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# Effects of Fuel and Air Impurities on PEM Fuel Cell Performance

## 2010 Annual Merit Review

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Los Alamos National Laboratory

Project ID #FC045

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# Researchers

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# Overview

## Timeline

- Project start date FY-07
- Project end date FY-11
- Percent complete 80%

## Budget

- Total project funding
  - DOE share %100
- Funding received in FY09 - 800K
- Funding for FY010- 1M

## Barriers

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

## Collaborators:



*Ammonia impurity studies*



*X-ray Tomography*



**CIDETEC**  
IIC4 research alliance

*S impurity studies*



*Modeling*



*Fuel cell impurity studies*

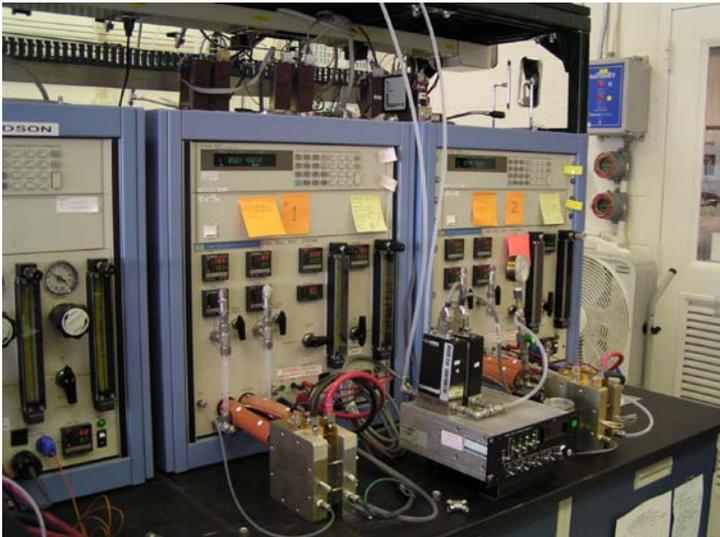
# Relevance

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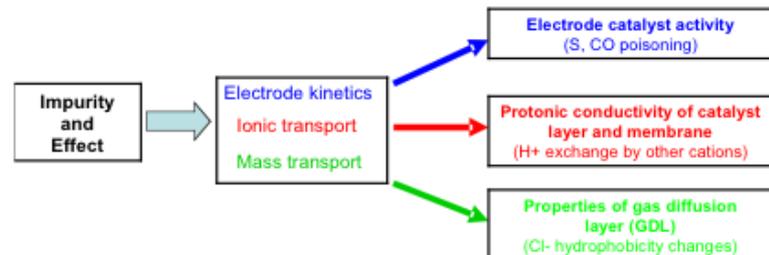
- Objectives
  - Understand the effects of fuel cell operation with less than pure fuel and air; simulate “real world” operation.
  - Understand how impurities affect DOE fuel cell cost and performance targets
  - Contribute to the scientific understanding of impurity-fuel cell component interactions 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.  $\text{H}_2\text{S}$ , CO and  $\text{SO}_2$  adsorption onto Pt catalysts
  - Reduce ionomer conductivity-  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{NH}_3$
  - 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



# 1000hr Drive Cycle Testing Effects of 10 ppb H<sub>2</sub>S

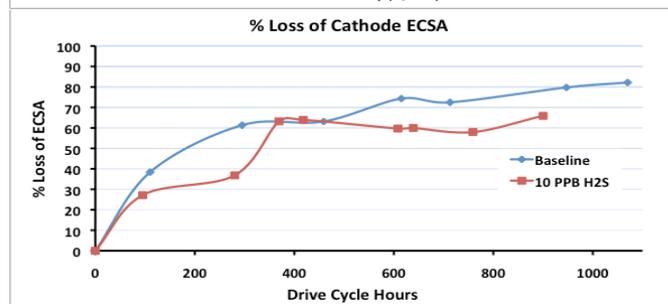
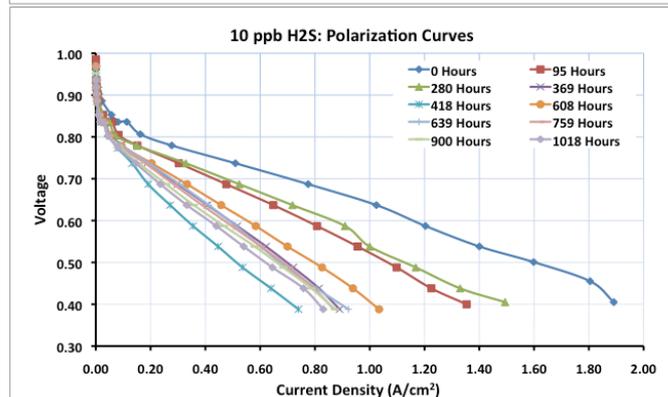
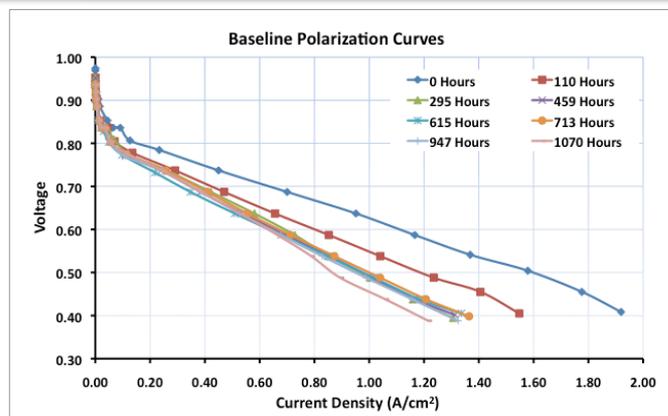
## *milestone*

Cell: 50 cm<sup>2</sup>

- MEA- Gore 720, anode- 0.10 mg Pt/cm<sup>2</sup>, cath- 0.20 mg Pt/cm<sup>2</sup>
- Drive Cycle Durability Test:
- Constant voltage mode 0.85V-0.6V
- Conditions— cell temp. 80C, H<sub>2</sub>: 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 H<sub>2</sub>S, 10 PPB

Characterization:

- 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,



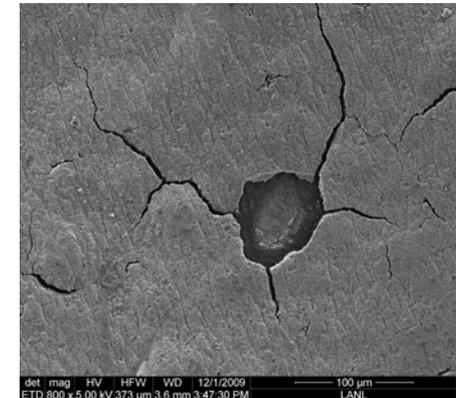
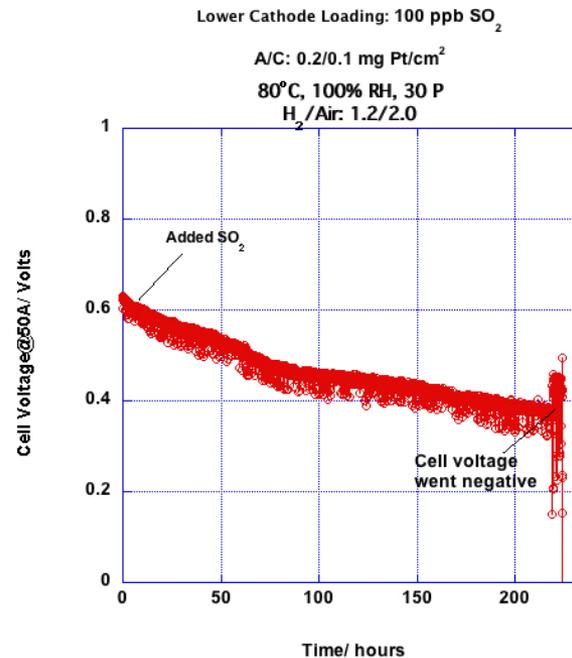
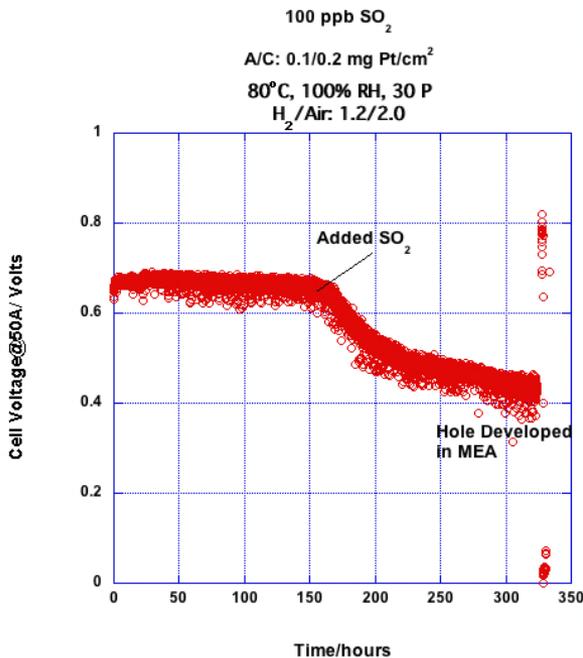
Degradation of fuel cell performance with respect to baseline

Increased fuel cell losses in the kinetic region

Cathode ECSA not significantly different

The effect of hydrogen sulfide at this concentration would probably be recoverable by air purging or voltage pulsing

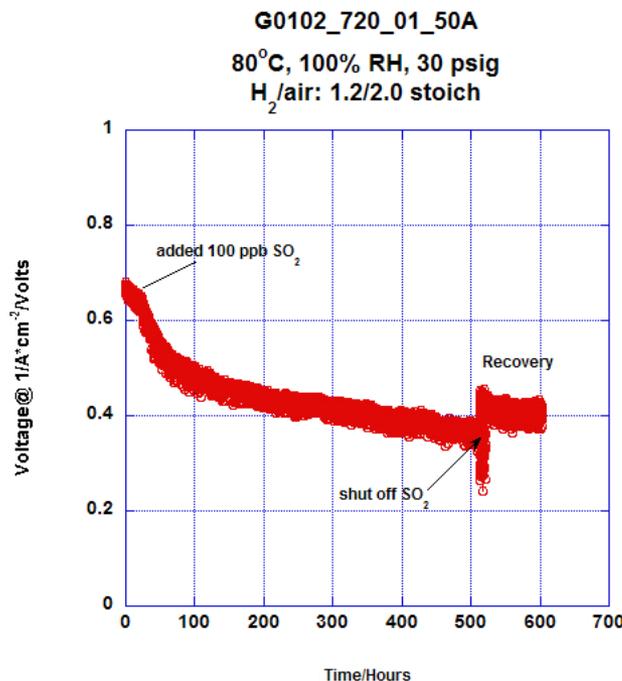
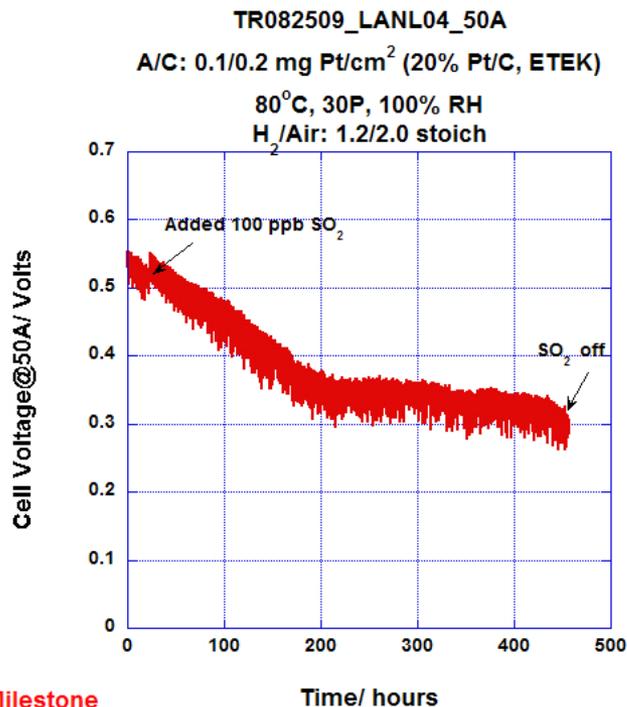
# Cathode Loadings: 100 ppb SO<sub>2</sub>



Under identical condition, we probe the impact SO<sub>2</sub> on cathode loadings: (0.1 and 0.2 mg Pt/cm<sup>2</sup>) Catastrophic failure in both expt's: further analysis showed a hole developed. We are currently revisiting the impact of cathode loadings.

