



DOE Hydrogen Program

2008 DOE Hydrogen Program Review:

Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

- *Presented by: Fernando Garzon*
- Los Alamos National Laboratory
- June 12, 2008

Project ID
#FC30

This presentation does not contain any proprietary, confidential, or otherwise restricted information

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Overview

Timeline

- Project start -FY07
- Status- ongoing

Budget

- Funding in FY08: \$1000 K
- Funding for FY07: \$1200 K
- Non-cost shared

Near Term Targets:

- *5000 hrs durability*
- *30\$/kW by 2010*
- *55% energy conversion efficiency*
- *0.3g/kW Pt loading*

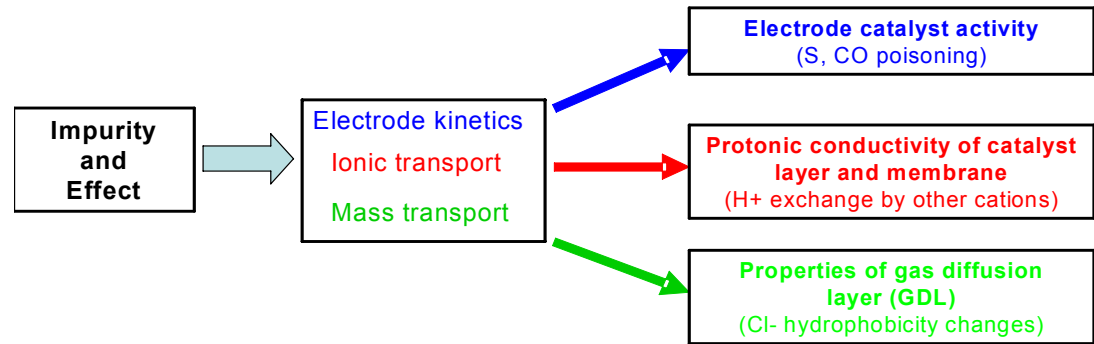
Barriers

- Fuel cell systems must cost less than \$50/kw
 - Fuel and air purifications systems add cost
 - Higher Pt loading required to maintain performance in presence of impurities increases cost
- 5000 hr lifetime needed. Durability may decrease in the presence of impurities

Partners



Technical Approach



- 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

- Impurities affect fuel cells in many ways:
 - Electrocatalyst poisoning e.g. H₂S, CO and SO₂ adsorption onto Pt catalysts
 - Reduce ionomer conductivity- Na⁺, Ca⁺⁺, NH₃
 - Block proton access to electrochemically active interface
 - GDLs become hydrophilic and flood at high current densities

Objectives

Overall Objective: Contribute to the scientific understanding of the effects of fuel and air impurities on fuel cell performance and how it affects DOE fuel cell cost and performance targets.

Specific Objectives:

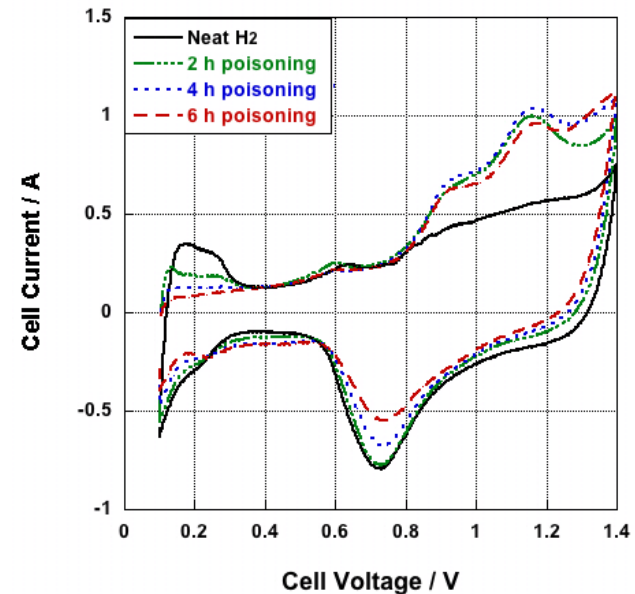
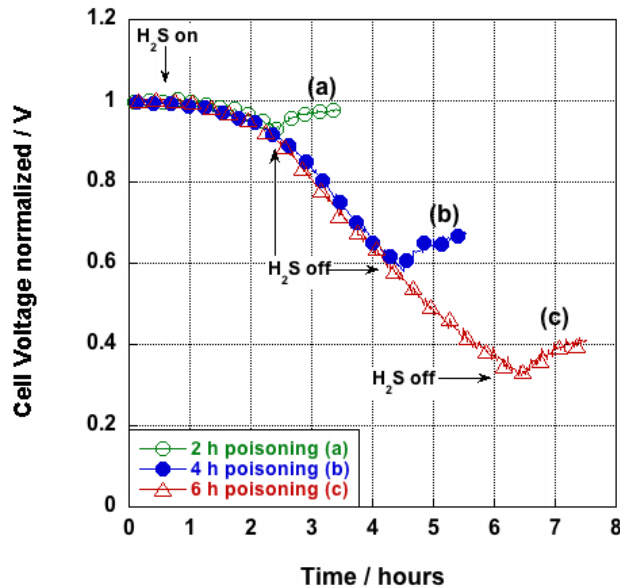
- Investigate effects of impurities on catalysts and other FC components
- Understand the effect of catalyst loadings on impurity tolerance
- Investigate the impacts of impurities on catalyst durability
- Develop methods to mitigate negative effects of impurities
- Develop models of fuel cell-impurity interactions
- Collaboration with USFCC, Fuel Cell Tech Team, Industry and other National Laboratories to foster a better understanding of impurity effects

Milestones

Month/Year	Milestone or Go/No-Go Decision
Mar-08	Milestone: report on the performance degradation due to H ₂ S anode poisoning as a function of catalyst loading (0.1 and 0.05 mg Pt/cm ²). Completed
Apr-08	Milestone: Modeling and validation of impurity effects in PEMFCs. We have developed a model for understanding the effects of alkali contaminants on fuel cell response and experimentally validated the results using novel experimental methods. Completed
May-08	Milestone: Determination of multiple contaminant effects carbon monoxide and hydrogen sulfide, on fuel cell response. Completed

