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

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FC_22_Garzon

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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:



Modeling



X-ray Tomography



S impurity studies



Modeling



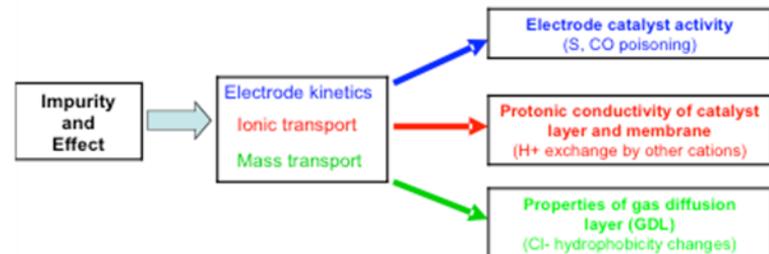
Fuel cell impurity studies

Relevance

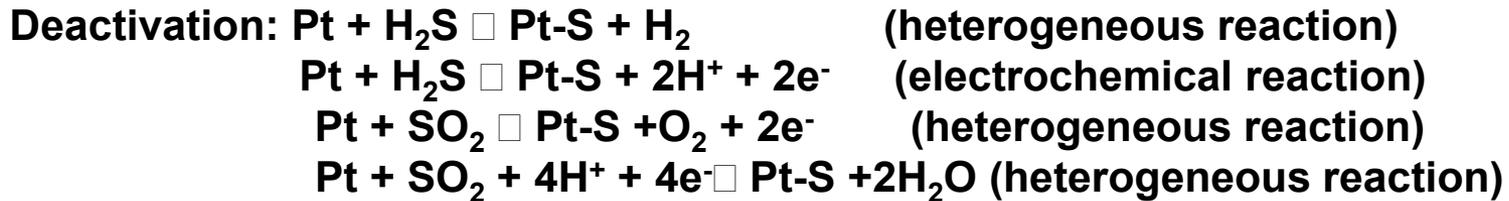
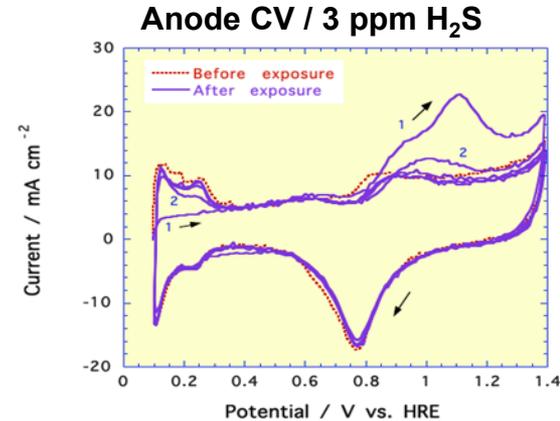
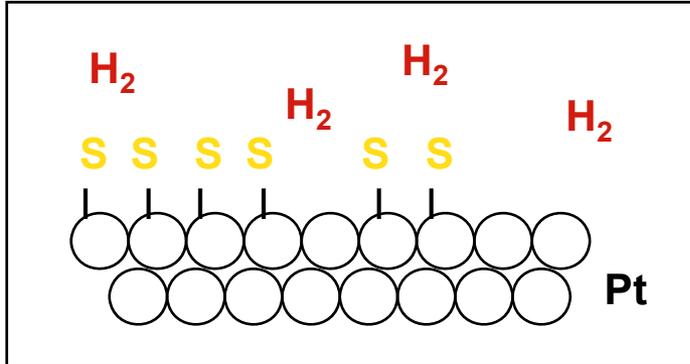
- Objectives
 - Understand the effects of fuel cell operation with less than pure fuel and air; simulate “real world” operation.
 - Understand how impurities affect DOE fuel cell cost and performance targets
 - Contribute to the scientific understanding of impurity-fuel cell component interactions and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



Basic S-Degradation Mechanism



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

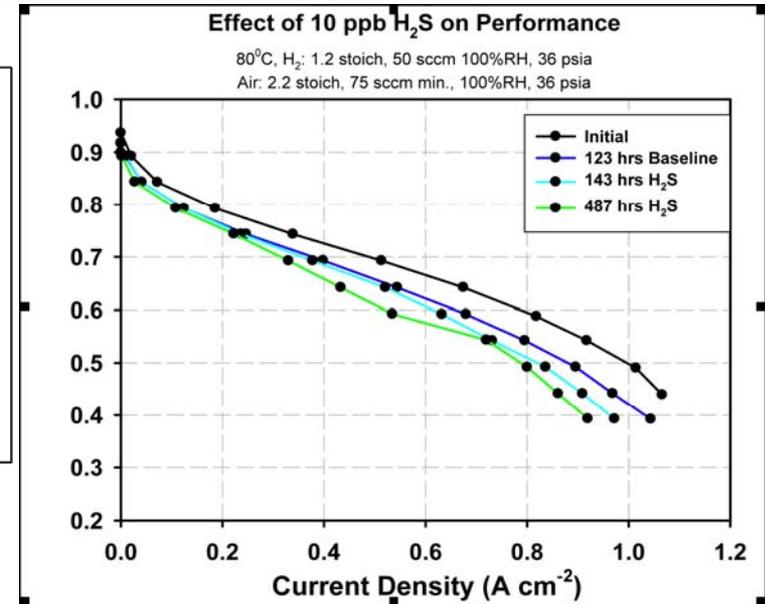
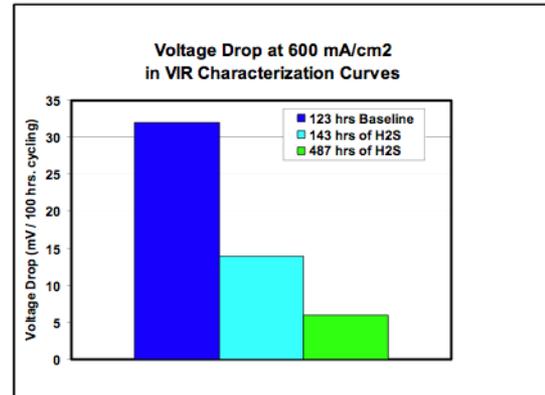
Drive Cycle Testing Effects of 10 ppb H₂S *New Results*