# Cathode Impurities:

## 100 ppb SO<sub>2</sub> Studies: 500h test *milestone*



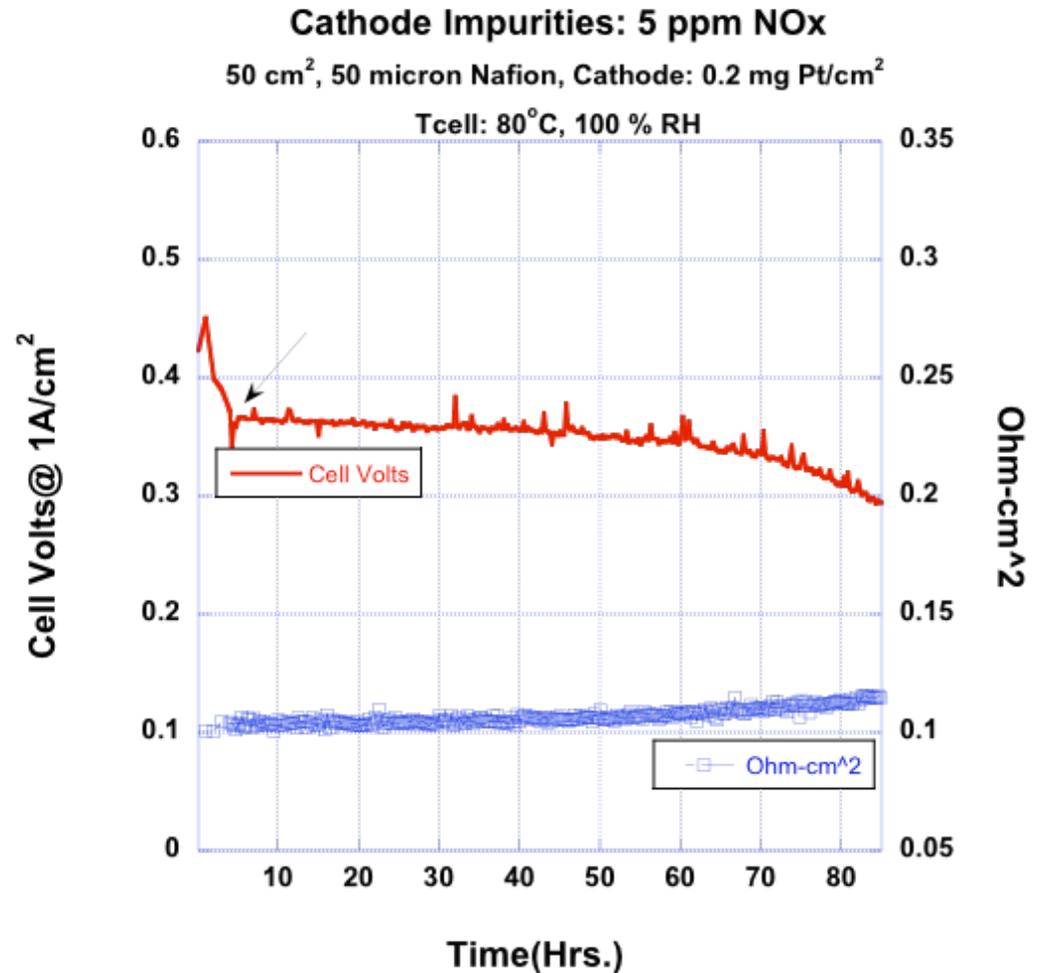
### Test Conditions:

- A/C: 0.1/0.2 mg Pt/cm<sup>2</sup>
- 50 cm<sup>2</sup>, 100%Rh, 30 Psig
- H<sub>2</sub>/Air: 1.2/2.0 stoich
- 50A constant current

Two cells were tested using 100ppb SO<sub>2</sub> in the cathode (LANL MEA vs Commercial)  
Losses were both ~200 mV,  
Recovery stage showed very little performance increase

# NO<sub>x</sub> Influence on Membrane Resistance

- High frequency resistance rising indicative of cation poisoning
- Strong evidence of ammonium ion formation from NO reduction by hydrogen



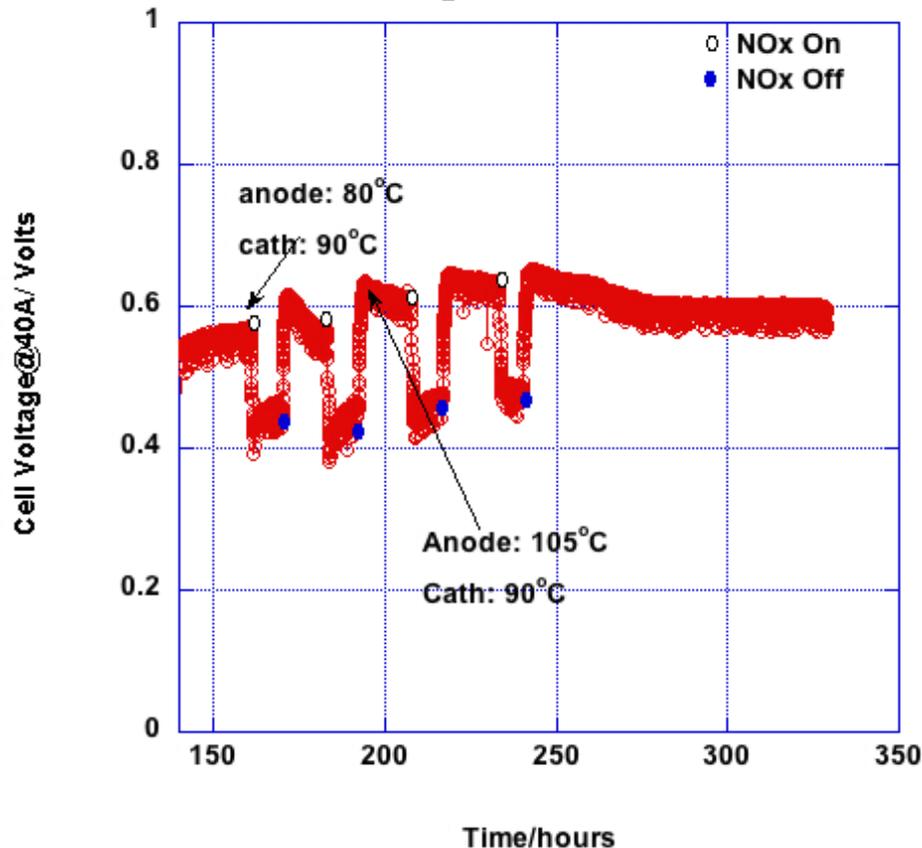
# NO<sub>x</sub> tests: On and Off Cycling

NO<sub>x</sub> Recovery: On and Off cycles with 5 ppm

A/C: 0.1/0.2 mg Pt/cm<sup>2</sup>

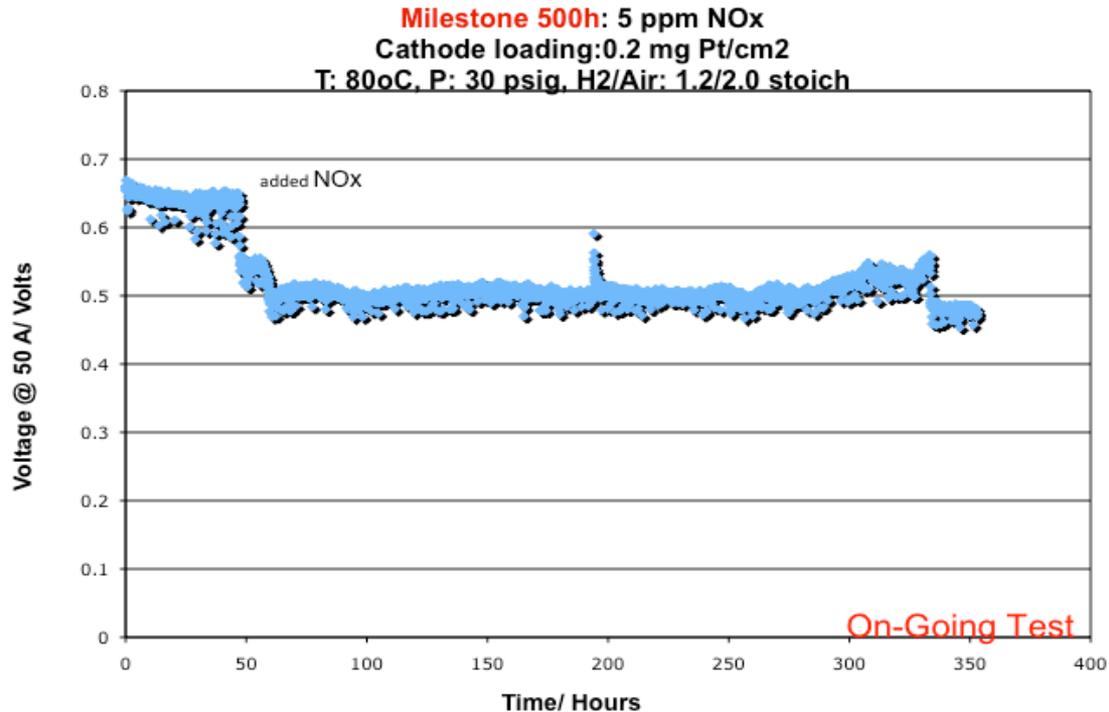
80°C, 30 P

H<sub>2</sub>/Air: 1.2/2.0



- 5 ppm NO<sub>2</sub> exposure
- 0.8 A/cm<sup>2</sup> constant current
- Full recovery after short-term exposure
- Increasing RH did significantly change recovery rate

# Long-term-NO<sub>x</sub> tests



- 5 ppm NO<sub>2</sub> exposure
- 1 A/cm<sup>2</sup> constant current
- Steady state response is reached
- Probably ammonia water flux equilibrium

# Ammonia Air or Fuel Impurities

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## Air Sources:

- Agriculture environment:
  - Potential source of ammonia ( $\text{NH}_3$ )
  - Ammonia can also be present in industrial environments
- Potential impact of  $\text{NH}_3$  on the cathode of a PEMFC

## Fuel Sources

### Conversion of a fossil fuel into a hydrogen-rich gas:

- Byproduct of autothermal reforming process (if nitrogen is present)
- Reforming process three main byproducts:
  - $\text{CO}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$
- Ammonia, as a fuel impurity, affects the performance of a PEMFC<sup>1,2</sup>
- There is also evidence<sup>3</sup> that the concentration profile of cations across the membrane changes with the current density

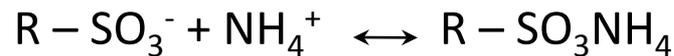
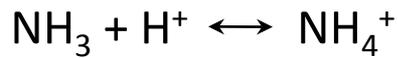
# Possible Effects of Ammonia on PEMFCs

## ■ Oxygen reduction reaction (ORR)

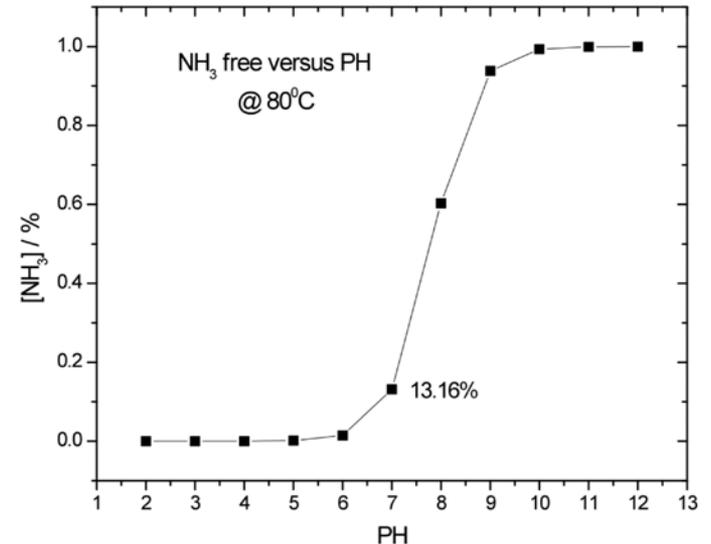
- Reduction of available active Pt sites for ORR
- NH<sub>3</sub> oxidation

## ■ Nafion<sup>®</sup>

- NH<sub>3</sub> in a PEMFC (acid media) forms NH<sub>4</sub><sup>+</sup> and bonds with sulfonic groups



- Reduction of water content in membrane (Membrane conductivity and ORR<sup>5</sup>)
- $\lambda_{\text{H}^+} = 20^6$
- $\lambda_{\text{NH}_4^+} = 13^6$



5. F. Uribe, T. Zawodzinski, S. Gottesfeld, *J. Electrochemical Society*, 149, A293 (2002); 6. R Halseid, P. J. S. Vie and R. Tunold, *J. Electrochemical Society*, 151, A381 (2004)

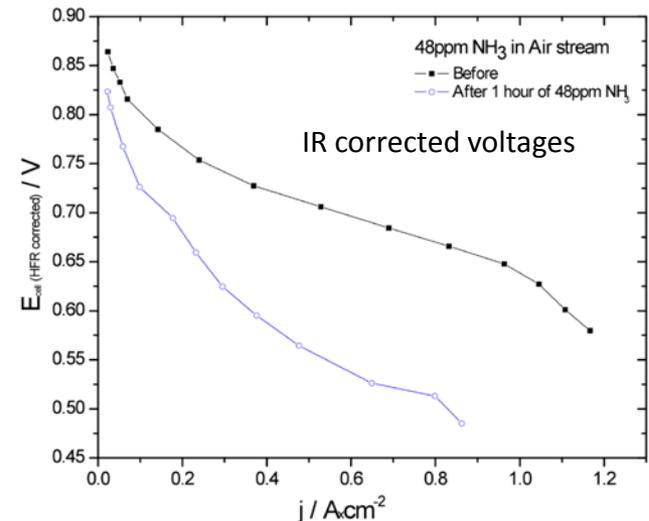
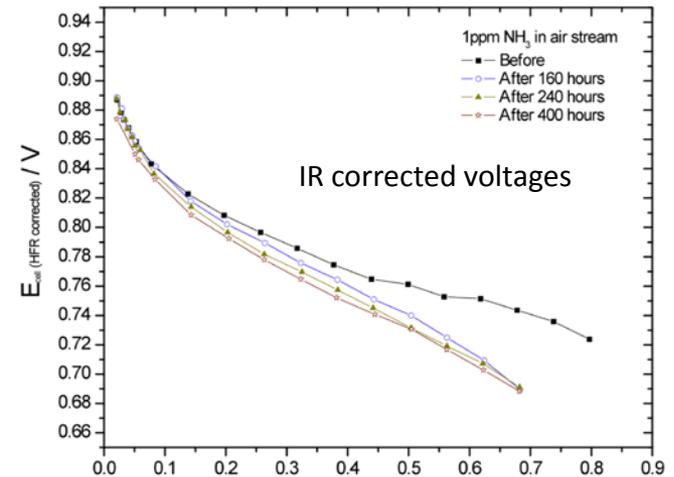
# Ammonia in the Air (cathode)

- The increase in High Frequency Resistance (HFR) alone does not explain the loss in fuel cell performance

1ppm NH<sub>3</sub> on the cathode side, versus the time of contamination. Anode/Cathode/Cell: 80°C; Anode/Cathode: 0.2/0.2mg<sub>Pt</sub>·xcm<sup>-2</sup>; Nafion® 117; 30/30psi back pressure.

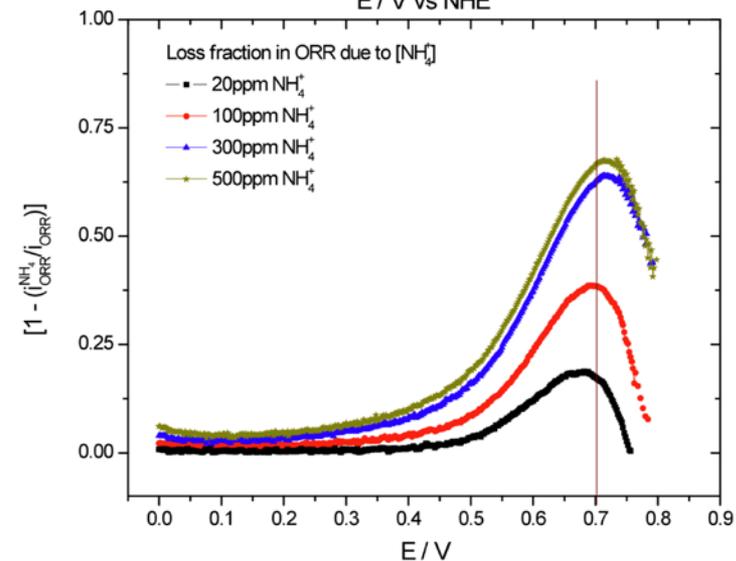
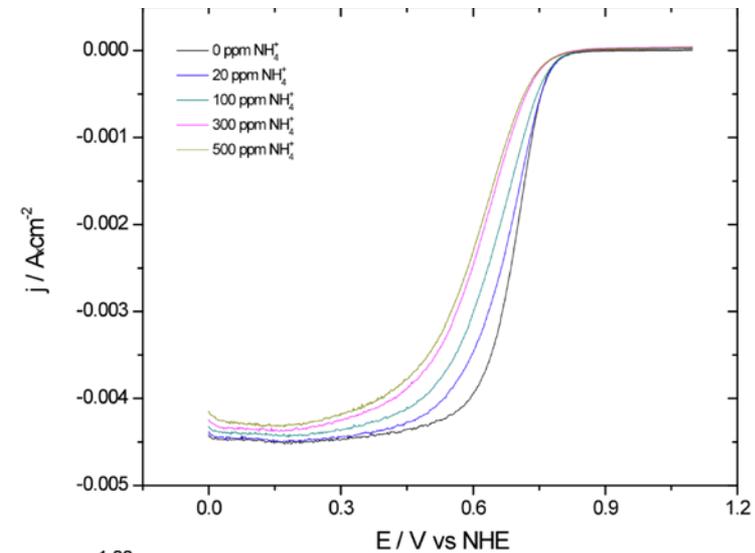
- Performance degradation increases with concentration

48ppm NH<sub>3</sub> on the cathode side 80°C  
Anode/Cathode: 0.2/0.2mg<sub>Pt</sub>·xcm<sup>-2</sup>  
Nafion® 117; 30/30psi of back pressure



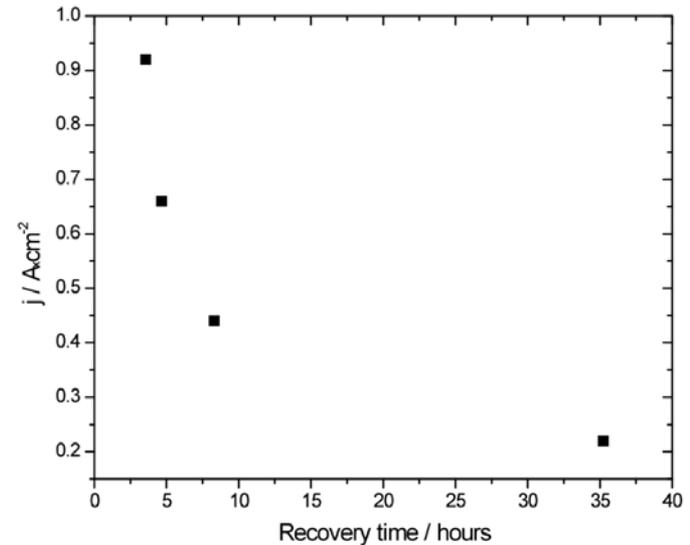
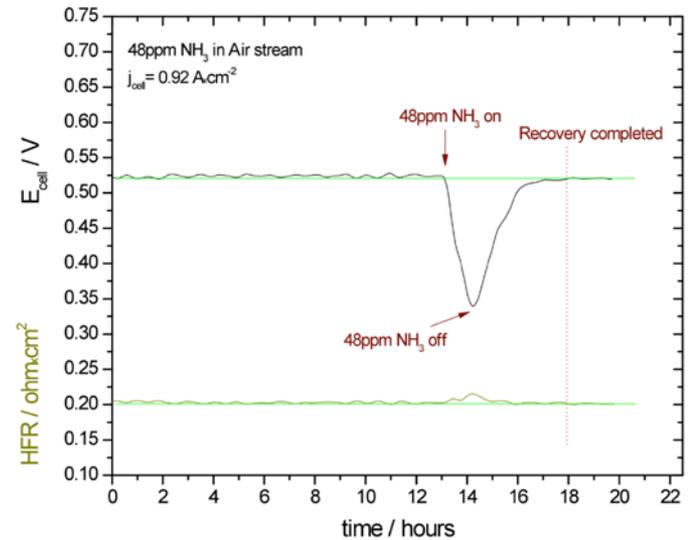
# ORR in Presence of Ammonium Ions RDE study

