

2005 Mid Year DOE Fuel Cell Program Review

Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

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P#:FC 37

Project Overview

Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

Timeline

“Started” FY05
End date not established
25% Complete

Barriers

B. Cost
C. Fuel Cell Performance
A. Materials Durability

Budget

100% DOE
Total FY05 = \$800k

Partners

ORNL: *MEA material analysis (Karren More)*
USFCC (Materials and Components Working Group)
Technical Training

- **University of California, Berkeley**
- **University of Oklahoma**
- **De Nora N.A. ETEK**

Project Objectives

Overall Objective: Contribute to DOE effort in developing an efficient, durable, direct hydrogen fuel cell power system for transportation.

Specific goals:

- Evaluate the effects of fuel and air impurities on FC performance
- Evaluate catalyst durability under the effects of impurities
- Investigate effect of impurities on other FC components
- Find ways to mitigate negative effects of impurities.
- Continue collaborations with Industry and other National Laboratories

Project Objective: Identifying Origins of Impurities in FC

- Fuel Impurities
- *Hydrogen source and Reforming Process*

Natural gas
Gasolines \longrightarrow **CO, NH₃, H₂S, HCN**
Diesel
Methanol

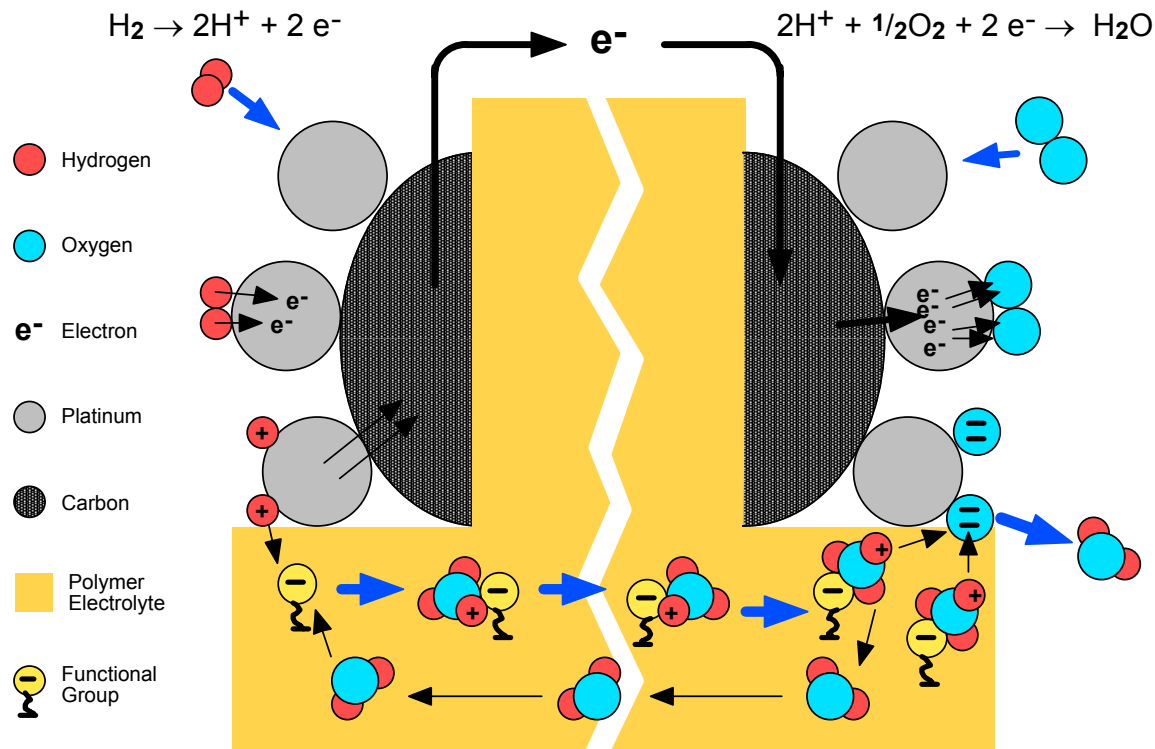
- Air Impurities
 - * *From fuel combustion pollution:* **SO₂, NO₂, diesel fumes**
 - * *From natural sources:* **Ocean salts, dust**

- Other
 - * *De-icers:* **NaCl, CaCl₂**
 - * *Corrosion products from FC system:* **cations**

During the last six months studies focused H₂S, and SO₂

Project Objective: Understanding Impurity Adsorption Effects

- Impurities may adsorb onto:
 - Pt surface
 - CO, H₂S, SO₂, Cl⁻
 - Carbon support
 - H₂S, SO₂
 - Ionomer
 - M⁺, NH₄⁺
 - Gas diffusion layer
 - Salts, wetting agents



