2004 DOE Hydrogen, Fuel Cell and Infrastructure Technologies Program Review

Electrodes for Hydrogen-Air Fuel Cells

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Collaborations and Interactions

1. **Brookhaven National Laboratory:** *Low Pt content catalysts (R. Adzic).*
2. **Oak Ridge National Laboratory:** *MEA material analysis (Karren More).*
3. **DuPont (CRADA):** *MEA testing and evaluation.*
4. **Donaldson Co. (CRADA):** *Studies on Effects of Air Impurities on FC Performance (E. Stenersen).*
5. **University of New Mexico:** *Materials Durability and Education (P. Atanassov).*
6. **USFCC (Materials and Components Working Group):** *Development of a "Single Cell Testing Protocol".*
7. **GM Fuel Cell Center:** *Technical Presentation.*
8. **UTC Fuel Cells:** *Technical Presentation*
9. **USCAR FredomCAR Comitee:** *Technical Presentations*.

Project Objectives

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

Specific goals:

- Lower Pt-catalyst content in the MEA's
- Improve Pt-catalyst utilization.
- Develop low-cost, high surface area support materials that "replace" precious-metal supports or improve Pt activity for ORR.
- Evaluate catalyst durability.
- Evaluate the effects of fuel and air impurities on FC performance
- Find ways to mitigate negative effects of impurities.
- Continue collaborations with Industry and other National Laboratories
- FY04 Budget: 1.1 M$

Technical Barriers and Targets

Components Barriers
O. Stack Materials and Manufacturing Cost
P. Durability
Q. Electrode Performance

FredomCAR Technical Targets:

Characteristic	Units	DOE 2003 Status	Year 2005	Year 2010
Precious Metal Loading	g/peak kW	<2	0.6	0.2
Durability	hours	1000	2000 [a]	5000 [b]

[a] includes thermal cycling , [b] thermal and driving cycles

Project Mayor Tasks and Approach

<u>Tasks:</u>

a. Effect of Fuel and Air Impurities
b. Electrocatalyst Supports
c. Electrode Structure and Characterization
d. Catalyst Migration in MEA's
e. Special Task: USFCC Single Cell Test Protocol

- ***Study the effects of ambient air impurities on FC performance*** *(e.g. SO_2, NO_2, NaCl).*
- ***Study the effects of low concentrations H_2S on anode performance.***
- ***Find materials and devices able to mitigate negative effects of impurities.***
- ***Evaluate performance of low Pt-content catalysts (BNL catalysts).***
- ***Test low Pt-content catalysts for long term performance.***
- ***Correlate MEA component changes and performance after long term operation.***
- ***Study Pt-alloys catalysts durability in fuel cell*** *(e.g. measure Ru crossover).*
- ***Prepare new high-surface area supports for Pt catalysts.***
- ***Collaborate with USFCC to develop a "Single Cell Testing Protocol".***

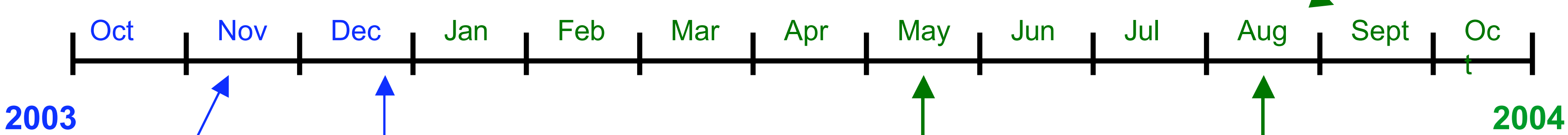
Work Timeline / Milestones

Complete 500 hr test with 50 ppm CO and 2% air bleed with 0.02 mg Pt/cm^2 at the anode. BNL catalyst: 1% Pt-10% Ru
Status:Completed

Effect of 400 ppb NO_2 on cathode performance with filter
Status: Completed [1]

Determine the rate of loss of Ru from the anode under various FC operational conditions.
Status: In progress

Develop techniques to catalyze support materials with surface areas of at least 200 m^2/g Pt.



