# 2006 Annual DOE Fuel Cell Program Review

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

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FC#24

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**This presentation does not contain proprietary or confidential information.**

# Project Overview

## Timeline

- Start:FY05
- Status: Ongoing

## Barriers:

Electrode performance decreased by impurities(fuel cell efficiency decreases)

Higher Pt loading required to maintain performance in presence of impurities increases cost

Durability may decrease in the presence of impurities

## Budget:

FY06: 800K

## Targets (2010):

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

## Partners:

FreedomCAR and Fuel Partnership
USFCC

# Project Objectives

**Overall Objective**: Contribute to the understanding of the effects of fuel and air impurities on fuel cell performance

**Specific Goals:**

Develop analytical methods for trace measurements

Test fuel cell performance under simulated multi-component hydrogen impurity gas mixtures

Investigate effect of impurities on catalysts and other FC components

Develop methods to mitigate negative effects of impurities

Develop models of fuel cell-impurity interactions

Continue collaborations with USFCC, Fuel Cell Tech Team, Industry and other National Laboratories to foster a better understanding of impurity effects

# Impurities And Their Sources in Polymer Fuel Cells

- **Fuel Impurities**
- ***Hydrogen Source and Reforming Process***

  ***Natural gas***
  ***Coal*** → **$CO$, $NH_3$, $H_2S$, HC's**
  ***Fuel Oil***

- **Air Impurities**

  * ***From fuel combustion pollution*: $SO_2$ , NO & $NO_2$ , Soot**
  * ***From natural sources*: Ocean salts, dust**

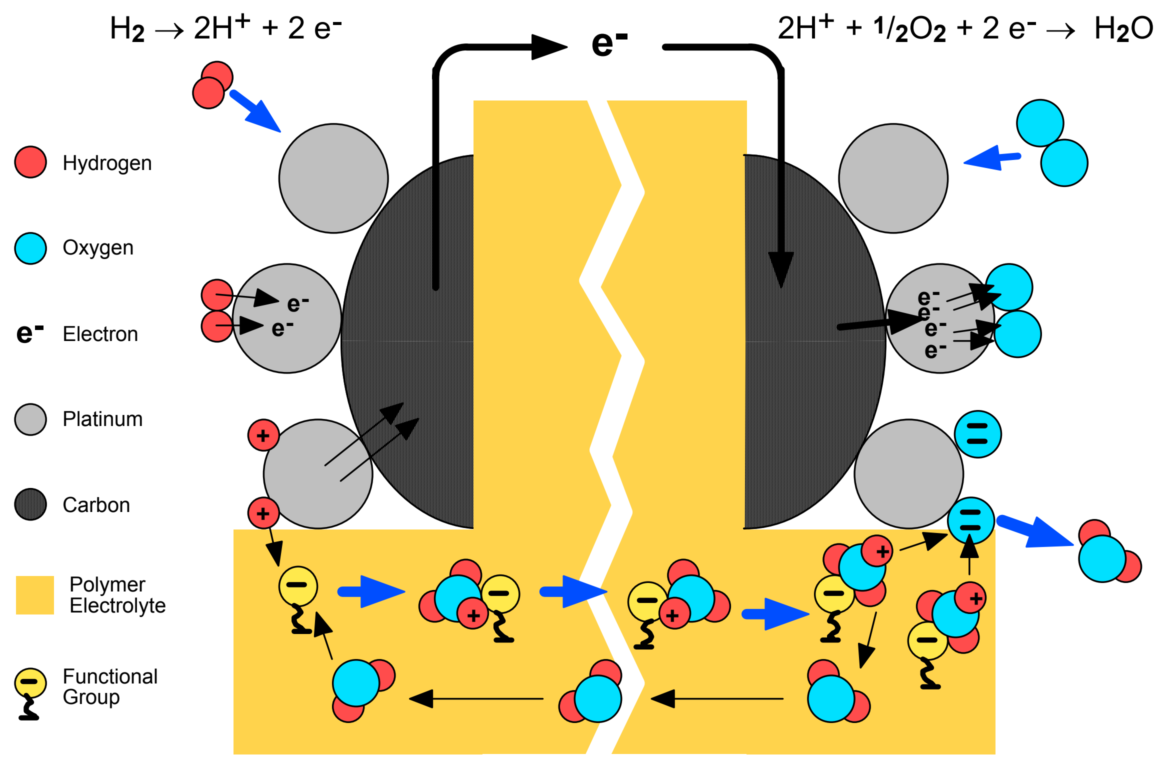
- **Other**

  * ***De-icers:* NaCl, $CaCl_2$**
  * ***Corrosion products from FC system:* cations**

***Recent FC-Tech Team focus on gas mixtures to simulate common fuel impurities***

# Understanding Impurity Adsorption Effects

- Impurities may adsorb onto:
- Pt surface
  - CO, $H_2S$, $SO_2$ , $Cl^-$
- Carbon support
  - $H_2S$, $SO_2$
- Ionomer
  - M+, $NH_4^+$
- Gas diffusion layer
  - Salts,wetting agents

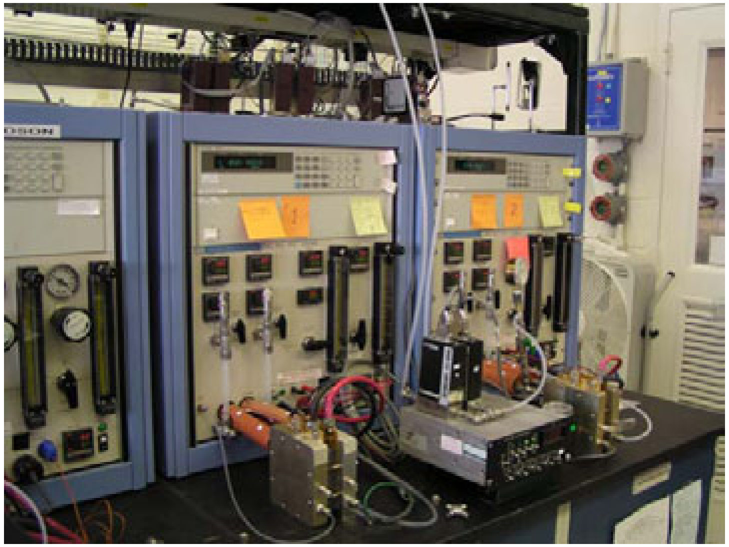



**•Impurities may block reaction sites for: *chemisorption*, *charge transfer* and/or *impede protonic conduction*.**

**•May also *change GDL properties* affecting mass transport**

# Research Approach

- Fabricate and operate fuel cells under controlled impurity gases
  - Multi-gas mixing manifolds and FC test stations
  - Pre-blend impurity gas
  - Measure performance
    - Understand degradation mechanisms
    - Study mitigation approaches
- Develop analytical tools for studies
  - Electroanalytical methods
  - *In situ* diagnostics
  - Sub PPM gas analysis
- Analyze and model data



