth (z-dir) and along the membrane surface (x-dir)



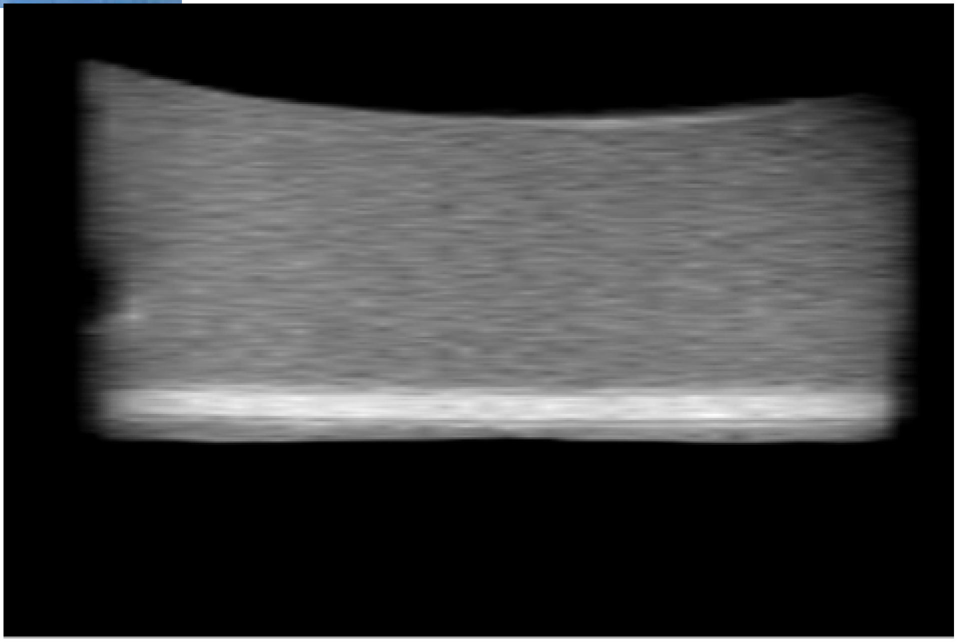
Time Dependent Diffusion of Xe Gas in Model Glass bead Pack

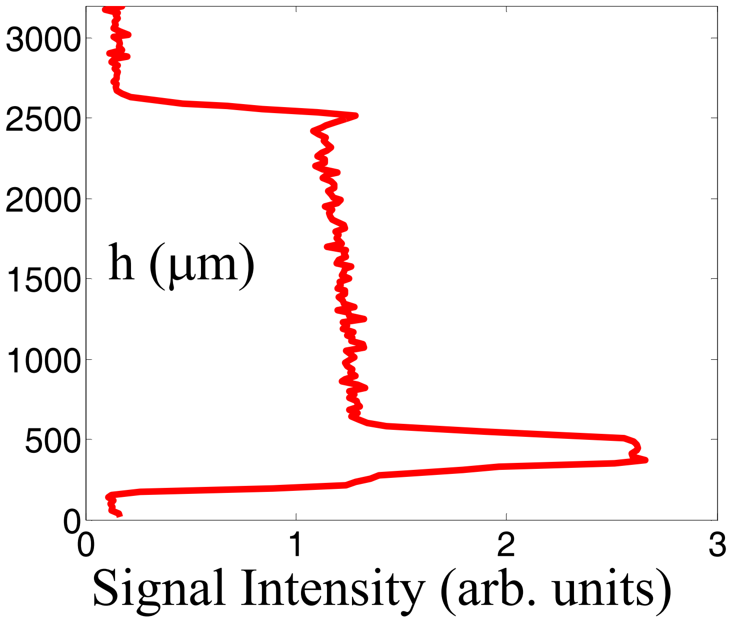
[R. W. Mair, et. al., *Phys. Rev. Lett.* **83** 3324 (1999)]