- Ammonium decreases both the onset potential and current of the oxygen reduction reaction
- RDE Linear Sweep Voltammetry for oxygen reaction reduction on a polycrystalline platinum electrode, 1600rpms.  $10\text{mV/s}^{-1}$ , in  $0.1\text{M HClO}_4$  at  $25^\circ\text{C}$ , at different  $[\text{NH}_4^+]$  added as  $(\text{NH}_4)\text{ClO}_4$
- Ammonium ions mainly affects the ORR in the fuel cell operating potential region (*the higher  $[\text{NH}_3]$ , the higher  $i_{\text{ORR}}$  losses*)



# PEMFC Cathode Exposed to NH<sub>3</sub>

- PEMFC exposed to 48ppm NH<sub>3</sub> on the cathode side
- Anode/Cathode/Cell: 80°C
- Anode/Cathode: 0.2/0.2mg<sub>PtX</sub>cm<sup>-2</sup>
- Nafion® 117; 30/30psi of back pressure
  
- Recovery time: 3.55 hours
- Voltage drop: 184mV
- HFR increase: 0.0125 Ohm-cm<sup>-2</sup>
- Voltage drop related to HFR increase: 11.5mV
- % of losses related to HFR increase: 6.3%
  
- Recovery time after PEMFC cathode exposed to 48ppm NH<sub>3</sub> for 1h, at different current densities
- Recover rate is much faster at high current densities
- Water Flux rather than ammonium ion oxidation is the primary recovery mechanism



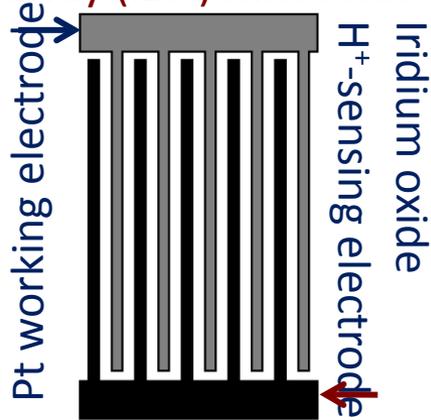
# Cation impurity effects on ORR

- Cation impurities affect ionomer conductivity, water ( $a_{\text{H}_2\text{O}}$ ) and  $\text{H}^+$  ( $a_{\text{H}^+}$ ) activities and affect oxygen reduction kinetics
- Lowered conductivity of Nafion<sup>®</sup> complicates quantitative estimates of the impurity effects on the ORR kinetics
- Determination of the interfacial activity of  $\text{H}^+$  would greatly improve understanding of the impurity effects on ORR and fuel cell performance
- Iridium oxide-coated Au electrodes have been used as pH sensors in aqueous electrolyte solutions

# Measurements of in situ $H^+$ activity

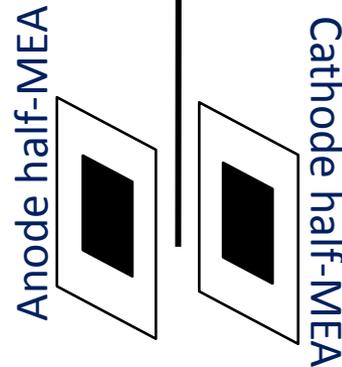
At ORR site

Nafion<sup>®</sup>-coated interdigitated array (IDA) microelectrode

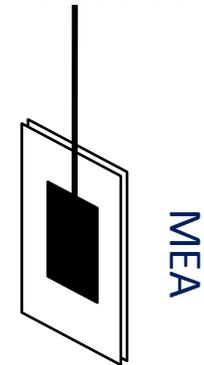


In an operating fuel cell

Iridium oxide-coated microwire



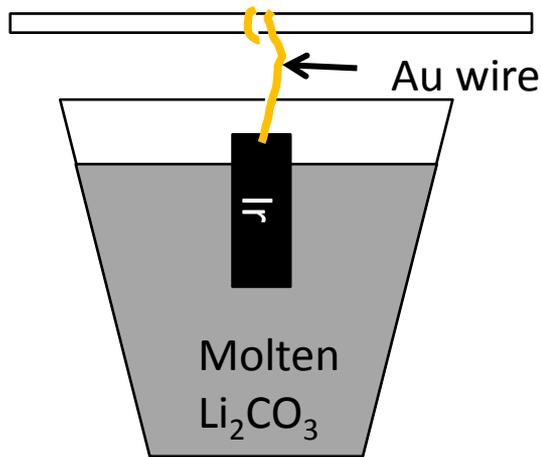
MEA with H<sup>+</sup>-sensing electrode



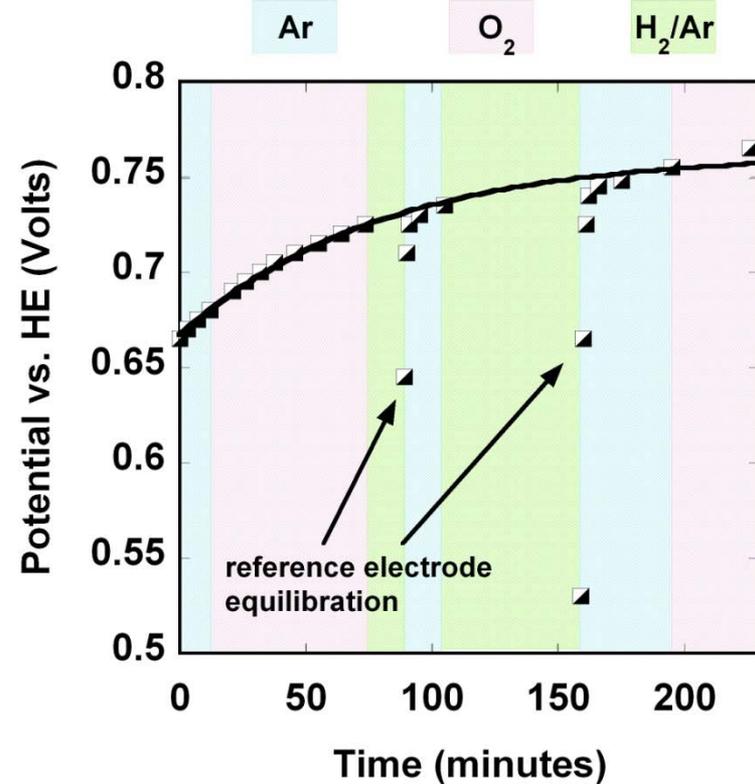
The measurements will help decouple the various effects of cationic impurities on ORR kinetics and fuel cell performance

# Ir/IrO<sub>x</sub> electrode By high temp oxidation of Ir

Ir oxide deposition



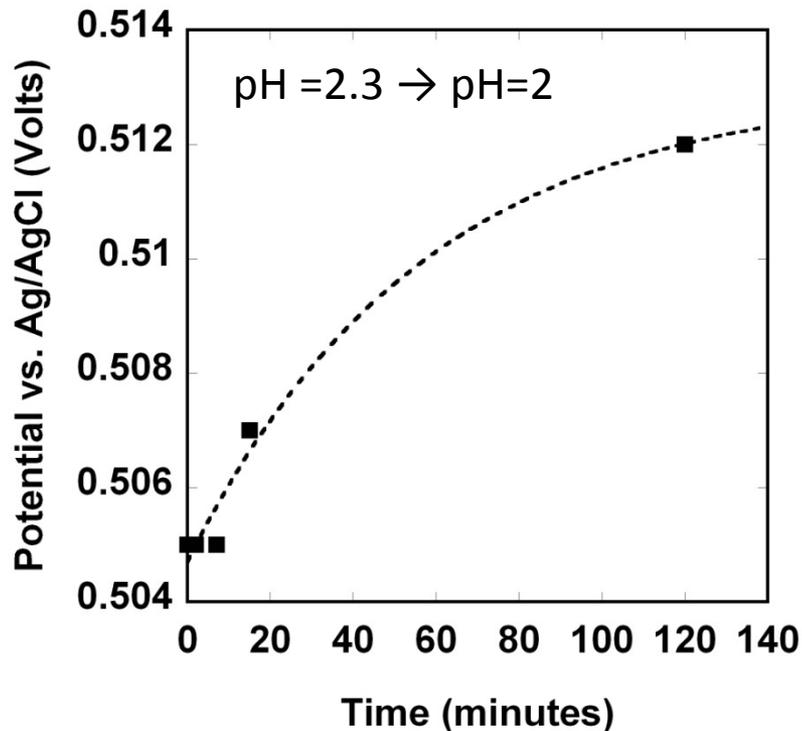
Potential response of freshly prepared electrode



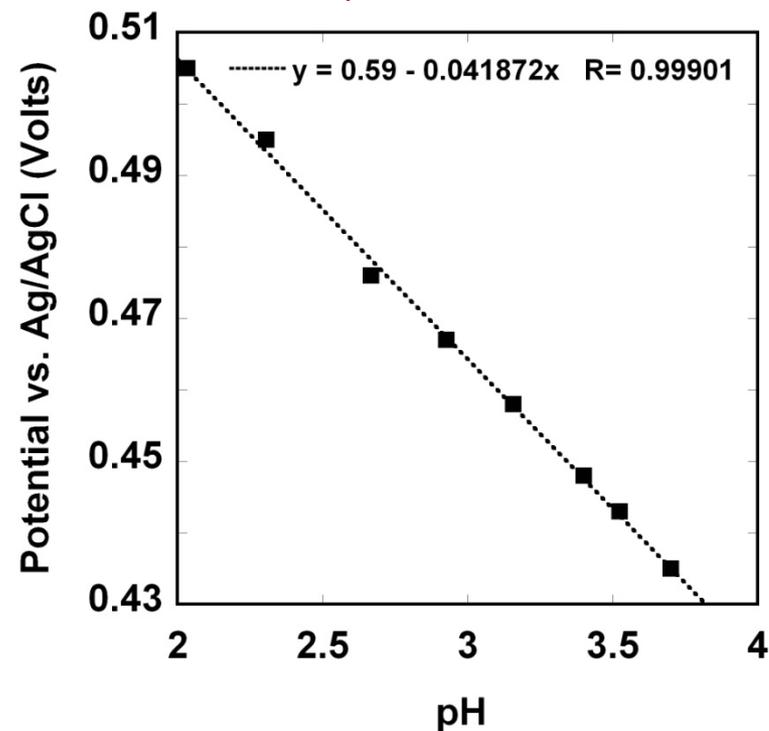
- Freshly prepared electrode has to be hydrated/broken in before use
- No or a weak effect of oxidizing/reducing agents on the measured potential

