2009 DOE Hydrogen Program Annual Review:
Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

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Overview

Timeline

- Project start date FY-07
- Project end date FY-11
- Percent complete 60%

Budget

- Total project funding
  - DOE share
  - Contractor share
- Funding received in FY08 - 1.2M
- Funding for FY09- 800K

Barriers

- Costs:
  - Fuel and air purification systems add cost
  - Impurity effects decrease fuel cell lifetime
  - Performance:
- Impurities and contaminants decrease fuel cell performance

Collaborators:

CASE WESTERN RESERVE UNIVERSITY EST. 1826 *Modeling*

xradia *X-ray Tomography*

CIDETEC Ik4 research alliance *S impurity studies*

BERKELEY LAB LAWRENCE BERKELEY NATIONAL LABORATORY Modeling

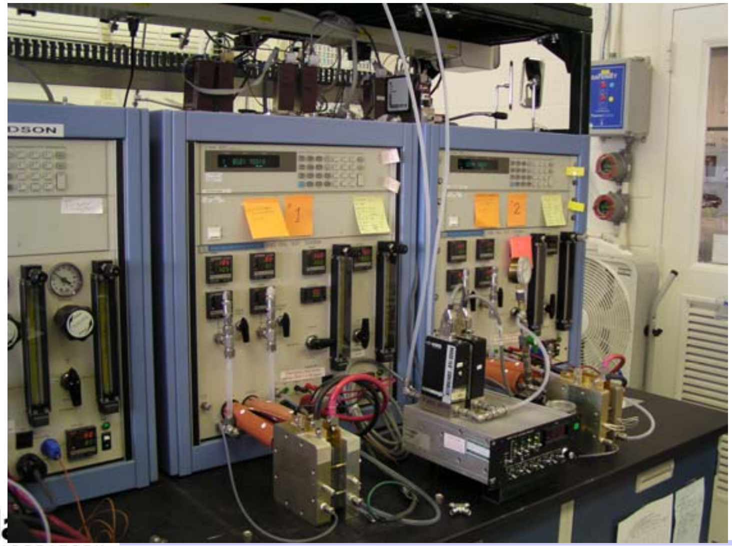
NRC·CNRC Institute for Fuel Cell Innovation *Fuel cell impurity studies*

Relevance

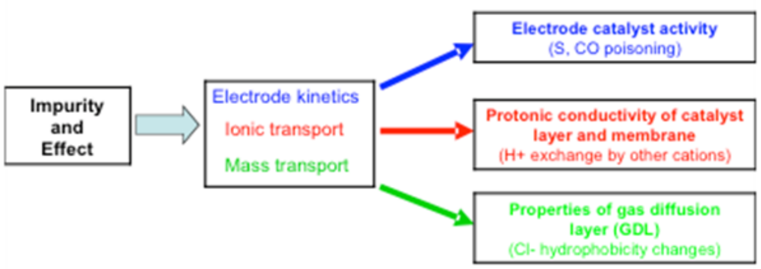
- Objectives
  - Understand the effects of fuel cell operation with less than pure fuel and air; simulate "real world" operation.
  - Understand how impurities affect DOE fuel cell cost and performance targets
  - Contribute to the scientific understanding of impurity-fuel cell component interactions and performance inhibition mechanisms
  - Develop science based models of impurity interactions upon fuel cell performance
  - *Experimental validation of models*
  - Develop mitigation strategies and methods
- Impact
  - Lowing cost of fuel cell operation by improving performance and increasing lifetime

Technical Approach

- Impurities affect fuel cells in many ways:
  - Electrocatalyst poisoning e.g. H_2S, CO and SO_2 adsorption onto Pt catalysts
  - Reduce ionomer conductivity- Na^+, Ca^{++}, NH_3
  - Block proton access to electrochemically active interface
  - Mass transport of water in ionmer may be reduced
  - GDLs may become hydrophilic and flood at high current densities



- Fabricate and operate fuel cells under controlled impurity gases
  - Multi-gas mixing manifolds and FC test stations
  - Pre-blend impurity gases
  - Measure performance
  - Steady state and *cycling* conditions
    - Understand degradation mechanisms
    - Study mitigation approaches
- Design supporting experiments to measure fundamental parameters needed for modeling
  - *Electroanalytical experiments*
  - *Adsorption studies*
  - *Permeation studies*
- Analyze and model data
  - Impurity impact on catalysis
  - Impurity impact on transport



Impurity and Effect

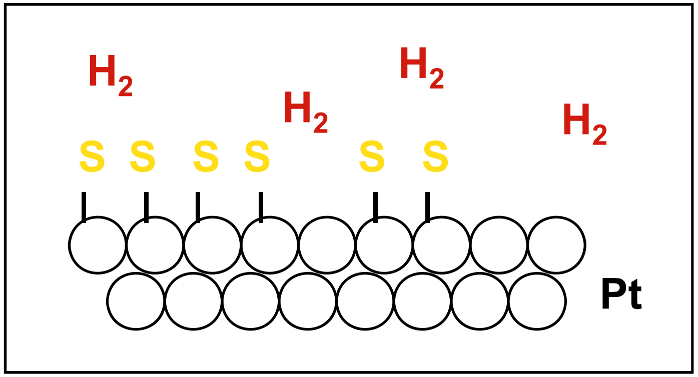
Electrode kinetics
Ionic transport
Mass transport

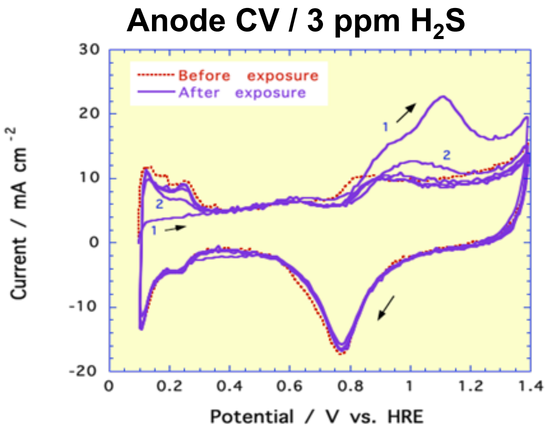
Electrode catalyst activity
(S, CO poisoning)

Protonic conductivity of catalyst layer and membrane
(H+ exchange by other cations)

Properties of gas diffusion layer (GDL)
(Cl- hydrophobicity changes)

Basic S-Degradation Mechanism





Deactivation: $Pt + H_2S$ □ $Pt\text{-}S + H_2$ **(heterogeneous reaction)**

$Pt + H_2S$ □ $Pt\text{-}S + 2H^+ + 2e^-$ **(electrochemical reaction)**

$Pt + SO_2$ □ $Pt\text{-}S + O_2 + 2e^-$ **(heterogeneous reaction)**

$Pt + SO_2 + 4H^+ + 4e^-$□ $Pt\text{-}S + 2H_2O$ **(heterogeneous reaction)**

Cleaning: $Pt\text{-}S + 4H_2O$ □ $Pt + SO_4^{2-} + 8H^+ + 6e^-$

- *Strong sulfur chemisorption onto Pt deactivates the catalyst*
- *Pt-coverage: more than one monolayer of sulfur*
- *PtS may form under severe conditions*

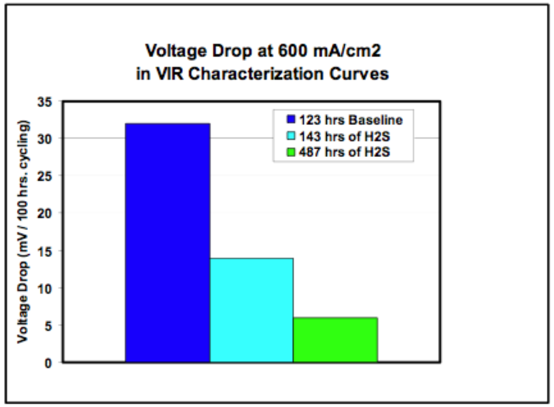
Drive Cycle Testing Effects of 10 ppb H_2S *New Results*