# Analytical Method Development

## $H_2S$ Detector and TPD

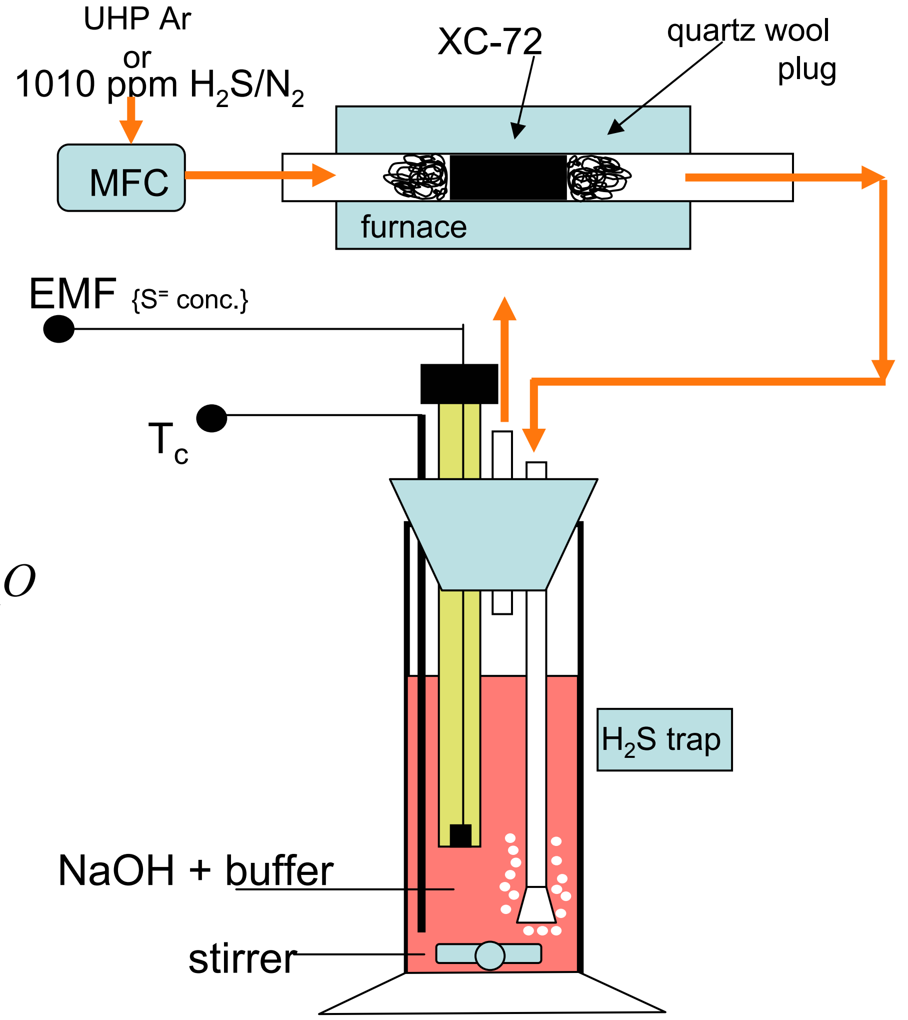
- *We have developed a reliable low cost method for sub-ppm $H_2S$ analysis- ppb sensitivity*
  - Ag/AgS Electrode Sulfide ion probe
  - Detects $S^=$

$$Ag + S^= \longrightarrow AgS + 2e^-$$

- Probe measures ppb quantities of $H_2S$ by $S^=$ concentration change

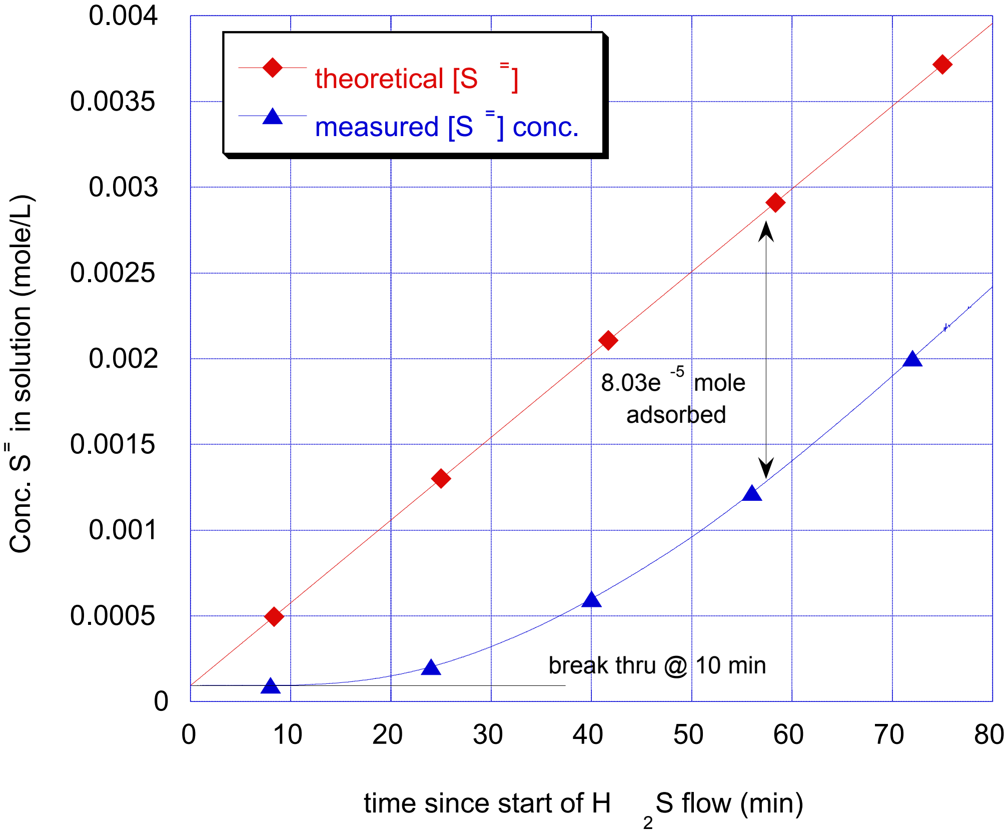
$$H_2S + 2NaOH_{aqueous} \xrightarrow[pH>12]{} S^= + 2Na^+ + 2H_2O$$

- $H_2S$ is a sticky gas: care must be taken in ppb measurements
  - Pre-treat gas lines
- Temperature Programmed Desorption performed by heating sample at 5° C/min.