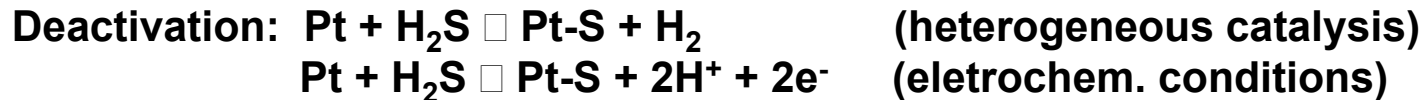
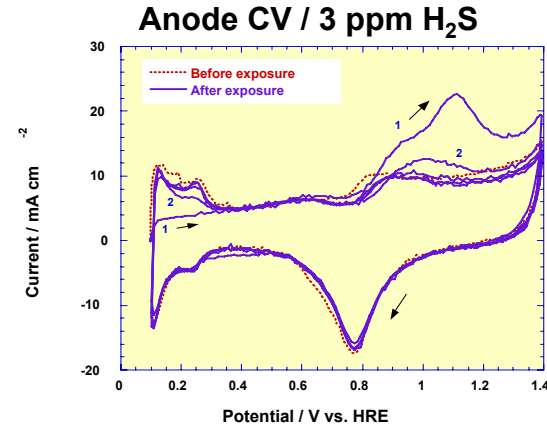
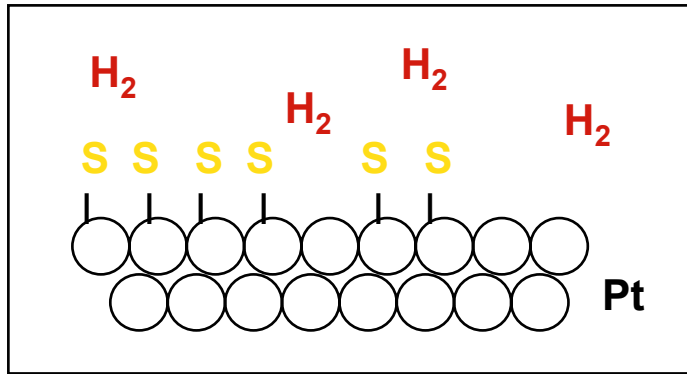
Impact of H₂S Exposure on Fuel Cell Performance

Exposure to 1.5 ppm H₂S for 2, 4 and 6 hour



- Performance degradation is more severe for larger dosages
- Catalyst poisoning is cumulative

Basic Degradation Mechanism

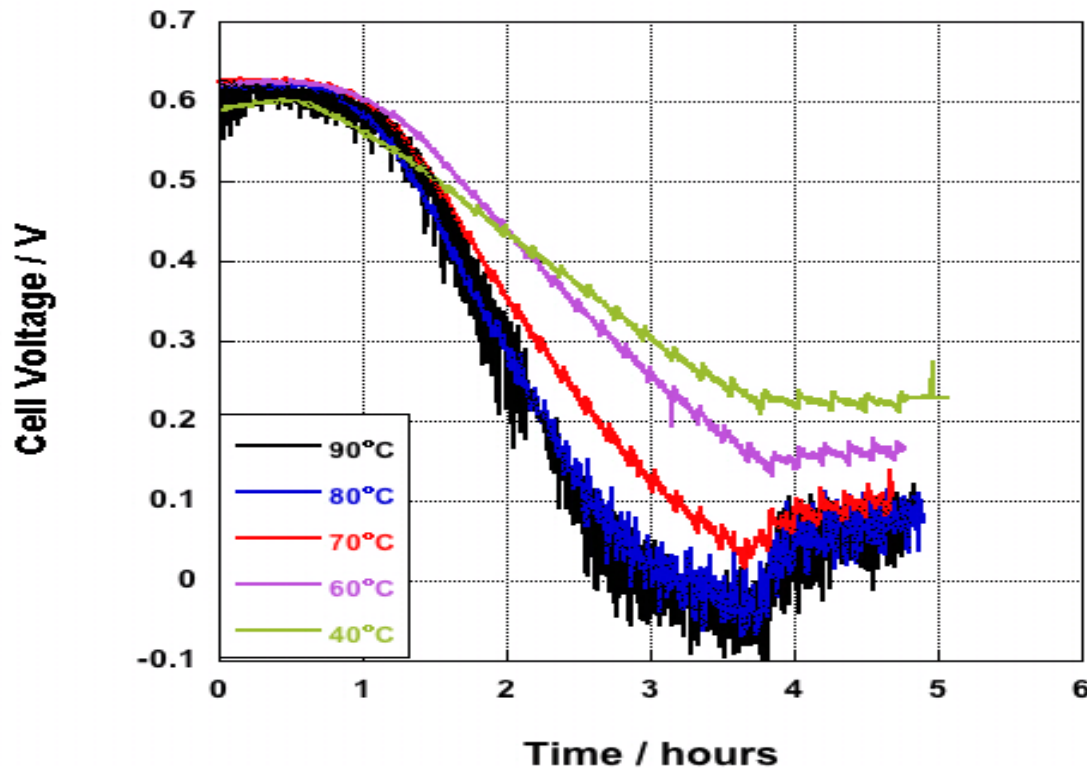


- Strong sulfur chemisorption onto Pt deactivates the catalyst
- Pt-coverage: more than one monolayer of sulfur
- PtS may form under severe conditions

1. T. Loucka, *J. Electroanal. Chem.*, **31**,319 (1971)
2. R. Mohtadi et al., *Electrochem. Solid State Lett.*, **6**, A272(2003)
3. Garzon, et al., *ECS Trans.* 3, (1) 695 (2006))
4. W. Shi et al., *Journal of Power Sources*, **164**, 272 (2007)
5. Z. Shi et al., *J. Electrochem. Soc.*, **154**, B609 (2007)