- Impurities block reaction sites for chemisorption, charge transfer and/or impede protonic conduction.
- Also changes GDL properties

Technical Approach

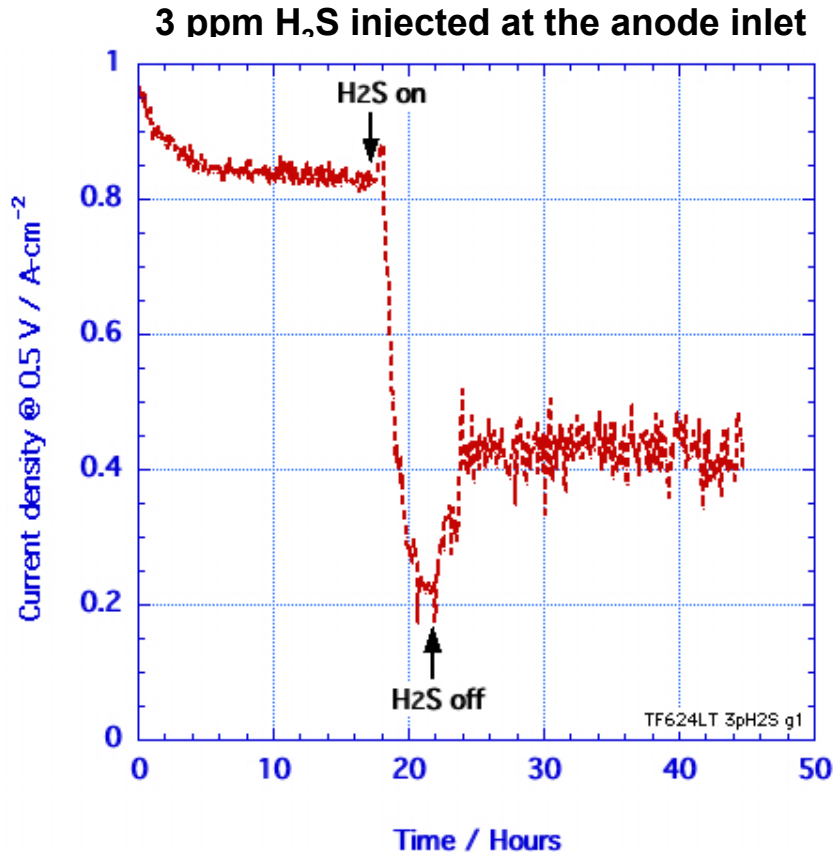
- ***Study the effects of ambient air impurities on FC performance (e.g. SO₂, NO₂, NaCl).***
- ***Study the effects of low concentrations H₂S on anode performance.***
- ***Study the effects of impurities under dry and humidified gas flows***
- ***Investigate the effects of actual diesel combustion fumes.***
- ***Determine specific effects of impurities on FC component (e.g. catalysts, membrane and GDL)***
- ***Find materials and devices able to mitigate negative effects of impurities.***
- ***Test procedures for reactivating electrodes poisoned with sulfur compounds.***
- ***Collaborate with USFCC to develop a “Single Cell Testing Protocol”.***

Technical Accomplishments

Month-Year	Milestone	Status
Feb 05	Report results of a method for cleaning sulfur-poisoned cathode Pt-catalyst with minimum interruption of cell operation.	<i>completed</i>
May 05	Report results of a method for cleaning sulfur-poisoned anode Pt-catalyst with minimum interruption of cell operation.	<i>completed</i>
Jun 05	Determine cathode threshold tolerance levels to SO ₂ .	<i>in progress</i>
Jul 05	Determine cathode threshold tolerance levels to NO ₂	<i>In progress</i>
Aug 05	Complete tests with actual diesel exhaust.	<i>in progress</i>
Sept 05	Identify potential approaches to attain sulfur tolerant catalysts.	<i>in progress</i>