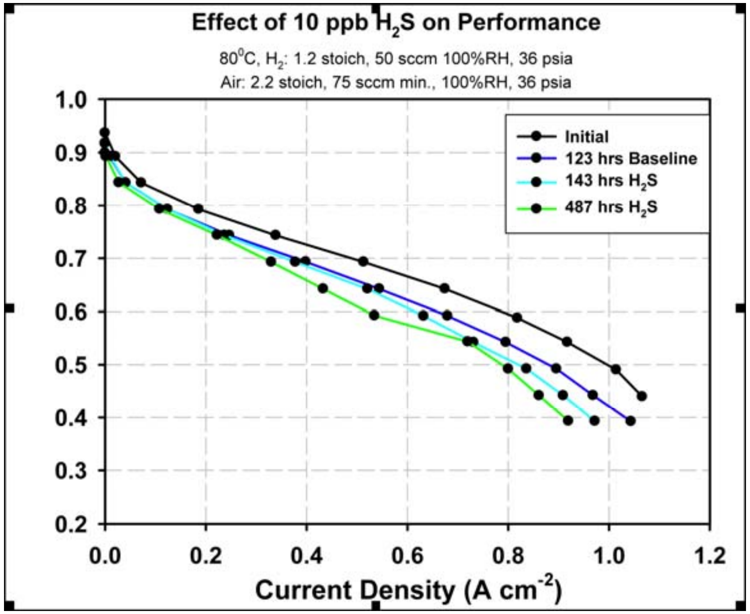
Cell:50 cm^2

- MEA- , anode- 0.10 mg Pt/cm^2, cath- 0.20 mg Pt/cm^2
- Drive Cycle Durability Test:
- Constant voltage mode 0.85V-0.6V
- Conditions— cell temp. 80C, H2: 1.2 stoich, 50 sccm min., 50% RH (63C), 14psig, AIR: 2.0 stoich, 75 sccm min., 50% RH (63C), 14 psig
- Initial pre-exposure run 100 hours
- After pre-exposure run, a 1000 hour H2S, 10 PPB

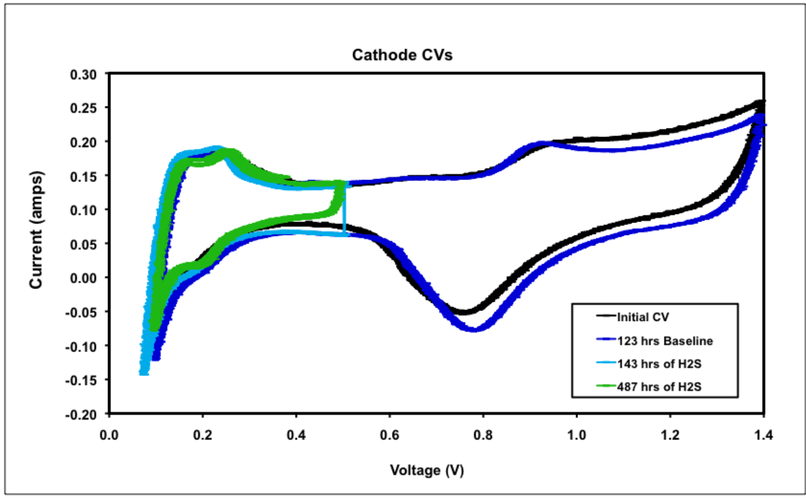
Characterizations:

- Collection of a sample of anode and cathode exhaust water for fluorine ion concentration testing
- Polarization tests— 0.95V - 0.40V
- CV Analysis for electrochemical surface area changes 0.100V – 0.5V,

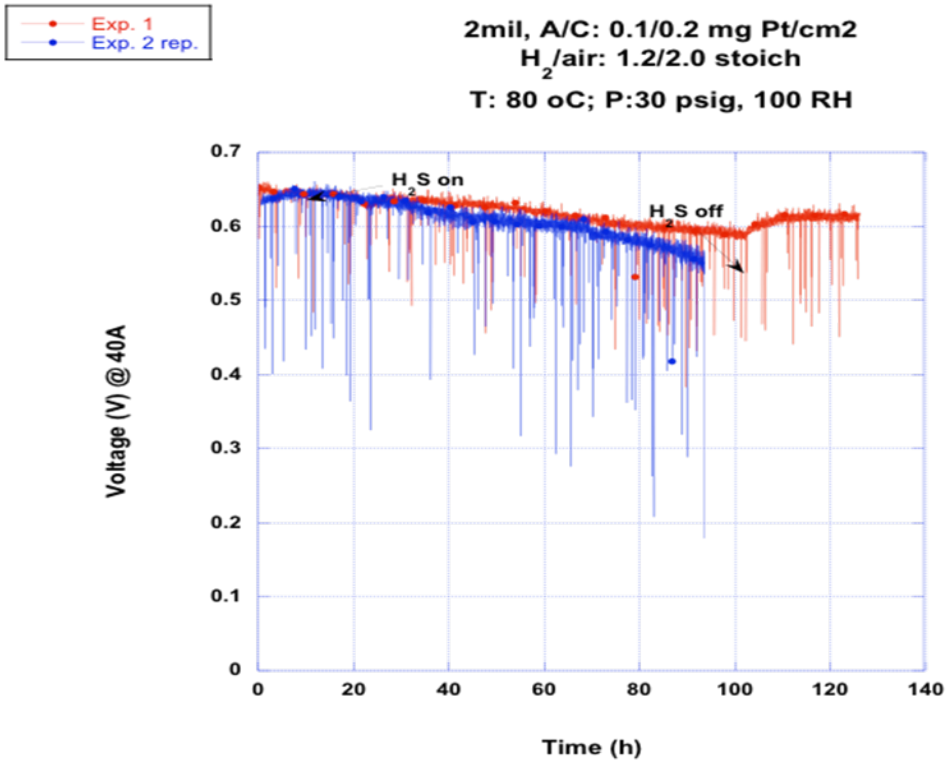


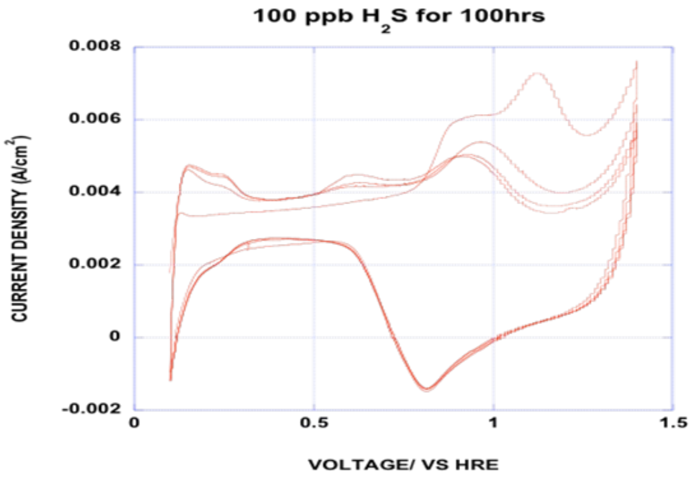


- *No additional degradation due to hydrogen sulfide observed*
- *membrane degradation on cycling is an issue with ultrathin low Pt loading MEAs*