# Electrochemical behavior of hydrated Ir/IrO<sub>x</sub> electrode

Potential vs. time  
dependence



Potential vs. pH  
dependence

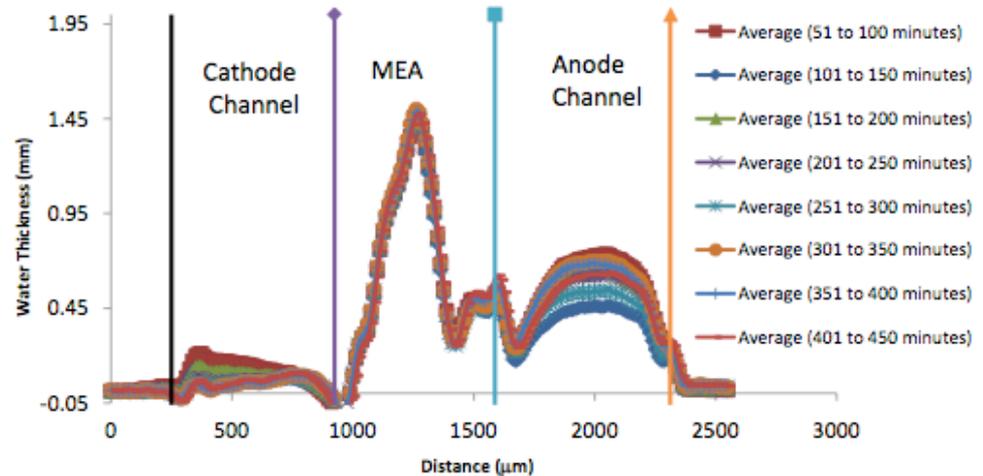
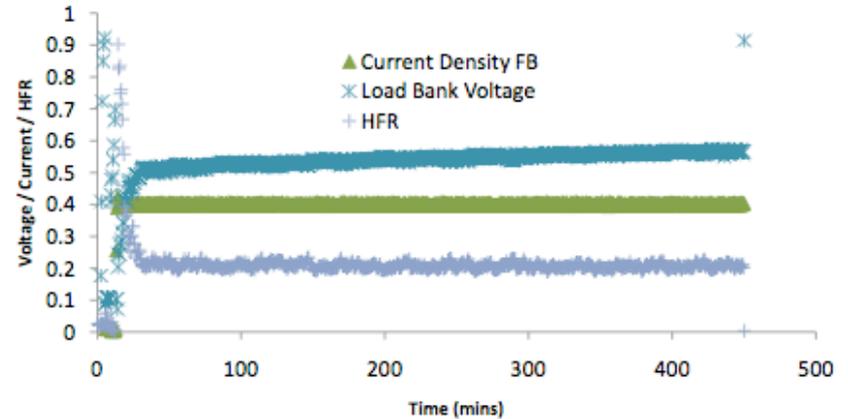
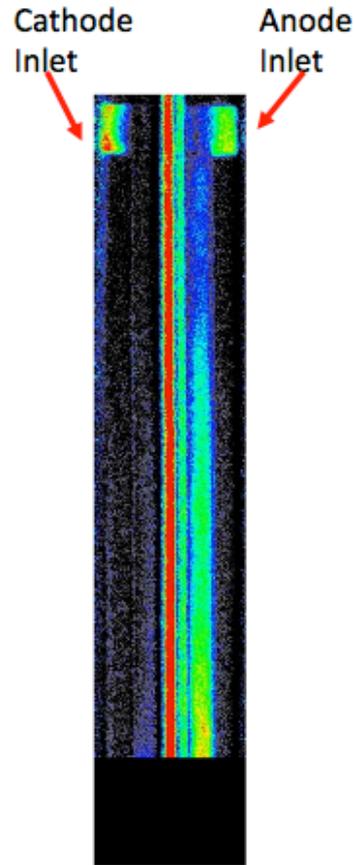


- Quicker response of hydrated electrode
- Very little dependence on redox state, hydrogen oxygen concentration

Well defined linear relationship between potential and solution pH

# Neutron Imaging Water in $\text{NH}_4^+$ Contaminated Fuel Cell

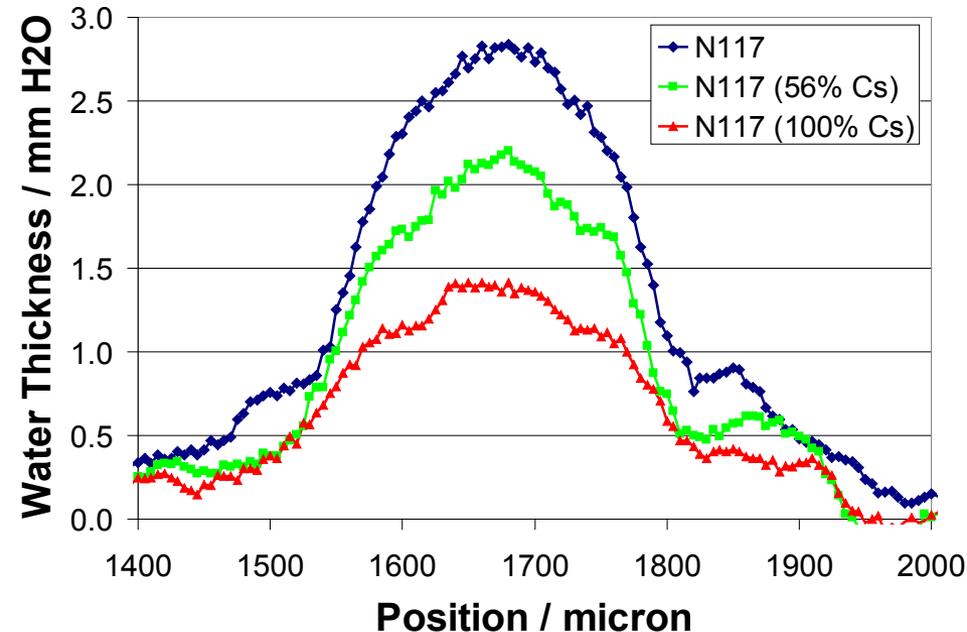
- Parallel channel fuel cell ~10% ammonia exchanged  $80^\circ\text{C}$  100% RH
- Fuel cell performance recovers
- Water distribution unchanged
- $\lambda$  similar to protons



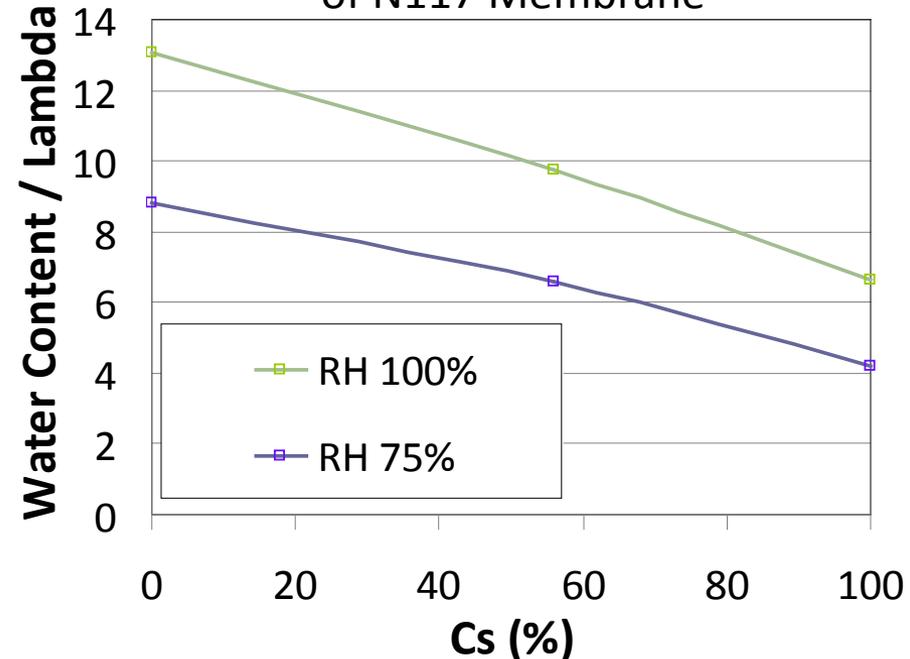
# Cation Effect on Membrane Water Content

*milestone*

Neutron Imaging Water Profile vs Cs (%)  
of N117 Membrane



Water Content vs Cs (%)  
of N117 Membrane



- Membrane water content measured *in situ* by neutron imaging
  - N117 and N117 sulphonic acids sites exchanged with Cs (56% and 100%)
- Cation contamination greatly reduces membrane water content
  - Reduced protonic conductivity due to lack of sulphonic acid sites

# Summary

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- H<sub>2</sub>S anode poisoning/durability test completed
  - low concentrations do not appear to affect durability
- SO<sub>2</sub> long term testing completed
  - low concentrations do not appear to affect durability
- NO<sub>x</sub> fuel cell poisoning shown to be largely reversible
- NH<sub>3</sub> poisoning was shown to behave like cation contamination
  - Anode or cathode introduction produces similar fuel cell response
  - water equilibrium is the predominate removal mechanism
- Some cationic impurities were shown to change water concentration in fuel cells

# Future Work

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- Measurements of proton activities in operating fuel cells
  - Study effects of cation impurities on proton concentrations in electrodes
  - Validate modeling
- Continue studies of cation removal mechanisms
- Investigate the effects of gas phase contaminants on ultra low loading fuel cells

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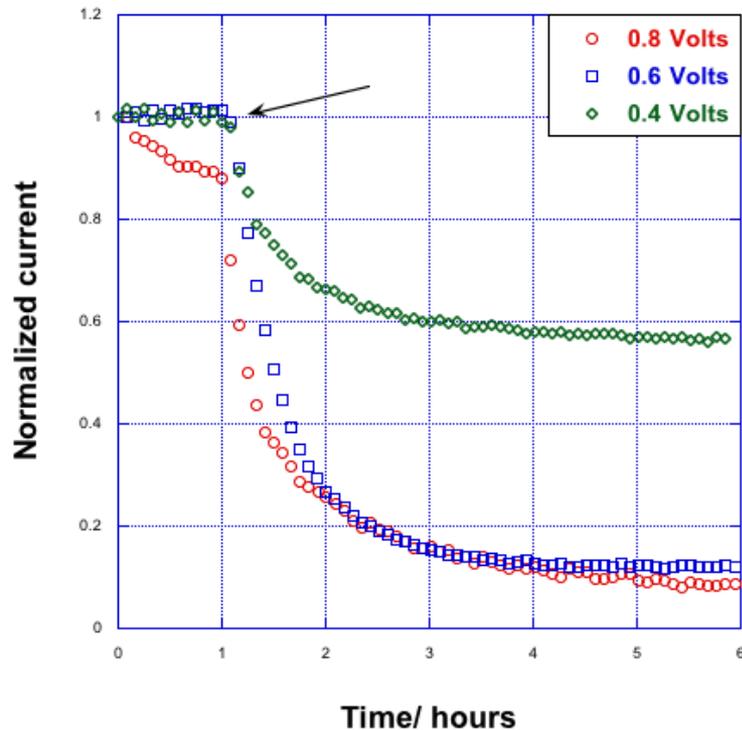
*We gratefully acknowledge funding from the US  
DOE Office of Fuel Cell Technologies*

