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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Fuel Cell Research

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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

 *S impurity studies*

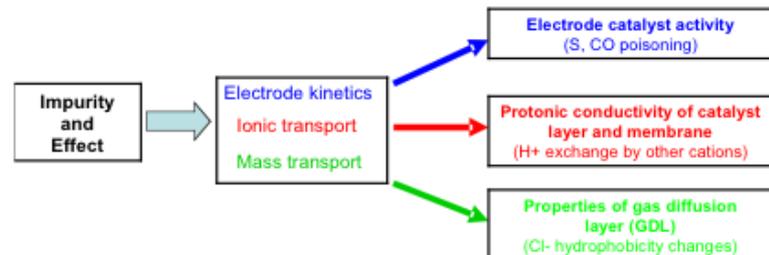 Modeling

 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
  - 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
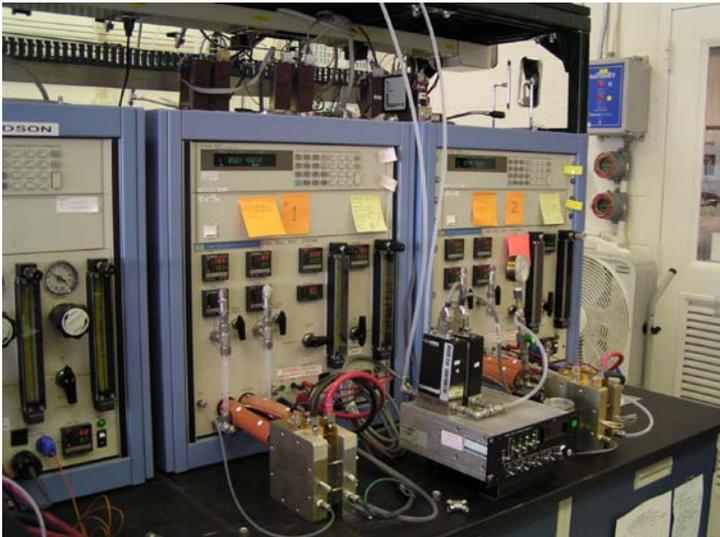
- Fabricate and operate fuel cells under controlled impurity gases

    - 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)

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# 1000hr Drive Cycle Testing Effects of 10 ppb H$_2$S
milestone

Cell:50 cm^2

- MEA- Gore 720, 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

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,

Baseline Polarization Curves

10 ppb H2S: Polarization Curves

% Loss of Cathode ECSA
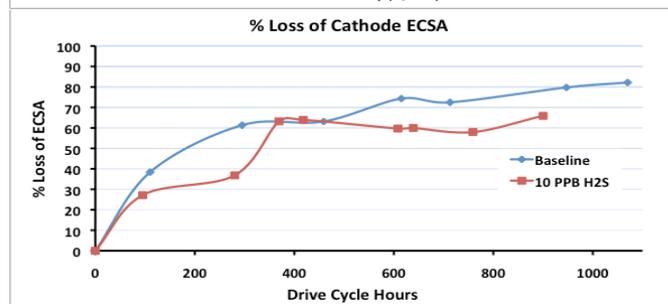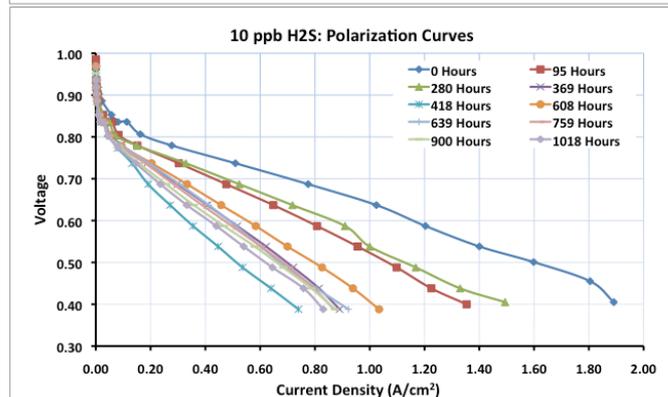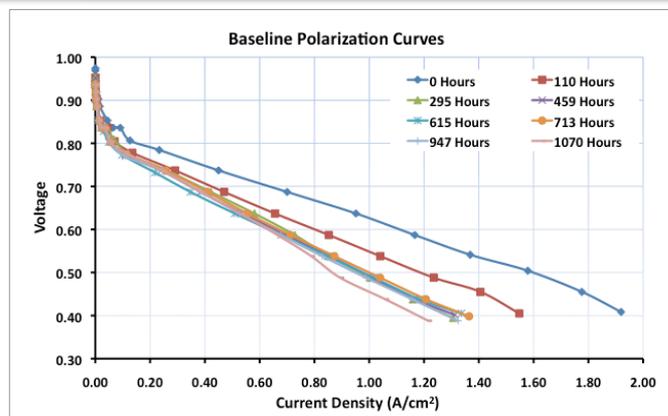
- Degradation of fuel cell performance with respect to baseline
- Increased fuel cell losses in the kinetic region
- Cathode ECSA not significantly different
- The effect of hydrogen sulfide at this concentration would probably be recoverable by air purging or voltage pulsing

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Fuel Cell Research

Cathode Loadings: 100 ppb SO$_2$
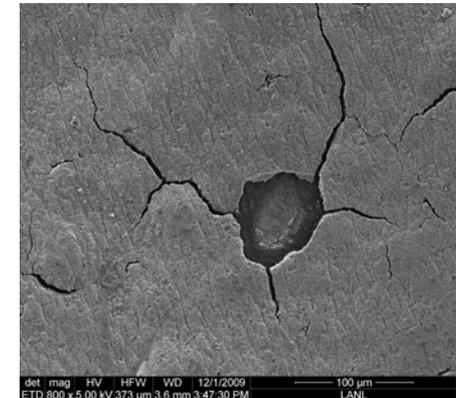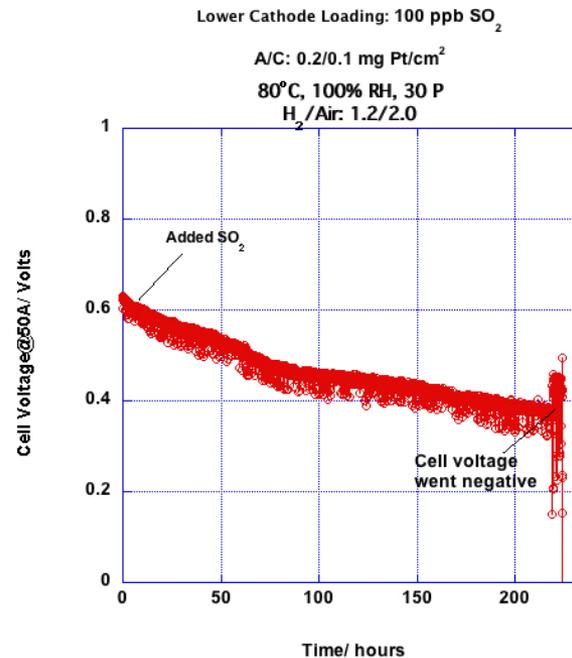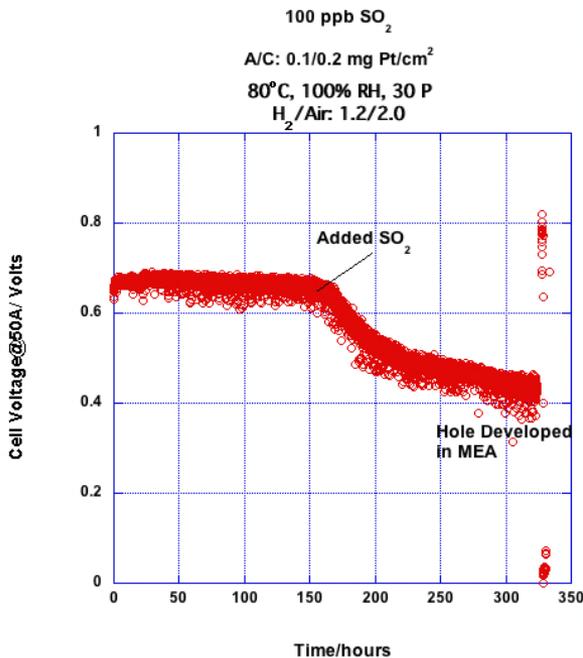
Under identical condition, we probe the impact SO$_2$ on cathode loadings: (0.1 and 0.2 mg Pt/cm^2) Catastrophic failure in both expt's: further analysis showed a hole developed. We are currently revisiting the impact of cathode loadings.

# Cathode Impurities:
100 ppb SO$_2$ Studies: 500h test *milestone*
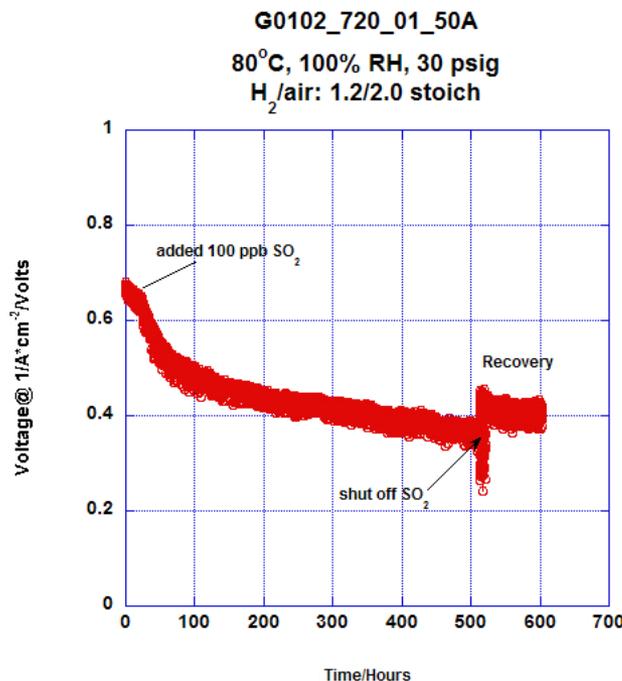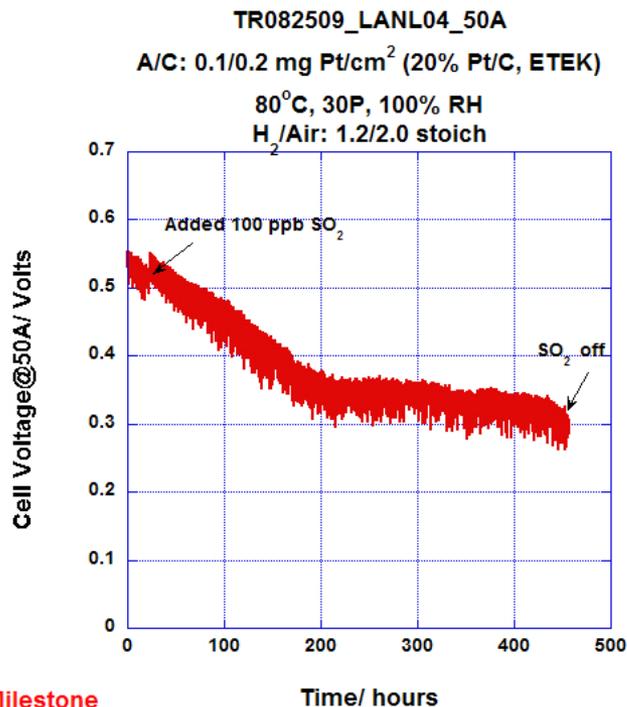
Test Conditions:
- A/C: 0.1/0.2 mg Pt/cm^2
- 50 cm^2, 100%Rh, 30 Psig
- H$_2$/Air: 1.2/2.0 stoich
- 50A constant current