H_2S Removal *New Results*



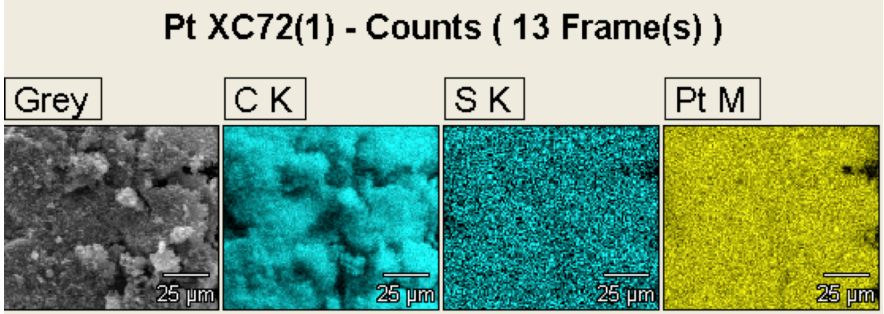


- 100 ppb H_2S for approx. 100 hrs.
- CV showed clean surface after 4 cycles
- Performance returned to original
- **Degradation larger** in subsequent poisoning

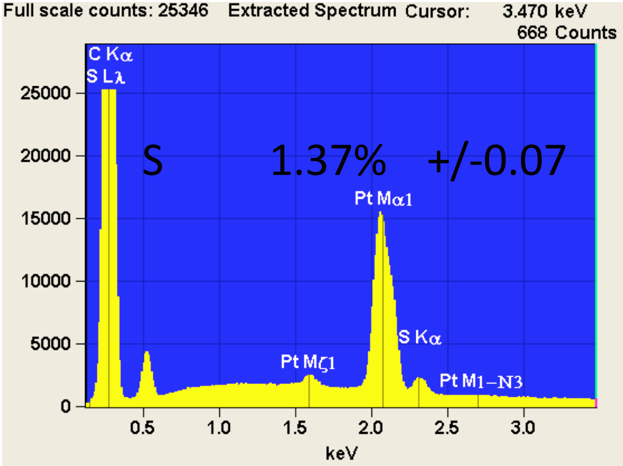
Did we really remove the H_2S?

Quantifying S adsorption on Pt-C catalysts

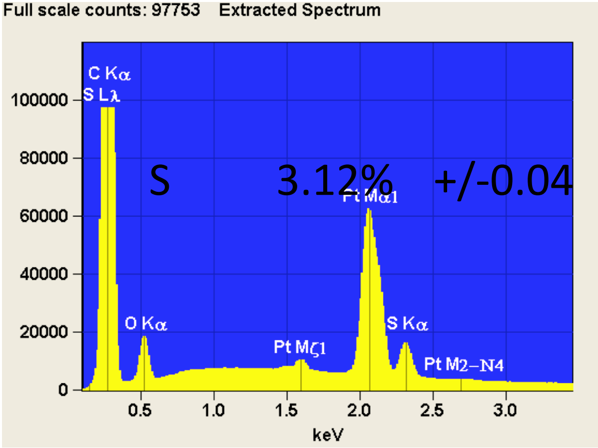
Quanta 400 ESEM Thermo Si-Drift EDS detector *New Results*



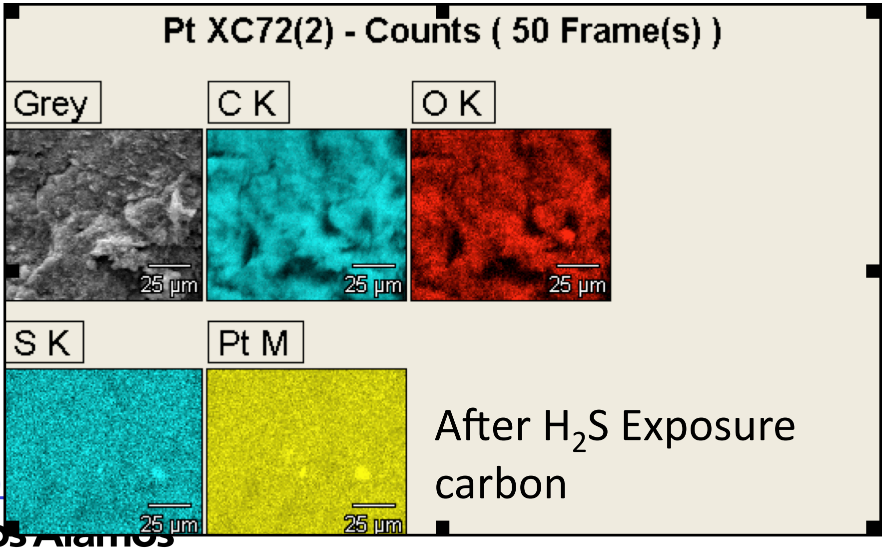
As received S from carbon support



S 1.37% +/-0.07



S 3.12% +/-0.04

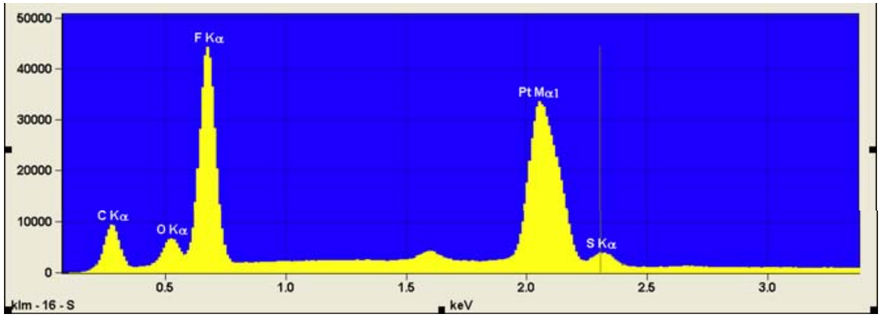


After H_2S Exposure carbon

2 weight % S gain in excellent agreement with TGA Study

Distribution of S Poisoning *New Results*

- Does S uniformly poison FCs?
- S adsorption detection difficult in conventional PEMFCS high S to Pt ratios
  - S in Nafion®
  - 1% S in C supports (50 to 80% catalyst weight
- Novel test fuel cell geometry
- Thin membrane Pt anode catalyst 0.86mg/cm^2 without support
  - minimize Ionomer content of layer
- Using high sensitivity Thermo Si Drift Detector S concentration can be accurately determined
- Validation in 5 cm cell
  - S concentrations vary from 0.9 to 2% from inlet to outlet while Pt&F (from ionomer) concentrations nearly constant
- *Next study: 50 cm segmented cell*

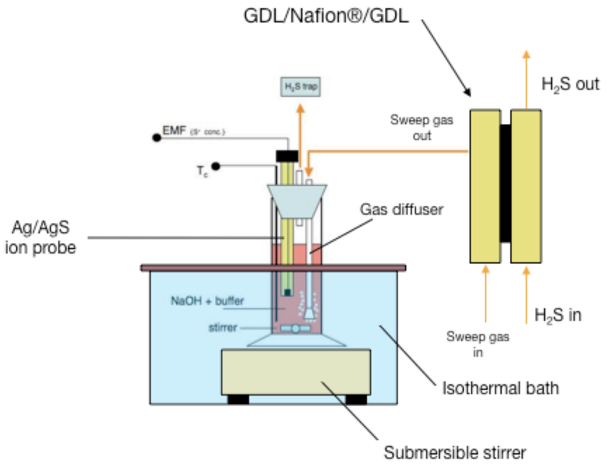


Si drift detectors

•Closer working distances & entire wafer is active
•Low Capacitance and noise
•Up to 10 times higher count than conventional EDS Si(Li)
•Improved accuracy under current conditions
•Higher count rates even at low beam current
•Enable chemical microscopy with high resolution for low energy peaks >50nm resolution