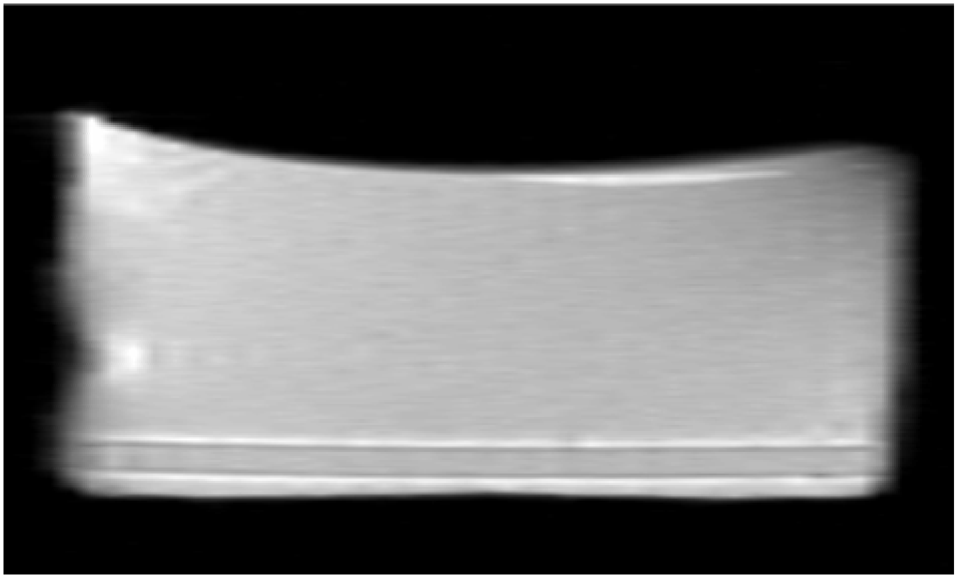
Heterogeneity in NMR Properties

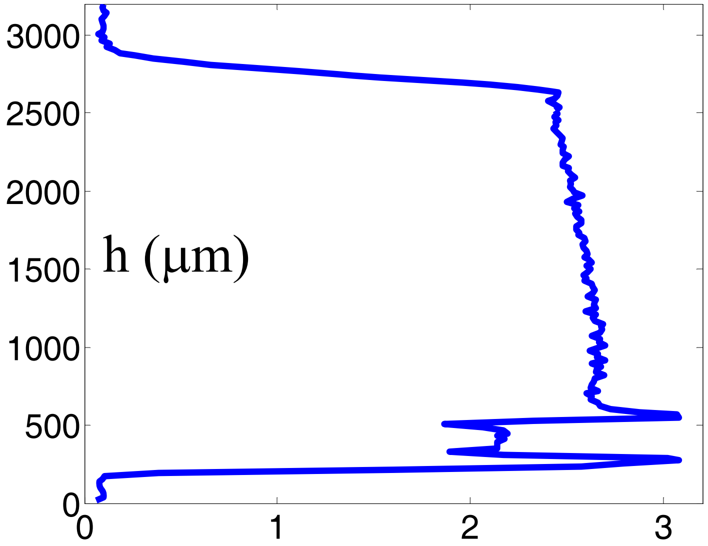
Diffusion weighted ^{1}H Image





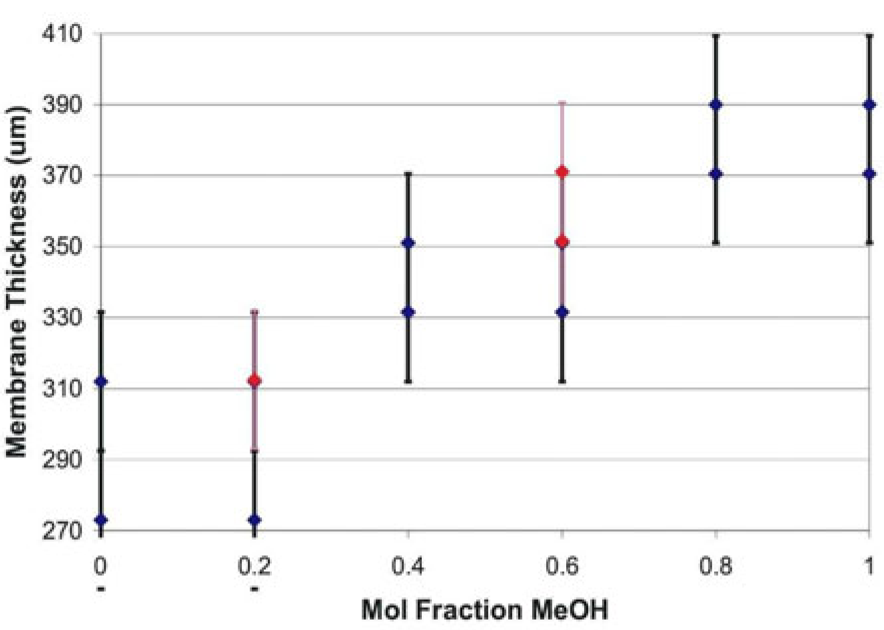
T$_2$ weighted ^{1}H Image



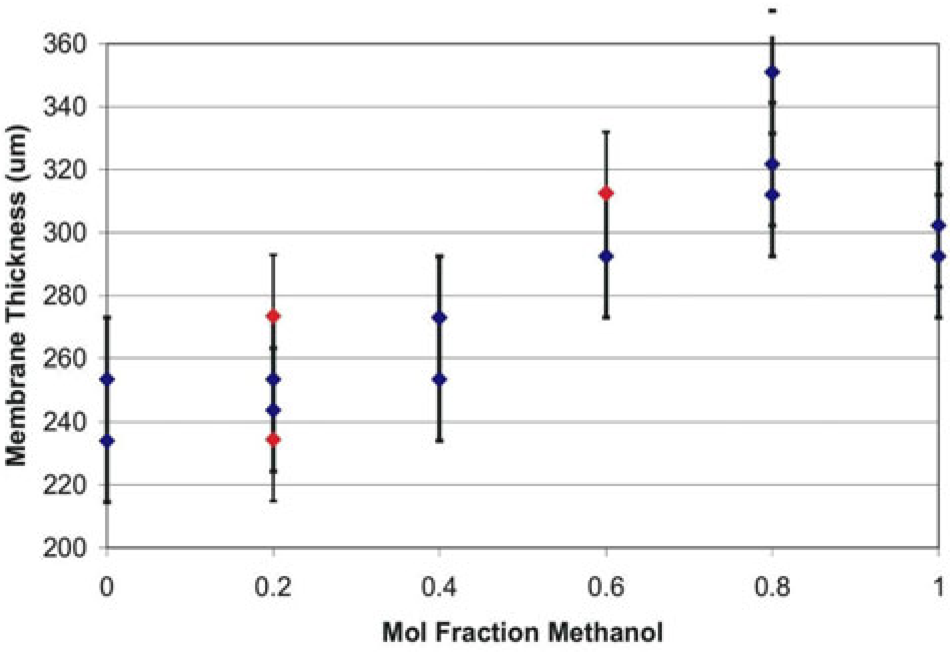


PEM Swelling

T_2 Image based thickness