Two cells were tested using 100ppb SO$_2$ in the cathode (LANL MEA vs Commercial)
Losses were both ~200 mV,
Recovery stage showed very little performance increase

NO$_x$ Influence on Membrane Resistance

•High frequency resistance rising indicative of cation poisoning

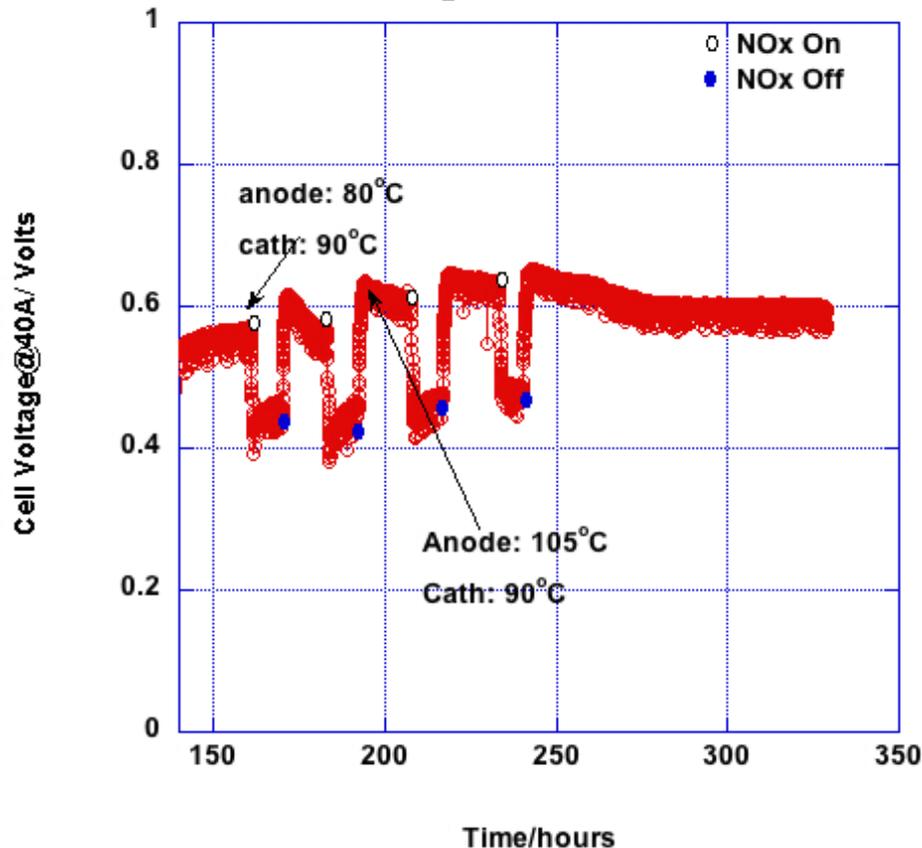•Strong evidence of ammonium ion formation from NO reduction by hydrogen

Cathode Impurities: 5 ppm NOx

50 cm^2, 50 micron Nafion, Cathode: 0.2 mg Pt/cm^2

Tcell: 80°C, 100 % RH
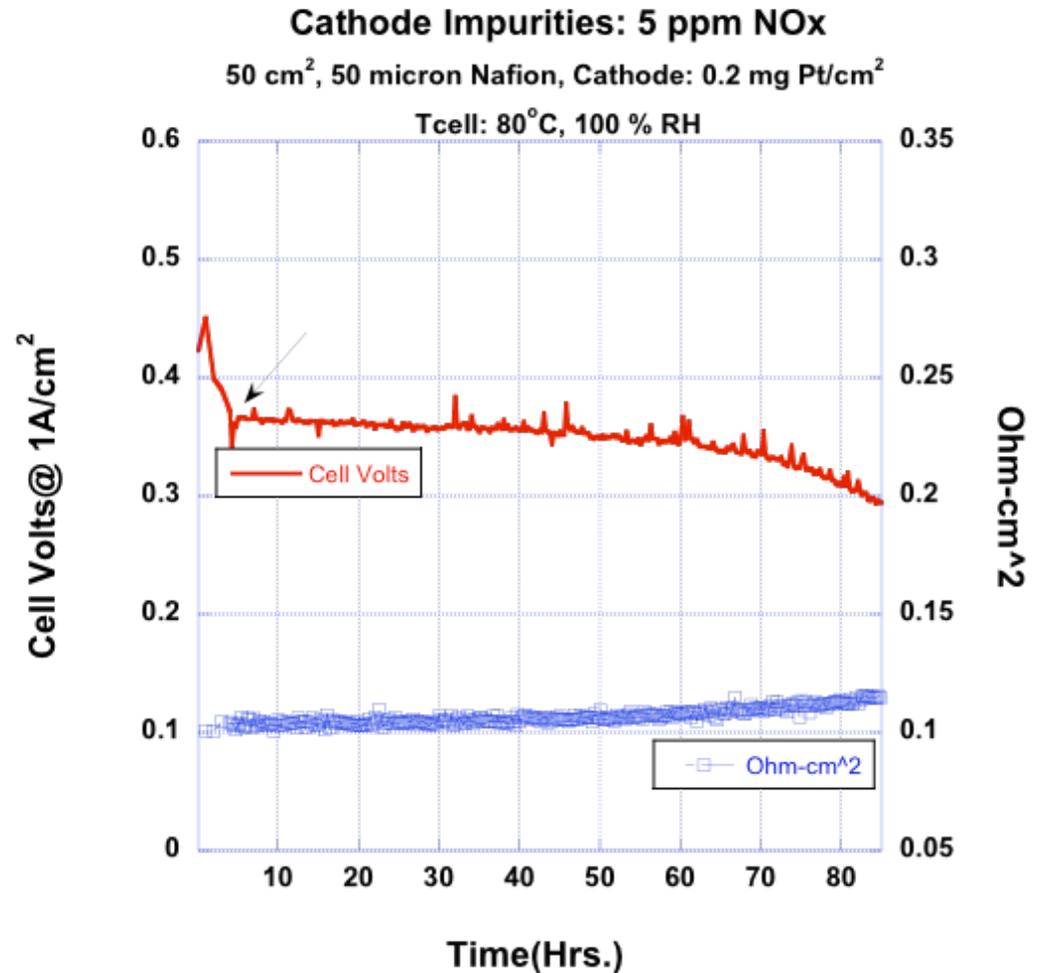
NO$_x$ tests: On and Off Cycling

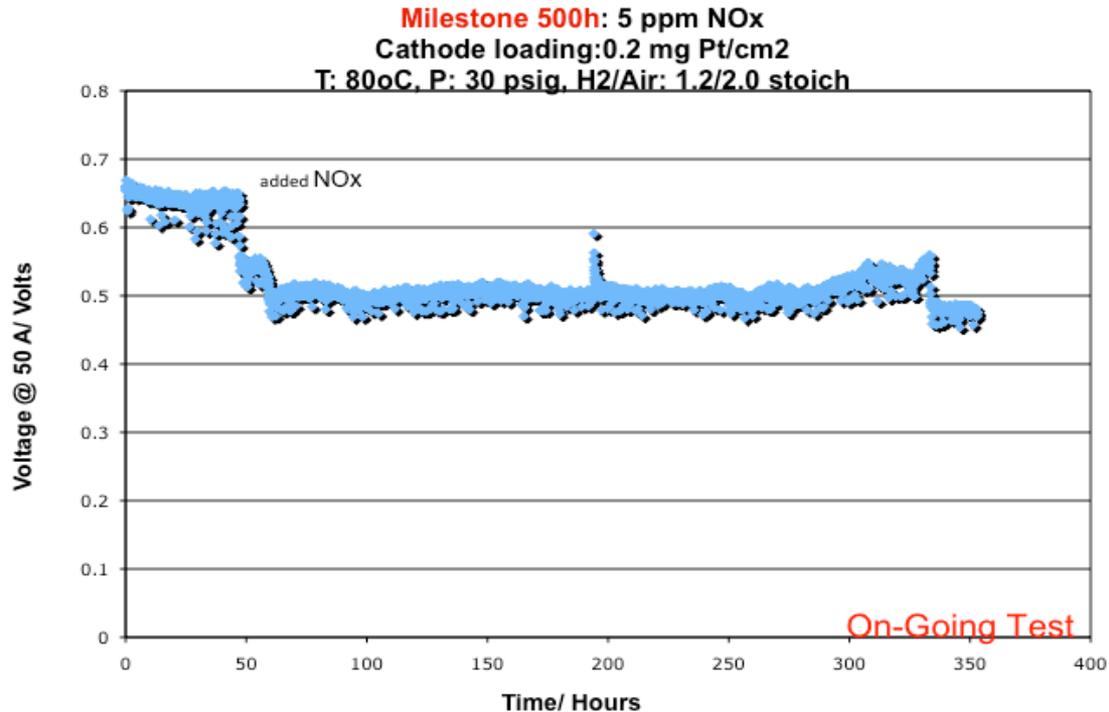NOx Recovery: On and Off cycles with 5 ppm
A/C: 0.1/0.2 mg Pt/cm^2
80°C, 30 P
H$_2$/Air: 1.2/2.0

- 5 ppm NO$_2$ exposure
- 0.8 A/cm^2 constant current
- Full recovery after short-term exposure
- Increasing RH did significantly change recovery rate

Long-term-NO$_x$ tests

Milestone 500h: 5 ppm NOx
Cathode loading:0.2 mg Pt/cm2
T: 80oC, P: 30 psig, H2/Air: 1.2/2.0 stoich

added NOx

On-Going Test

Voltage @ 50 A/ Volts

Time/ Hours

- 5 ppm NO$_2$ exposure
- 1 A/cm^2 constant current
- Steady state response is reached
- Probably ammonia water flux equilibrium

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Fuel Cell Research

Ammonia Air or Fuel Impurities

Air Sources:

- Agriculture environment:

    - Potential source of ammonia (NH_3)

    - Ammonia can also be present in industrial environments

- Potential impact of 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:

    - CO, H_2S, NH_3

- Ammonia, as a fuel impurity, affects the performance of a PEMFC[1,2]