Effect H₂S on FC Performance

Pt-Cu (1:1) Anode Catalyst

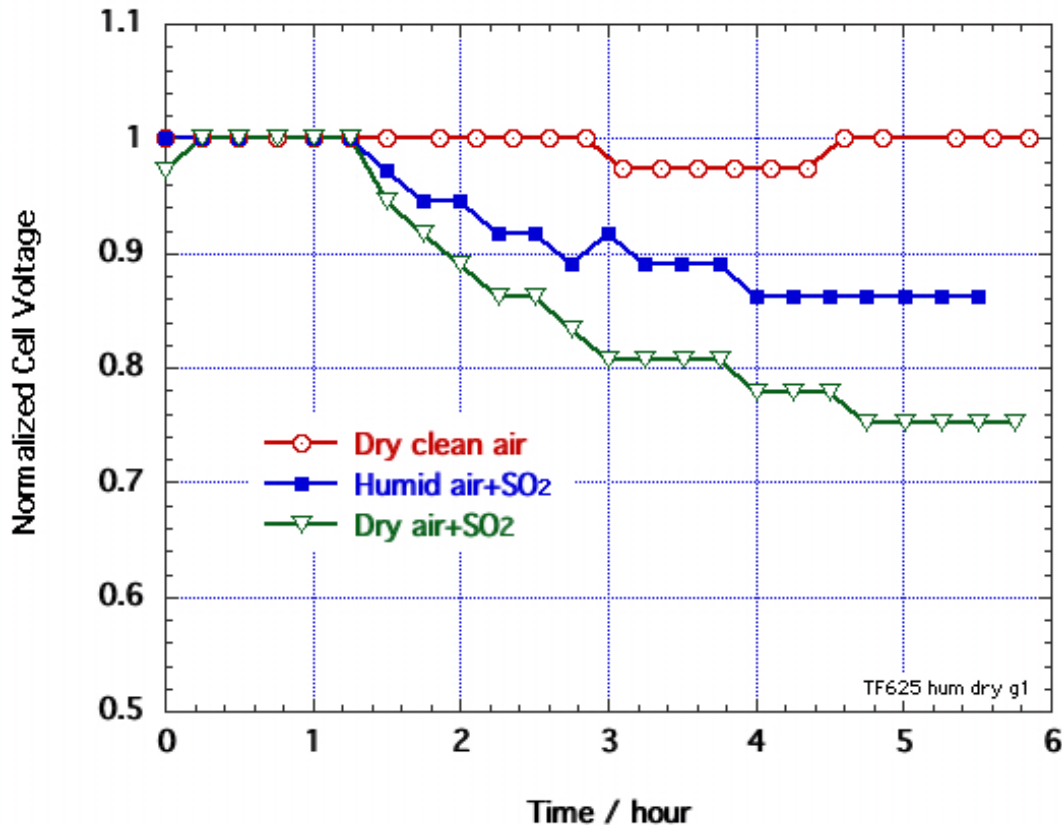


- H₂S irreversibly poisons Pt-Cu catalysts
- Operation on clean air does not reactivate the catalyst.
- Pt-Cu catalyst does not offer any advantage in comparison to Pt catalysts

H₂/Air FC TF624 (5cm²)
 N112 A: 0.22 mg Pt/cm² (20% Pt-Cu[1:1] ETEK)
 C: 0.21 mg Ptc/m² (20%Pt-C ETEK)
 T_{cell} : 80 °C , PSIG: 30/30

Effect of SO₂ on performance with dry and humidified air

Measurements at 0.6 A/cm² constant current
1.5 ppm SO₂ injected at the cathode inlet

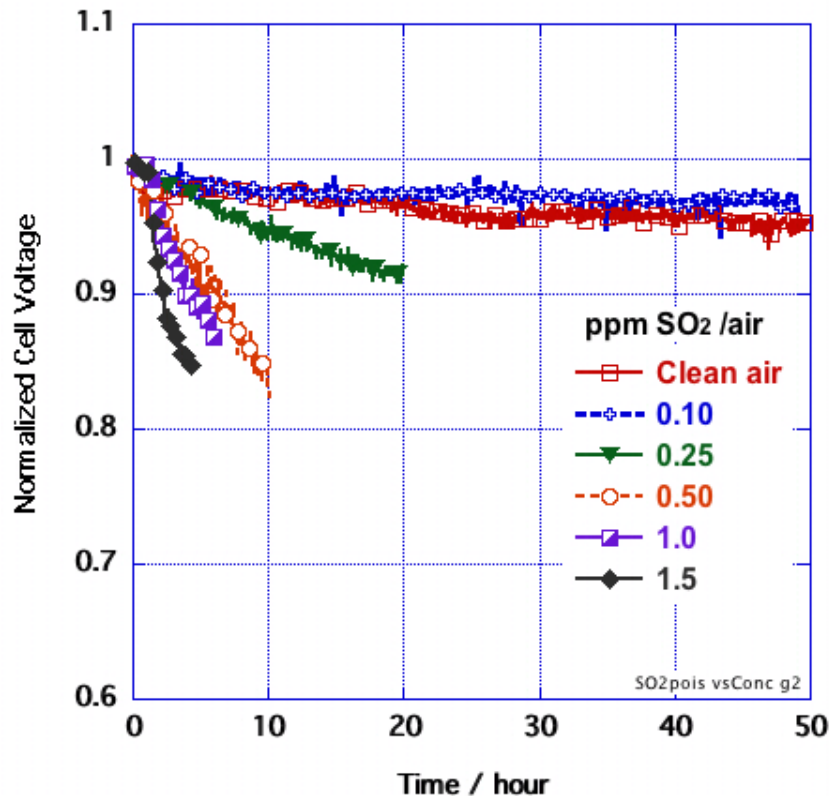


- The negative effect of SO₂ is more acute in dry air.
- Dry clean air does not affect performance under these conditions.