# Fuel Cell V Influence on SO<sub>2</sub> Poisoning

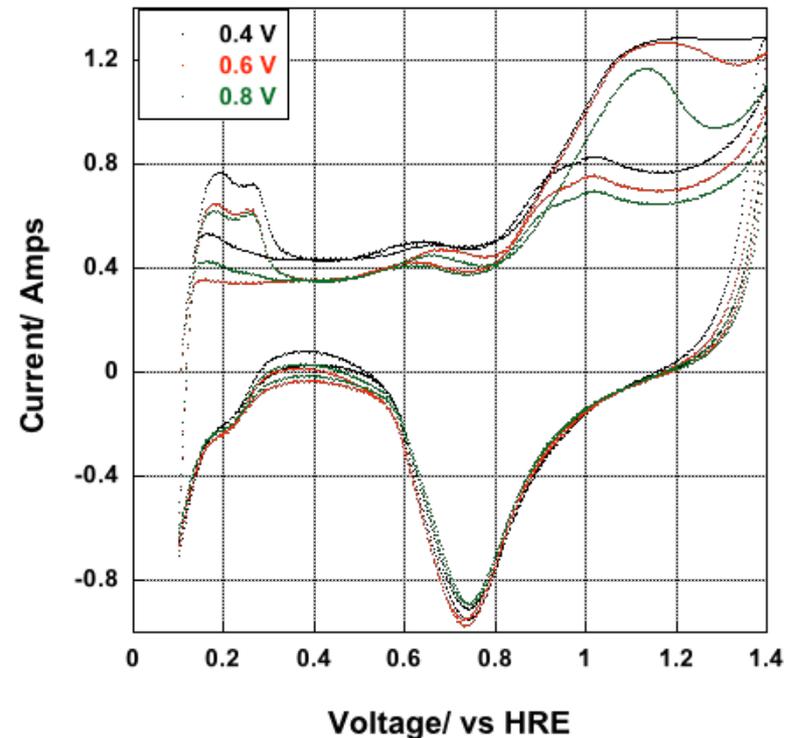
## Potential Dependence-5 ppm SO<sub>2</sub>

50cm<sup>2</sup>, 50 micron Nafion<sup>®</sup>, Cathode: 0.2 mg Pt/cm<sup>2</sup>

T<sub>cell</sub>: 80°C, 100% RH



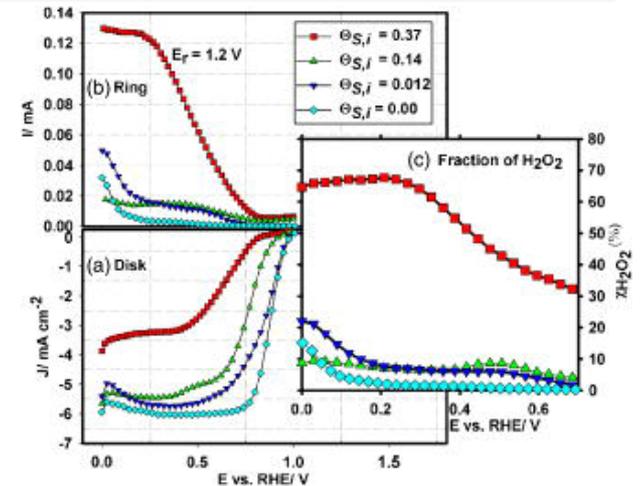
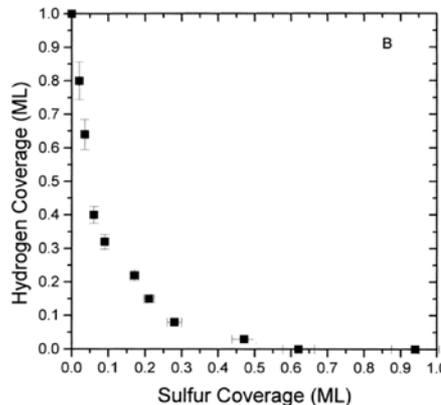
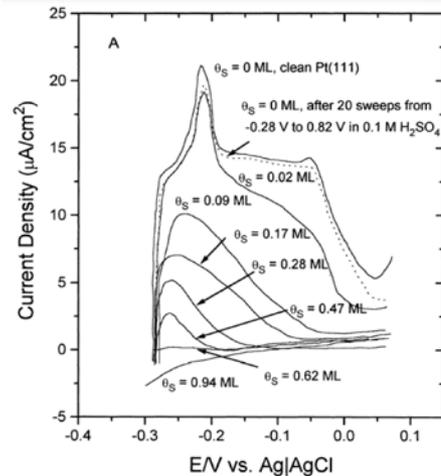
## Cathode CVs after exposure to 5 ppm SO<sub>2</sub>



- Cell operating voltage influences fuel cell poisoning rates
- More effect at higher cell voltages
- Crossover studies currently underway

# Sulfur on Pt Anodes and Cathodes

**The effect of sulfur on adsorption of hydrogen on Pt(111):** voltammetric profiles for hydrogen desorption at the indicated sulfur coverage in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution;  
 (B) hydrogen coverage versus sulfur coverage (in monolayers)  
 S hurts H adsorption

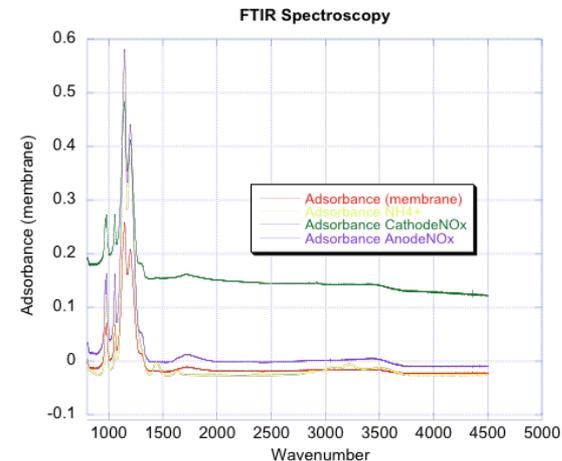
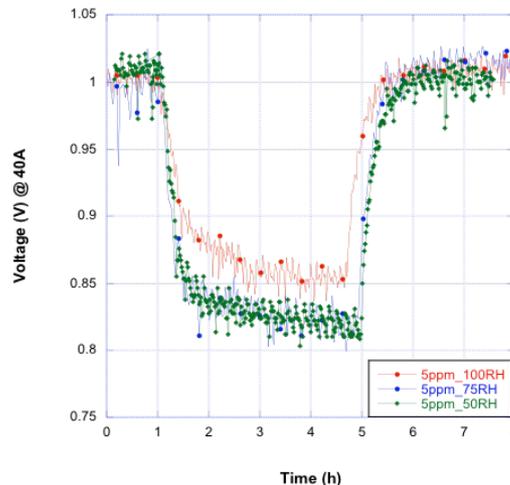
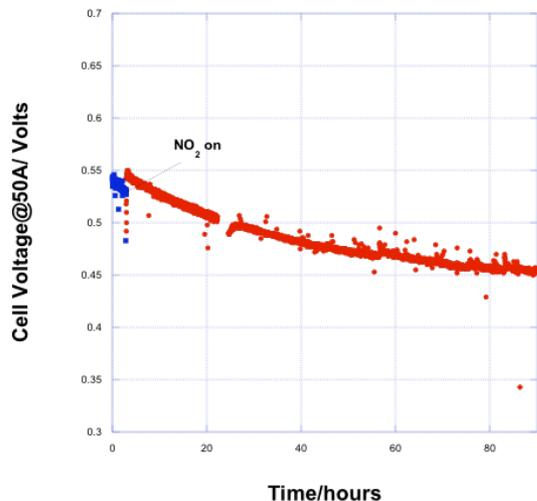


Y. Garsany, *et al J. ECS* 154, b670 (2007).

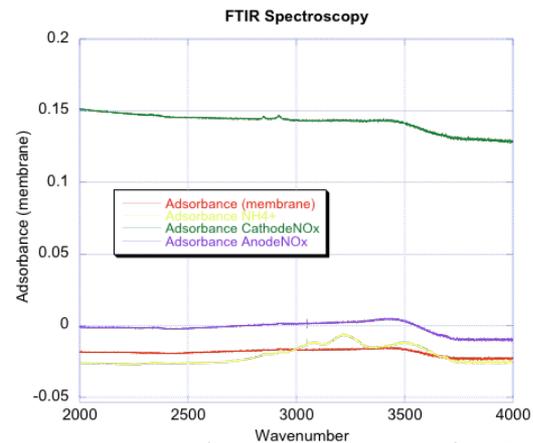
- SO<sub>2</sub> adsorption on to RRDE cathode
- Sulfur adsorption strongly affects Oxygen reduction kinetics and pathways
- Note large generation of peroxide for 0.37 of monolayer coverage

Y. E. Sung, W. Chrzanowski, A. Zolfaghari, G. Jerkiewicz, A. Wieckowski, *Journal of the American Chemical Society* 119, 194 (1997)

# NO<sub>x</sub> In Cathode Air

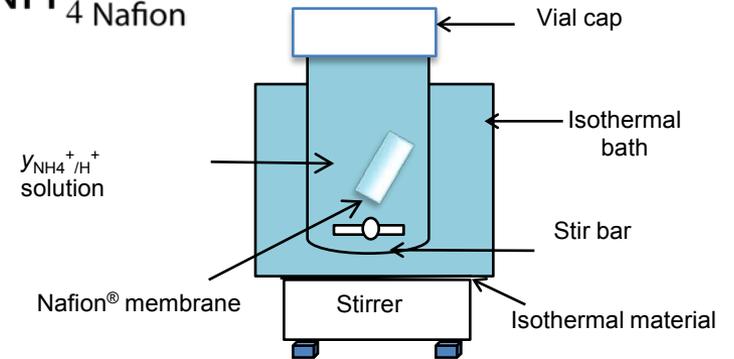
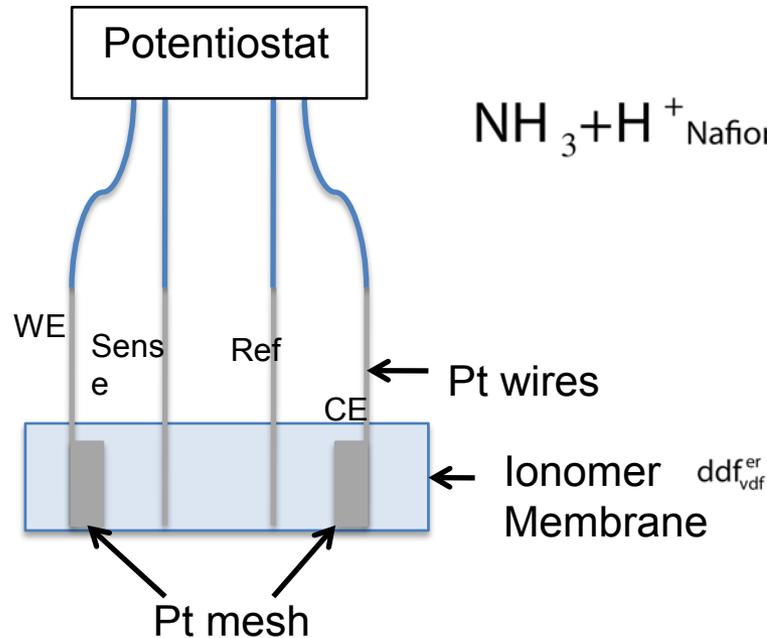


- 0.1mg/cm<sup>2</sup> Pt-C anode-0.2mg/cm<sup>2</sup> Pt-C cathode  
50μm ionomer
- Fuel Cell Testing of 5ppm NO<sub>2</sub> cathode 1 A/cm<sup>2</sup>  
80°C
- Steady decay in performance
- Some humidification dependence on performance losses
  - Higher humidification may remove more soluble NO<sub>2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



- Ammonium exchange membrane compared to NO<sub>2</sub> exposed MEA
- ammonium ions 2400–3200 cm<sup>-1</sup>
- Sharp peaks at 2800 cm<sup>-1</sup> may be amine vibrational modes

# Ammonium Ion Membrane Equilibrium



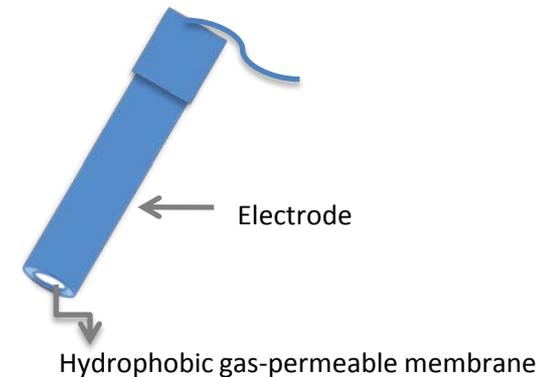
$$\mu_{\text{nafion}} = \mu_{\text{solution}} \quad (\text{system at equilibrium})$$



$$\text{Equilibrium: } K_{\text{eq}} = \frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_3)}$$

$\text{NH}_4^+$  concentration fixed

$$(\text{NH}_3) = \frac{(\text{OH}^-)}{K_{\text{eq}}}$$





# Concentrated Solution Transport Equations Used in Membrane

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

$C_t$  -  $SO_3^-$  conc. in ionomer

$\Phi$  - potential V

$\alpha$  -  $D_B/D_H$

$L$  - thickness cm

$\lambda$  -  $H_2O/SO_3^-$

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

$\xi_i$  - drag coef.