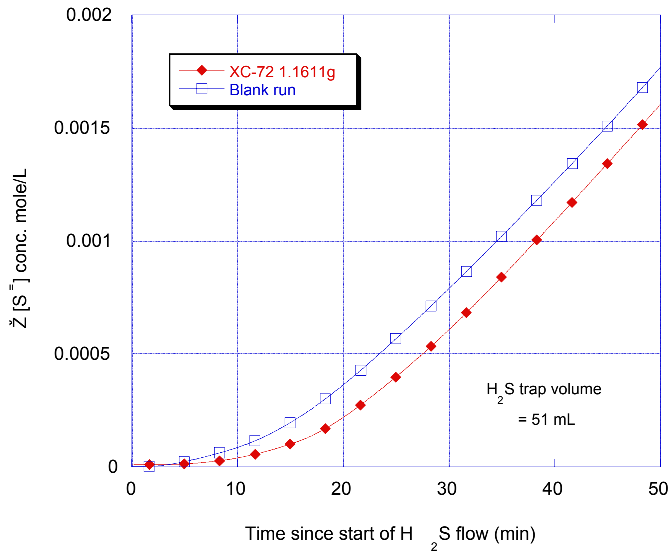


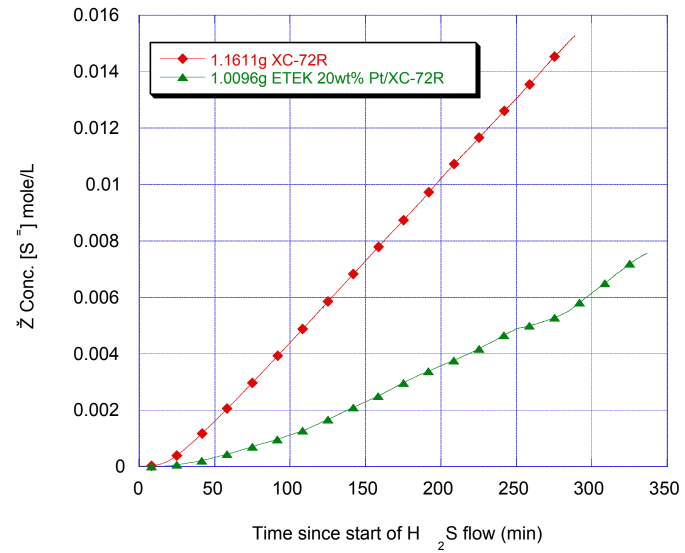
# XC-72R Comparison To Activated Carbon

- First experiment repeated using activated charcoal
- 0.24 wt% or 80 times greater absorption than on XC-72R form of carbon
- *Form of carbon is very important in determining $H_2S$ adsorption behavior*



# $H_2S$ Adsorption On XC-72 Carbon and E-TEK™ Pt/XC-72 Results




- XC-72 absorbs little $H_2S$ at RT
- *Pt 20%XC-72 adsorbs significant amounts of $H_2S$*
  - ~2%
  - Process exhibits slow kinetics- $H_2S$ dissociative adsorption?

$$H_2S_{gas} + Pt \rightarrow H_2S_{Pt}$$
$$H_2S_{Pt} \rightarrow S_{Pt} + 2H_{Pt}$$
$$S_{Pt} + 2H_{Pt} \rightarrow S_{Pt} + H_2$$

  - Desorption temperature >200° C

# Hydrogen Impurity Mixture

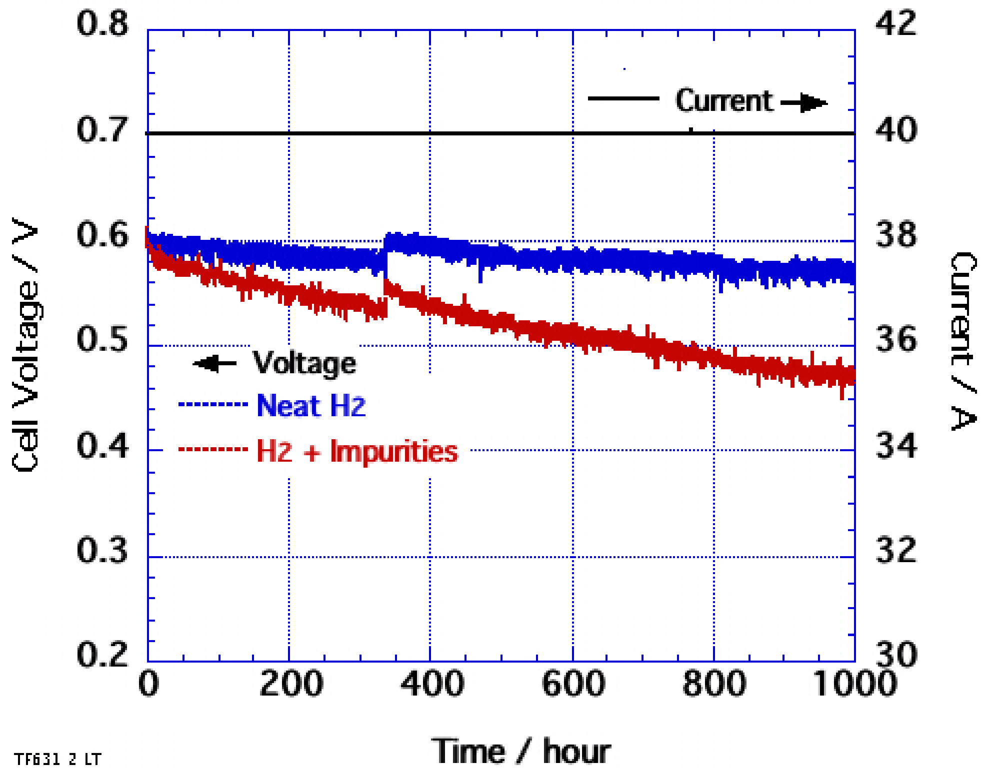
**FreedomCar Fuel Cell Tech Team proposed hydrogen impurity spec.**

| *Component* | *Level* | *LANL Test* |
|---|---|---|
| Hydrogen | > 99.9 | 95-99 * |
| Sulfur (as $H_2S$) | 10 ppb | 10 ppb |
| CO | 0.1 ppm | 0.1 ppm |
| $CO_2$ | 5 ppm | 5 ppm |
| $NH_3$ | 1 ppm | 1 ppm |
| NMHC | 100 ppm | 50 ppm ethylene |
| Particulates | Conform to ISO 14687 | not included in first test |