Technical Results: H₂S Temperature Effects

Poisoning with 2ppm H₂S for 3h 15 min
400/2100sccm



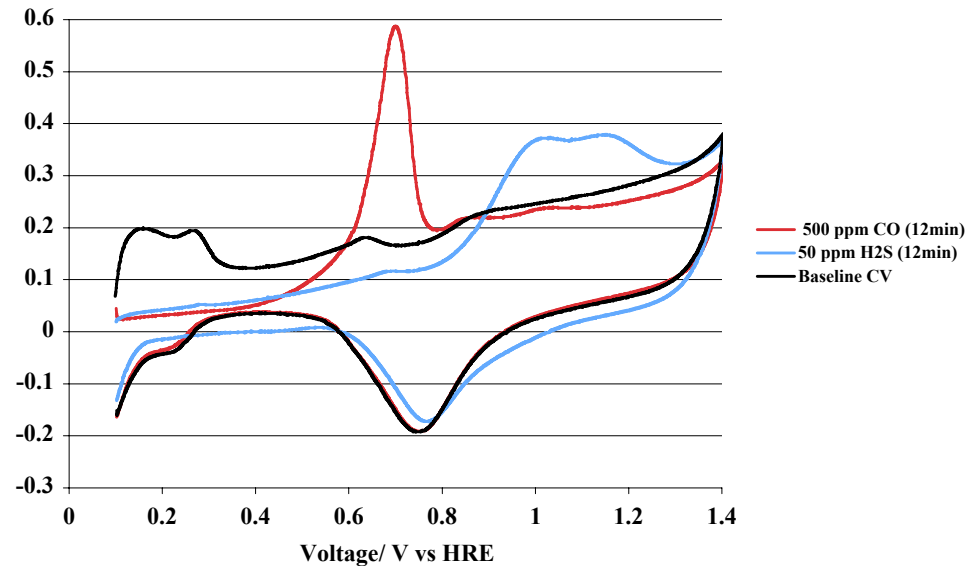
50 cm² / 40 A / 80 °C

- As T increases so does
- the degradation rate
- and extent.
- Relative recovery after
- returning to neat H₂
- is higher at the higher T
- but less total recovery

Technical Results: Co-adsorption of CO and H₂S

- *CO and H₂S often times occur together though CO concentration typically higher*
- *Both strong adsorbates CO peak 0.6-0.8V, S above 0.9V*
- *CO gas phase transport low water solubility; H₂S high water solubility*
- *Wet environment shows relatively more CO/H₂S*
- *Mix both gasses at 10:1 CO:H₂S ratio at concentrations for nearly complete poisoning*

Baseline CVs for H₂S and CO at
60°C



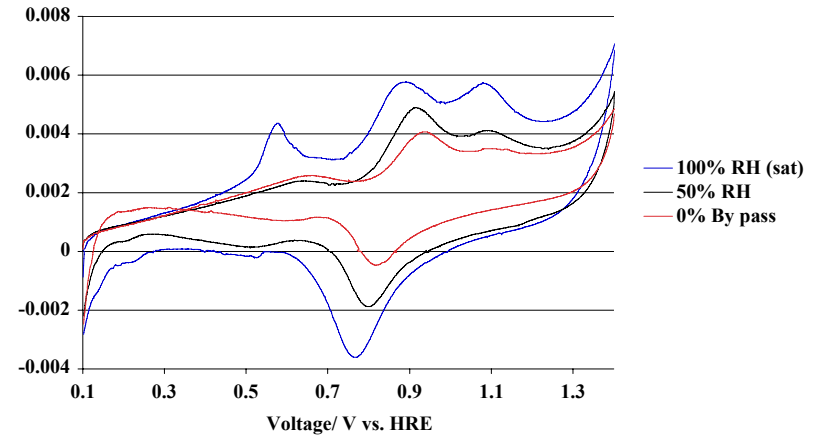
50 cm² cells / N112, 20 mV/s
 Loadings: 0.2 mg Pt at each electrode
 Cell Temperature: 80 °C. PSIG: 3.7/3.7

Technical Results: Co-adsorption of CO and H₂S

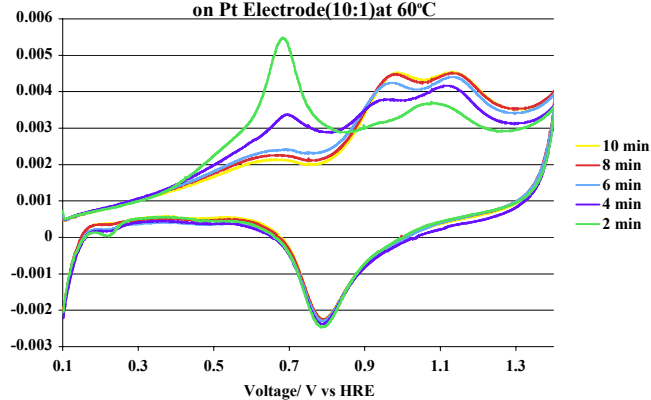
- CV indicates a larger presence of CO during short term exposure
- H₂S eventually replaces CO on the electrode surface
- CO kinetics are faster, H₂S has a higher adsorption strength
H₂S suppresses CO adsorption

Wet environment shows more relatively more CO/H₂S

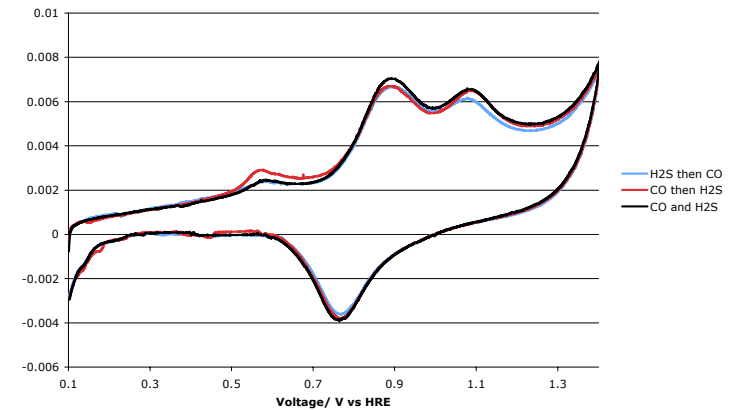
Co-Adsorption between CO and H₂S
on Pt Electrode(10:1)at 80°C
-Effects of RH