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

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

Diffusion

Migration

Drag

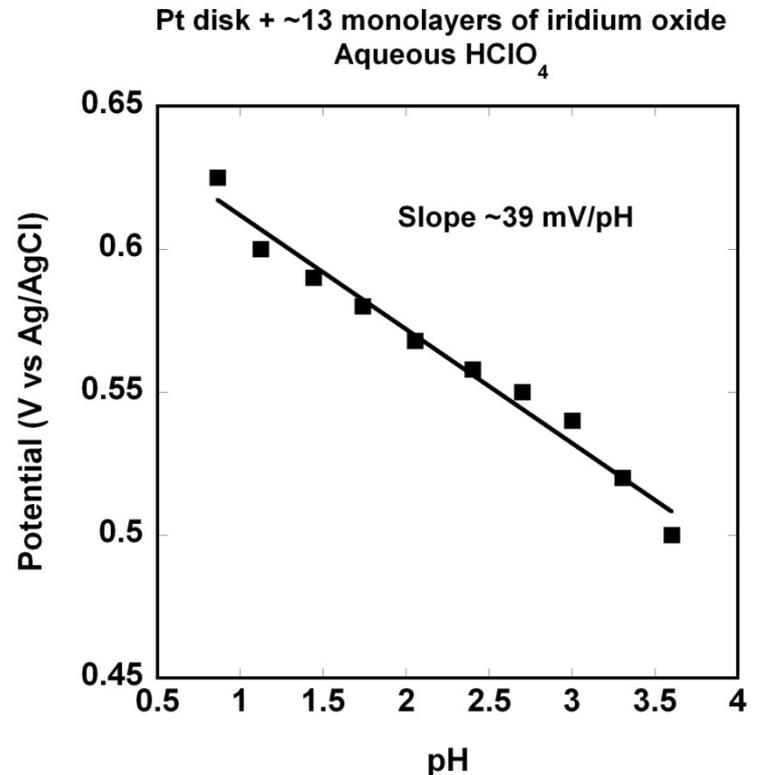
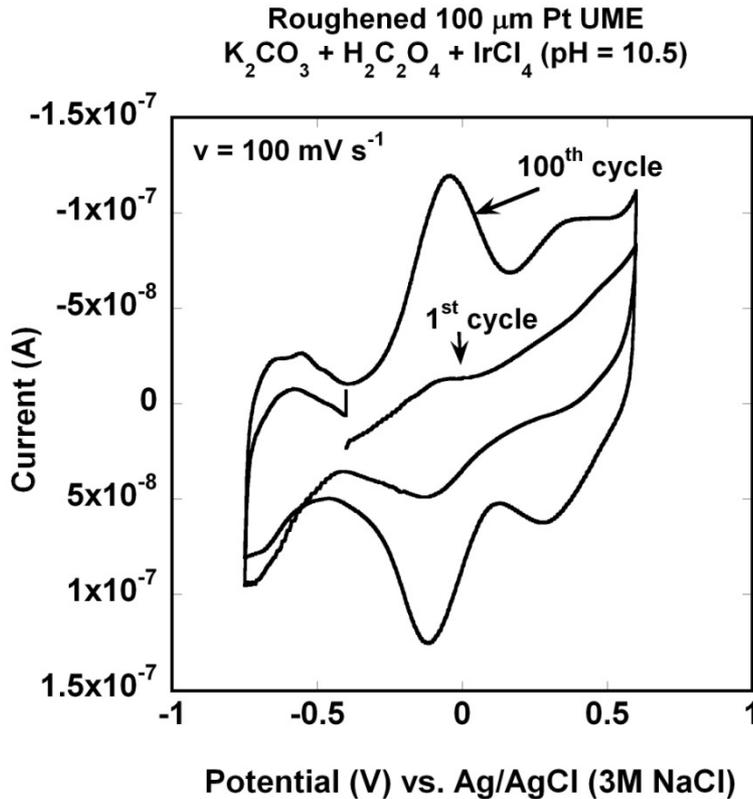
$$C_t \frac{\partial y_H}{\partial t} = \nabla \cdot \frac{D_H C_t}{L} \left[ \frac{\partial y_H}{\partial x} + \frac{y_H}{b} \frac{\partial \phi}{\partial x} + \xi_H y_H d_a \frac{\partial \lambda}{\partial x} \right] \quad H^+$$

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

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

Diffusion

# Platinum electrodes in aqueous media

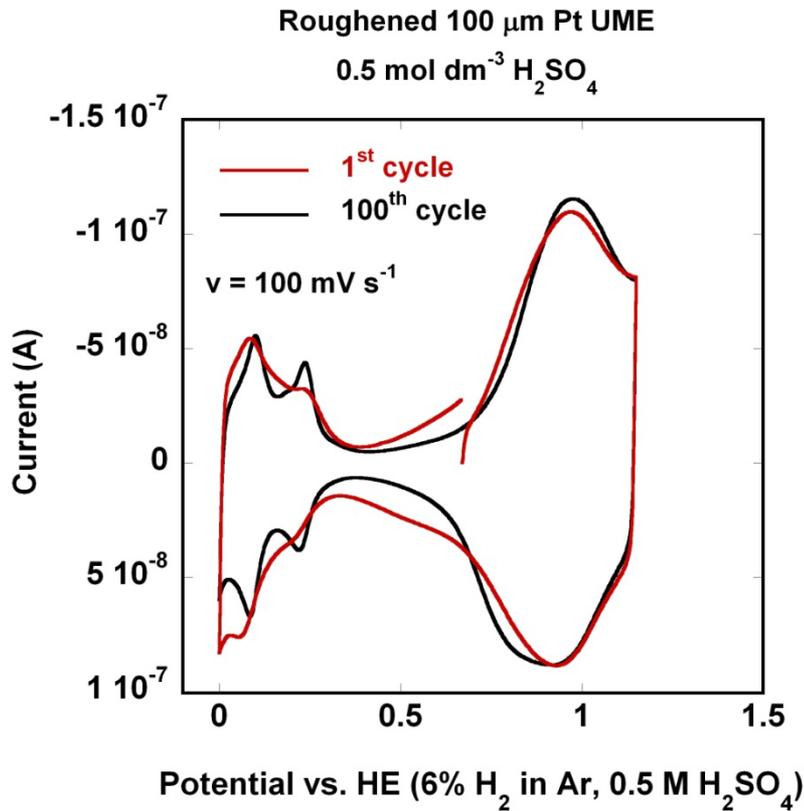


Iridium oxide easily deposited on platinum disk electrodes, ultramicroelectrodes (shown) and Pt sputtered on glass

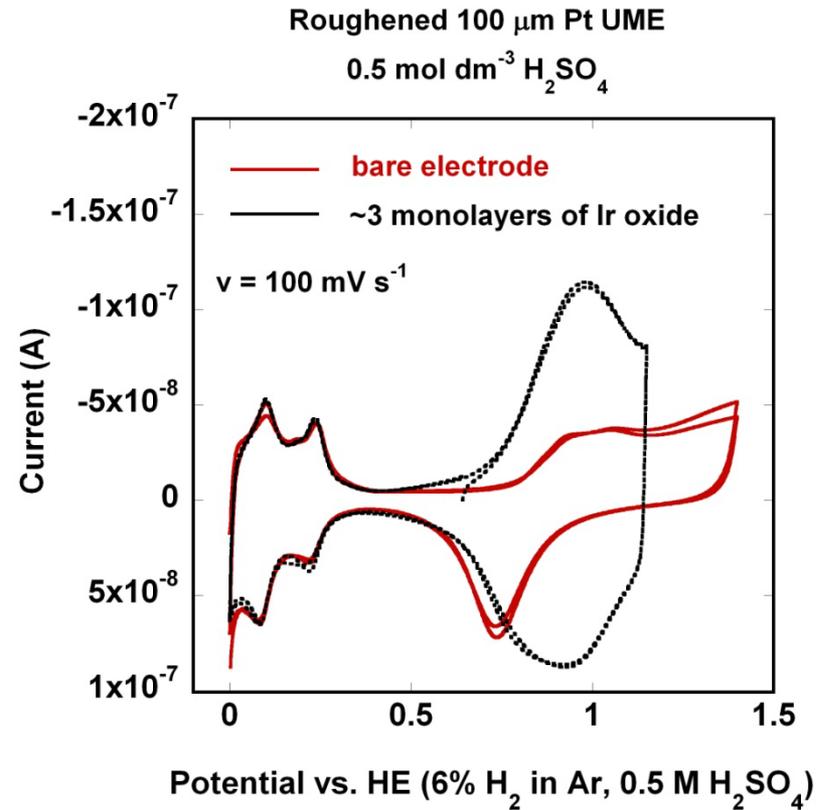
Clear, approximately linear E vs. pH dependence with sub-Nernstian slope in aqueous media with no  $\text{O}_2$  sensitivity

# Iridium oxide-coated Pt electrodes in aqueous media

## Voltammetry in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$



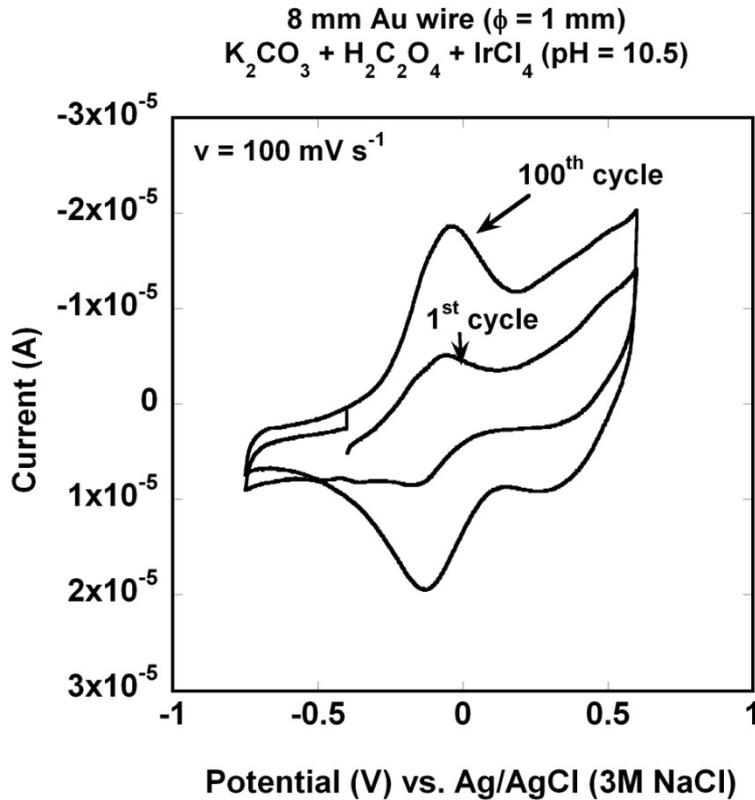
Well defined hydrogen UPD on Pt developed upon cycling



Presence of iridium oxide on Pt surface has no effect on hydrogen UPD!