- There is also evidence[3] that the concentration profile of cations across the membrane changes with the current density
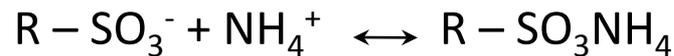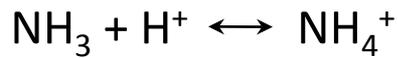
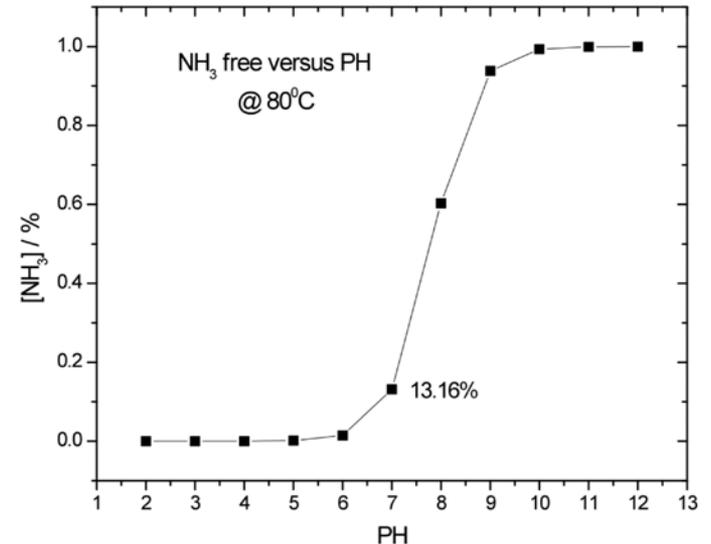# Possible Effects of Ammonia on PEMFCs

■ **Oxygen reduction reaction (ORR)**
  - Reduction of available active Pt sites for ORR
  - NH_3 oxidation

■ **Nafion®**
  - NH_3 in a PEMFC (acid media) forms NH_4^+ and bonds with sulfonic groups

$$NH_3 + H^+ \longleftrightarrow NH_4^+$$

$$R - SO_3^- + NH_4^+ \longleftrightarrow R - SO_3NH_4$$

NH₃ free versus PH @ 80°C

13.16%

  - Reduction of water content in membrane (Membrane conductivity and ORR[5])
  - $\lambda_{H^+} = 20$ [6]
  - $\lambda_{NH_4^+} = 13$ [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)

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Ammonia in the Air (cathode)

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

1ppm NH_3 on the cathode side, versus the time of contamination. Anode/Cathode/Cell: 80^0C; Anode/Cathode: $0.2/0.2mg_{Pt}xcm^{-2}$; Nafion® 117; 30/30psi back pressure.


• Performance degradation increases with concentration

48ppm NH_3 on the cathode side 80^0C Anode/Cathode: $0.2/0.2mg_{Pt}xcm^{-2}$ Nafion® 117; 30/30psi of back pressure

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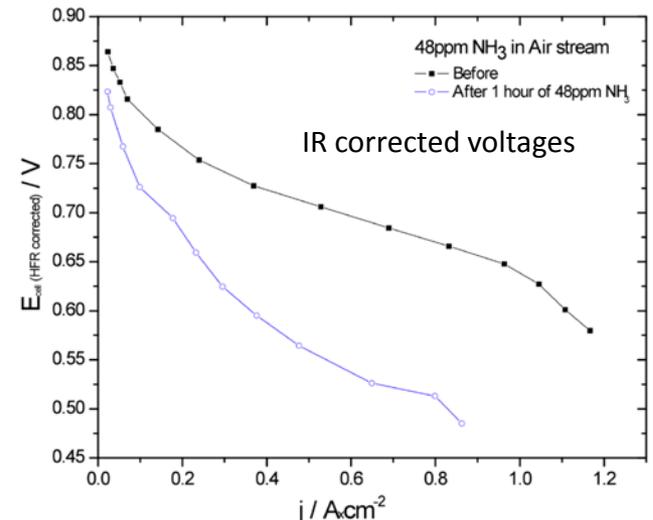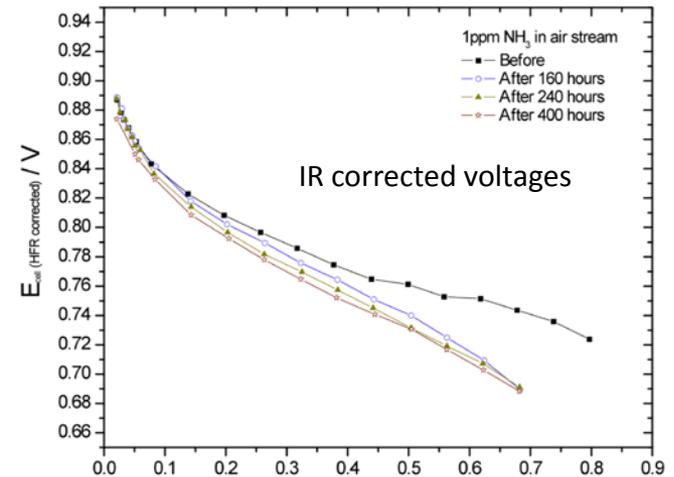
ORR in Presence of Ammonium Ions RDE study

• 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. 10mV/s^{-1}, in 0.1M HClO$_4$ at 25^{0}C, at different [NH$_4^+$] added as (NH$_4$)ClO$_4$

•Ammonium ions mainly affects the ORR in the fuel cell operating potential region *(the higher [NH$_3$], the higher i$_{ORR}$ losses)*
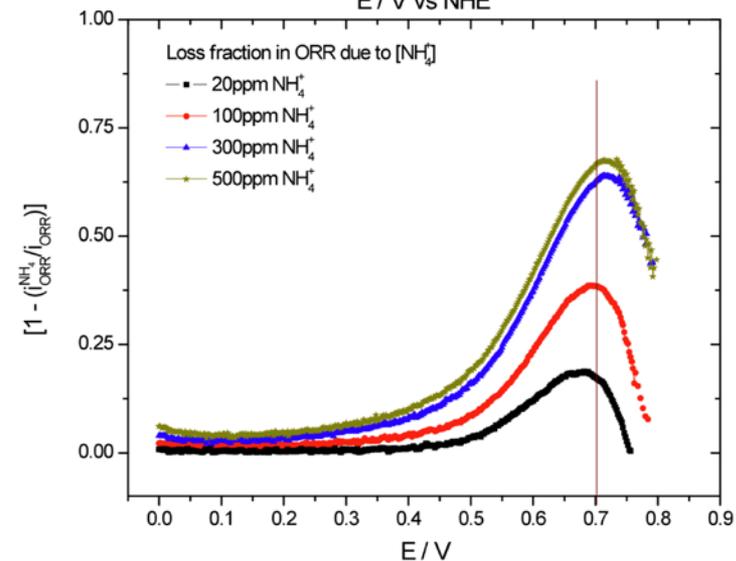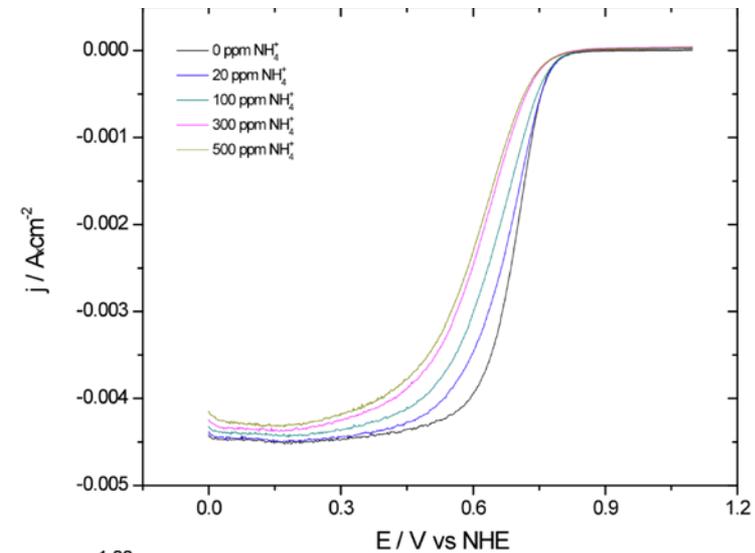
PEMFC Cathode Exposed to NH$_3$

- PEMFC exposed to 48ppm NH$_3$ on the cathode side
- Anode/Cathode/Cell: 80^{0}C
- Anode/Cathode: 0.2/0.2mg$_{Ptx}$cm^{-2}
- Nafion$^®$ 117; 30/30psi of back pressure

- Recovery time: 3.55 hours
- Voltage drop: 184mV
- HFR increase: 0.0125 Ohm-cm^{-2}
- 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$_3$ 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

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Fuel Cell Research
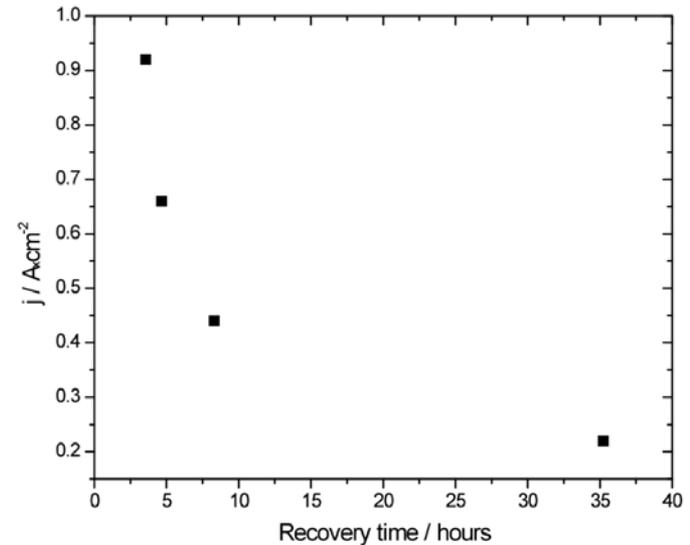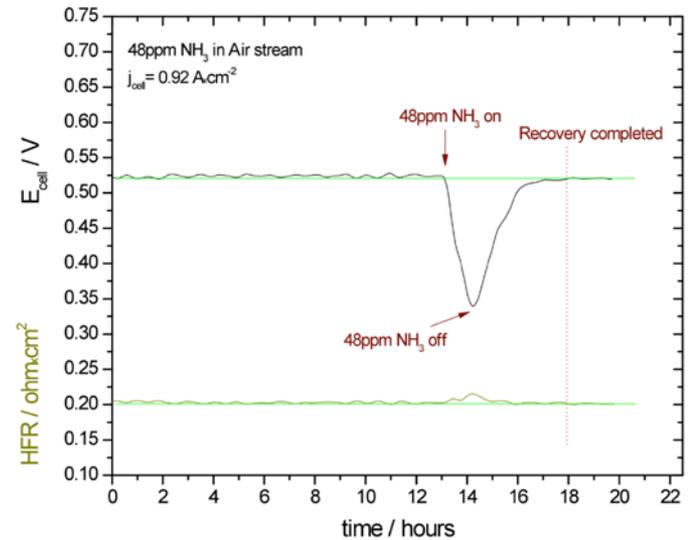
Cation impurity effects on ORR