***** *Includes dilution due to inert gas in stock mixtures***

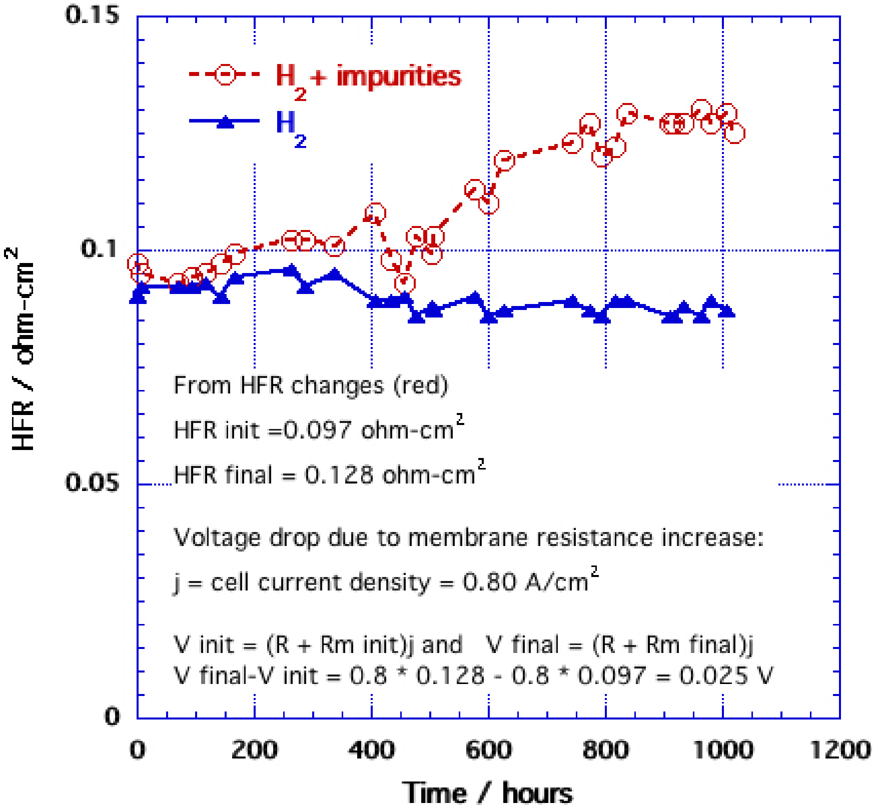
# Milestone: Constant Current Testing of Impurity Mixture

Voltage losses of two 50 cm² equivalent cells run at 0.8 A/cm² for 1000 hours




- *Impurity cell performance loss is significantly greater than hydrogen control cell*

# Impurity Mixture Effects On Membrane Conductivity




TF631 2 HFR

- High frequency resistance increases with time for impurity test mixture
- 25 mV loss from R increase
- $NH_4^+$ exchange for $H^+$ ?
- IR loss is not the only source of cell voltage drop

*•Ammonia gas forms cations and lowers membrane conductivity*

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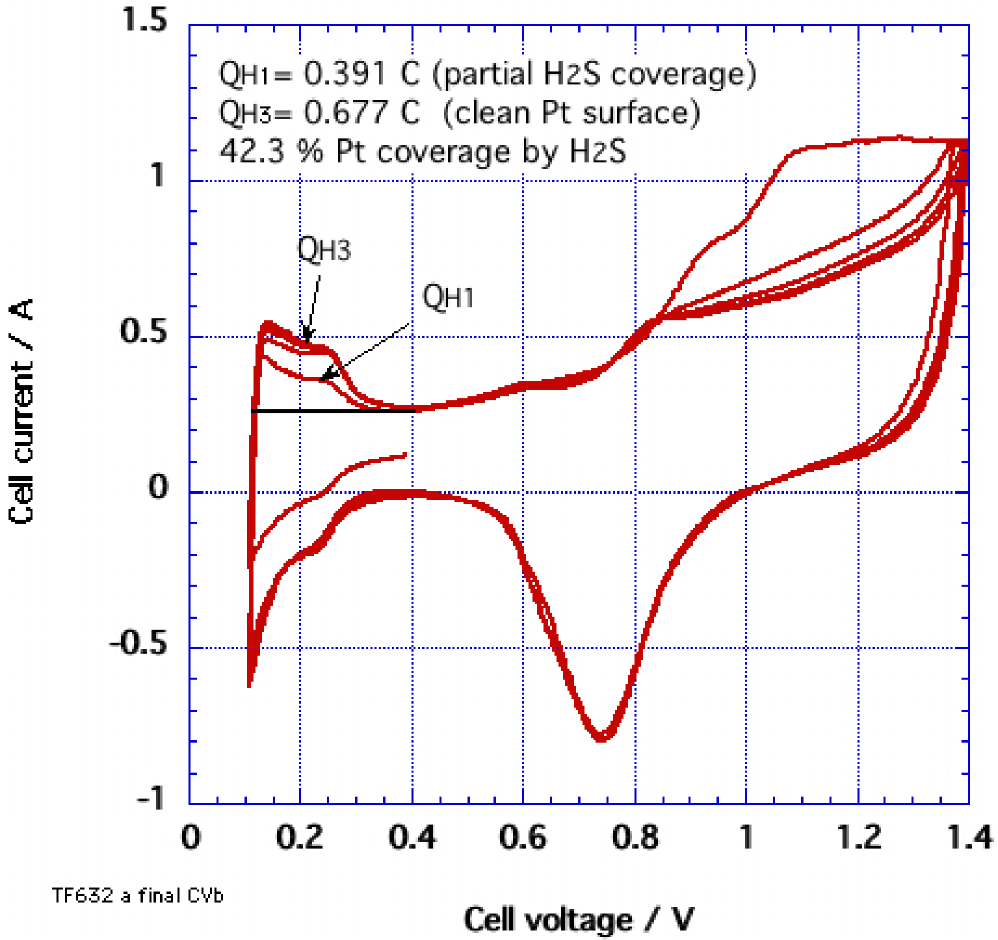
# Impurity Mixture Effects