Perform the 1st set of measurements for the “Single Cell Testing Protocol” development.
Status:Completed

Effect of 500 ppb SO_2 on cathode performance with filter/ 500 hr.
Status:Completed

Complete 500 hr test with 50 ppb H_2S on H_2 with a scrubber.
Status: Completed

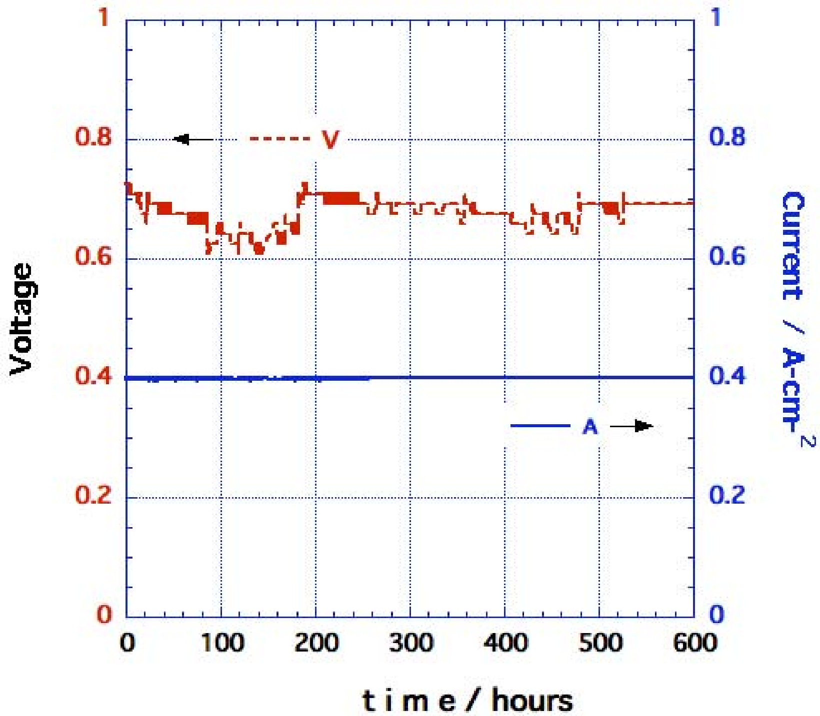
Complete 500 hr test with 50 ppm CO and 2% air bleed with 0.02 mg Pt/cm^2 at the anode. BNL catalyst: 2% Pt-20% Ru

[1] Test completed. Results still under analysis

Task a. Effect Impurities

Nov 03 Milestone Completed

Performance of Low Pt Content Anode Catalysts *
--- Catalyst content: 17 μg Pt/cm^2 (1% Pt - 10% Pt BNL) ---



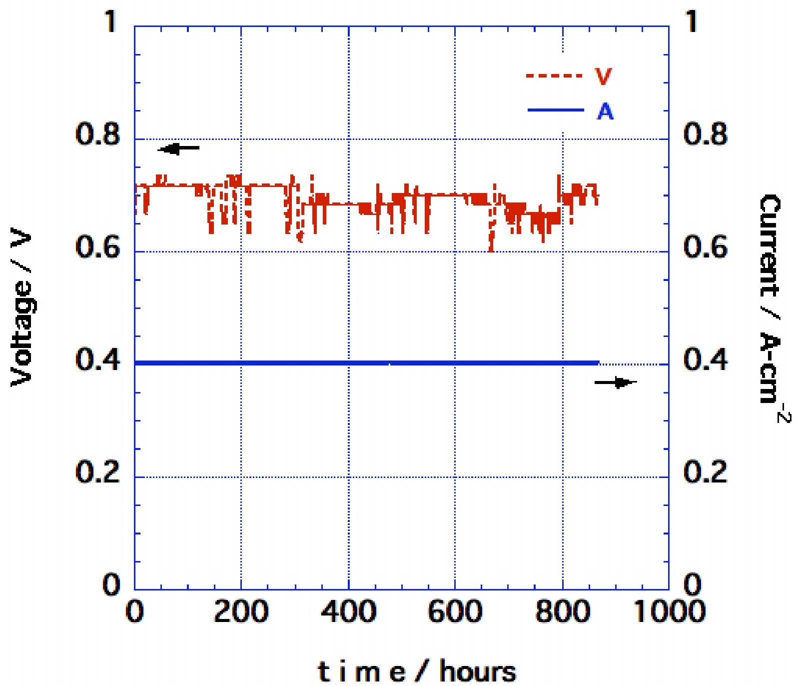
Voltage losses after 600 hr:
- * with neat H_2: **16 mV** (0.708-0.692 V)
- * with H_2+CO+2% air: **17 mV** (0.675-0.658 V)
- * total loss due to CO: **50 mV** (0.708-0.658 V)