Cell: 50 cm²

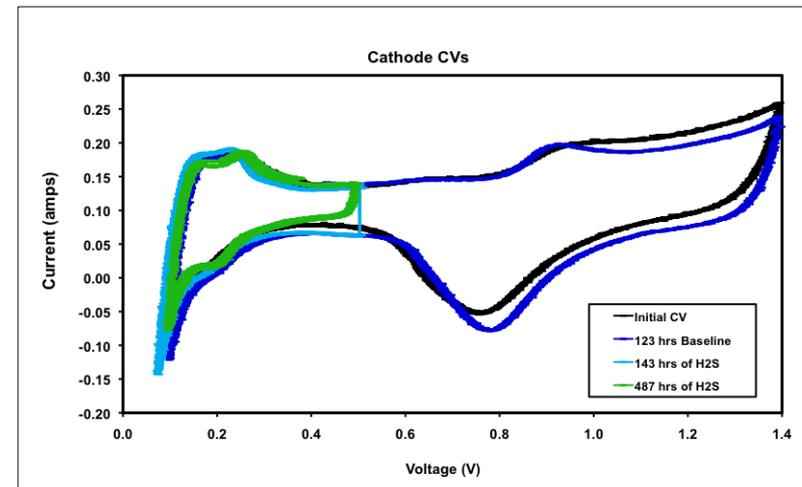
- MEA- , anode- 0.10 mg Pt/cm², cath- 0.20 mg Pt/cm²
- Drive Cycle Durability Test:
- Constant voltage mode 0.85V-0.6V
- Conditions— cell temp. 80C, H₂: 1.2 stoich, 50 sccm min., 50% RH (63C), 14psig, AIR: 2.0 stoich, 75 sccm min., 50% RH (63C), 14 psig
- Initial pre-exposure run 100 hours
- After pre-exposure 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,



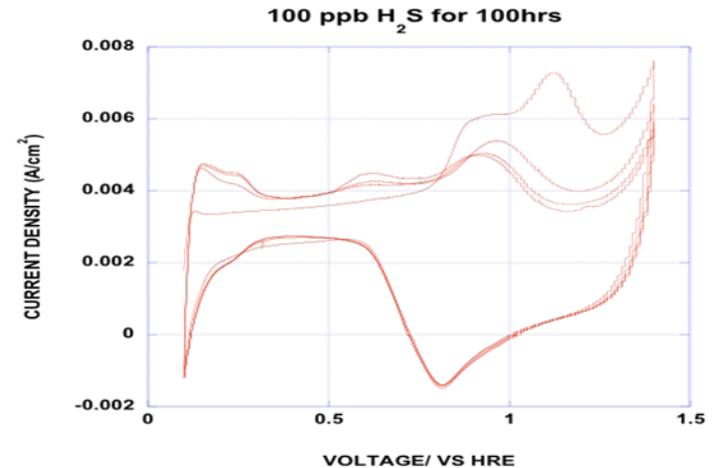
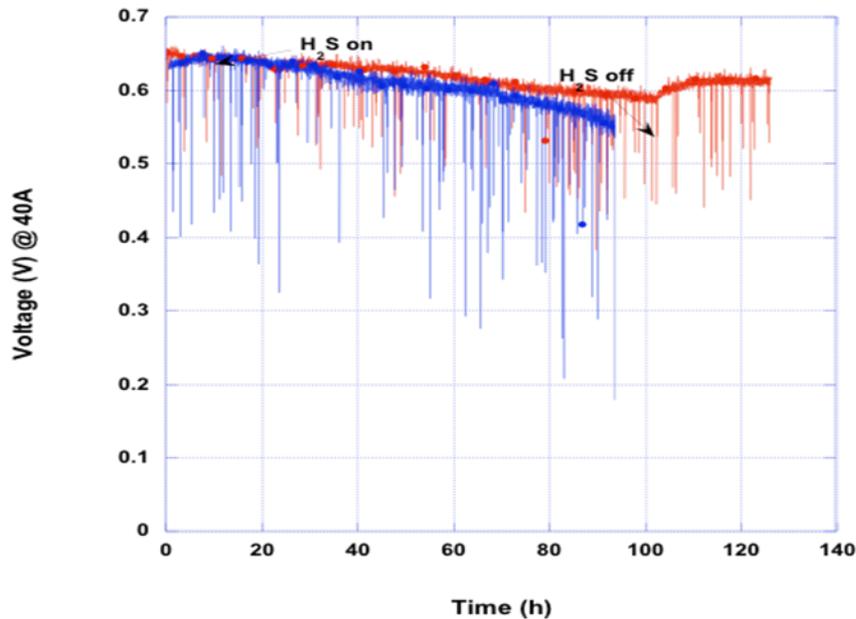
•No additional degradation due to hydrogen sulfide observed
•membrane degradation on cycling is an issue with ultrathin low Pt loading MEAs



H₂S Removal *New Results*

—●— Exp. 1
—●— Exp. 2 rep.