TF625-50 cm² ; N112,
A: 0.21 mg Pt/cm²
C: 0.22 mg Pt/cm²
T_{cell}: 80 °C, P: 30 psig
T_{humidifier}: A/C: 105/80 °C
H₂/Air: 1.3/2.0 stoich

Determining cathode threshold tolerance level to SO₂

A total of 0.011 μmoles of SO₂ injected at the cathode air inlet in each case



* Normalized voltage changes at 0.60 A/cm² constant current

* Under these conditions and exposure time, the threshold deleterious SO₂ level is between 0.1 and 0.25 ppm.

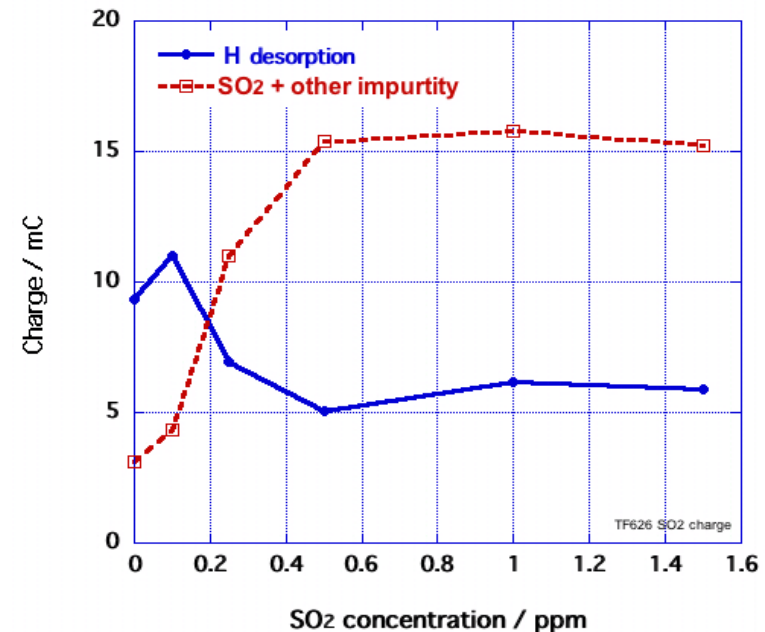
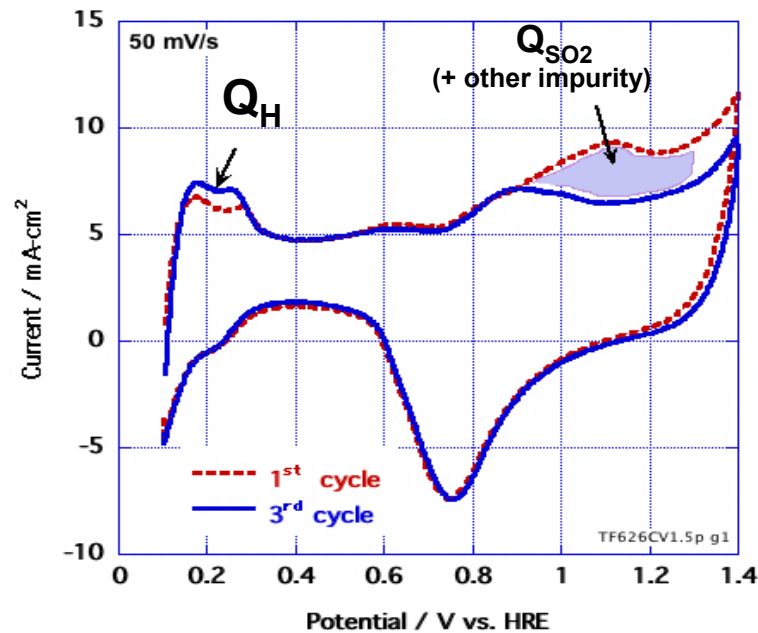
* Voltage drop is due to catalyst poisoning (see next slide)

H₂/Air FC,
 TF626, 50 cm², N112, 80 °C
 A: 0.21 mg Pt/cm² (20% Pt/C, ETEK)
 C: 0.22 mg Pt/cm² (20% Pt/C, ETEK)