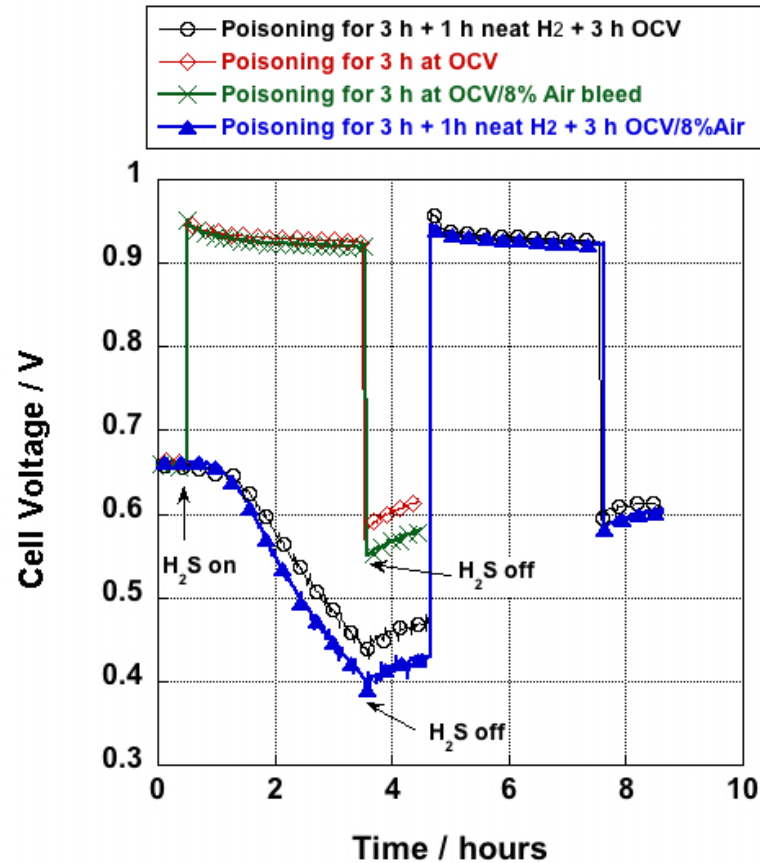
Co-Adsorption between CO and H₂S
on Pt Electrode(10:1)at 60°C



Co-Adsorption between CO and H₂S
on Pt Electrode(10:1)at 80°C
-Poisoning Order



Technical Results: Effect of Anode Air Bleeding



1.5 ppm H₂S

J = 0.8 A/cm²

T = 80 °C.

In contrast to CO mitigation, Anode air bleed does not have any significant benefit on poisoning or recovery for H₂S

H₂S crossover from anode to cathode ?

EVIDENCE:

1. *Open circuit will allow chemical oxidation of sulfur by O₂ at the cathode*
 1. *Possible reaction: Pt-S + 3/2O₂ + H₂O → Pt + SO₄²⁻ + 2H⁺ (slow)*
2. *FC operation at high voltage will induce partial electrochemical*
3. *oxidation of sulfur, only at the cathode*
4. *Diffusion of H₂S observed across the Nafion membrane*
5. *Injected H₂S at the cathode produces performance degradation*

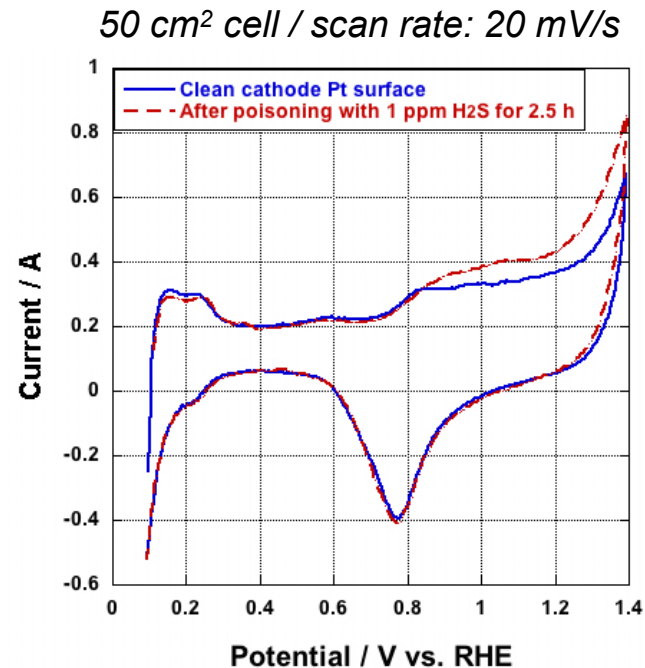
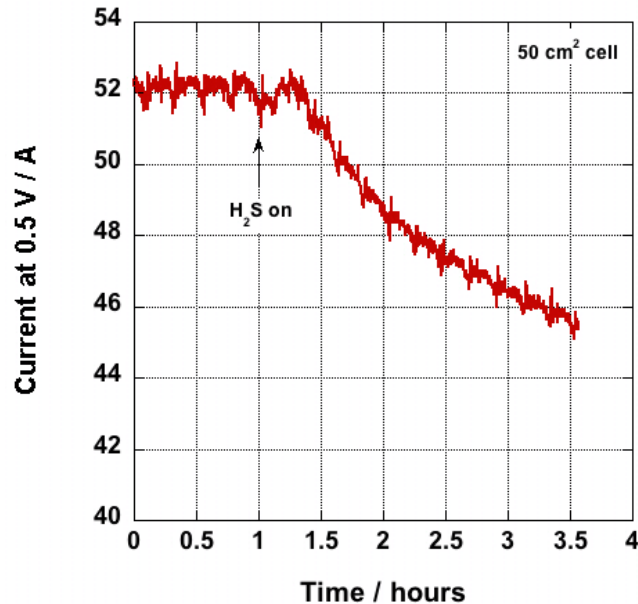
MECHANISMS:

- Dry membrane permeation:
 - Permeation by diffusion
 - Rate proportional to concentration gradient
- Wet membrane permeation:
 - co-permeation with water
 - Rate proportional to water activity and concentration gradient
- Proton drag:
 - moves with proton across cell
 - Rate proportional to current density
 - Need hydrogen pumping cell to study (avoids oxidation of H₂S)

- Hydrogen sulfide state in membrane is a polar molecule
- No ionic dissociation at low pH
- High solubility:3.4 g/l-atm at 25°C