2mil, A/C: 0.1/0.2 mg Pt/cm²
H₂/air: 1.2/2.0 stoich
T: 80 oC; P:30 psig, 100 RH

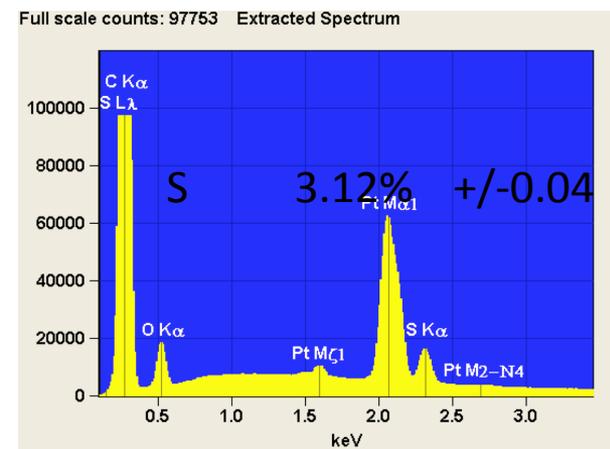
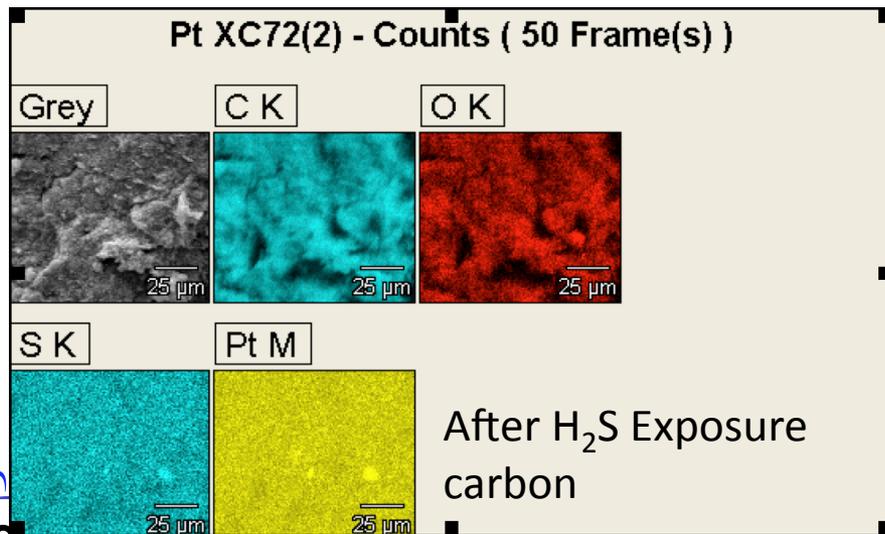
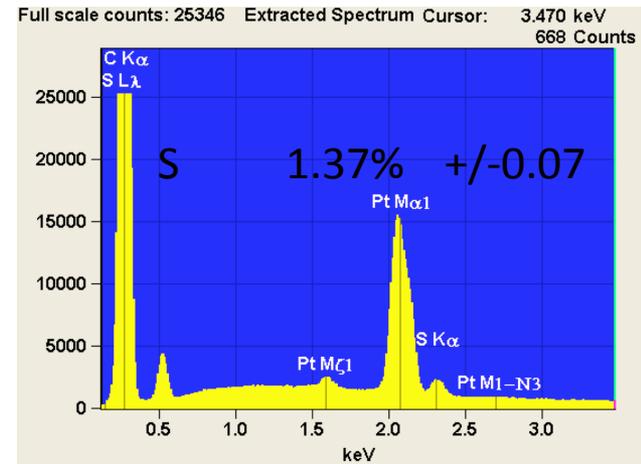
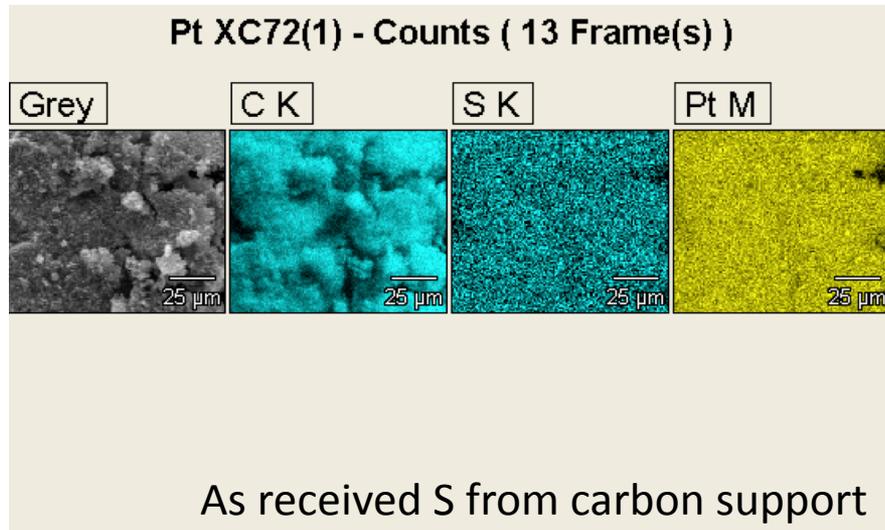


- 100 ppb H₂S for approx. 100 hrs.
- CV showed clean surface after 4 cycles
- Performance returned to original
- **Degradation larger** in subsequent poisoning

Did we really remove the H₂S?

Quantifying S adsorption on Pt-C catalysts

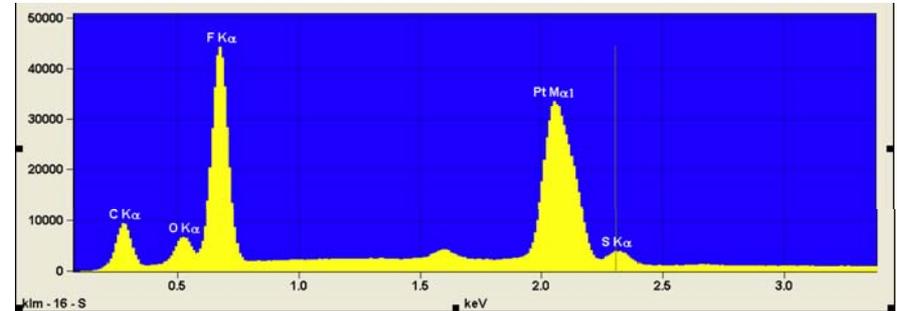
Quanta 400 ESEM Thermo Si-Drift EDS detector *New Results*



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/cm² 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*

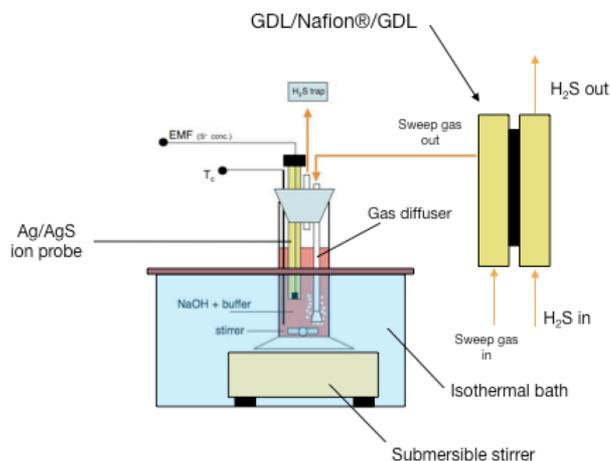


Si drift detectors

- 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

H₂S Crossover Measurements *New Results*

- Analytical technique using commercial Ag/AgS ion probes to trap H₂S 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 cm² with GDL (no catalyst), 1000ppm and 96 ppm sources of H₂S used, mixed from pure H₂S



Results of comprehensive crossover study:

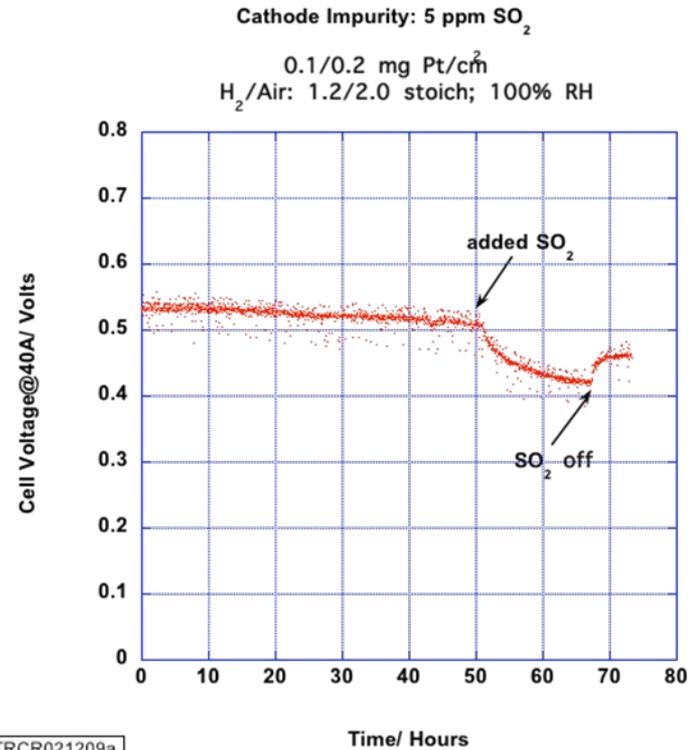
| H ₂ S Concentration (Source gas) | Nafion® Membrane | Humidification State | Crossover/H ₂ S trapping rate (g/s) | Permeation Constant (g/s•atm•cm) |
|---|--|-----------------------|--|----------------------------------|
| 1000 ppm | 212 | dry | 7.46×10^{-9} | 7.58×10^{-10} |
| | | wet | 2.68×10^{-8} | 2.72×10^{-9} |
| | 117 (a) 117 (b) 117 (a) 117 (b) | dry | 2.51×10^{-9} | 8.79×10^{-10} |
| | | dry | 2.43×10^{-9} | 8.50×10^{-10} |
| | | wet | 6.86×10^{-9} | 2.40×10^{-9} |
| | | 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*

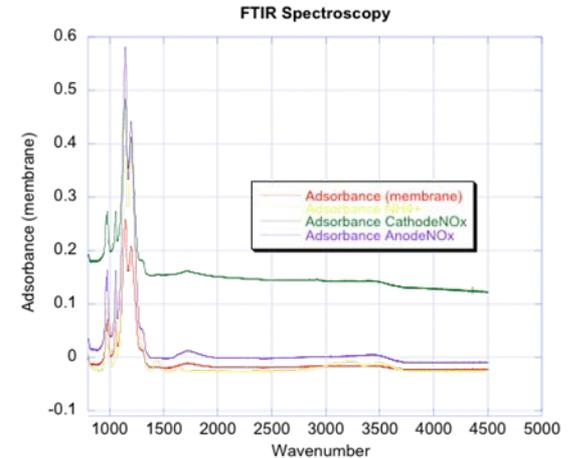
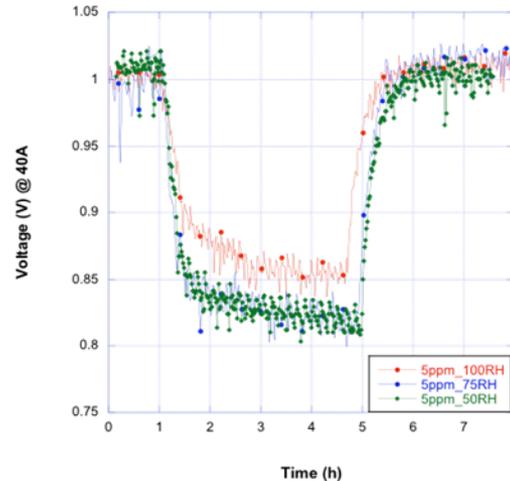
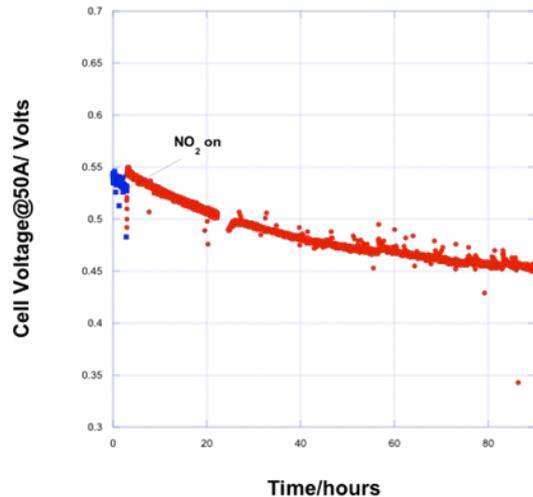
E.L. Brosha, T. Rockward, F.A. Uribe, and F. Garzon, "Measurement of H₂S Crossover Rates in Fuel Cell Nafion® Membranes Using Ion-probe Techniques." To be submitted: *J. Electrochem. Soc.* Spring 2009.

Thin-Ionomer PEMFC Exposure to SO₂ *New Results*

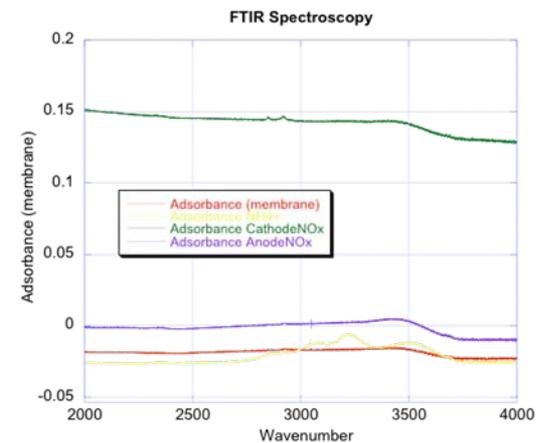
- Sulfur dioxide emissions are very large in developing economies
- Major culprit for fuel cell failure in some Asian test markets
- Source -coal and high sulfur petroleum fuel combustion
- 50 cm² 5ppm SO₂ cathode injection: 0.8 A/cm²
- 0.1mg/cm² anode-0.2mg/cm² cathode 25μm ionomer
- Voltage loss with partial recovery
- Similar performance loss to thicker membrane FC's previously tested



NO_x *New Results*



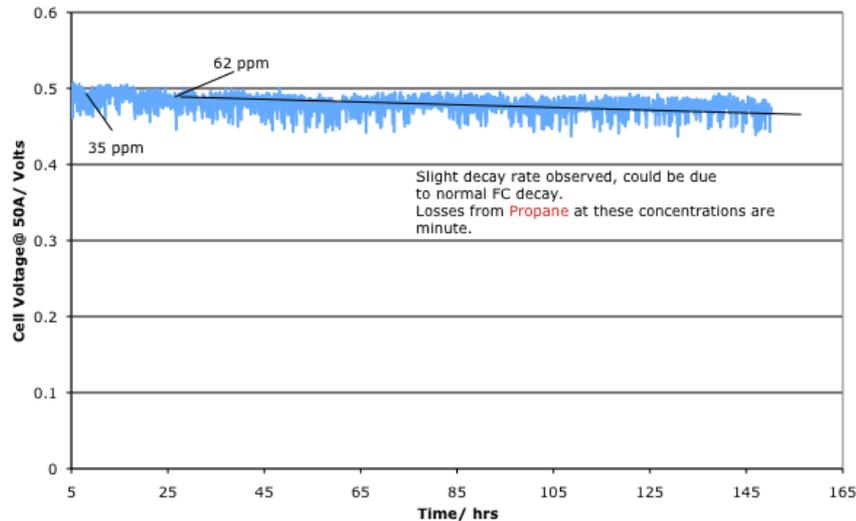
- 0.1mg/cm² Pt-C anode-0.2mg/cm² Pt-C cathode
50μm ionomer
- Fuel Cell Testing of 5ppm NO₂ cathode 1 A/cm²
80°C
- Steady decay in performance
- Some humidification dependence on performance losses
 - Higher humidification may remove more soluble NO₂
- FTIR spectroscopy to detect speciation