Determining cathode threshold tolerance level to SO₂

(Cont'd)

CV of partially poisoned cathode after
3.2 hrs of exposure to 1.5 ppm SO₂



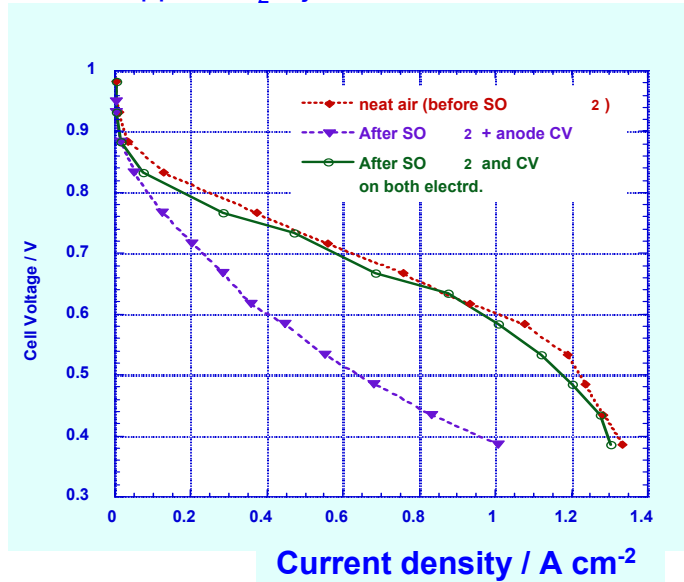
- * SO₂ poisoning decreases H-adsorption
- * SO₂ is oxidized at high potential
- * 3rd cycle CV features indicates that the Pt catalyst becomes clean

- * Charge values for H-desorption and for SO₂ oxidation also show that the threshold value lies between 0.25 and 0.1 ppm.

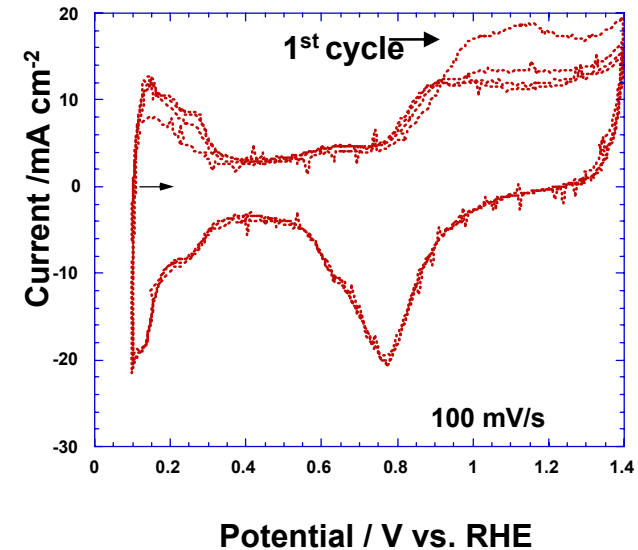
SO₂ as an air impurity

Effect on the cathode catalyst

5 ppm SO₂ injected at the cathode



CV after 17.6 hr exposure / 5 ppm SO₂

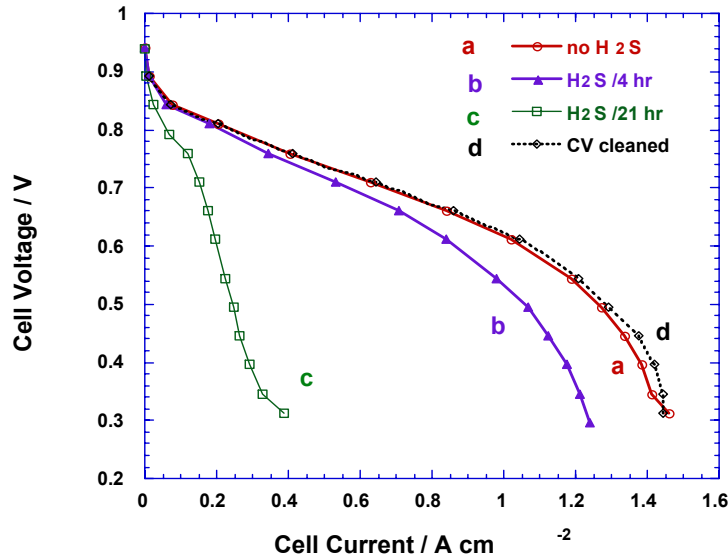


- * Cathode catalyst poisoning by SO₂ is irreversible
- * In-situ voltammetric polarization (CV to 1.4 V vs. RHE) results in a complete cathode catalyst reactivation
- * This reactivation cannot be carried-out during normal cell operation.