50 cm^2 cell / T= 80 C
A: 0.19 mg BNL/cm^2 (10% Ru; 1% Pt)
C: 0.22 mgPt/cm^2 (ETEK)
Running Mode: 20 A constant current
a) H_2 at @ 1.5 stoich, 474 hr (30 psig)
(overnight & weekends)
b) H_2 at @ 1.5 stoich+CO+2% air bleed,
126 hr (day time)
Air flow: constant @ 2100 sccm (30 psig)

*** Catalysts prepared by R. Adzic et al., Brookhaven National Laboratory**

Performance of Low Pt Content Anode Catalysts*

--- Catalyst content: 18 µg Pt/cm^2 (2% Pt-20% Ru BNL) ---



50 cm^2 cell, N112 / T= 80 C
A: 0.20mg BNL/cm^2 (20% Ru; 2% Pt)
C: 0.24mg Pt/cm^2 (ETEK)
Running Mode: 20 A constant current
a) H_2 at @ 1.3 stoich (30 psig)
b) H_2 at @ 1.3 stoich+CO+3% air bleed
Air flow: constant @ 2100 sccm (30 psig)

Voltage losses after 868 hr of testing:

	initial V	final V
* with neat H_2:	0.717	0.717 (± 0.009)
* H_2+CO+3% air:	0.697	0.701 (± 0.013)

* total loss due to CO: 16 mV (0.717-0.701 V)

* **No losses when operating with H_2**
* **Result demonstrate good catalyst stability**

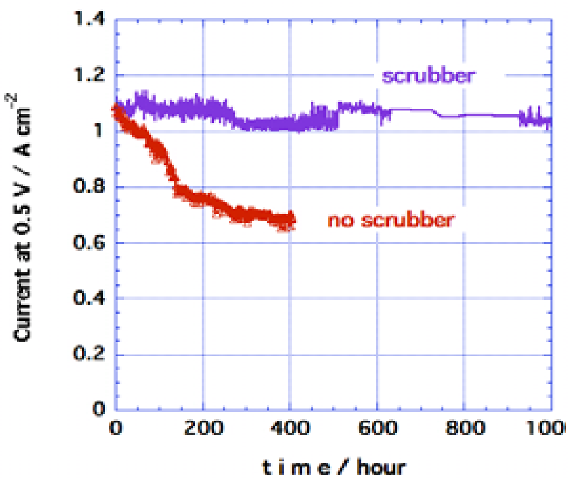
* **630 hr with neat H_2**
* **238 hr with 50 ppm CO + 3% air**
* **Cell failed after 870 hr (probably H_2 cross over)**

Milestone Aug 04 requires 20 µg Pt/cm^2 with cell running on H_2+ 50 ppm CO + 2% air

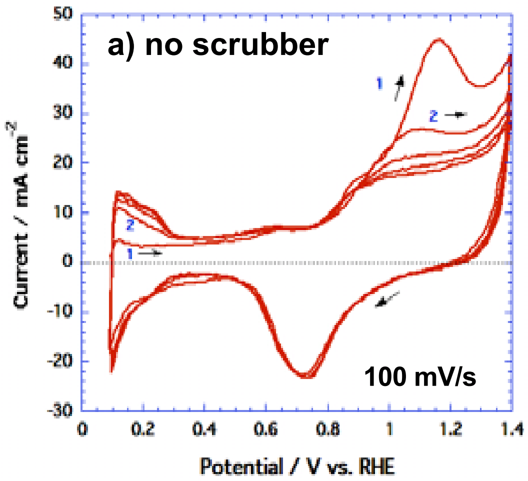
*** Catalysts prepared by R. Adzic et al., Brookhaven National Laboratory**