- Cation impurities affect ionomer conductivity, water (a_{H2O}) and H^+ (a_{H+}) activities and affect oxygen reduction kinetics

- Lowered conductivity of Nafion® complicates quantitative estimates of the impurity effects on the ORR kinetics

- Determination of the interfacial activity of 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
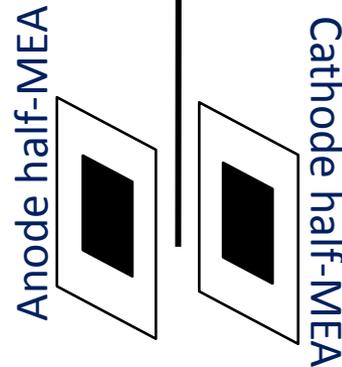
Measurements of in situ H⁺ activity

At ORR site

In an operating fuel cell

Nafion®-coated interdigitated array (IDA) microelectrode

Pt working electrode
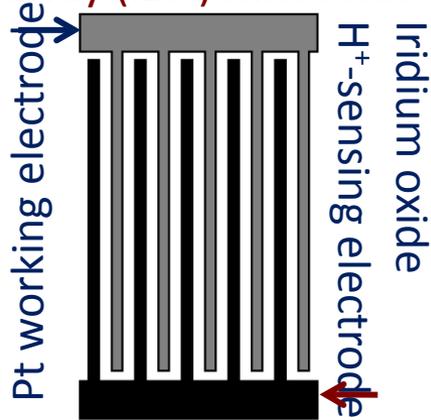
Iridium oxide H⁺-sensing electrode

Iridium oxide-coated microwire

MEA with H⁺-sensing electrode

Anode half-MEA

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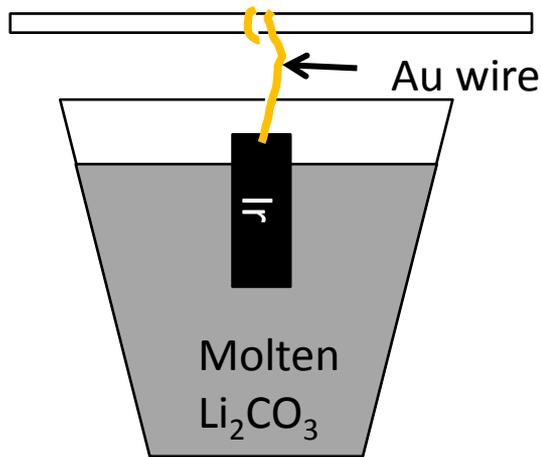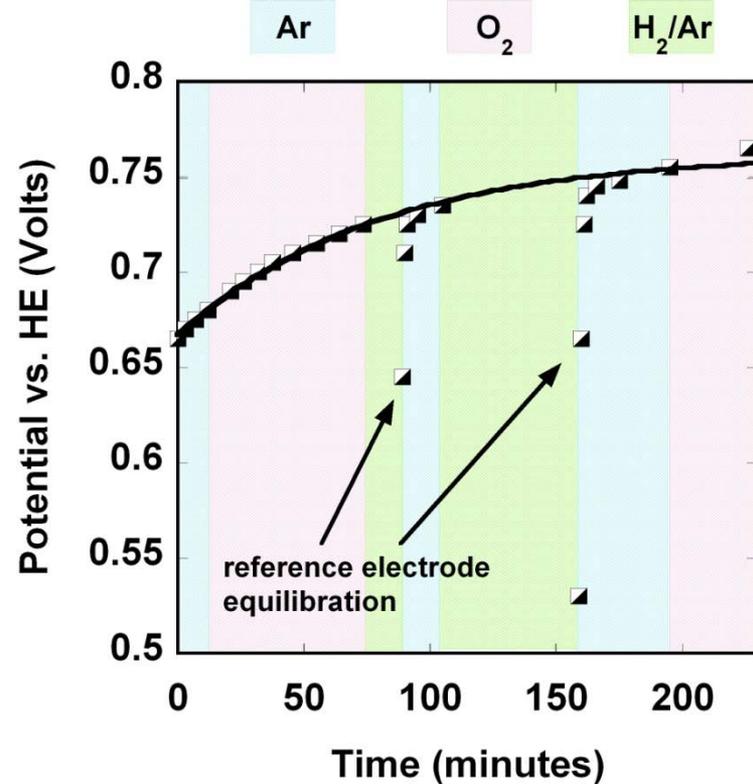
MEA
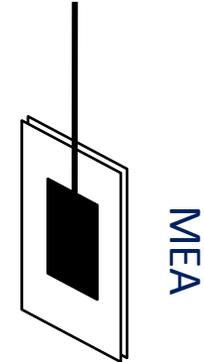
The measurements will help decouple the various effects of cationic impurities on ORR kinetics and fuel cell performance

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Ir/IrO$_x$ electrode By high temp oxidation of Ir

Ir oxide deposition
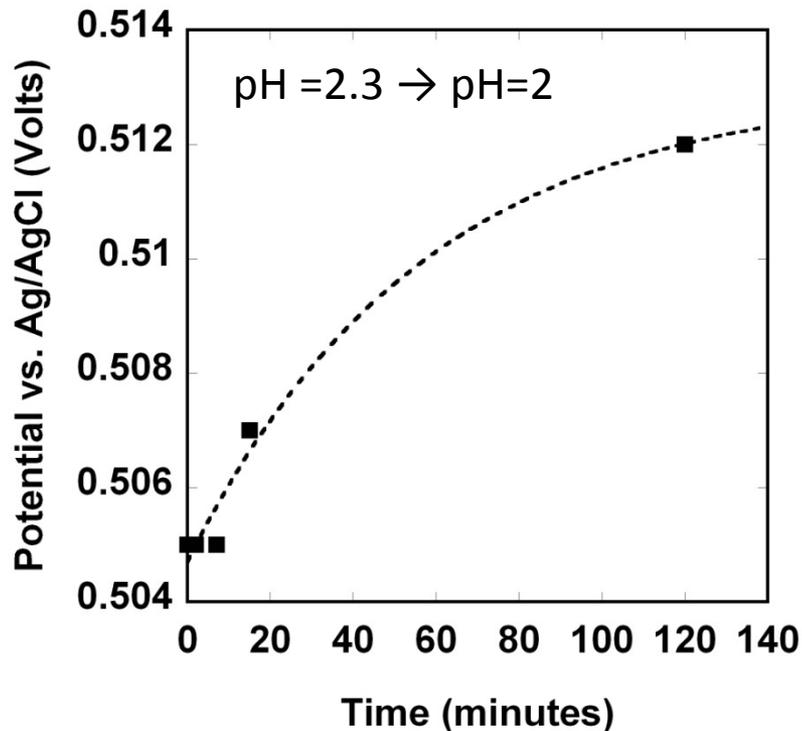

Au wire

Ir

Molten Li$_2$CO$_3$

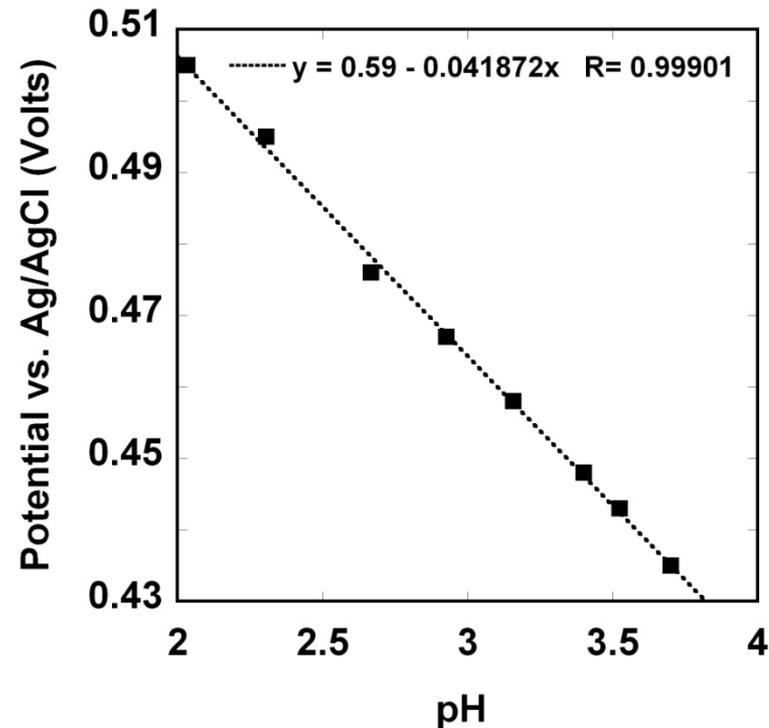### Potential response of freshly prepared electrode

- 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$_x$ electrode

Potential vs. time dependence

pH =2.3 → pH=2

Potential vs. pH dependence

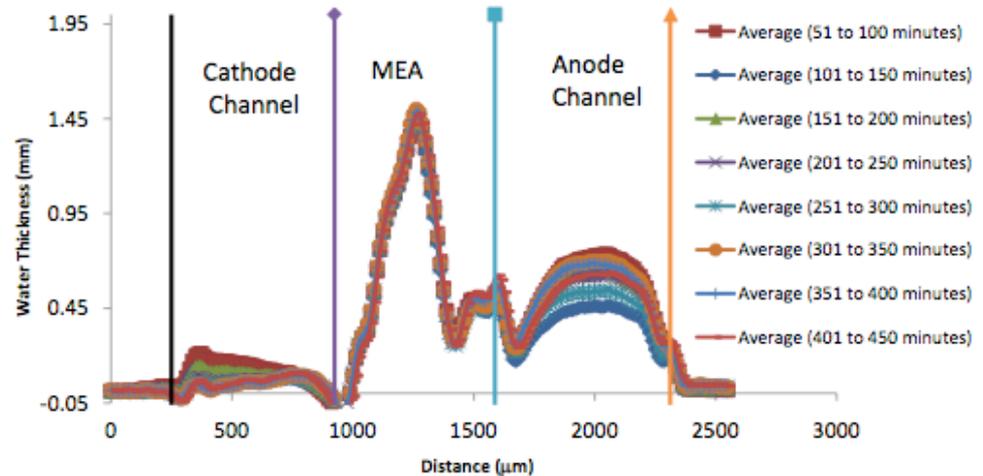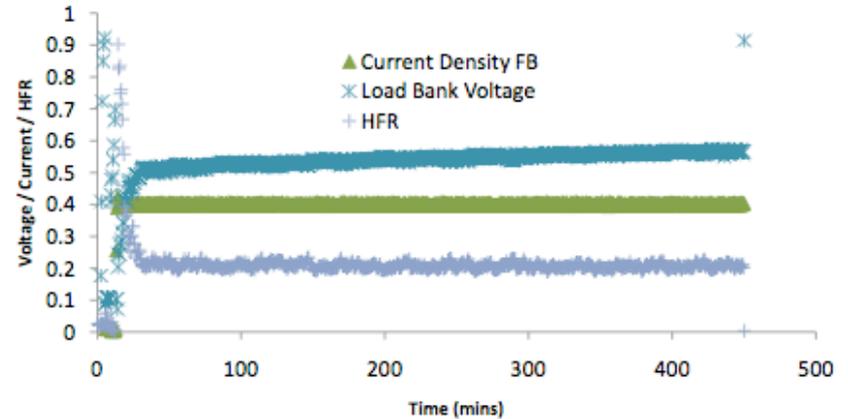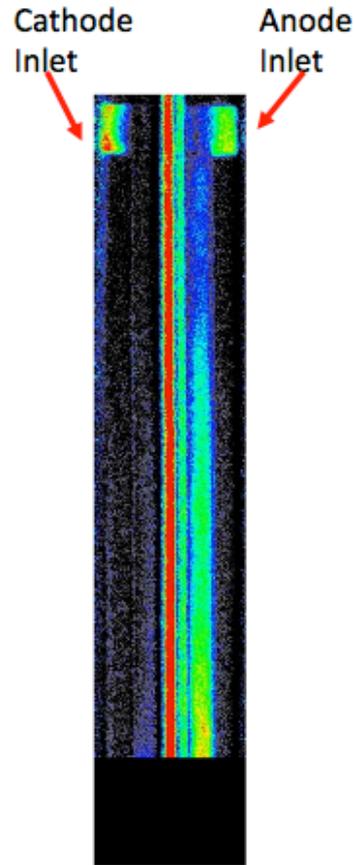
$y = 0.59 - 0.041872x$ R= 0.99901