H_2S Crossover Measurements *New Results*

- Analytical technique using commercial Ag/AgS ion probes to trap H_2S that permeates through Nafion® has been developed and used to measure rates.
- Technique was focus in previous reviews/updates.
  - Chemical trap followed by lead nitrate titration using ion probe to determine endpoint.
  - Methods used for N117, N112, and N212 membranes at 25°C
  - 50 cm^2 with GDL (no catalyst), 1000ppm and 96 ppm sources of H_2S used, mixed from pure H_2S



Results of comprehensive crossover study:

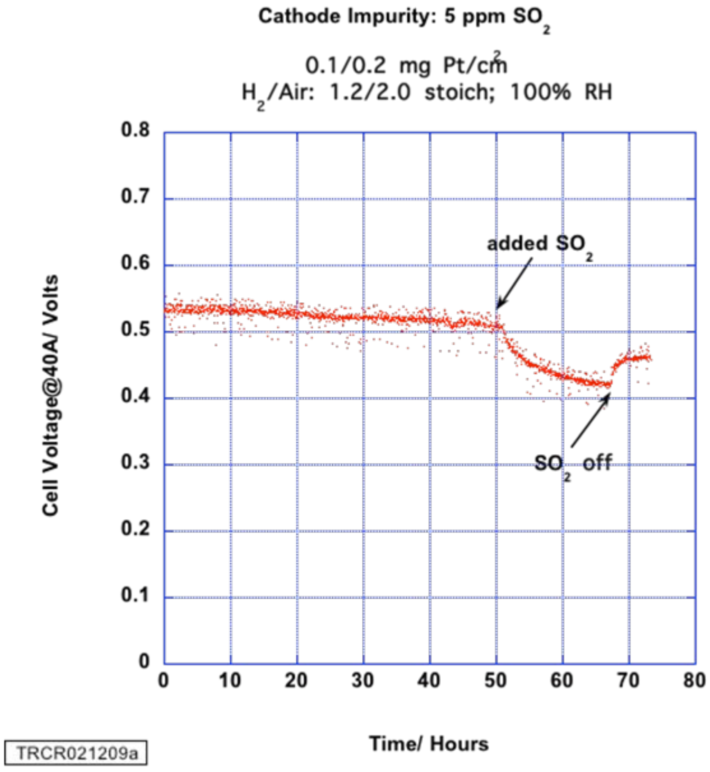
H_2S Concentration (Source gas)	Nafion® Membrane	Humidification State	Crossover/H_2S trapping rate (g/s)	Permeation Constant (g/s•atm•cm)
1000 ppm	212	dry	7.46×10^{-9}	7.58×10^{-10}
		wet	2.68×10^{-8}	2.72×10^{-9}
	117 (a)	dry	2.51×10^{-9}	8.79×10^{-10}
	117 (b)	dry	2.43×10^{-9}	8.50×10^{-10}
	117 (a)	wet	6.86×10^{-9}	2.40×10^{-9}
	117 (b)	wet	5.94×10^{-9}	2.08×10^{-9}
	112	wet	3.59×10^{-8}	3.44×10^{-9}
		wet	4.86×10^{-8}	4.65×10^{-9}
96 ppm	112	wet	2.23×10^{-9}	2.36×10^{-9}
		wet	2.24×10^{-9}	2.36×10^{-9}

- *Hydrogen sulfide crossover rates well-characterized*

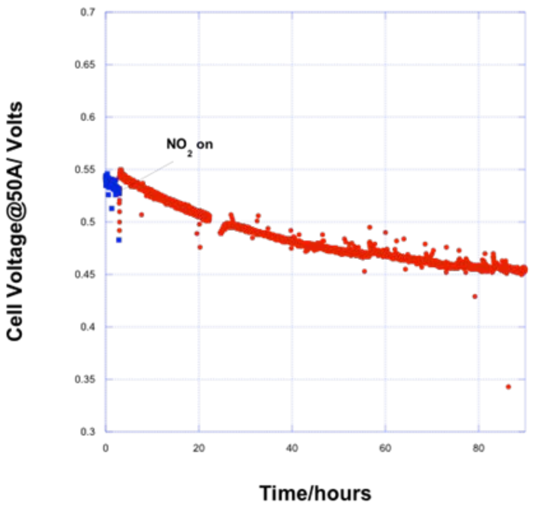
E.L. Brosha, T. Rockward, F.A. Uribe, and F. Garzon, "Measurement of H_2S Crossover Rates in Fuel Cell Nafion® Membranes Using Ion-probe Techniques." To be submitted: *J. Electrochem. Soc.* Spring 2009.

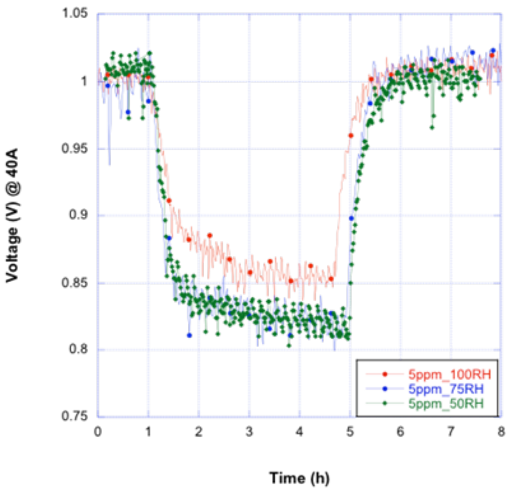
Thin-Ionomer PEMFC Exposure to SO_2 *New Results*

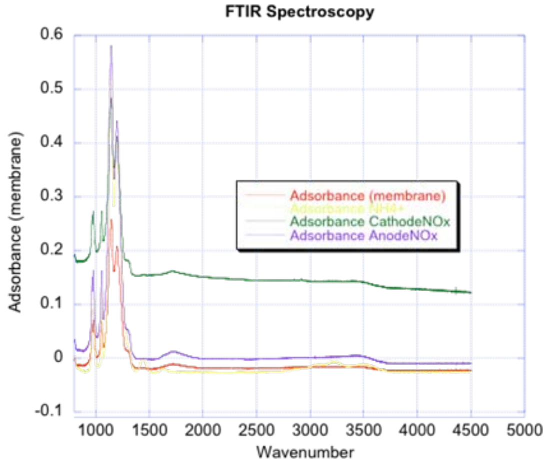
- Sulfur dioxide emissions are very large in developing economies
- Major culprit for fuel cell failure in some Asian test markets
- Source -coal and high sulfur petroleum fuel combustion
- 50 cm^2 5ppm SO_2 cathode injection:0.8 A/cm^2
- 0.1mg/cm^2 anode-0.2mg/cm^2 cathode 25µm ionomer
- Voltage loss with partial recovery
- Similar performance loss to thicker membrane FC's previously tested