- Ammonium exchange membrane compared to NO₂ exposed MEA
- ammonium ions 2400–3200 cm⁻¹
- Sharp peaks at 2800 cm⁻¹ may be amine vibrational modes

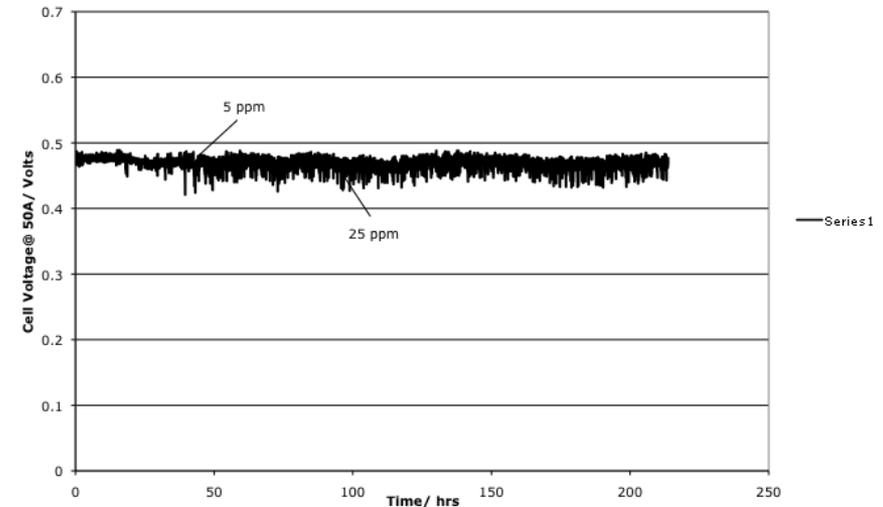
Hydrocarbon Effects *New Results*

Hydrocarbons: Effects of Propane
A/C: 0.1/0.2 mg Pt/cm²
2 mil, 50cm², 80°C, 100 % RH



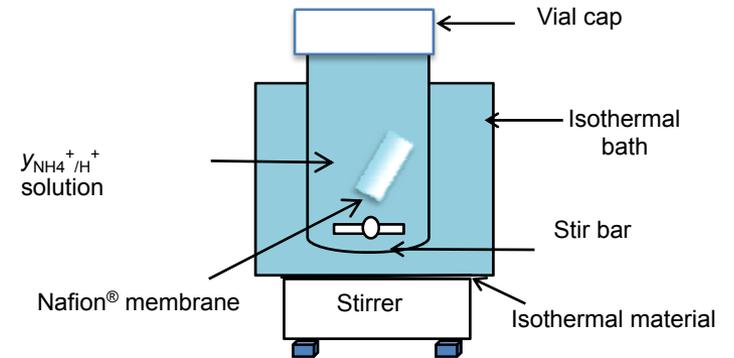
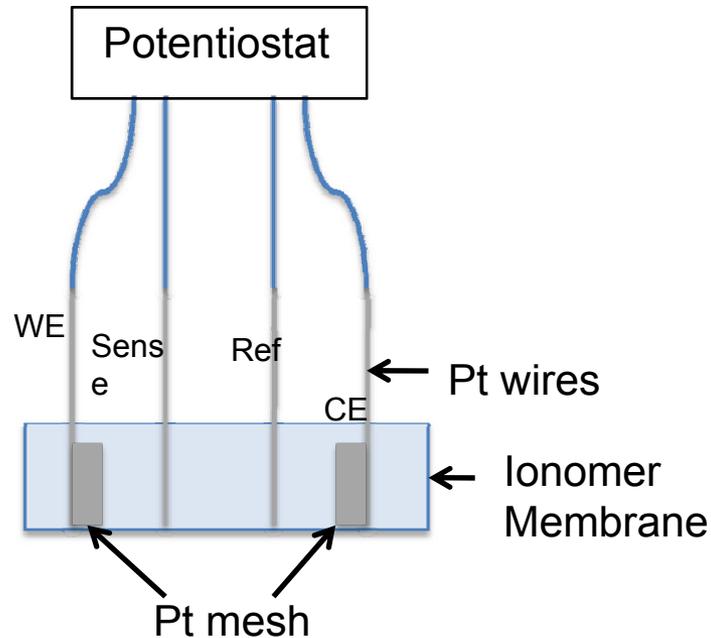
- 0.1mg/cm² Pt-C anode-0.2mg/cm² Pt-C cathode 50μm ionomer
- Propane injected resulted in little performance loss
- Increasing concentration did not change loss rate at 1 amp/cm² constant current

Hydrocarbons: Effects of Propylene
A/C: 0.1/0.2 mg Pt/cm²
2 mil, 50cm², 80°C, 100 % RH



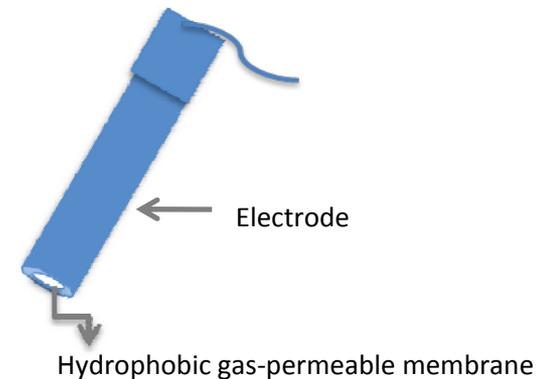
- 0.1mg/cm² Pt-C anode-0.2mg/cm² Pt-C cathode 50μm ionomer
- No effect of 5 to 25ppm injection of Propylene C₃H₆