50 $cm^2$ cells / N112, 50 mV/s
Loadings: 0.2 mg Pt at each electrode
Cell Temperature: 80 °C. PSIG: 30/30

- ***Cyclic voltammetry is indicative of sulfur poisoning: ~40% coverage of Pt surface***
- ***No Evidence of CO in CV***
  - **S adsorbed onto Pt strongly blocks CO adsorption in gas phase studies:** ***V.D. Thomas et. al. Surface Science 464(2000) 153-164***

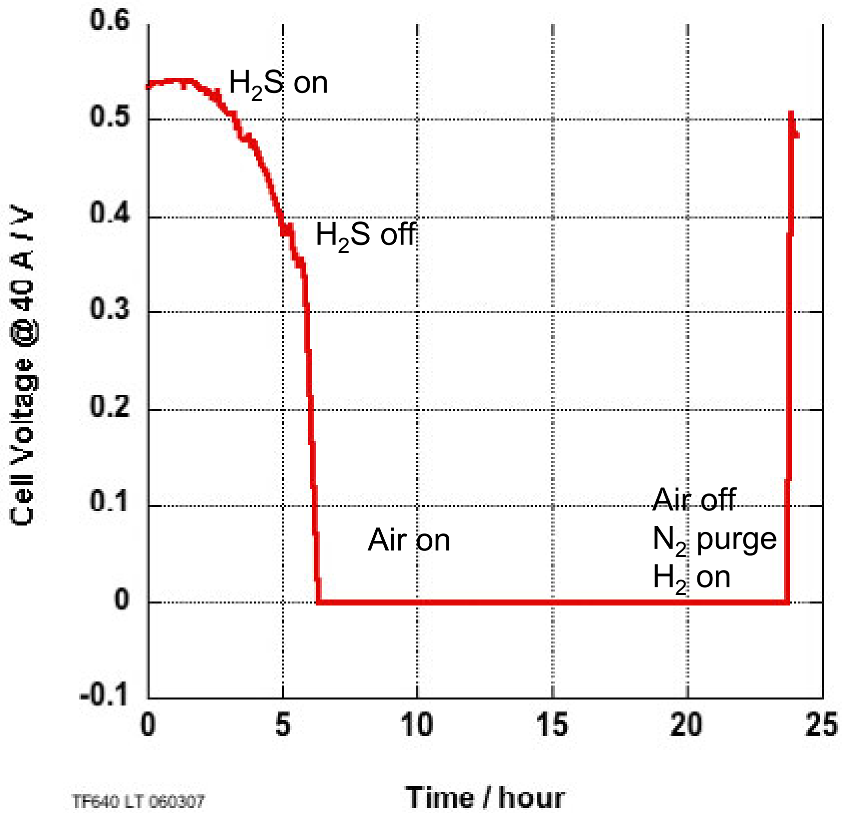
Possible reactions:

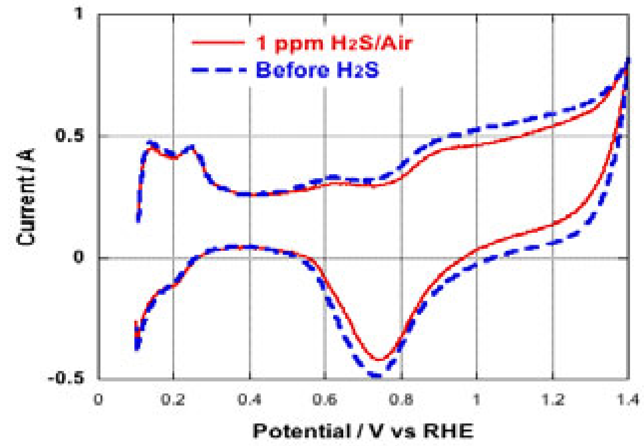
$$H_2S_{gas} + Pt \rightarrow H_2S_{Pt}$$

$$H_2S_{Pt} \rightarrow S_{Pt} + 2H^+ + 2e^-$$

$$H_2S_{Pt} \rightarrow HS_{Pt} + H^+ + e^-$$

# Milestone:Air Effect on Anode Due To Shut-down



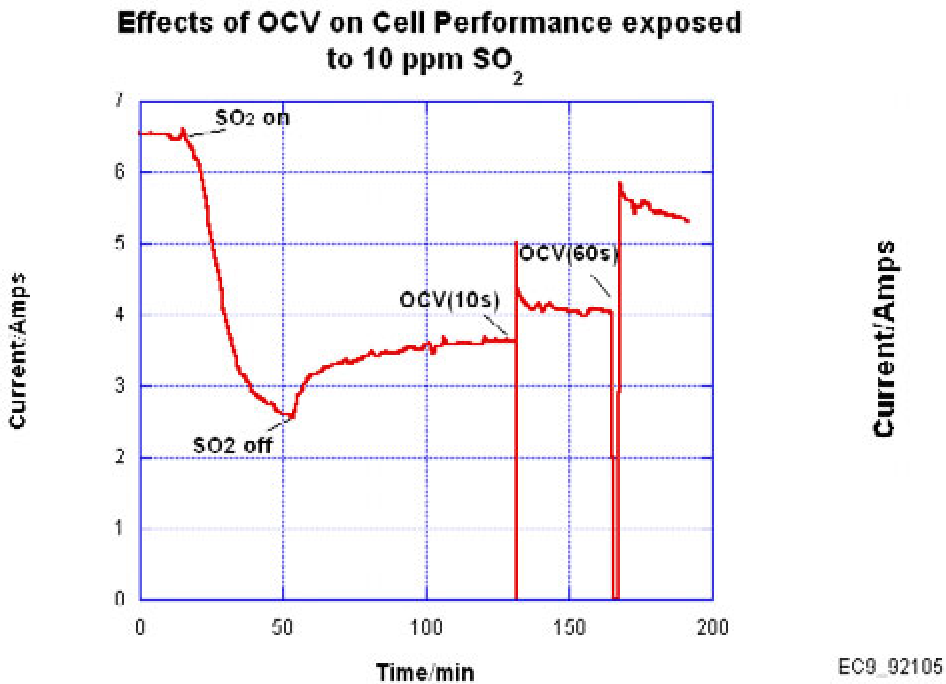

- Anode poisoned with 1 ppm $H_2S$
- Anode is at OCV before air exposure
- Air bled overnight
- ***Cell recovered almost fully***