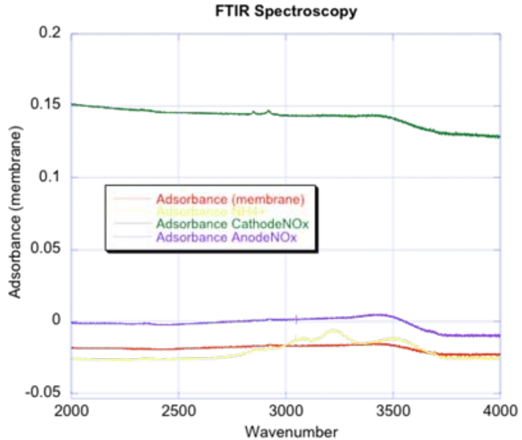
NO$_X$ *New Results*





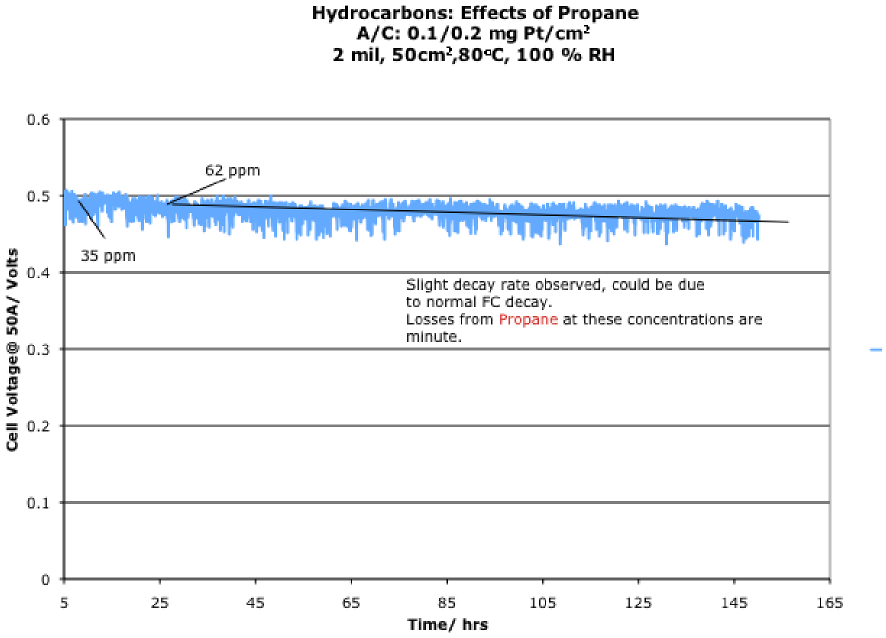


- 0.1mg/cm^2 Pt-C anode-0.2mg/cm^2 Pt-C cathode 50µm ionomer
- Fuel Cell Testing of 5ppm NO$_2$ cathode 1 A/cm^2 80°C
- Steady decay in performance
- Some humidification dependence on performance losses
  - Higher humdification may remove more soluble NO$_2$
- FTIR spectroscopy to detect speciation

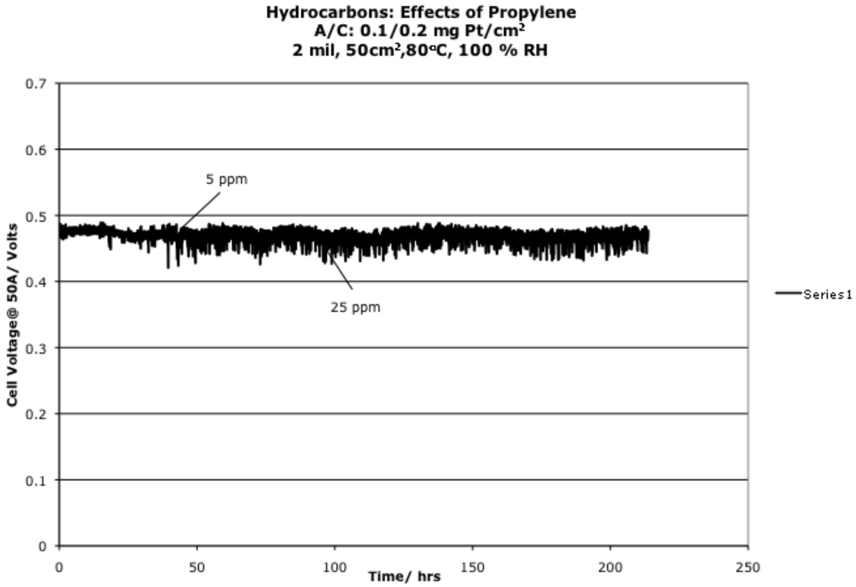


- Ammonium exchange membrane compared to NO$_2$ exposed MEA
- ammonium ions 2400–3200 cm^{-1}
- Sharp peaks at 2800 cm^{-1} may be amine vibrational modes

Hydrocarbon Effects *New Results*


Hydrocarbons: Effects of Propane
A/C: 0.1/0.2 mg Pt/cm^2
2 mil, 50cm^2,80°C, 100 % RH

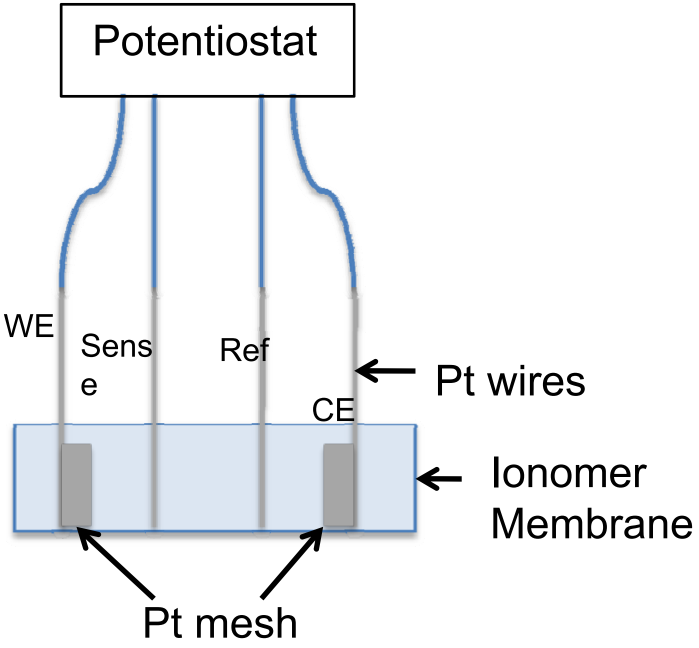
Slight decay rate observed, could be due to normal FC decay.
Losses from Propane at these concentrations are minute.

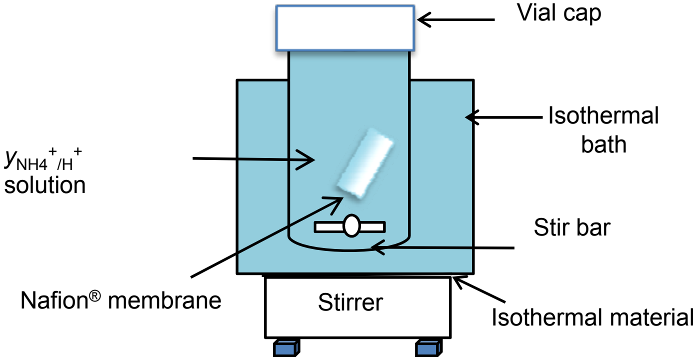

Hydrocarbons: Effects of Propylene
A/C: 0.1/0.2 mg Pt/cm^2
2 mil, 50cm^2,80°C, 100 % RH

- 0.1mg/cm^2 Pt-C anode-0.2mg/cm^2 Pt-C cathode 50µm ionomer
- Propane injected resulted in little performance loss
- Increasing concentration did not change loss rate at 1 amp/cm^2 constant current

- 0.1mg/cm^2 Pt-C anode-0.2mg/cm^2 Pt-C cathode 50µm ionomer
- No effect of 5 to 25ppm injection of Propylene C_3H_6