- 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 NH_4^+ Contaminated Fuel Cell

- Parallel channel fuel cell ~10% ammonia exchanged 80°C 100% RH

- Fuel cell performance recovers

- Water distribution unchanged

- λ similar to protons

Cathode Inlet

Anode Inlet

Voltage / Current / HFR vs Time (mins)

- ▲ Current Density FB
- ✕ Load Bank Voltage
- + HFR

Water Thickness (mm) vs Distance (µm)

Cathode Channel   MEA   Anode Channel

- ■ Average (51 to 100 minutes)
- ● Average (101 to 150 minutes)
- ▲ Average (151 to 200 minutes)
- ✕ Average (201 to 250 minutes)
- ✳ Average (251 to 300 minutes)
- ● Average (301 to 350 minutes)
- + Average (351 to 400 minutes)
- — Average (401 to 450 minutes)

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Cation Effect on Membrane Water Content
milestone

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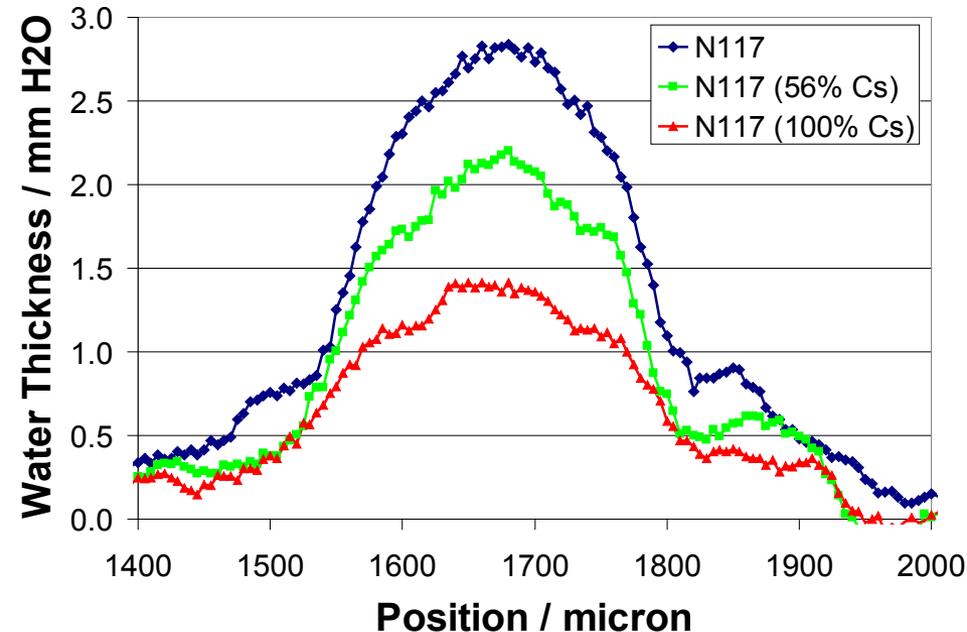
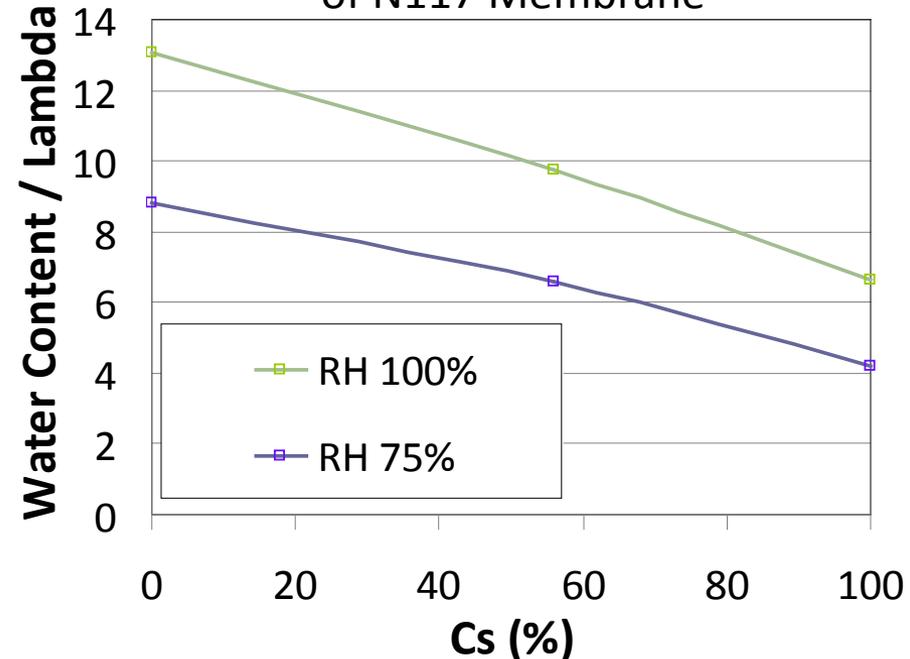Water Content vs Cs (%) of N117 Membrane

- 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

- H_2S anode poisoning/durability test completed
  - low concentrations do not appear to affect durability
- SO_2 long term testing completed
  - low concentrations do not appear to affect durability
- NO_x fuel cell poisoning shown to be largely reversible
- NH_3 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

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Future Work

- 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
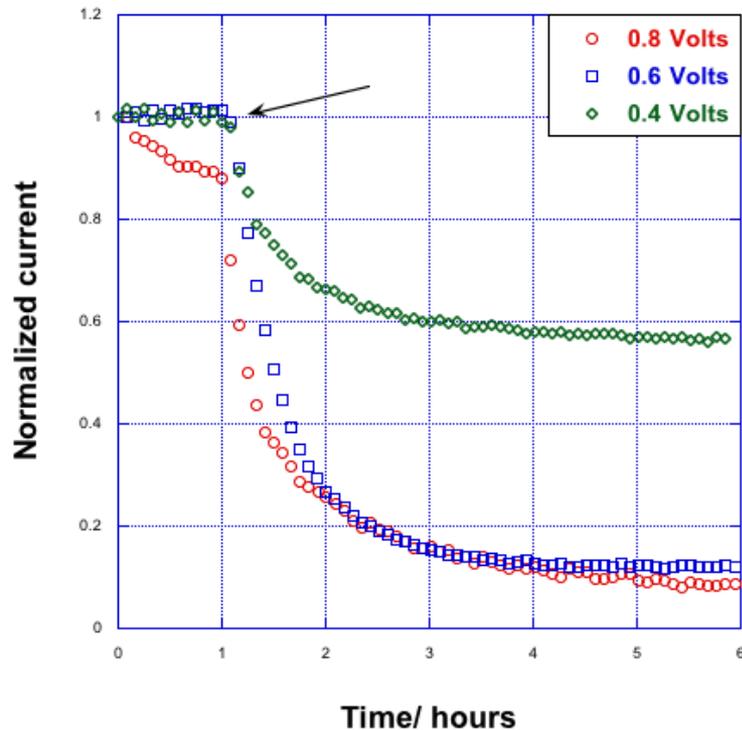- Investigate the effects of gas phase contaminants on ultra low loading fuel cells

We gratefully acknowledge funding from the US DOE Office of Fuel Cell Technologies
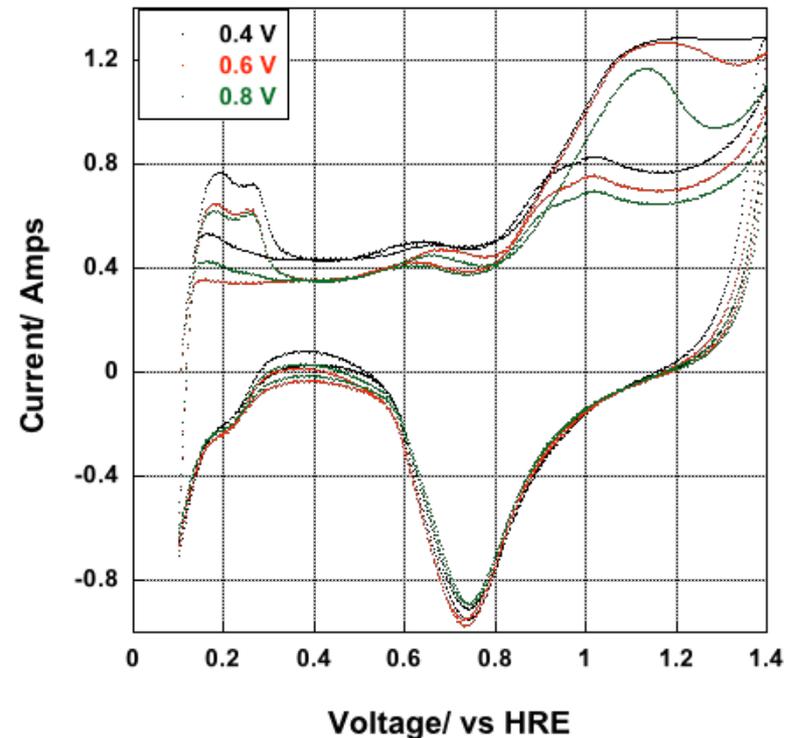
Fuel Cell V Influence on SO$_2$Poisoning