Ammonium Ion Membrane Equilibrium



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

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



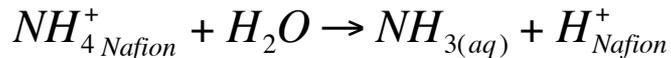
Ammonia Removal Mechanisms *New Results*

- Two possible mechanisms for ammonia removal from membranes:

– Electro-oxidation:

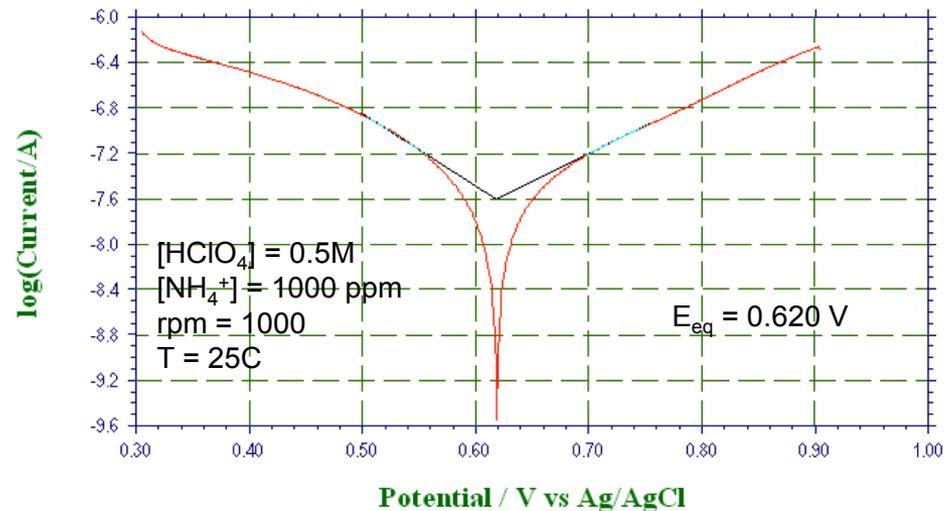


– Water solubility:

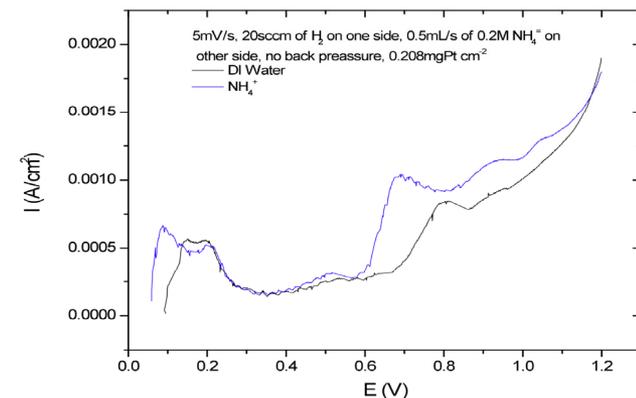


$$[NH_4^+_{Nafion}] = \frac{[NH_{3(aq)}][H^+_{Nafion}]}{k_{eq}[H_2O]}$$

Ammonium ion oxidation rate in PEMFC- also very slow

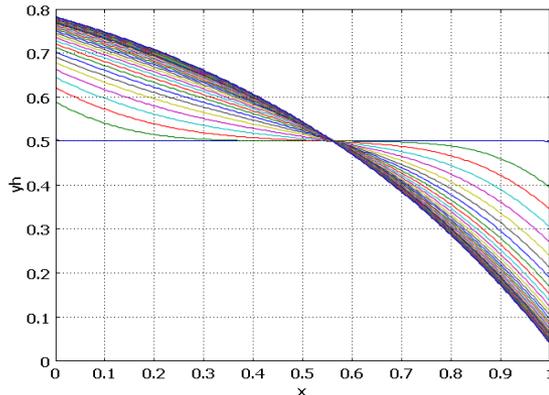
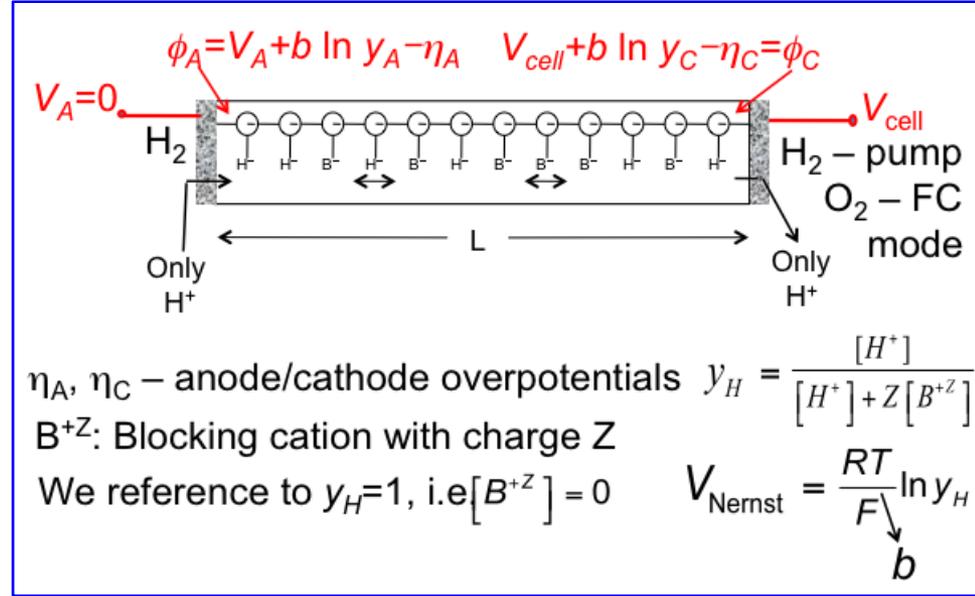


Ammonium ion oxidation rate in perchloric acid-very slow

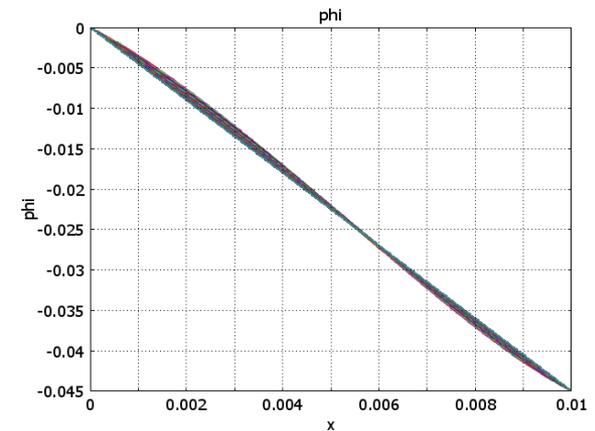


Membrane Blocking Cation Model and Validation

- 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 $\lambda=14 \text{ H}_2\text{O}/\text{SO}_3^-$.
- H-pump, not FC, model focuses on membrane effects, simplifies experimental verification and understanding.
- Time response, limiting current discussed
- AC impedance model



Initial uniform 50% H^+ and NH_4^+ distribution
 Step current from 0 to 0.25 A/cm^2
 $D_H = 1.73 \cdot 10^{-5} \text{ cm}^2/\text{s}$, $D_B = 3.63 \cdot 10^{-6}$
 y_h and ϕ plotted every 0.2 s



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 - $d(\text{activity})/d\lambda$

ξ_i - drag coef.