Technical Results: H₂S crossover, cont'd

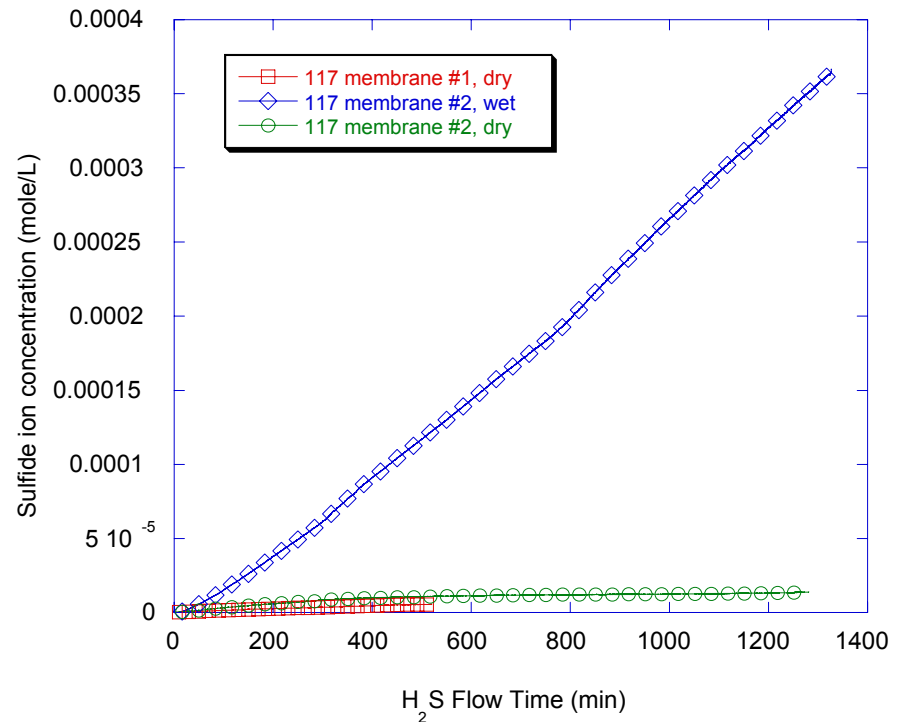
1 ppm H₂S injected at the cathode



- *H₂S at the cathode degrades cell performance*
- *Similar effect observed when SO₂ is injected at the cathode*

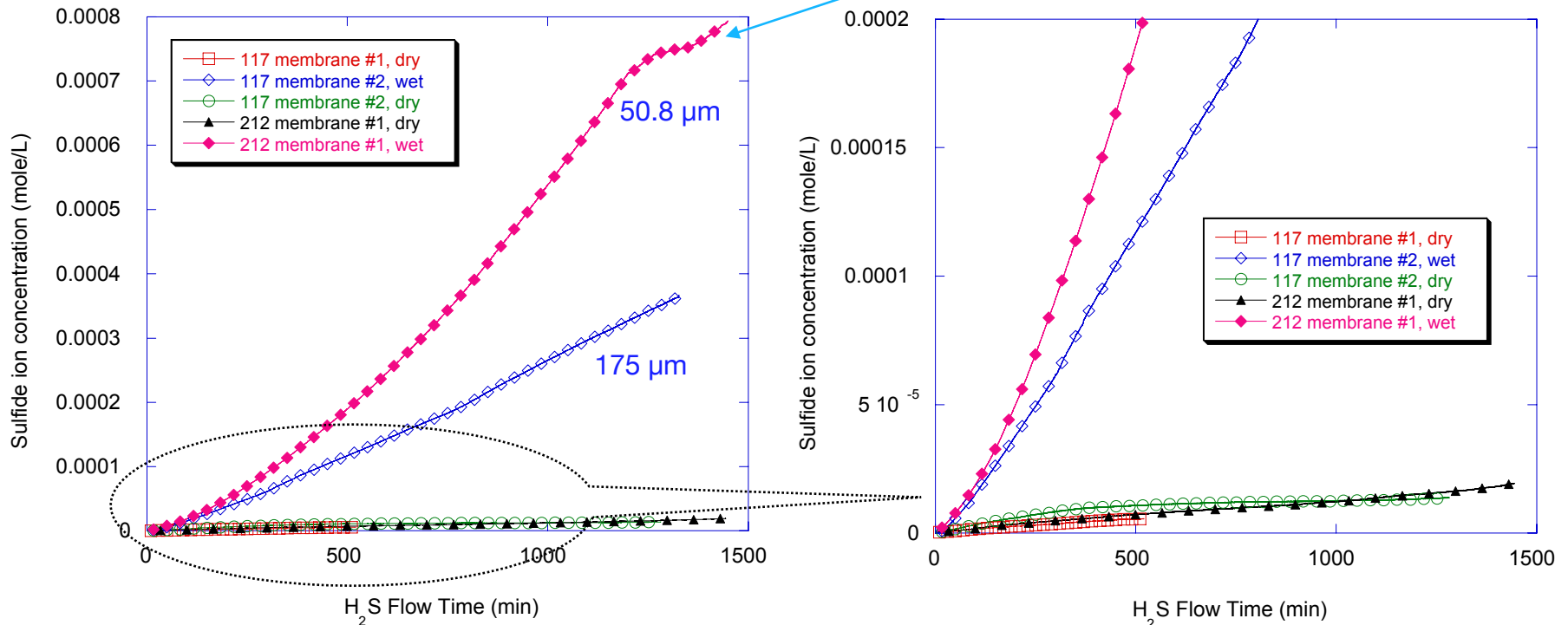
Technical Results: Wet Versus Dry Gas Permeation for Hydrogen Sulfide

- 1030 ppm of H_2S (wet/dry) and 6% H_2 (wet/dry) were flowed across the sides of a 117 membrane 50 cm^2 for 72 hours.
- The H_2S trap was placed in line after sufficient H_2S crossed over to passivate GDL and flow fields.
- Trapping experiment was run between 500 and 1300 min alternating between humidified and dry membrane state.
- Dry : $3.2\text{e-}8\text{g/min } H_2S$ crossover
- Wet: $5.9\text{e-}7\text{g/min } H_2S$ crossover
- Gas humidification greatly increases rate of crossover