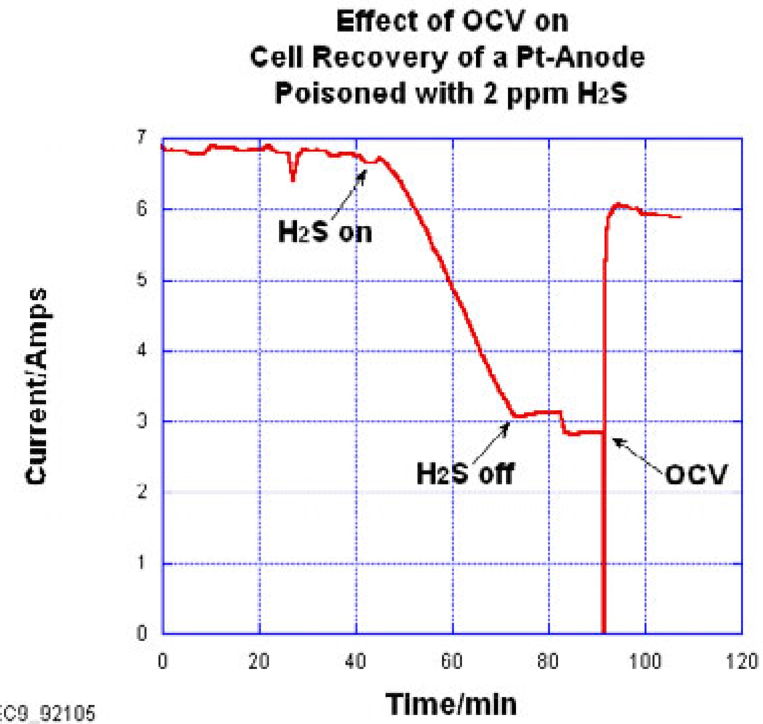
Possible mechanisms?

$$S_{Pt} + H_2 \rightarrow H_2S_{gas} \uparrow$$

$$S_{Pt} + O_2 + H_2O \rightarrow SO_3^{=}{}_{aq} + 2H^{+}{}_{aq}$$

# Effect of OCV on Sulfur Poisoned Cathodes and Anodes



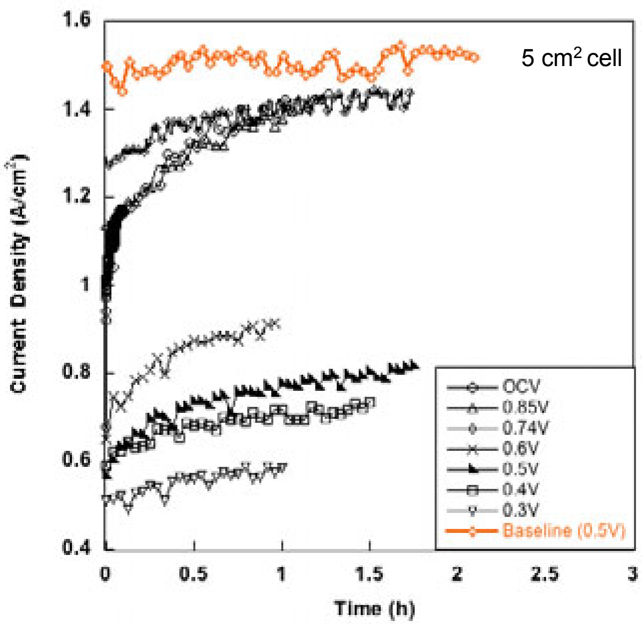

$$cathode: SO_{2Pt} + O_2 + 2H^+ \rightarrow H_2SO_4\ ?$$

$$anode: S_{Pt} + H_2 \rightarrow H_2S_{gas}\uparrow \quad ?$$

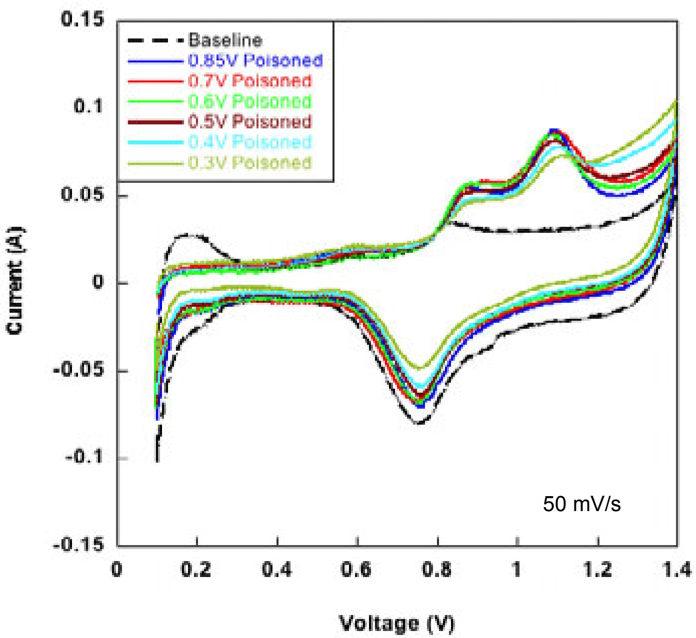
- *Cells are poisoned for 50 min (2X amount of $H_2S$ needed for full poisoning at 100% adsorption efficiency)*
- *The application of Open Circuit Voltage on S-poisoned electrodes indicates partial recovery*

# Effect Of Cell Voltage on $H_2S$ Anode Poisoning

Cell performance recovery (at 0.5 V) after anode exposure to $H_2S$ at different voltages