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

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

Diffusion

Migration

Drag

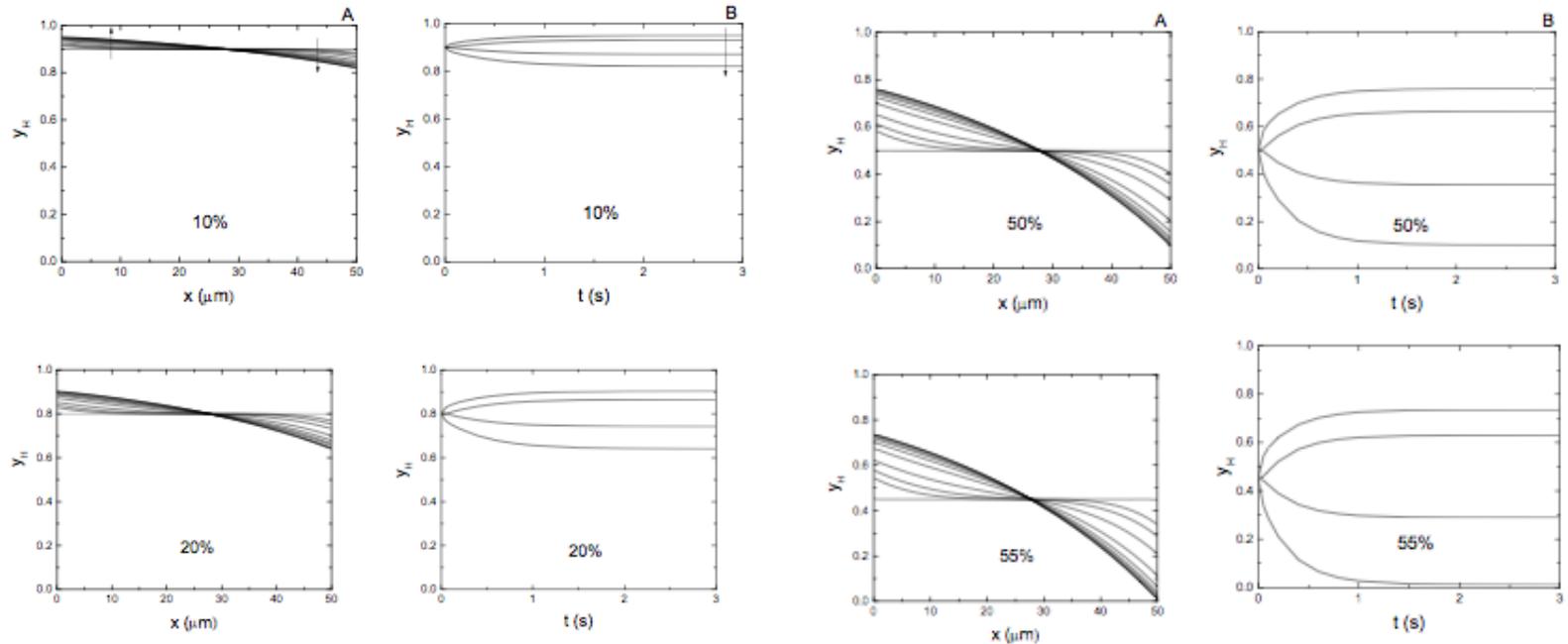
$$C_t \frac{\partial y_H}{\partial t} = \nabla \cdot \frac{D_H C_t}{L} \left[\frac{\partial y_H}{\partial x} + \frac{y_H}{b} \frac{\partial \phi}{\partial x} + \xi_H y_H d_a \frac{\partial \lambda}{\partial x} \right] \quad H^+$$

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

$$C_t \frac{\partial \lambda}{\partial t} = \nabla \cdot \frac{-D_H C_t}{L} \left[\left(\frac{\alpha \xi_B}{Z_B} - \xi_H \right) \frac{\partial y_H}{\partial x} + \frac{((\alpha \xi_B - \xi_H) y_H - \alpha \xi_B)}{b} \frac{\partial \phi}{\partial x} + \left(\left(\frac{\alpha \xi_B^2}{Z_B} - \xi_H^2 \right) y_H - \frac{\alpha \xi_B^2}{Z_B} - \frac{C_t D_w \lambda}{c_1 L} \right) d_a \frac{\partial \lambda}{\partial x} \right] \quad \text{Water}$$