Potential Dependence-5 ppm SO$_2$

50cm^2 , 50 micron Nafion®, Cathode: 0.2 mg Pt/cm^2
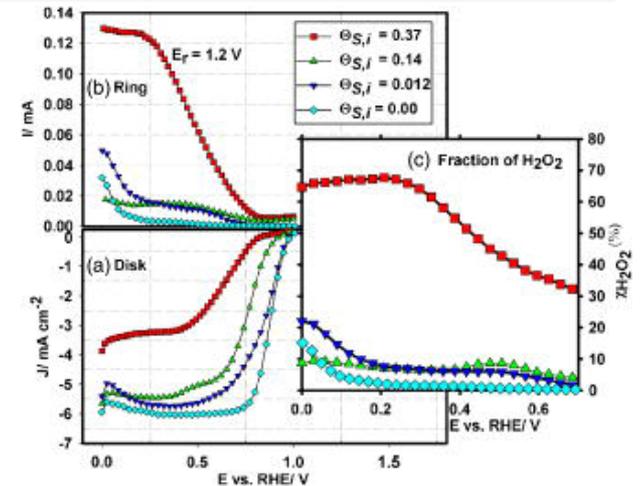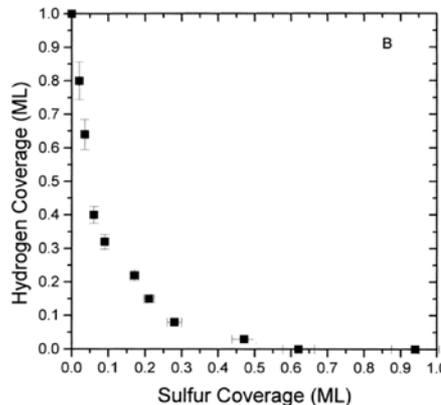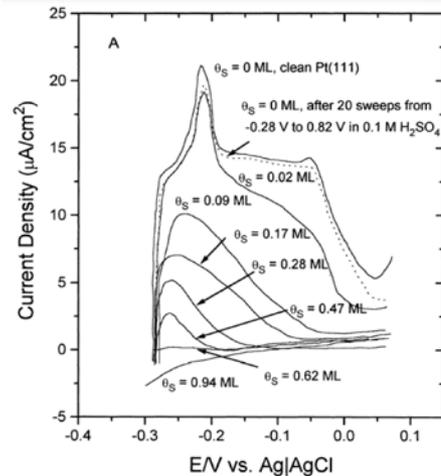
T$_{cell}$: 80°C, 100% RH

Cathode CVs after exposure to
5 ppm SO$_2$

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

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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_2SO_4 solution;
(B) hydrogen coverage versus sulfur coverage (in monolayers) S hurts H adsorption

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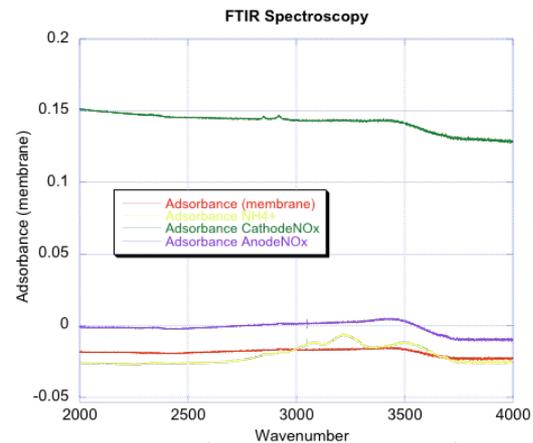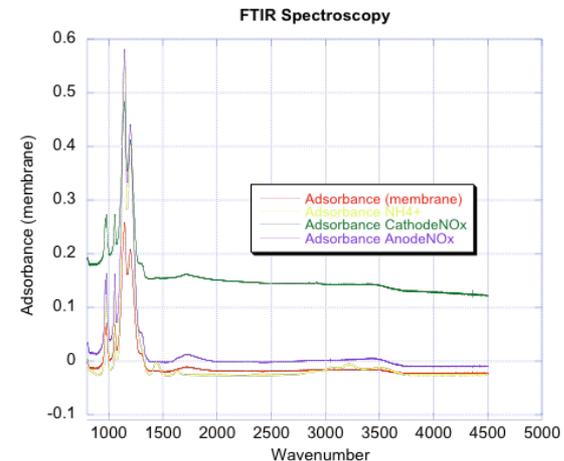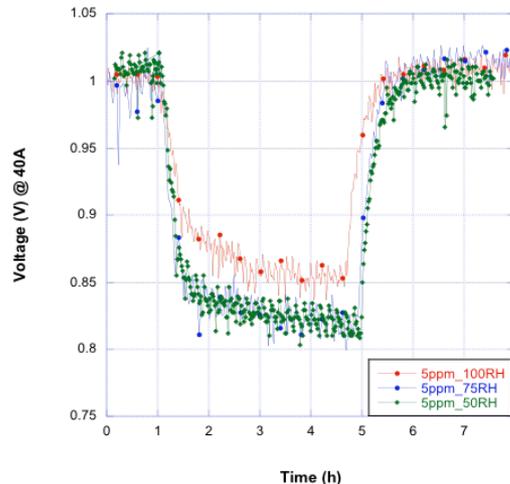

Y. Garsany, *et al J. ECS* 154, b670 (2007).

- SO$_2$ 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

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NO$_X$ In Cathode Air
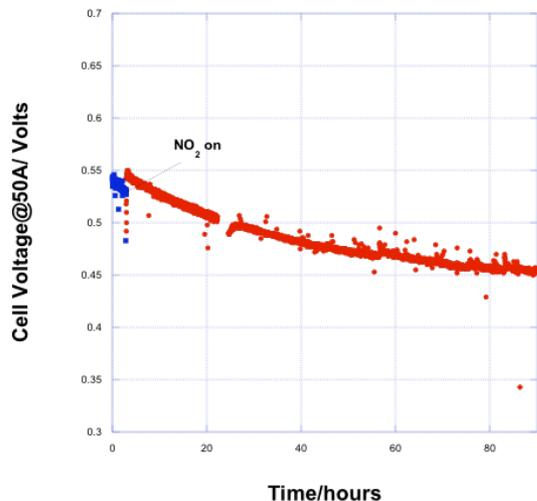
- 0.1mg/cm^2 Pt-C anode-0.2mg/cm^2 Pt-C cathode 50μm ionomer

- 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

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Ammonium Ion Membrane Equilibrium

Potentiostat

$$NH_3 + H^+_{\text{Nafion}} \leftrightarrow NH^+_{4\,\text{Nafion}}$$

WE

Sense

Ref

CE

Pt wires

Ionomer ddf^{er}_{vdf}
Membrane

Pt mesh

Vial cap

y_{NH4^+/H^+} solution

Isothermal bath

Stir bar

Nafion® membrane

Stirrer

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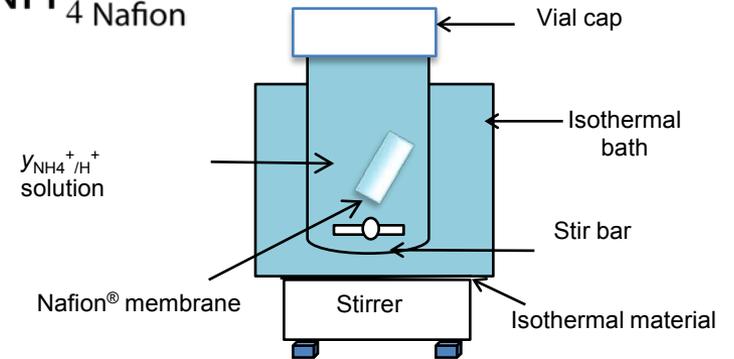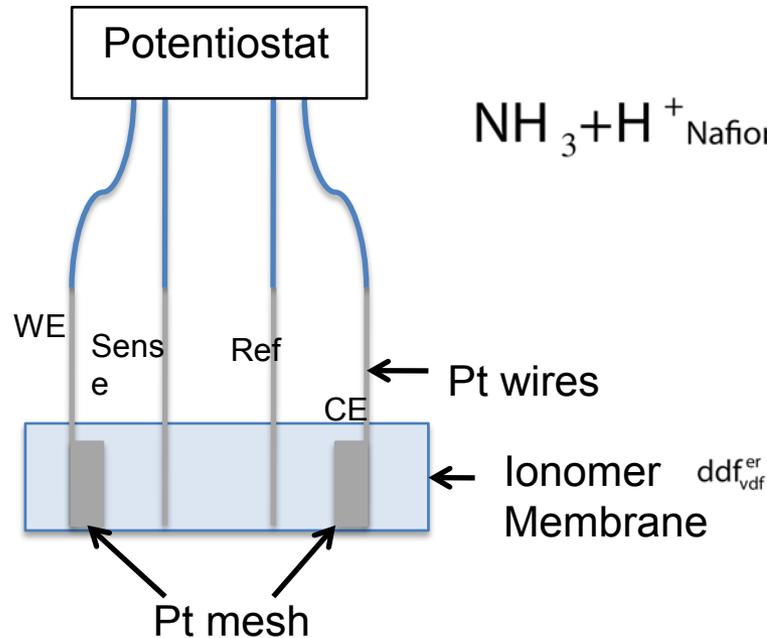
$$\mu_{\text{nafion}} = \mu_{\text{solution}} \text{ (system at equilibrium)}$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$\text{Equilibrium}: \quad K_{eq} = \frac{(NH_4^+)(OH^-)}{(NH_3)}$$

NH_4^+ concentration fixed

$$(NH_3) = \frac{(OH^-)}{K_{eq}}$$

Electrode

Hydrophobic gas-permeable membrane
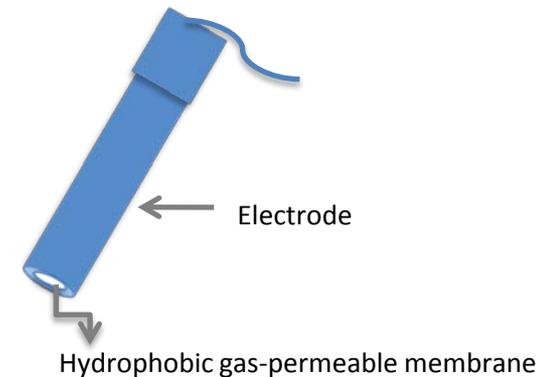
Membrane Blocking Cation Model and Validation

- *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 $\lambda=14$ 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*