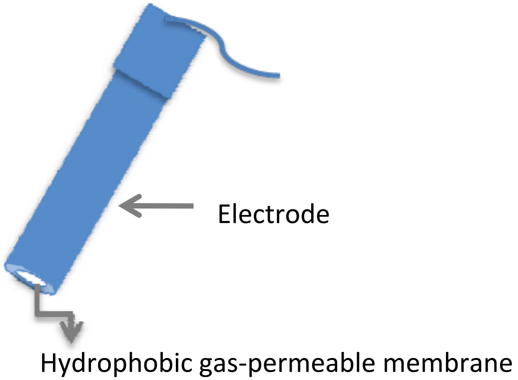
Ammonium Ion Membrane Equilibrium





$\mu_{nafion} = \mu_{solution}$ (system at equilibrium)

- Ammonia oxidation rate is insignificant
- removal mechanism is aqua ammonia-equilibrium



Ammonia Removal Mechanisms *New Results*

- Two possible mechanisms for ammonia removal from membranes:
  - Electro-oxidation:

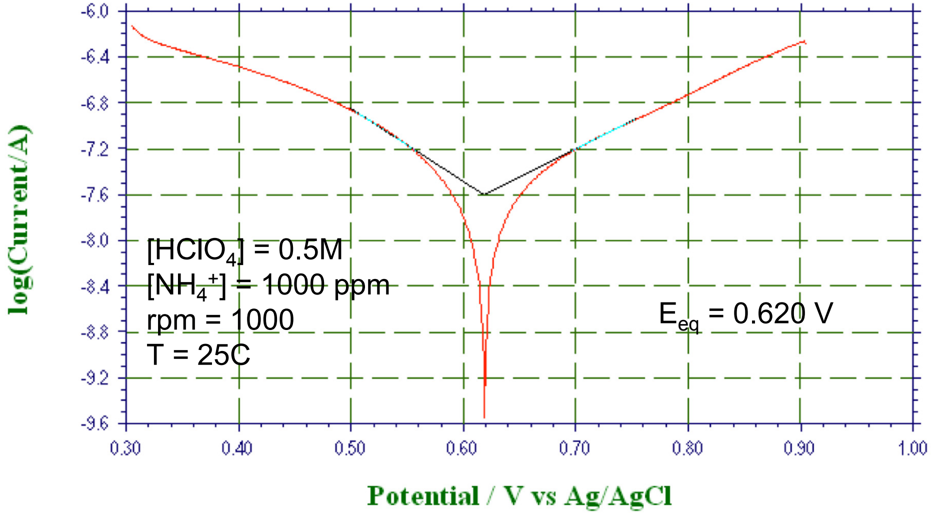
$$2NH_{4\,Nafion}^{+} \rightarrow 8H^{+}{}_{Nafion} + N_2 + 6e^{-}$$

  - Water solubility:

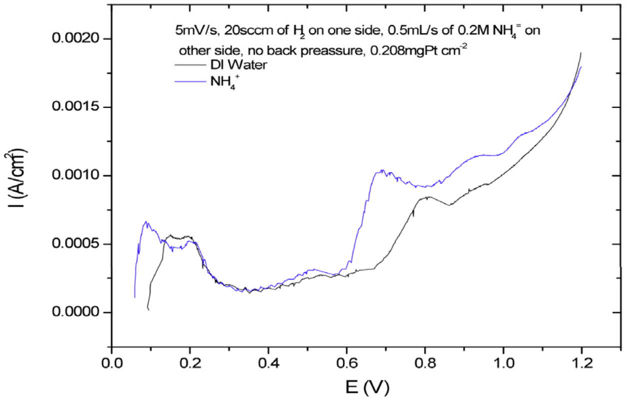
$$NH_{4\,Nafion}^{+} + H_2O \rightarrow NH_{3(aq)} + H_{Nafion}^{+}$$

$$[NH_{4\,Nafion}^{+}] = \frac{[NH_{3(aq)}][H_{Nafion}^{+}]}{k_{eq}[H_2O]}$$

Ammonium ion oxidation rate in PEMFC- also very slow

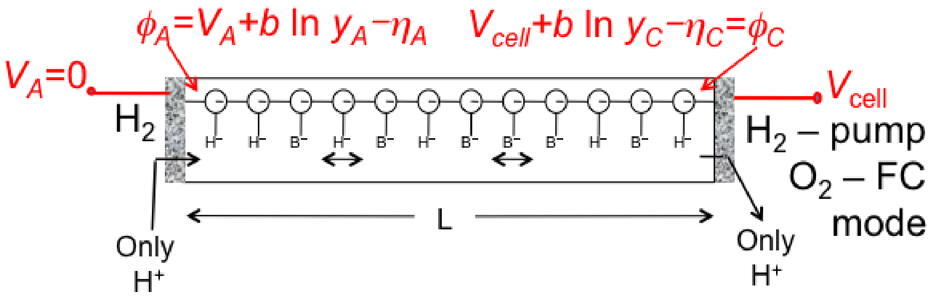


Ammonium ion oxidation rate in perchloric acid-very slow



Membrane Blocking Cation Model and Validation

- *Na^+, K^+, NH_4^+, Ca^{+2}, Cs^+ enter/leave on a long time scale and affect conductivity dynamically. Only H^+ enters/leaves membrane on short time scale.*
- *Water transport/electroosmotic-drag included, but boundary content maintained at λ=14 H_2O/SO_3^-.*
- *H-pump, not FC, model focuses on membrane effects, simplifies experimental verification and understanding.*
- *Time response, limiting current discussed*
- *AC impedance model*

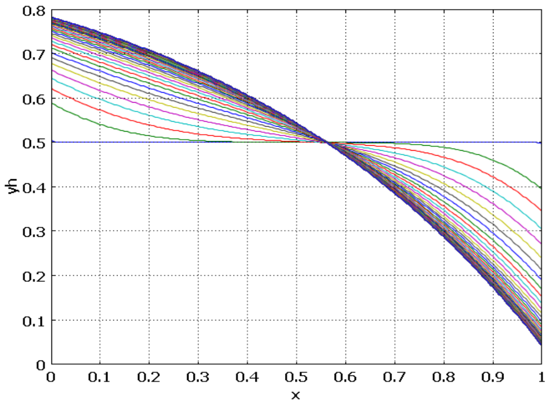


$\phi_A = V_A + b \ln y_A - \eta_A$ $\quad$ $V_{cell} + b \ln y_C - \eta_C = \phi_C$

η_A, η_C – anode/cathode overpotentials $\quad y_H = \dfrac{[H^+]}{[H^+] + Z[B^{+Z}]}$

B^{+Z}: Blocking cation with charge Z

We reference to y_H=1, i.e $[B^{+Z}] = 0$ $\quad V_{Nernst} = \underbrace{\dfrac{RT}{F}}_{b} \ln y_H$



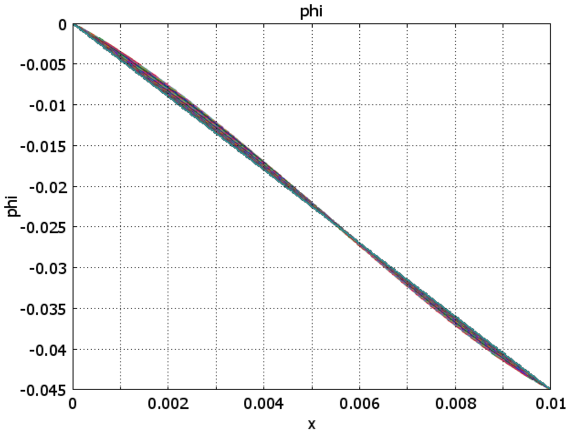
Fractional distance

Initial uniform 50% H^+ and NH_4^+ distribution

Step current from 0 to 0.25 A/cm^2

$D_H = 1.73 \cdot 10^{-5}$ cm^2/s, $D_B = 3.63 \cdot 10^{-6}$

y_h and ϕ plotted every 0.2 s



Length cm

Concentrated Solution Transport Equations Used in Membrane

D_i - dif. coef. of H^+,B^+ cm^2/s

C_t - SO_3^- conc. in ionomer

Φ - potential V

α - D_B/D_H

L - thickness cm

λ - H_2O/ SO_3^-

d_a- d(activity)/dλ

ξ_i - drag coef.