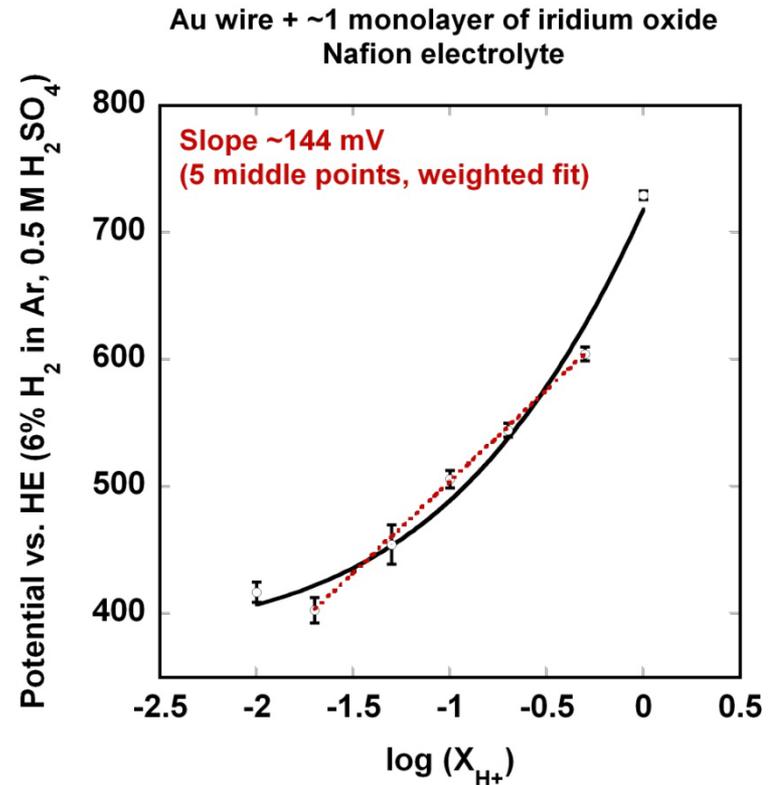
# Au/iridium oxide electrodes coated with Cs<sup>+</sup>-spiked Nafion<sup>®</sup>

## Ir oxide deposition



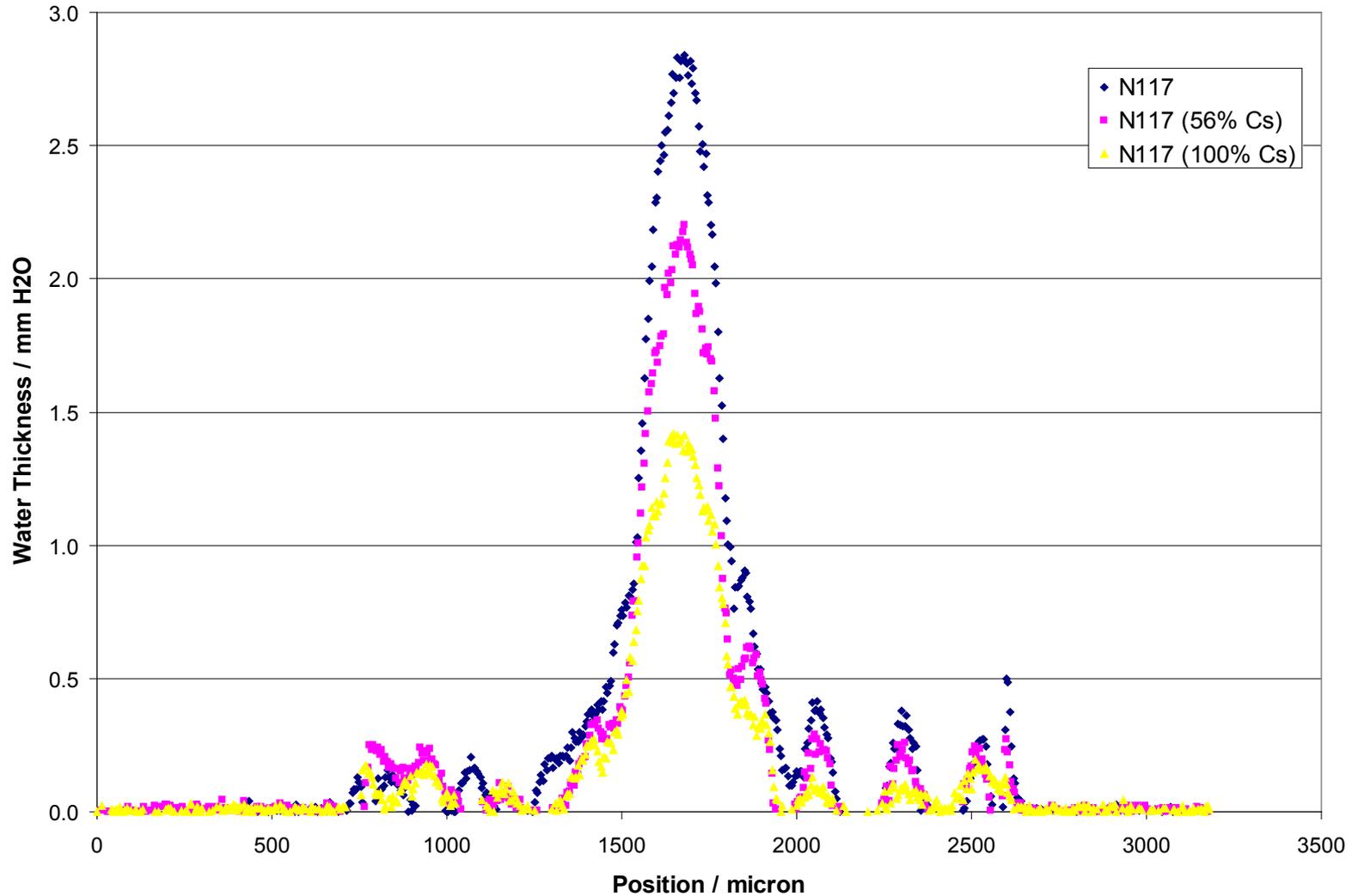
Well defined hydrogen UPD on Pt developed upon cycling

## H<sup>+</sup> (Cs<sup>+</sup>) sensing

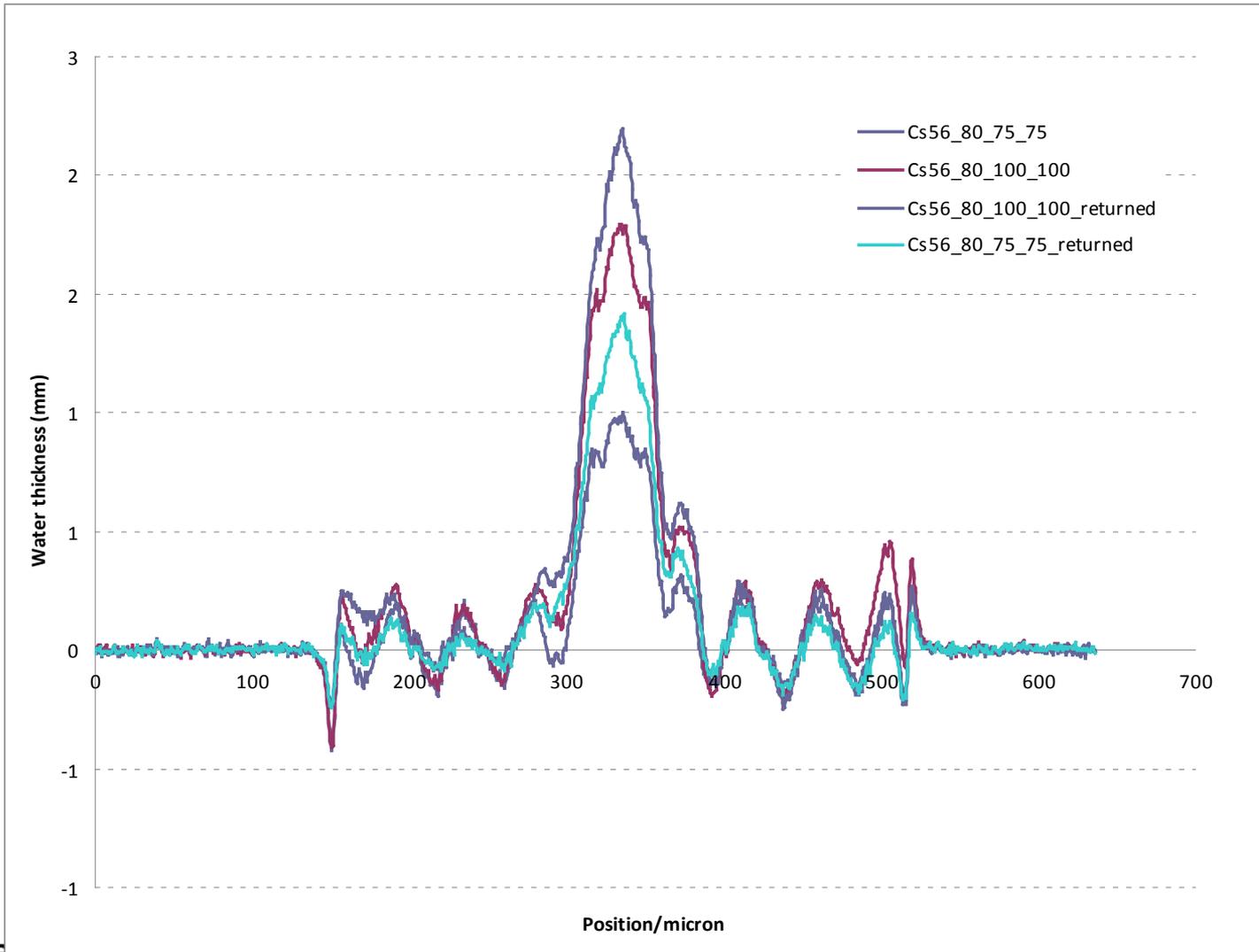


Strong non-linear E vs.  $\log(X_{H^+})$  dependence – possibility of accurate H<sup>+</sup> (Cs<sup>+</sup>) determination *in situ*

# Water Profiles for N117 showing Cs Effect



# Measured Water Thickness for a N117 Nafion<sup>®</sup> membrane with 56% Cs



# Measured Water Thickness for a N117 Nafion<sup>®</sup> membrane with 100% Cs