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

$V_A = 0$ V_{cell}

H_2 — pump

O_2 — FC mode

Only H^+ Only H^+

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

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

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

b

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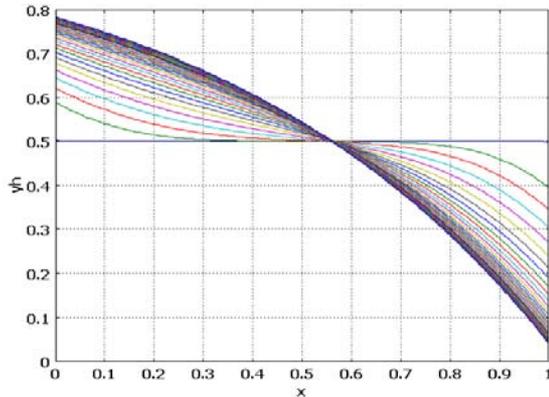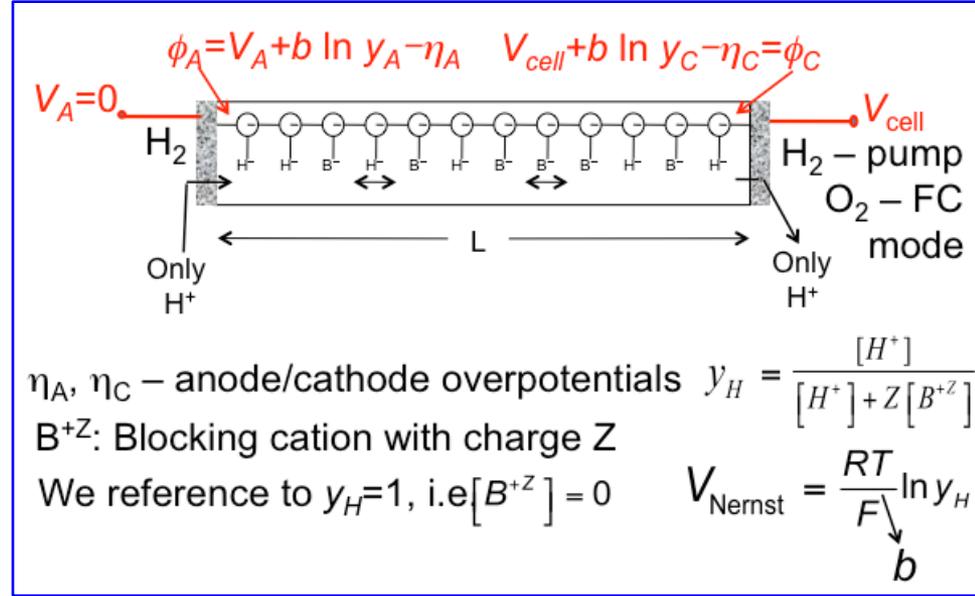
Initial uniform 50% H^+ and NH_4^+ distribution

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
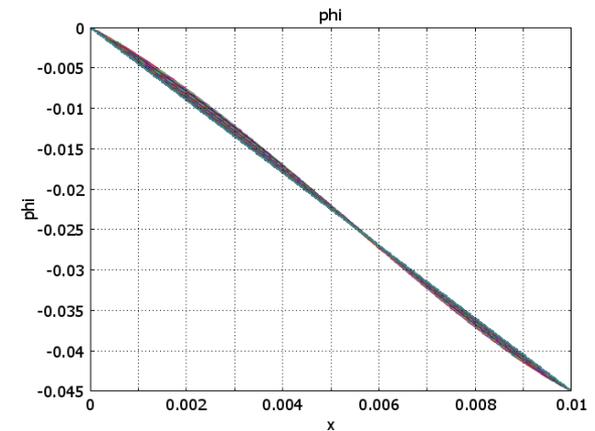
Concentrated Solution Transport Equations Used in Membrane

D_i - dif. coef. of H^+,B^+ cm²/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.

$\dfrac{FD_i}{RT}$ - mobility cm²/V-s

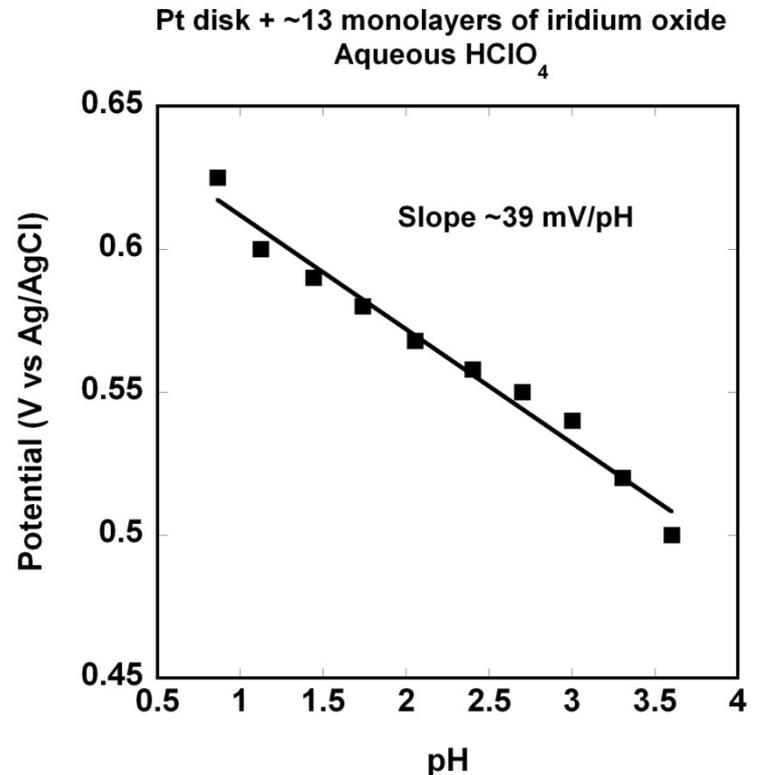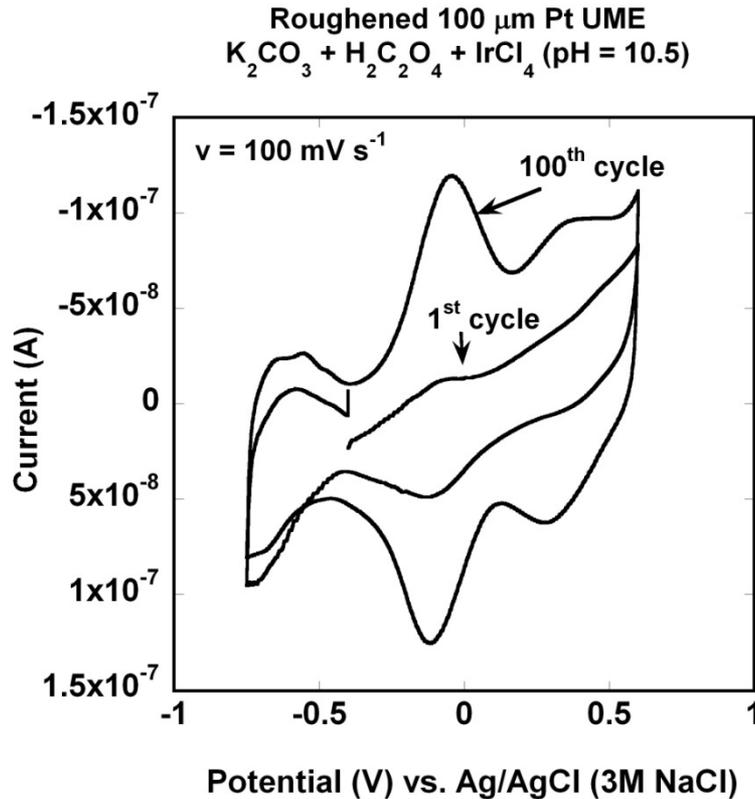b - $\dfrac{RT}{F}$ V

Diffusion   **Migration**   **Drag**

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

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

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

Diffusion

Fuel Cell Research

Platinum electrodes in aqueous media

Roughened 100 μm Pt UME
$K_2CO_3 + H_2C_2O_4 + IrCl_4$ (pH = 10.5)

v = 100 mV s^{-1}

100th cycle

1st cycle

Current (A)

Potential (V) vs. Ag/AgCl (3M NaCl)

Pt disk + ~13 monolayers of iridium oxide
Aqueous $HClO_4$
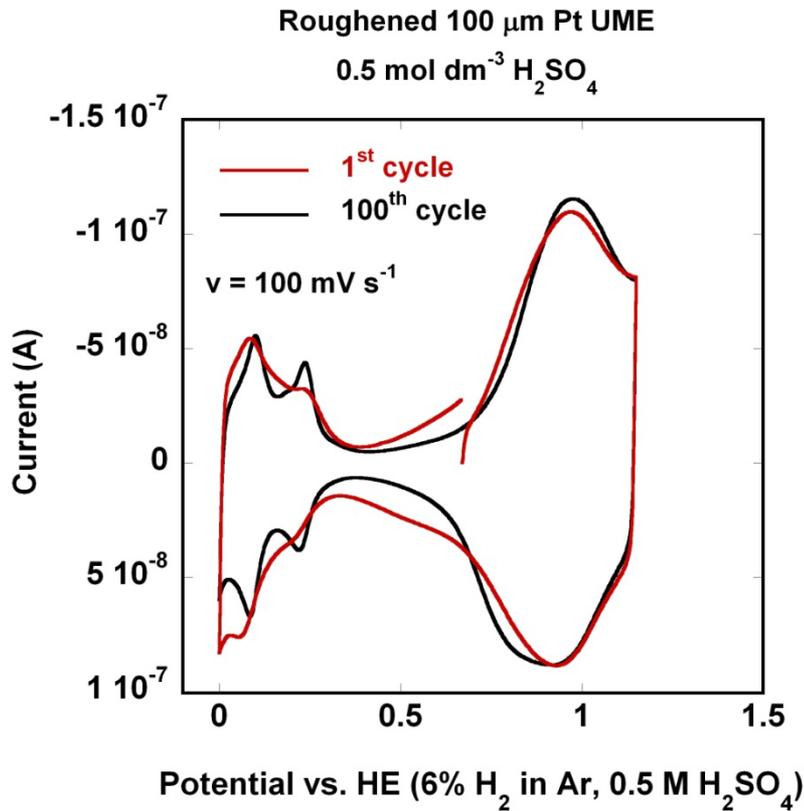
Slope ~39 mV/pH

Potential (V vs Ag/AgCl)

pH

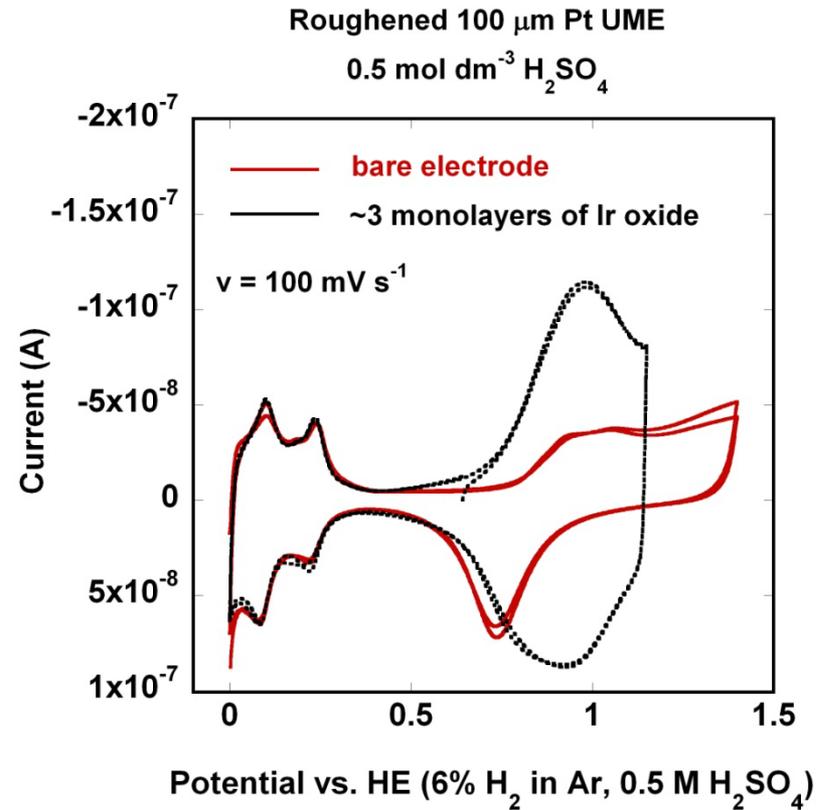Iridium oxide easily deposited on platinum disk electrodes, ultramicroelectrodes (shown) and Pt sputtered on glass