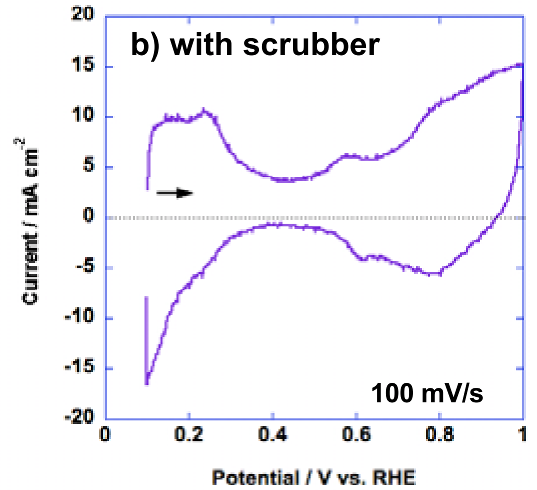
May 04 Milestone Completed

Effect of 50 ppb H_2S on Anode Performance



FC Anode CV's after long-term operation





Cell with a scrubber
A: 0.21 mg Pt/cm^2
C: 0.25 mg Pt/cm^2

Cell without a scrubber
A:0.18 mg Pt/cm^2
C: 0.19 mg Pt/cm^2

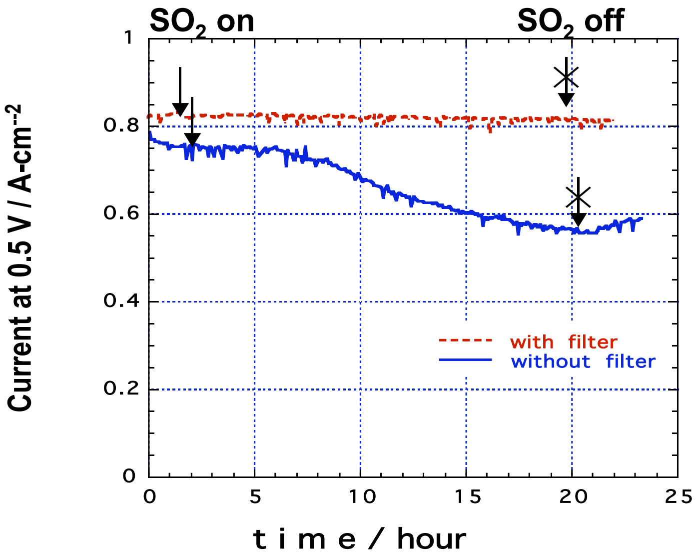
1. **A homemade scrubber (CuO/ZnO/alumina, United Catalysts) is efficient for cleaning H_2S from the H_2 fuel stream.**
2. **First cycle in CV (a) shows extensive H_2S poisoning and the large wave at 1.15 V indicates strong sulfur adsorption on Pt catalyst.**
3. **After operation with a scrubber, CV (b) indicates only small losses of catalyst activity.**

International Standard ISO 14687:1999(E) Hydrogen Fuel-Product specification: Hydrogen fuel Type I, grade A for internal combustion engines/fuel cells for transportation; residential/commercial appliances is allow to have up to 2 ppm of sulfur.