Technical Results: Membrane Thickness Affects H₂S Crossover Rates

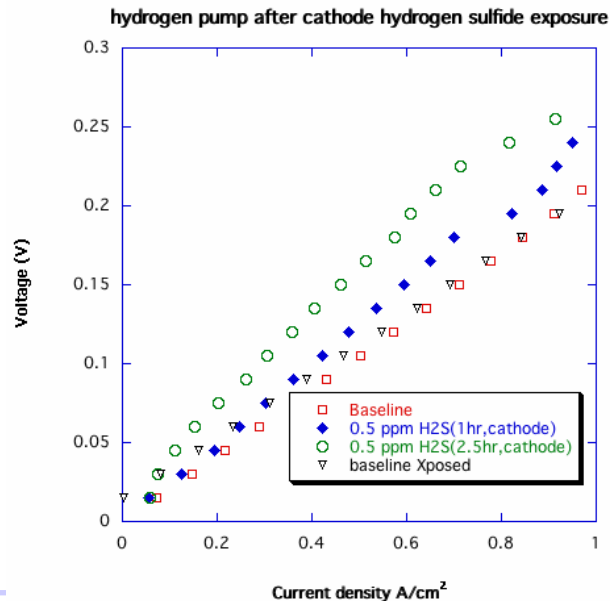
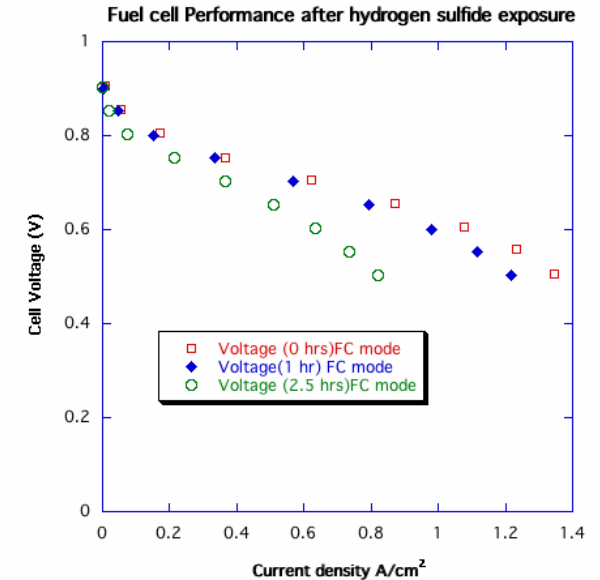
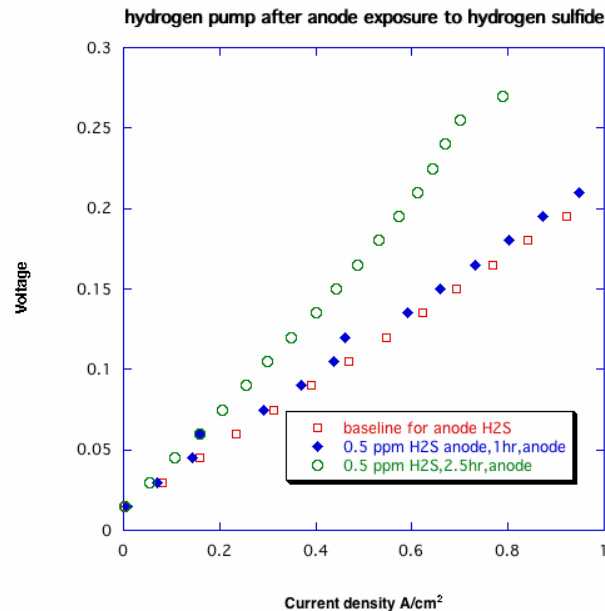
Rate of H₂S crossover in wet 212 membrane is $1.8e^{-6}$ g/min.



- Thinner membranes show higher crossover rates; scales with thickness
- Wet membranes show higher permeation rates
- however humidification decreases H₂S concentration reaching electrode

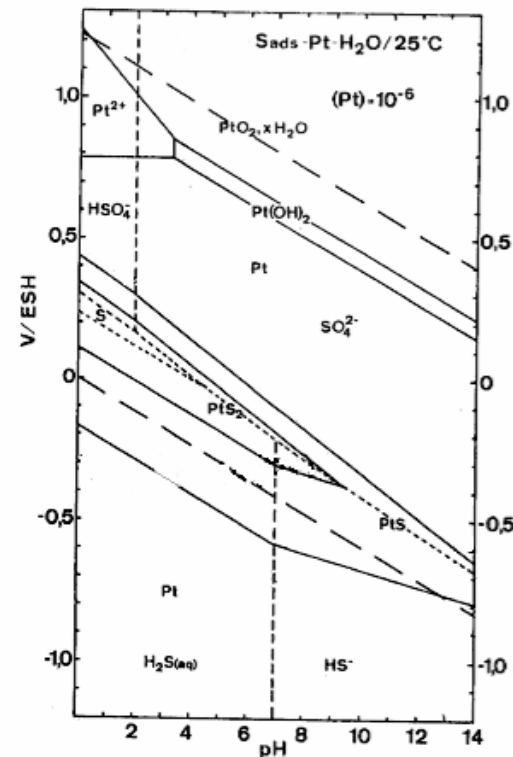
Technical Results: Hydrogen Pump Cell

- Use hydrogen pump cell to study anode poisoning and crossover
 - Measure polarization behavior before and after poisoning from either the anode or cathode compartment
 - Compare to fuel cell behavior
- 0.5 PPM H_2S in humidified H_2



Significant voltage losses created by H_2S in hydrogen pump mode

- Surface/speciation model pH Temp and S concentrations
 - Predominate sulfur species are H_2S , S -Pt, PtS , PtS_2 and HSO_4^-
 - SOx species are not stable in acid fuel cells
 - Explains similarity in poisoning results from using H_2S , SO_2 or Na_2S
 - CANNOT be displaced by hydrogen or CO
- Pt sulfur coverage at -0.15 volts with increasing coverage as anode potential is raised for 1 ppb H_2S
- At higher potentials transition from S adsorbed on Pt to PtS with surface reconstruction
- Oxidation cleaning mechanism is inhibited by kinetics not thermodynamics @ 0.450 mV
- Surface speciation model coupled to fuel cell electro-kinetics model
 - Activity coefficient corrections for strong electrolytes (Pitzer model)
 - nanoparticle free energies data (+ than bulk Pt)
 - Surface thermodynamics for nanoparticles

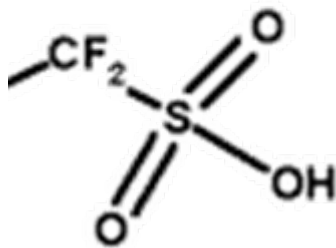


P. Marcus, E. Protopopoff, *Comptes Rendus de L Academie Des Sciences Serie Ii* **308**, 1685 (1989).

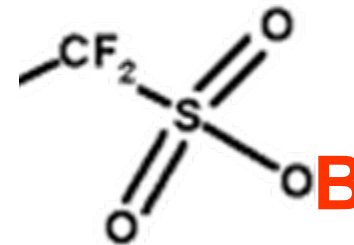
Cation Contamination

Cationic contaminants

- Displace protons in the ionomer phase
- Have higher affinity for the membrane
- Have a lower conductivity than protons
- Originate from aerosols or corrosion
- Have been shown to affect fuel cell performance
- Removal mechanism poorly understood