$\frac{FD_i}{RT}$ - mobility $cm^2/V\text{-}s$

b - $\frac{RT}{F}$ V

Diffusion Migration Drag

$$C_t \frac{\partial y_H}{\partial t} = \nabla \cdot \frac{D_H C_t}{L}\left[\frac{\partial y_H}{\partial x} + \frac{y_H}{b}\frac{\partial \phi}{\partial x} + \xi_H y_H d_a \frac{\partial \lambda}{\partial x}\right]$$

H^+

$$0 = \nabla \cdot \frac{D_H C_t}{L}\left[(\alpha - 1)\frac{\partial y_H}{\partial x} + \frac{((\alpha - 1) y_H - \alpha)}{b}\frac{\partial \phi}{\partial x} + ((\alpha \xi_B - \xi_H) y_H - \alpha \xi_B) d_a \frac{\partial \lambda}{\partial x}\right]$$

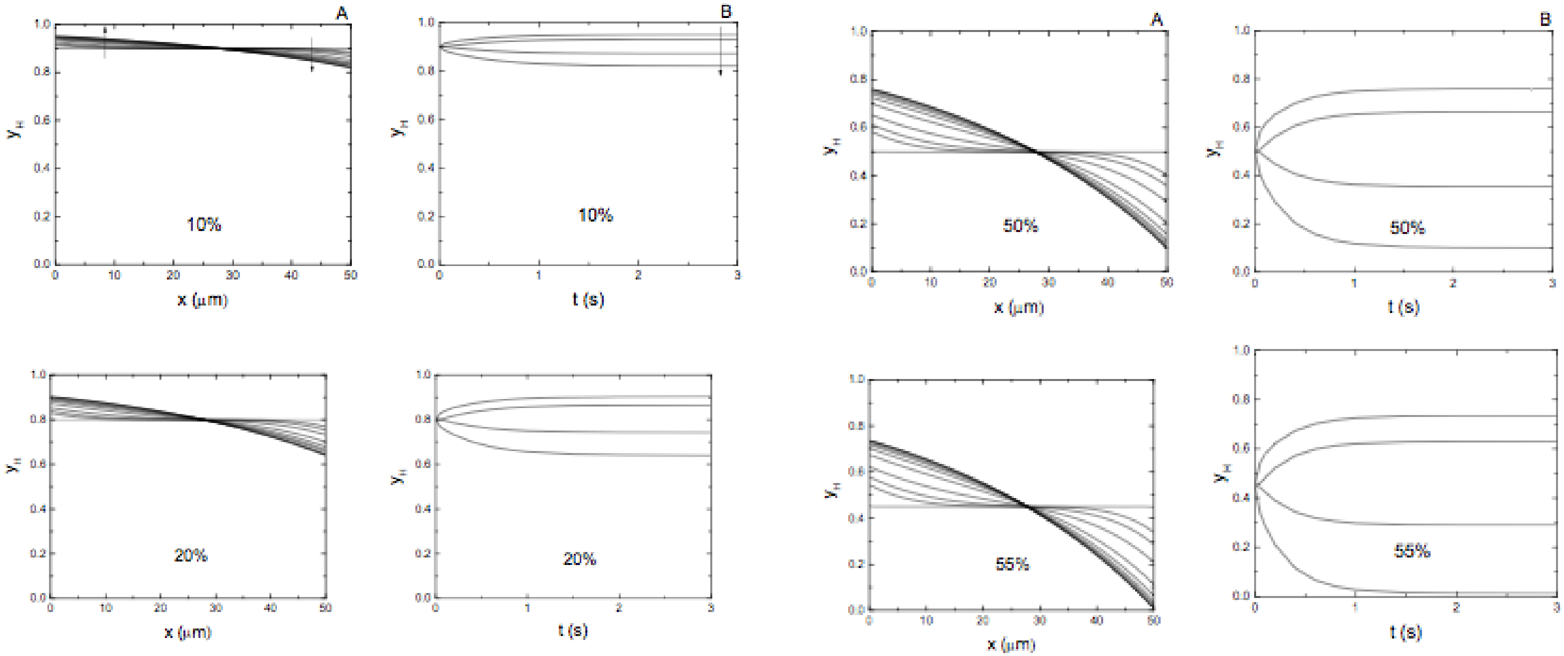
Total Charge

$$C_t \frac{\partial \lambda}{\partial t} = \nabla \cdot \frac{-D_H C_t}{L}\left[\left(\frac{\alpha \xi_B}{Z_B} - \xi_H\right)\frac{\partial y_H}{\partial x} + \frac{((\alpha \xi_B - \xi_H) y_H - \alpha \xi_B)}{b}\frac{\partial \phi}{\partial x} + \left(\left(\frac{\alpha \xi_B{}^2}{Z_B} - \xi_H{}^2\right) y_H - \frac{\alpha \xi_B{}^2}{Z_B} - \frac{C_t D_w^{'} \lambda}{c_1 L}\right) d_a \frac{\partial \lambda}{\partial x}\right]$$

Water

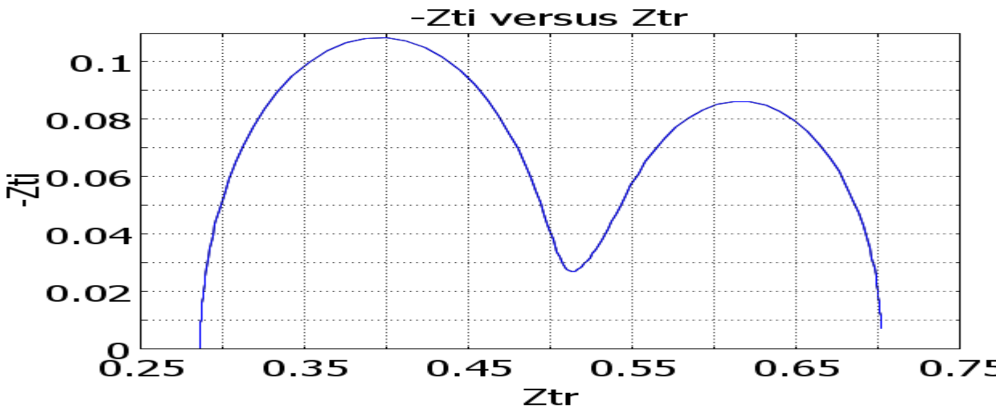
Diffusion

Transient Concentration Profiles *New Results*

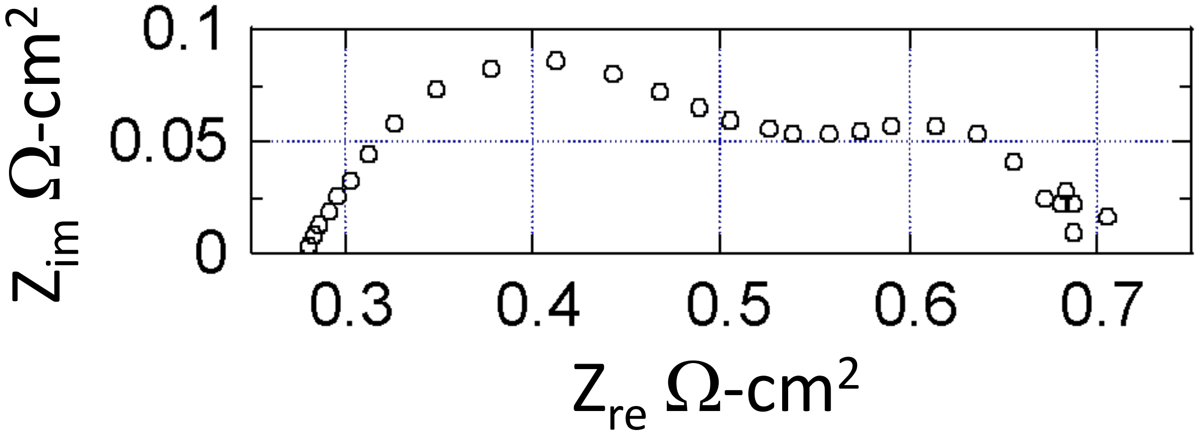


- •Modeled transient concentration profiles across a monvalent cation-contaminated fuel cell (50 μm ionomer) operating at constant current density of 1.0 A/cm^2
- •Protons strongly depleted at cathode
- •Membrane HFR would shift only slightly for low cation impurity levels
- •Time scale of cation migration event may be probed in the 0.1-1 Hz range by AC impedance