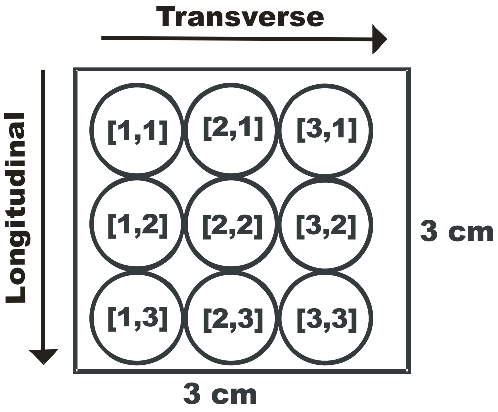


Diffusion Image based thickness



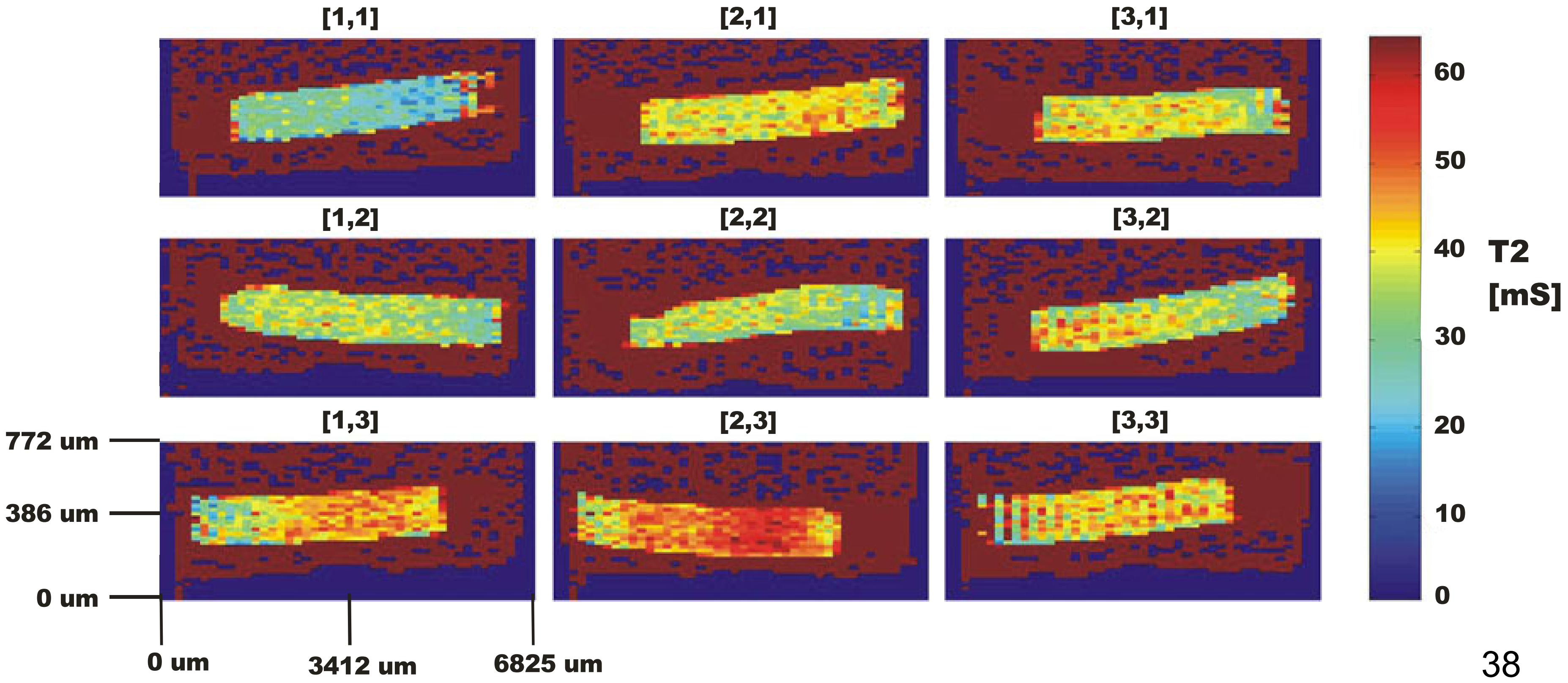
Thickness values calculated from solvent self-diffusion values are consistently smaller indicating the solvent translational diffusivity begins varying as a function of spatial position at the membrane surface at a different location than the rotational mobility indicated by T_2. This could be due to the so called “Schroeder’s Paradox” in which the surface of Nafion is found to be of high fluorocarbon concentration [Mauritz and Moore, *Chem. Rev*. **104** 4535-4585 (2004); Codd et al. *Appl. Mag. Res*. In press (2006).]