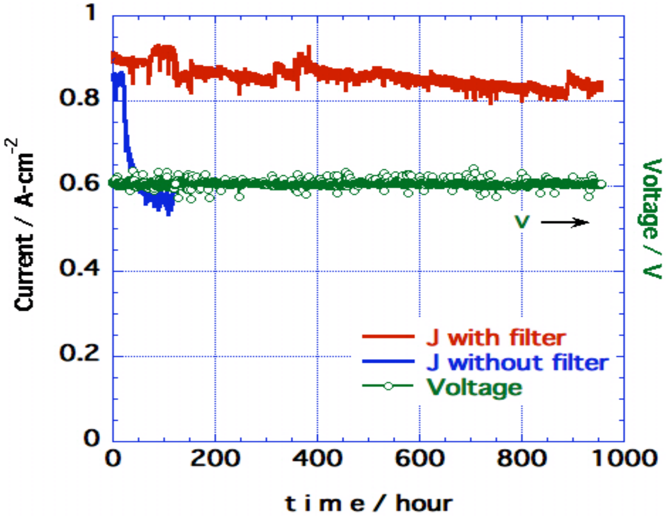
Milestone Dec 03
Completed

Effect of SO_2 on Cathode Performance

Effect of 1 ppm SO_2 on PEMFC performance with and without filter



Complete 500 hr testing with 500 ppb SO_2 with filter

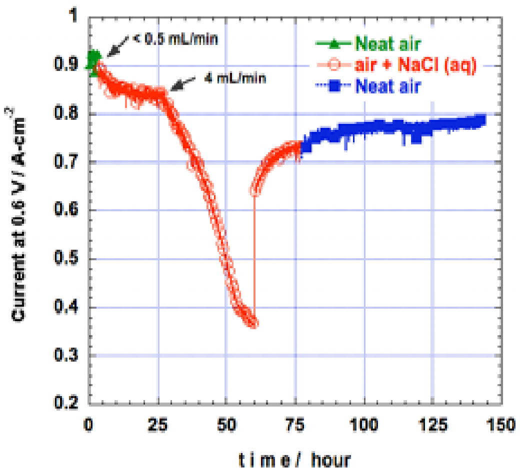


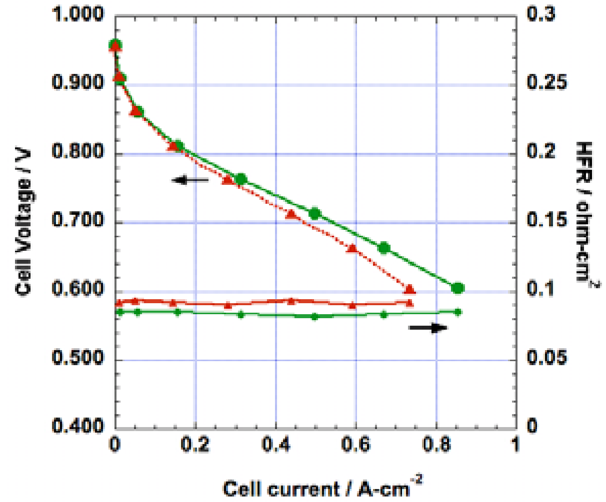
- **Even ppb levels of SO_2 have acute and irreversible negative effects on FC performance.**
- **Filtration of air provides a viable solution to SO_2 contamination.**

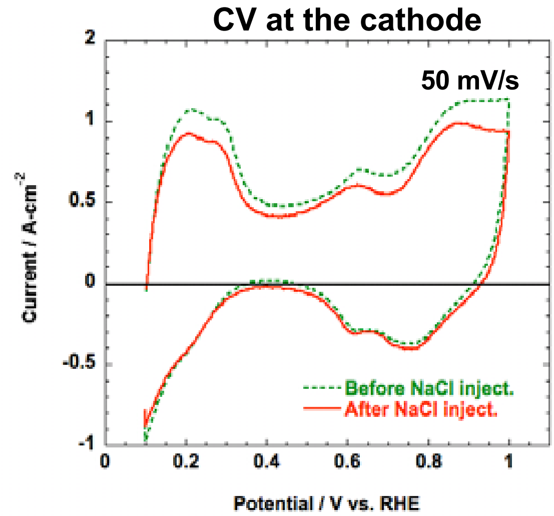
SO_2 injected at the cathode inlet
50 cm^2 cell, Nafion 112
A:0.23 mg Pt/cm^2; C:0.22 mg Pt/cm^2
H_2:1.5 stoich; Air: 2.0 stoich; T= 80 °C
Donaldson FC Test Air Filter FCX400027