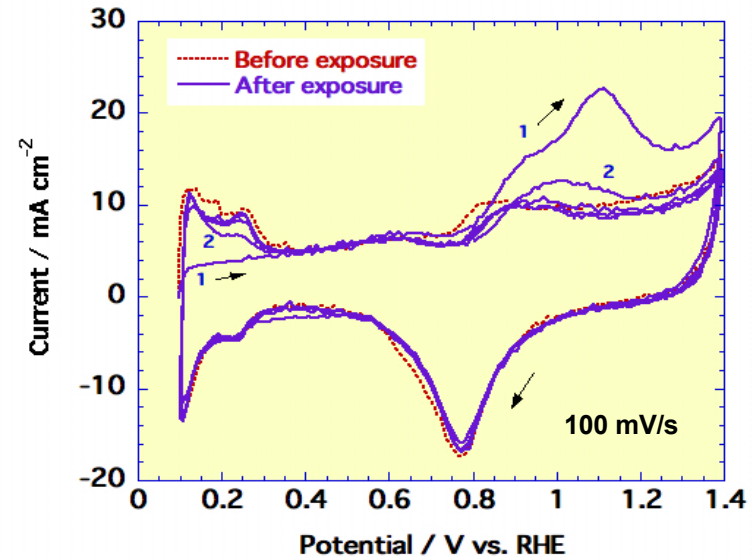
H₂S as fuel impurity

Effect on the anode catalyst

1 ppm H₂S injected at the anode

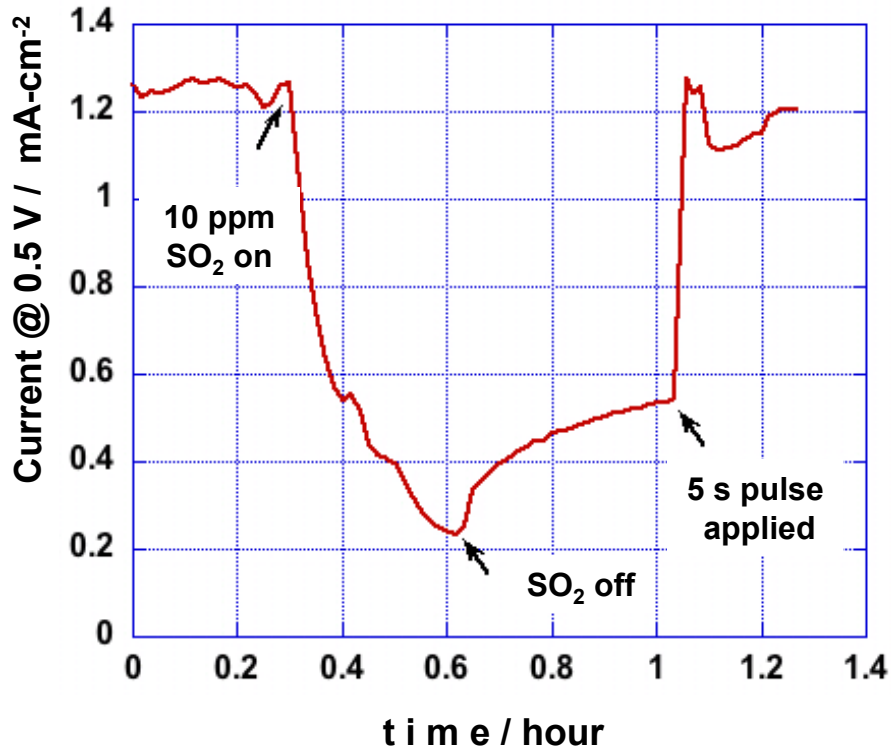


CV before and after full poisoning with 1 ppm H₂S

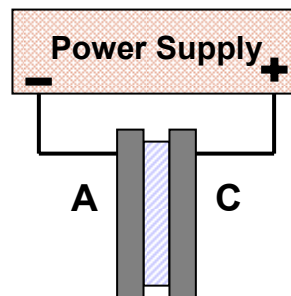


- * Anode catalyst poisoning by H₂S is irreversible
- * *In-situ* voltammetric polarization (CV to 1.4 V vs. RHE) results in a complete anode catalyst reactivation
- * This reactivation cannot be carried-out during normal cell operation.