Impedance Response *New Results*



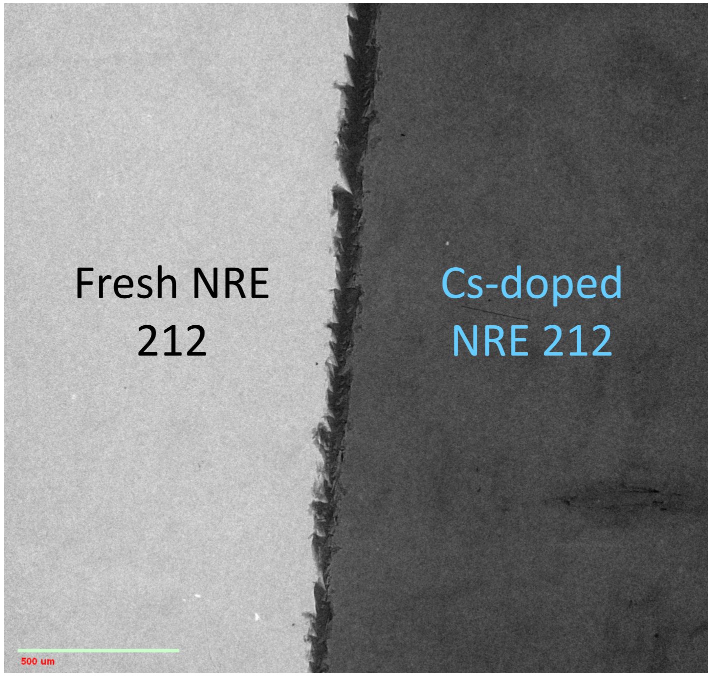
Point electrode simulation for Nafion® 117 50% Cs exchange C_D 0.1F/cm^2 j=0.3A/cm^2



AC impedance data .01-10KHz Nafion® 117 50% Cs exchange Pt loading 6mg/cm^2

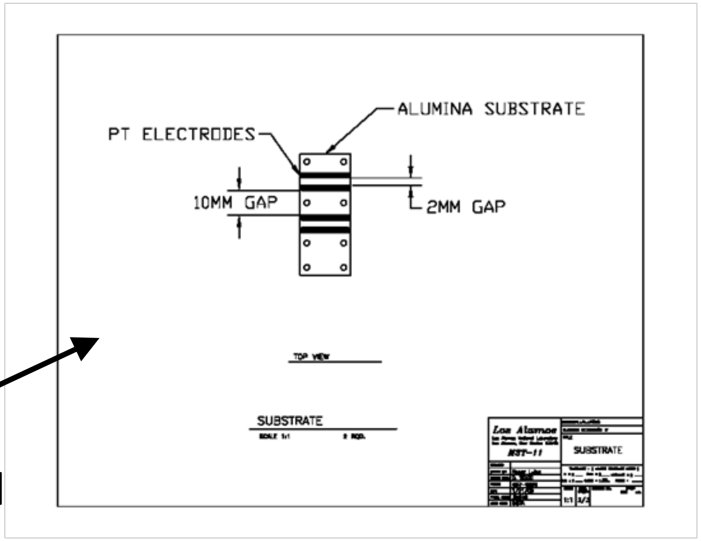
Visualization of Impurity Metal Cation Transport Using X-Ray Radiography *New Results*

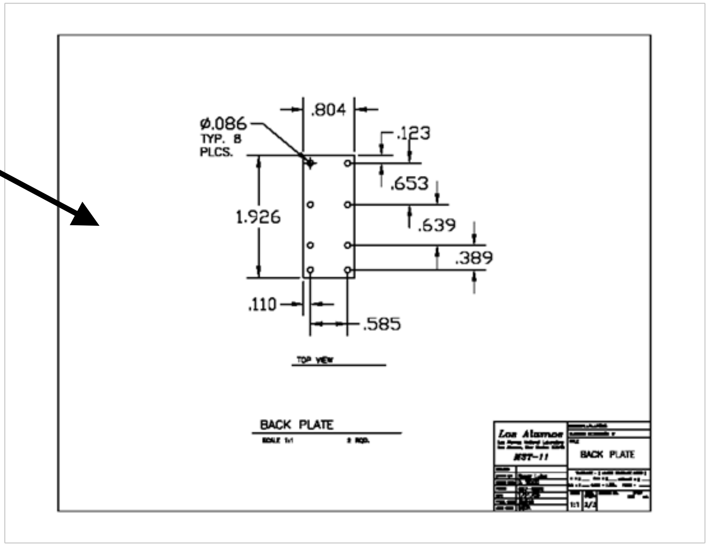
40 keV, 30 s Exposure Time



Ability to study cation diffusion using contrast differentiation (Cs^+ is baseline marker cation).

H_2-pump strip cell for studying proton transport.





Milestones

Month/Year	**Milestone or Go/No-Go Decision**
Feb-09	Milestone: Report on the hydrogen sulfide membrane permeability Completed
Feb-09	Milestone: Completed determination of alkane and alkene hydrocarbon effects on PEMFC performance. Completed
March-09	Milestone: We have expanded our cation contamination model to include water effects in membranes.
March-09	Milestone: Experimental validation of AC response of the cation impurity effects model
March-09	Milestone: determination of the electrochemical oxidation rates of ammonia in acidic solutions and PEMFCS

Summary/*Future Work*

- Low concentrations of S poisoning are not decreasing performance of prototype thin membrane/ low Pt loading MEAs
- S poisoning is probably not uniform
  - *Future segmented cell and impurity imaging studies on 50 cm^2 cells*
- Common hydrocarbons C1-C3 at PPM concentrations do not impact fuel cell performance
- SO_2 decreases fuel cell performance of low loading thin ionomer PEMFCs in a similar manner to the older generation-thicker membrane PEMFCs
- NO_2 decreases fuel cell performance
  - May be converted into other N-species at electrodes
  - *Future work: improved understanding of membrane speciation via spectrocopy*
- NH_3 exists in membranes as NH_4^+
  - slow equilibrium with water
  - Electrochemical oxidation rate is negligible in acidic conditions
  - Removal via water equilibrium
  - *Future work: Membrane transport studies-water equilibrium studies & FC testing of loss rates*
- Validated cation impurity models-explain why low levels of contaminants can cause significant performance losses
  - Need to model water effects (λ) in electrodes
  - Extend model to analyze slowly diffusing divalent metal cations
  - *Future experiments at NIST to determine cation- impurity effects on water transport*
  - *Future in situ imaging of operating cation fuel cells by X-ray tomography*

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