Protonated SO_3^- site



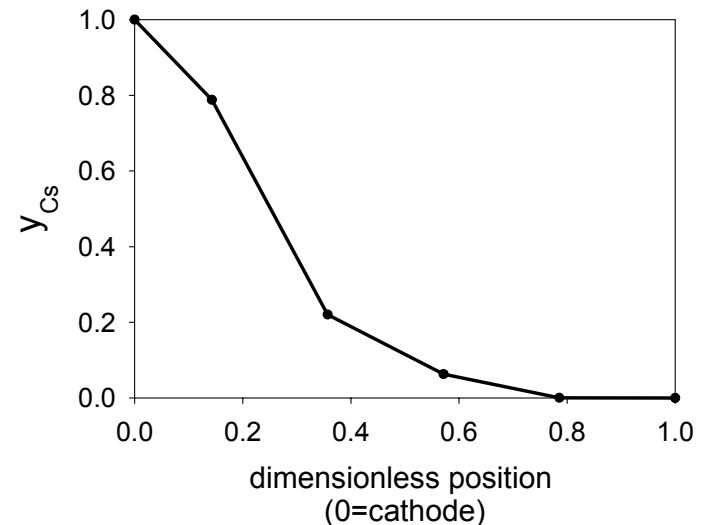
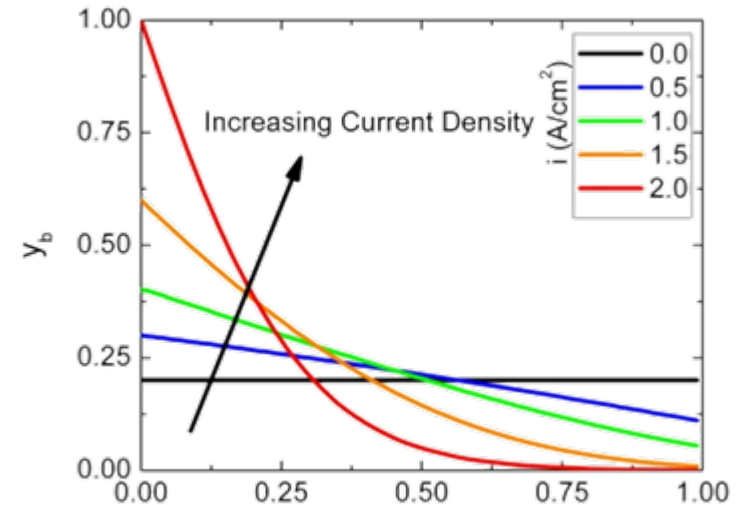
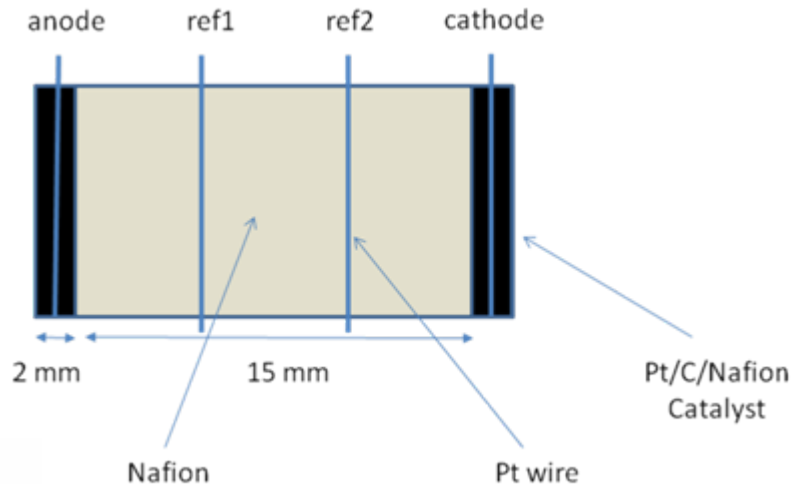
Contaminated SO_3^- site
 $\text{B} = \text{Na}^+, \text{NH}_4^+, \text{Cs}^+, \text{Ni}^{2+}, \text{Fe}^{3+}, \dots$

Technical Results: Membrane Contaminant Profiles

- Cations move due to electro-migration and chemical diffusion:

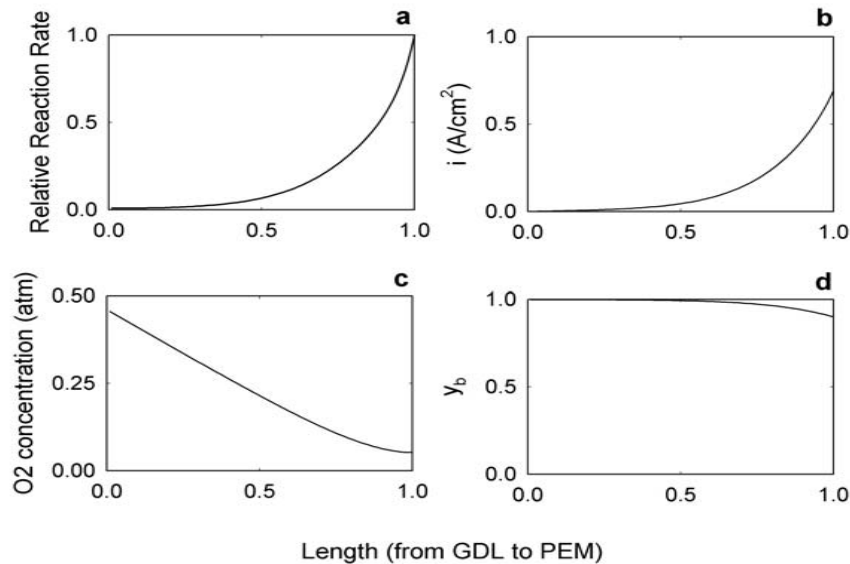
$$j_{i^+} = -D_{i^+} \frac{dC_{i^+}}{dx} + u_{i^+} C_{i^+} \frac{d\Phi}{dx}$$

- Contaminants build up near the cathode
- Novel strip cell was used to show concentration profiles exist
- Contaminate concentration measured by XRF

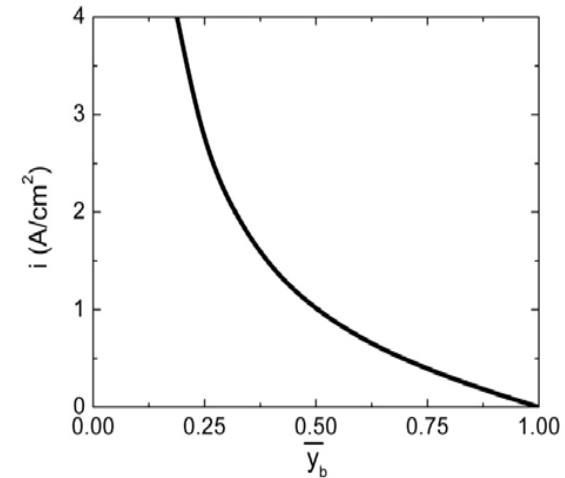


Technical Results: Electrode Effects Model

- Contaminants replace protons in the electrode
- Cathode overpotential increases account for most performance loss
- Lack of protons leads to proton limited currents