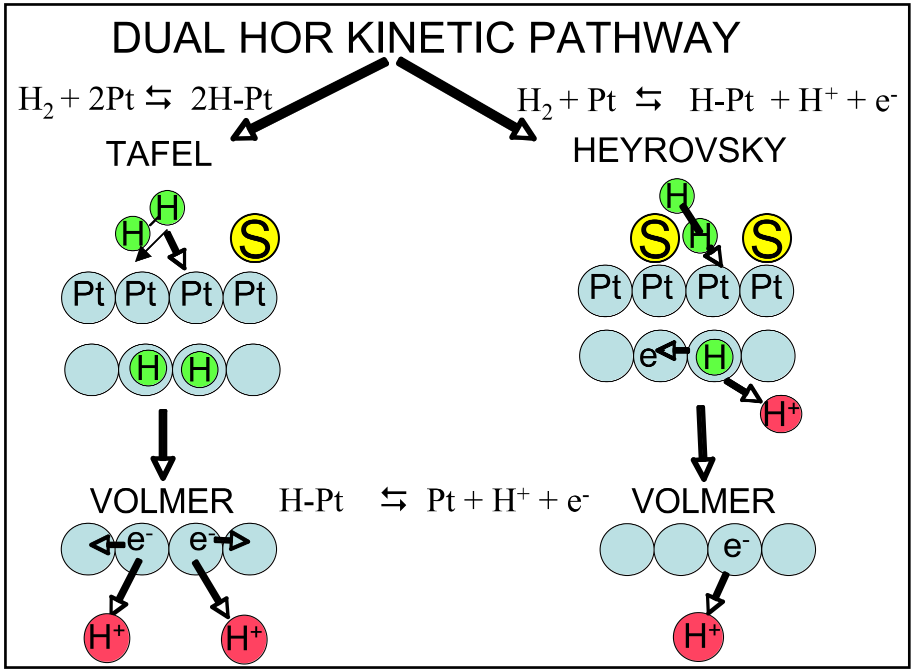

CV's for $H_2S$ poisoned anodes at different cell voltages

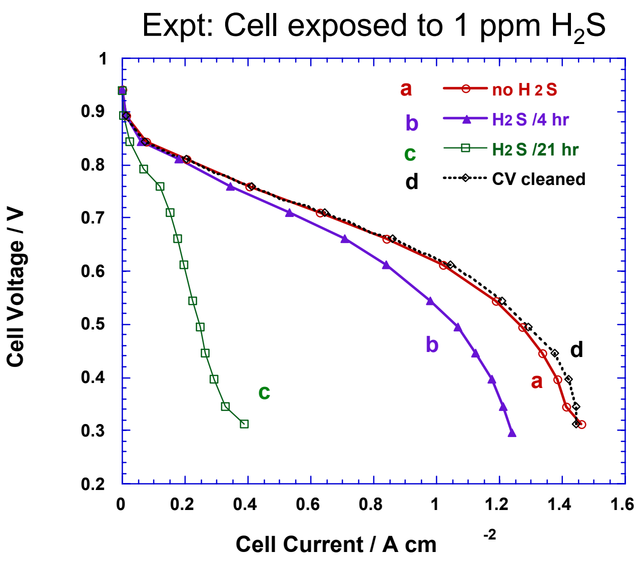


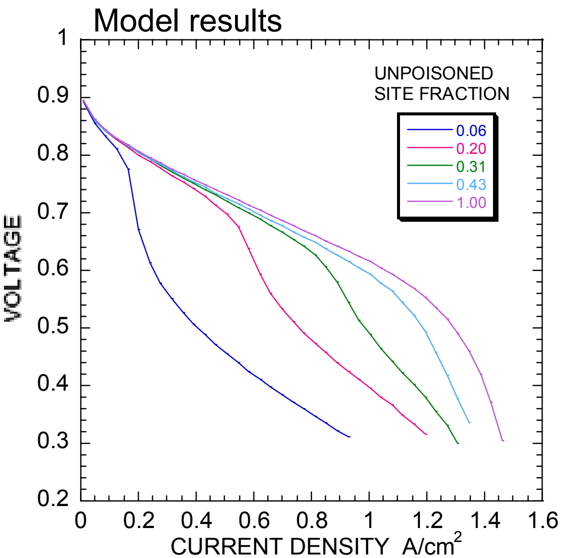

- *Cell voltage at which $H_2S$ exposure occurs influences amount of performance loss and recovery rate*
- *More poisoning at low cell voltages*

| Operating Voltage / V | $Q_{anodic}$ / C | $Q_{oxide\ reduction}$ / C | $Q_{Sulfur}$ / C |
|---|---|---|---|
| 0.85 | 0.0315 | 0.0123 | 0.0192 |
| 0.74 | 0.0342 | 0.0108 | 0.0234 |
| 0.6 | 0.0349 | 0.0109 | 0.0241 |
| 0.5 | 0.0341 | 0.00977 | 0.0243 |
| 0.4 | 0.0350 | 0.0107 | 0.0242 |
| 0.3 | 0.0338 | 0.00952 | 0.0243 |