Cleaning Sulfur (SO_2) Poisoned Cathode Pt-Catalyst

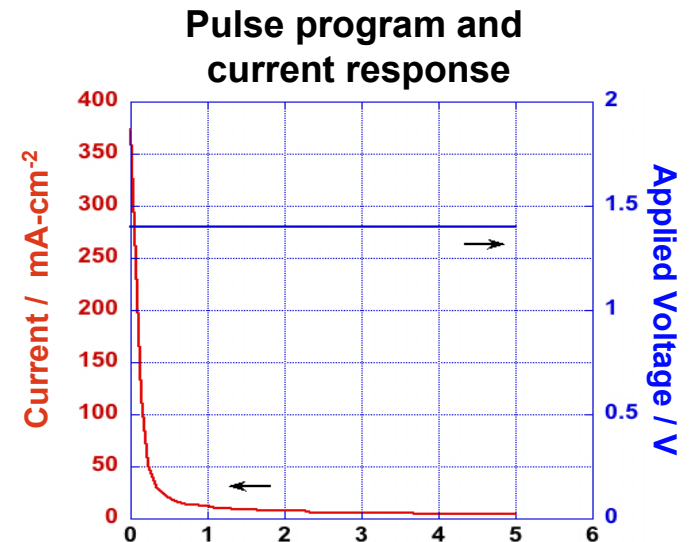


H₂/Air FC, N112, 5cm²
 A: 0.18 mg Pt/cm² (20% Pt/C)
 C: 0.22 mg Pt/cm² (20% Pt/C)
 P: 30/30; T: 80/105/80°C

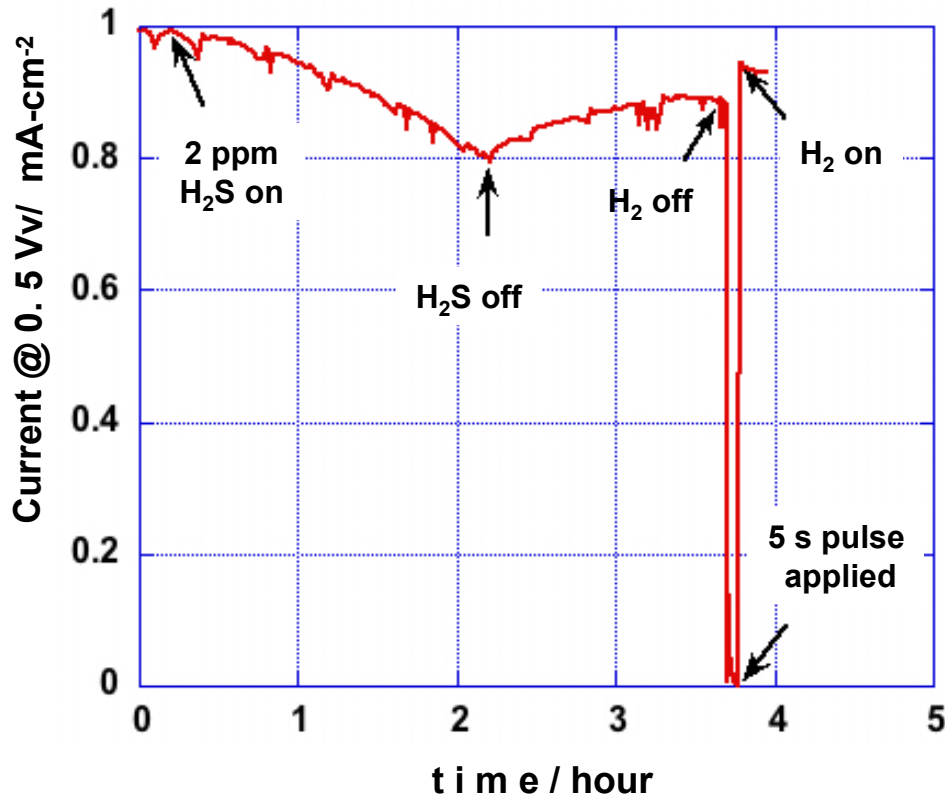


** A current-voltage pulse is applied to the cell using an external power supply*

** Performance recovery is practically complete*

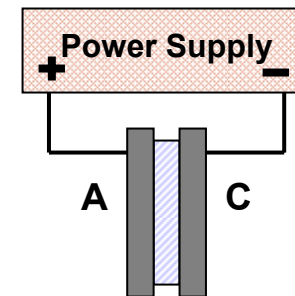


Cleaning Sulfur (H_2S) Poisoned Anode Pt-Catalyst



** A current-voltage pulse is applied to the cell using an external power supply*

** Recovery of performance is almost complete*



50 cm² cell, Nafion 112
 A: 0.22 mgPt/cm² ;
 C: 0.22 mgPt/cm²
 H₂: 1.3 stoich; Air: 2.0 stoich / T= 80 °C