Technical Progress



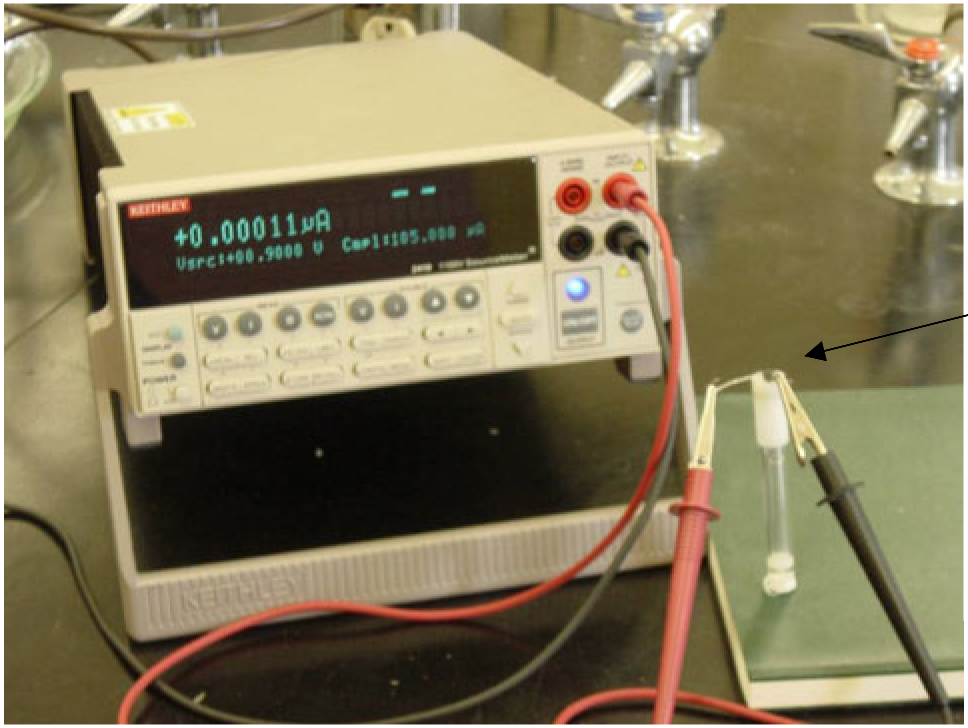
T_2maps of Nafion® 117 Hetrogeneity

[Codd et al. *Appl. Mag. Res*. In press (2006).]



ENMR Probe

An Electrophoretic NMR (ENMR) probe following the design of Holz *et al*. has been constructed for use with membrane samples. A programmable Kiethley power supply allows an electric field pulse train to be applied to the sample with NMR the rf and gradient pulses. Integration with the Bruker DRX 250 spectrometer is ongoing.



458 *M. Holz et al. / Magnetic Resonance Imaging 19 (2001) 457–463*

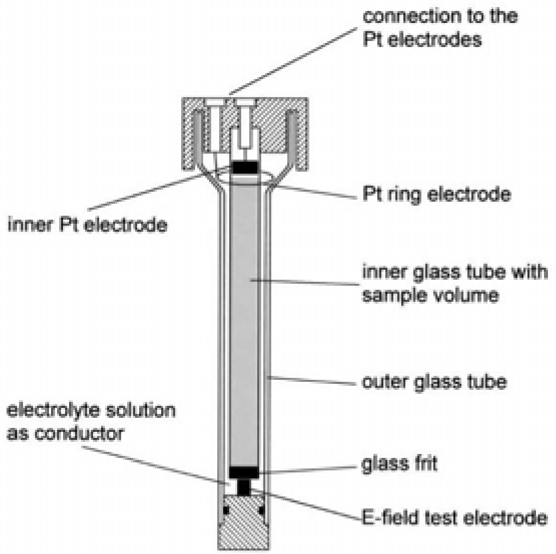


Fig. 1. Electrophoretic cell used in the present work for the ENMR experiments. The porous medium under observation is located in the inner tube of the concentric glass tube arrangement. The two Pt-electrodes are vented to the atmosphere in order to avoid problems with gas bubbles. The sample volume is mechanically separated from the conductor electrolyte in the outer glass tube by a glass frit.

Publications and Presentations

- Sarah L. Codd, Daniel T. Howe, Joseph D. Seymour, E. Hubble Werre, Scott C. Busse, and Eric S. Peterson, “Magnetic Resonance Microscopy of Heterogeneity in Polymer Electrolyte Membranes”, in press, *Applied Magnetic Resonance* (2006).
- Invited Lecture: Joseph D. Seymour, "Magnetic Resonance Microscopy of Membranes," 14th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg Tennesseee, October 23-27, 2005.
- D.T. Howe, J.D. Seymour, S.L. Codd, S.C. Busse, E.S. Peterson, E.H. Werre and B.F. Taylor, "MRM Measurement of Material Heterogeneity in Polymer Electrolyte Membranes", Oral Presentation O34, 8th International Conference on Magnetic Resonance Microscopy, Utsunomiya, Japan, August 22-26, 2005.
- “Instrumentation for PEM fuel cell transient degradation monitoring” S.R. Shaw IEEE-Power-Engineering-Society-General-Meeting-IEEE 67. 2004: 1646-9 Vol.2
- S. Pasricha, M. H. Nehrir, M. Keppler and S. R. Shaw. ``A Comparison of Static Electrical Terminal Fuel Cell Models", submitted to IEEE Transactions on Energy Conversion, accepted pending modifications.
- S. Pasricha and S. R. Shaw. ``A Dynamic PEM Fuel Cell Model", accepted for publication, IEEE Transactions on Energy Conversion.

Responses to Previous Year Reviewers' Comments

- No reviewer comments were provided.

(See Notes page for further information)

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.