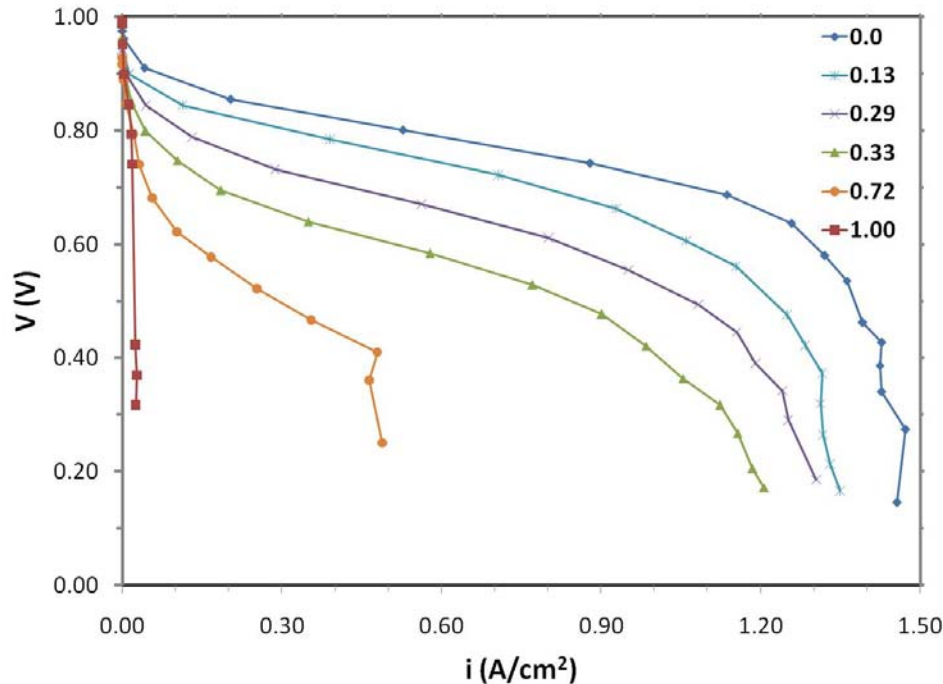
Species and reaction rate profiles across the electrode near proton limitation



Proton limited current for base case parameters

Technical Results: Alkali Contamination

- We are using Cs^+ as a model alkali cation (behaves like Na^+ , K^+)
- Very low detection limits with X-ray fluorescence Spectroscopy

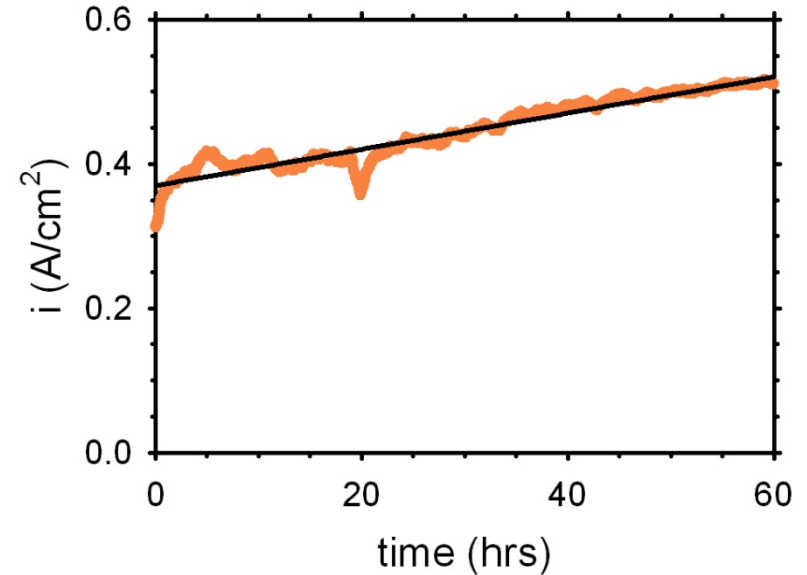


H₂/Air 30 PSI Temp A/C/Cell 85/80/85

Legend represents fraction of sites contaminated

Increasing contamination

- Decreases ionomer conductivity
- Lowers limiting current
- Affects kinetics



	level	i @ 0.5 V	HFR
Clean	0	1.31	0.048
Contaminated	0.716	0.37	0.114
After 60 hours	0.567	0.53	0.104

Cs^+ ions leave the membrane slowly ($2.5 \mu\text{g}/\text{cm}^2/\text{hr}$) but other cations show no recovery

Cationic Contamination Summary

- Fuel cell cationic contamination
 - Decreases ionomer conductivity
 - Lowers limiting current
 - Affects kinetics
- Modeling shows the mechanisms of performance degradation
 - Greatly increases cathodic overpotential due to loss of protons in the ionomer phase
 - Can lead to proton limited current
- Fuel cell recovery
 - 50% of Cs can leave in 2 days of operation
 - Some other ions also show recovery
 - Rate of recovery is still small compared to proton flux

Technical Achievements

- Measurement of increased degradation of fuel cell performance by H_2S with increasing temperature
- Measurements of H_2S membrane crossover for wet and dry membranes
- CO and H_2S co-adsorption kinetic studies
 - fast adsorption kinetics for CO but eventually displaced by H_2S
- H_2S anode poisoning studied by H_2 pump cells
- Model development and measurement of alkali cation contaminant behavior in perfluorosulfonic acid membranes
- Experimental measurement of fuel cell losses due to alkali cation contamination- good agreement with model

Future Work

- Continued contaminant crossover studies: Proton drag of H₂S
- Fundamental electrokinetic measurements of poisoned electrodes
- Lower cathode loading impurity studies
- Impurity effects on durability studies
 - New commercial MEAs with 2010 loadings
- Refine and validation of electrode impurity modeling efforts
- Studies of the effect of divalent cations on Fuel Cell performance
- Air contaminate studies: hydrocarbons and particulates