Special Task: USFCC Single Cell Test Protocol

(Materials and Components Working Group)

- * Major Goal: Develop a Conventional Test Protocol that includes:
 - Measure H_2 crossover*
 - Initial break-in procedure*
 - Generate reproducible polarization curves at given conditions*

- * A set of 4 equivalent 50 cm² cells tested in several laboratories
 - Round Robin Testing Participants:*
 - LANL*
 - Teledyne*
 - Greenlight Power Technologies*
 - Electrochem Technologies*

- * Data Collection and Report: LANL
 - Presentations: *FC Seminar, San Antonio, TX , 2004*
 - *ECS Meeting, Quebec City, Canada, May 2005*

Technical Accomplishments and Progress Summary

- 1 . Completed milestones up to date.*
- 2. Demonstrated a simple procedure for reactivating Sulfur- poisoned catalysts from exposure to SO₂ and H₂S.*
- 3. The procedure does not require gas purging or and expensive instrument and is carried out in few minutes.*
- 4. Demonstrated that the negative effects of SO₂ on the cathode are more severe under dry conditions.*
- 5. Actively participated in the USFCC by developing and performing the “Single Cell Testing Protocol”. LANL carried the first and the last set of measurements in the round robin.*

Publications and Presentations

1. P. A. Adcock, S. Pacheco, K. Norrman, F. Uribe," Transition metal oxides as reconfigured fuel cell anode catalysts for improved CO tolerance: Polarization data". *J. Electrochem. Soc.*, 152, A459-A466 (2005).
2. T. Rockward, E. Teather, D. Lane, F. Uribe, D. McNeil, R. Bailey and M. Pien, "Establishing a Standardized Single Cell Testing Procedure through Industry Participation Concensus and Experimentation". Fuel Cell Seminar, San Antonio, TX. November 2004.
3. T. Rockward and F. Uribe, "Cleaning (de-poisoning) PEMFC Electrodes from Strongly Adsorbed Species on the Catalyst Surface. Submitted for patent application, April 2005.
4. J. Wang, F. Uribe and R. Adzic, "A Simple Semi-Analytic Method for Analyzing Fuel Cell Polarization Curves". "Second International Conference on Polymer Batteries and Fuel Cells Symposium " The PBFC-2 Meeting The Electrochemical Society, Las Vegas, Nevada June 12 -17, 2005. Abstract #203.

Future Work

1. Dependence of the effects of H₂S, SO₂ and NO₂ on operating conditions such as: temperature, relative humidity and operating current or voltage.
2. Modeling performance including the effects of these impurities, starting with H₂S and SO₂ whose effects are best known.
3. Study the adsorption of H₂S and SO₂ on carbon supports.
4. Study the effects of diesel fumes as a function of temperature and relative humidity.
5. Electrochemical testing of the effects of impurities will include complementary gas chromatography analysis. We are implementing GC for measuring low impurity levels for SO₂, NO₂ and H₂S.
6. Continue studying the effect of salts (NaCl and CaCl₂) on performance. Test will include performance of pre-exposed components (catalyst layer, membrane and GDL).

2004 Reviewers Comments

1. The effect of SO₂ is reported but methods to reverse the effect are not proposed.

Here we present a simple method for reactivation of severely sulfur-poisoned Pt catalysts.

2. Can benefit from more focused systematic study on effects of one factor that is considered to be most important.

Emphasis on effects of sulfur compounds on FC performance during this period

3. Collaboration with USFCC is valuable - industry needs test protocol for establishing/measuring impurity levels of H₂ specification because existing specifications are inappropriate

This collaboration has continued with strong LANL participation

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Hydrogen leak in the hydrogen supply leading to accumulation in the room with ignition leading to an explosive event.

Hydrogen Safety

- Our approach to deal with this hazard is:
- *In labs with hydrogen supply from cylinder banks or from a hydrogen generator, hydrogen sensors have been installed and are interlocked with the hydrogen gas supply.*
- *Two sensors are installed in every room for redundancy.*
- *Sensors installed at ceiling level where accumulation is most severe.*
- *H₂ sets off the alarm at 10% of Lower Flammability Limit (LFL).*
- *In rooms that use only bottled hydrogen, only a single cylinder is in the room at any given time and bottle sizes are limited to ensure being safely below the LFL of the room even with complete release of a full cylinder.*
- *Work has been reviewed and approved through Los Alamos National Lab's safety programs:*
 - *Hazard Control Plan (HCP) - Hazard based safety review*
 - *Integrated Work Document (IWD) - Task based safety review*
 - *Integrated Safety Management (ISM)*