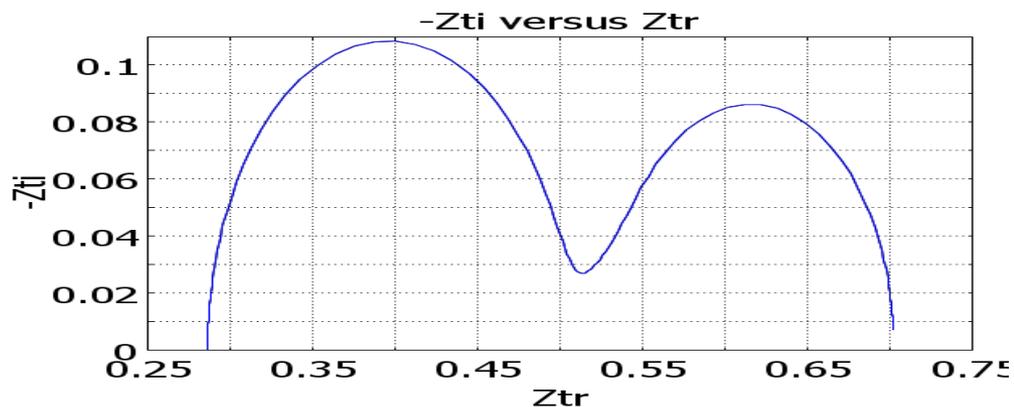
Diffusion

Transient Concentration Profiles *New Results*

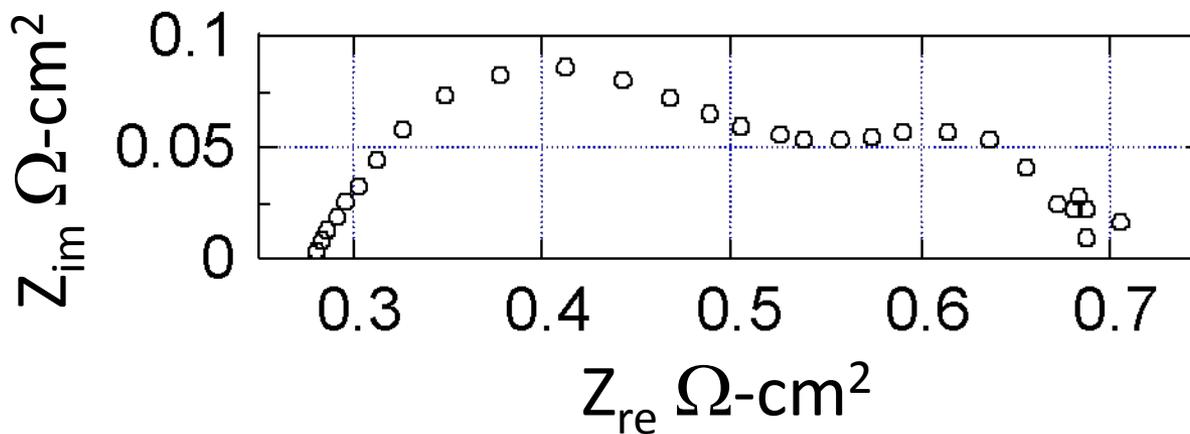


- Modeled transient concentration profiles across a monvalent cation-contaminated fuel cell (50 μm ionomer) operating at constant current density of 1.0 A/cm²
- Protons strongly depleted at cathode
- Membrane HFR would shift only slightly for low cation impurity levels
- Time scale of cation migration event may be probed in the 0.1-1 Hz range by AC impedance

Impedance Response *New Results*

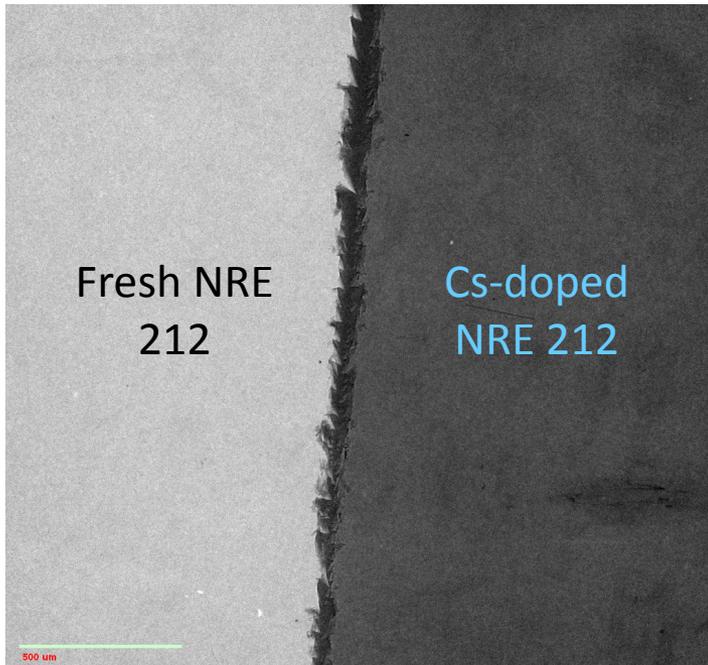


Point electrode simulation for Nafion[®] 117 50% Cs exchange C_D 0.1F/cm² $j=0.3$ A/cm²



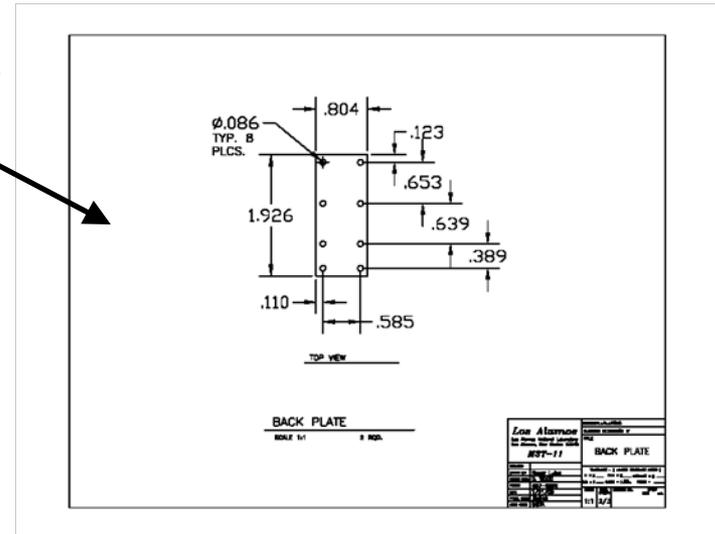
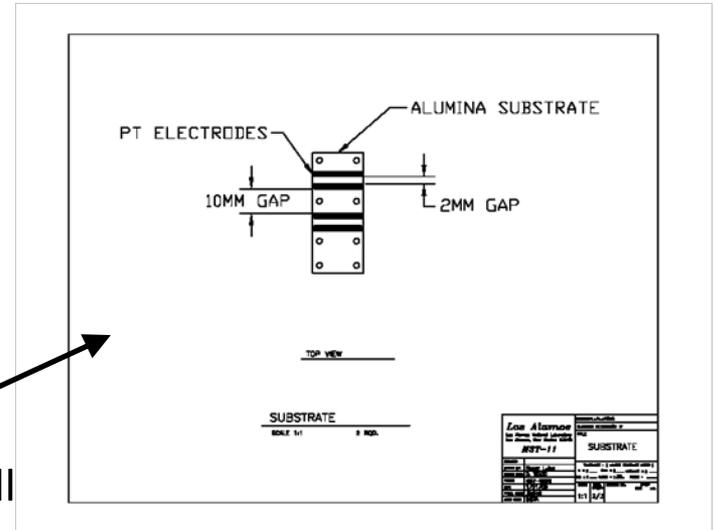
Visualization of Impurity Metal Cation Transport Using X-Ray Radiography *New Results*

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 cm² cells*
- Common hydrocarbons C1-C3 at PPM concentrations do not impact fuel cell performance
- SO₂ decreases fuel cell performance of low loading thin ionomer PEMFCs in a similar manner to the older generation-thicker membrane PEMFCs
- NO₂ decreases fuel cell performance
 - May be converted into other N-species at electrodes
 - *Future work: improved understanding of membrane speciation via spectroscopy*
- NH₃ exists in membranes as NH₄⁺
 - 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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