# Hydrogen Oxidation Model Aids Understanding of Impurity Effects



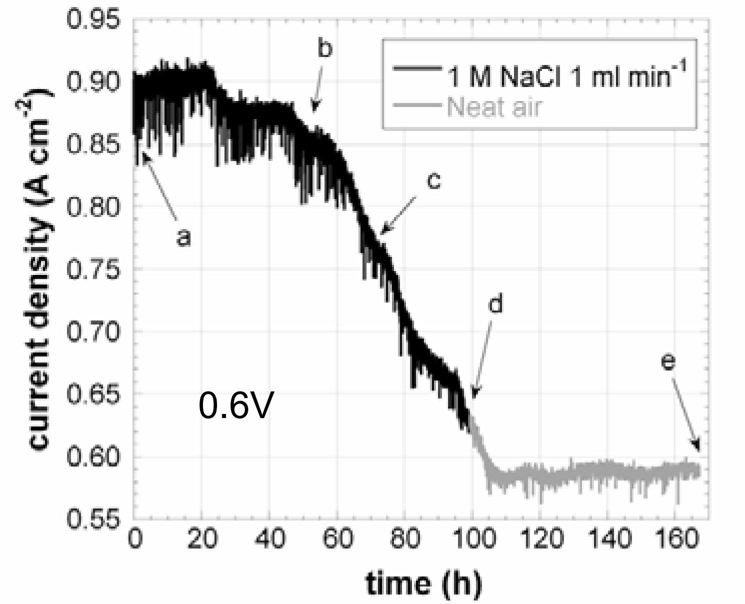



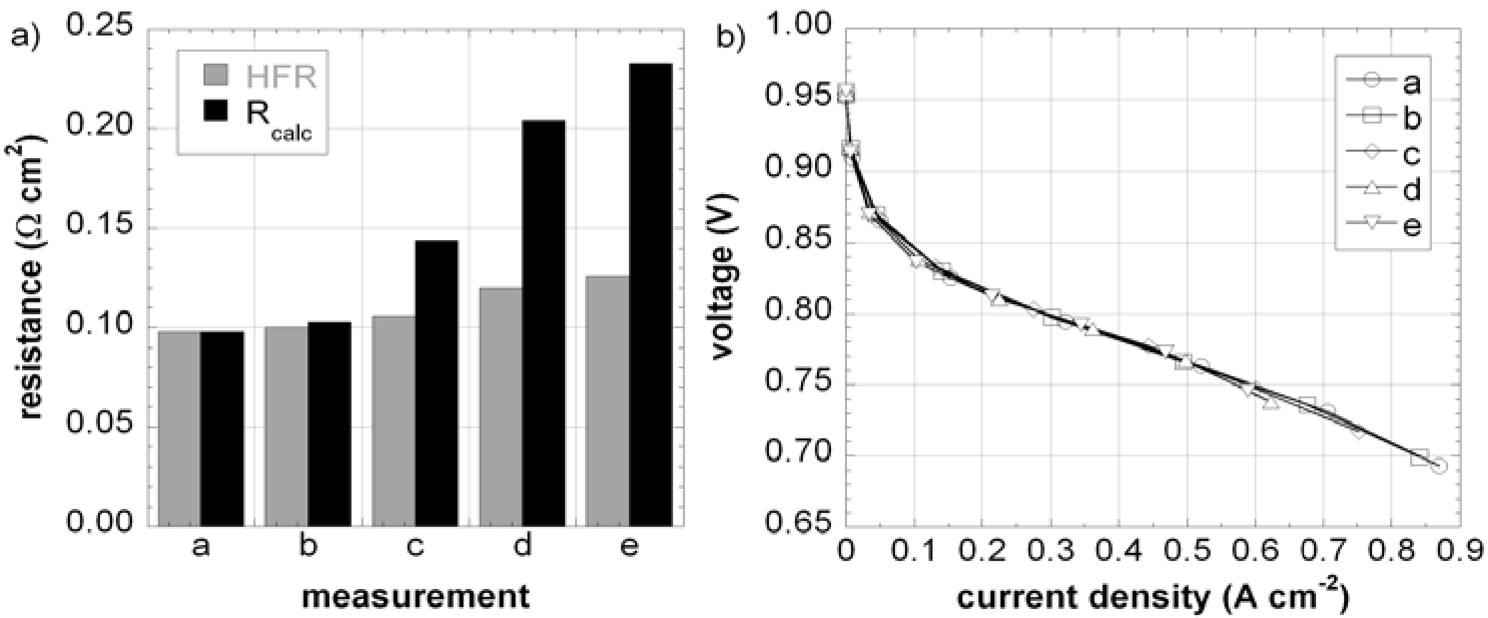




- Dual path HOR kinetics model needed to explain $H_2S$ poisoning data
- S poison acts as an irreversible H site blocker
- Old Butler-Volmer kinetics cannot explain results

# Modeling NaCl Contamination

- NaCl was introduced with the air feed (at high concentration and flow rate – enough $Na^+$ for complete exchange every 15 seconds)
- CVs show $Cl^-$ at cathode plays no role
- HFR measures ion conductivity (combination $H^+$ and $Na^+$)
  - IR corrections necessary for VI agreement much larger
  - HFR (complete Na+ exchange) ~ 171 mΩ/cm$^2$



# Summary

- $H_2S$ in fuel test mixture is primarily responsible for anode polarization losses
  - Little effect from CO in mixture-competitive adsorption
  - Almost no adsorption onto XC-72 but other carbons behave differently
- Ammonia is ion exchanging for protons and causing conductivity losses
- $SO_2$-poisoned cathode can be partially cleaned at OCV
- Fuel cell operating voltage strongly affects extent of anode $H_2S$ poisoning
- On shut-down OCV appears to be also an important factor for cleaning $H_2S$ poisoned anode
- Air purging $H_2S$ contaminated anode results in partial performance recovery
- Dual H oxidation pathway model provides insights in fuel cell behavior

# Future Near Term Work

- Continue $H_2S$ studies and begin $SO_2$ adsorption on other materials components of the fuel cell
  - Pt immersed in aqueous solution
  - Pt/XC-72R
  - Carbon paper
- Continue investigation of impurity speciation on Pt surfaces
- Determine performance threshold of $H_2S$ and $NH_3$ allowed in fuel
- Elucidate cleaning mechanism by OCV in S-poisoned electrodes
- Continue development of impurity models
- Characterize effects of $H_2S$ on anode durability and $SO_2$ on cathode durability
- Measure effects of Ca and Mg salt ions on fuel cell performance
- Commence particulate injection studies

# Publications, Presentations and Patents

- M. Mikkola, T. Rockward, F. Uribe and B. Pivovar, *“The Effect of NaCl in Cathode Air Stream on PEMFC Performance,"* Submitted to *Fuel Cells - From Fundamentals to Applications* (2006).

- F. Uribe and T. Rockward, *"Cleaning (de-poisoning) PEMFC electrodes from strongly adsorbed species on the catalyst surface"* 104229 Non-Provisional patent application (2006).

- F. Uribe and T. Rockward, *"Cleaning PEMFC Electrodes with Adsorbed S-species"*. 208 ECS Meeting, Los Angeles, CA. October (2005)

- F. Uribe *et al*, *“Electrode Structures and Effects Of Fuel Cell Impurities”* invited talk INRS, Quebec Canada, (2006)

# Review Comments

- Focus on basic understanding rather than empirical testing
  - We are coupling electro-analytical studies to reaction pathway modeling for first principles understanding.
- Focus on component generated impurities rather than fuel impurities
  - LANL & ORNL have previously and are currently studying fuel cell impurity generation and membrane uptake from metallic bipolar plates. The FreedomCAR tech team has suggested this project research priorities focus on fuel impurities.
- Increase interaction with FreedomCAR Codes and Standards Team
  - We have a project member participating at all FCCS meetings and we have tested their proposed impurity limits mixture.