Clear, approximately linear E vs. pH dependence with sub-Nernstian slope in aqueous media with no O_2 sensitivity

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Fuel Cell Research

Iridium oxide-coated Pt electrodes in aqueous media

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

Roughened 100 μm Pt UME
0.5 mol dm^{-3} H$_2$SO$_4$

- 1st cycle
- 100th cycle

v = 100 mV s^{-1}

Current (A)

Potential vs. HE (6% H$_2$ in Ar, 0.5 M H$_2$SO$_4$)

Roughened 100 μm Pt UME
0.5 mol dm^{-3} H$_2$SO$_4$

- bare electrode
- ~3 monolayers of Ir oxide

v = 100 mV s^{-1}

Current (A)

Potential vs. HE (6% H$_2$ in Ar, 0.5 M H$_2$SO$_4$)

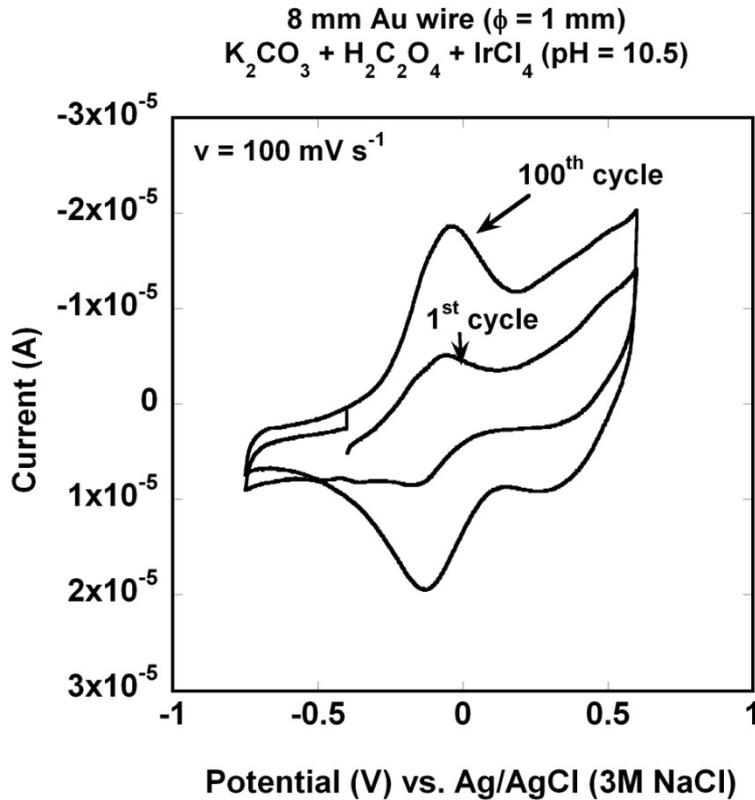Well defined hydrogen UPD on Pt developed upon cycling

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

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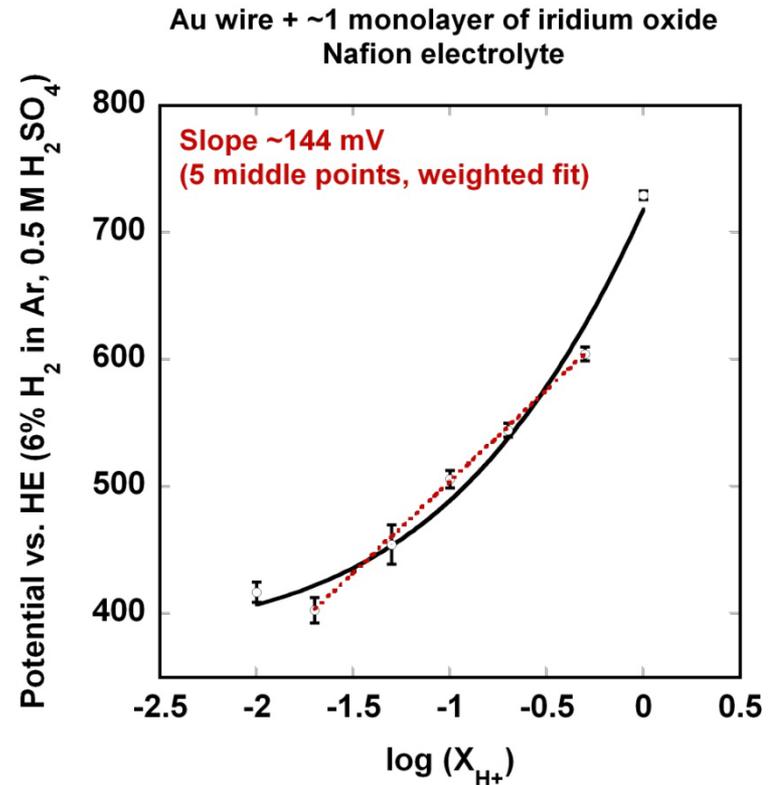NATIONAL LABORATORY

Fuel Cell Research

Au/iridium oxide electrodes coated with Cs⁺-spiked Nafion®

Ir oxide deposition

H⁺ (Cs⁺) sensing

8 mm Au wire (ϕ = 1 mm)
$K_2CO_3 + H_2C_2O_4 + IrCl_4$ (pH = 10.5)

v = 100 mV s^{-1}

100th cycle

1st cycle

Current (A)

Potential (V) vs. Ag/AgCl (3M NaCl)

Au wire + ~1 monolayer of iridium oxide
Nafion electrolyte

Slope ~144 mV
(5 middle points, weighted fit)
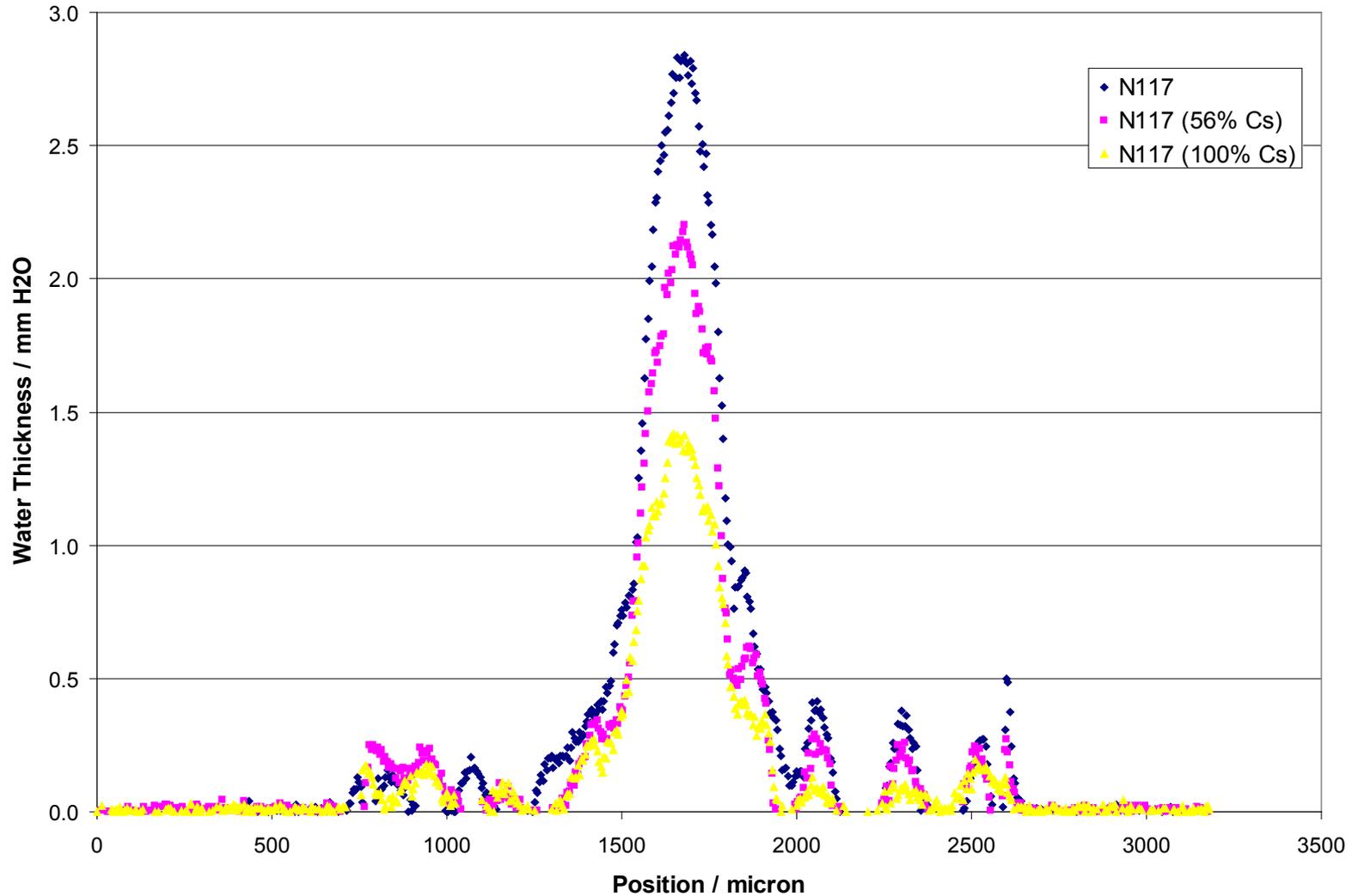
Potential vs. HE (6% H$_2$ in Ar, 0.5 M H$_2$SO$_4$)

log (X$_{H+}$)

Well defined hydrogen UPD on Pt developed upon cycling

Strong non-linear E vs. log(X$_{H+}$) dependence – possibility of accurate H⁺ (Cs⁺) determination *in situ*

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Water Profiles for N117 showing Cs Effect

Measured Water Thickness for a N117 Nafion® membrane with 56% Cs

Measured Water Thickness for a N117 Nafion® membrane with 100% Cs