50 cm^2 cell, Nafion 112
A: 0.22 $mgPt/cm^2$;C: 0.22 $mgPt/cm^2$
H2:1.3 stoich; Air: 2.0 stoich / T= 80 °C
Donaldson FC Test Air Filter FCX400027

Effect of NaCl on FC Performance







- *0.46 M NaCl solution was injected along with the air stream into the cathode.*
- *Performance dropped and did not fully recover on operation with neat air.*
- *NaCL decreases membrane conductivity (HFR increases).*
- *The presence of Cl^- does not significantly affect catalyst activity as shown by CV's.*
- *The presence of NaCl in the MEA may increase the hydrophilicity of the GDL.(see below)*
  XRF measurements indicated large amounts of salt in the GDL.

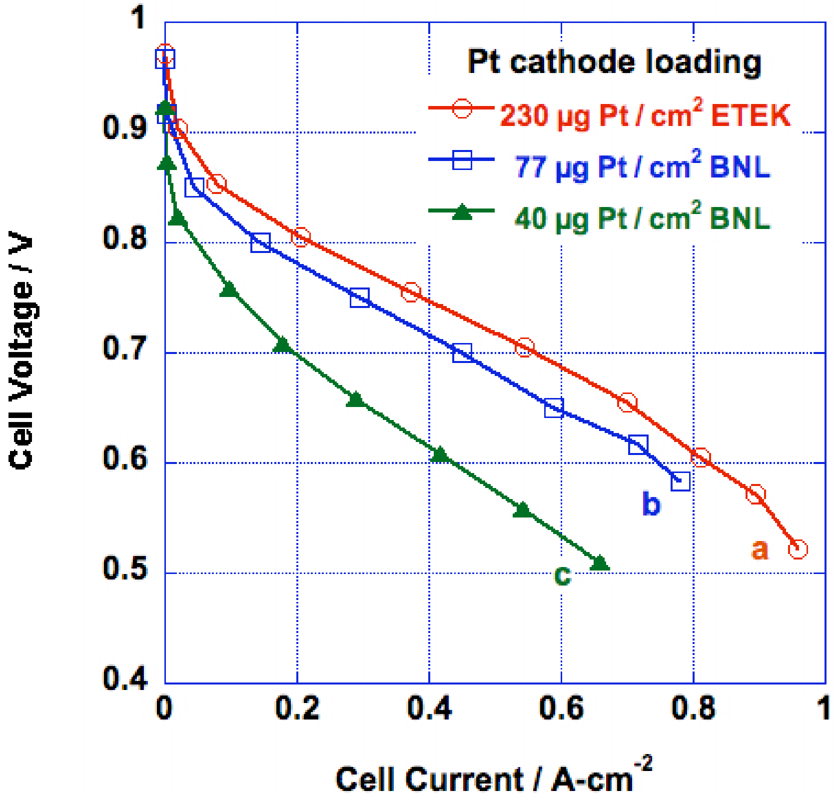
GDL(ELAT v2.22) Contact Angle Measurements

Sample soaked in water for 6 days: 113.5 deg.

Sample soaked in 0.46 M NaCl for for 6 days: 97.8 deg.

Performance of Low Pt content Cathode Catalysts

--- Catalyst content: 40 and 80 μg Pt/cm² (4% Pt-20% Pd, BNL) ---



50 cm² cell. T= 80° C
Membrane: Nafion® N1135.
Flows: H_2 1.3 stoich; Air 2100 sccm.
Back pressures: anode /cathode 30/30 psig.

Metal loading / kW (from power at 0.6 V)

cell	g Metal/kW	g Pt/kW
a	0.92	0.92
b	1.0	0.59
c	1.1	0.80

- **Performance of cell b represents a significant improvement in lowering the overall Pt loading.**

Metal loadings / cm²

cell	Anode mg Pt /cm²	Cathode mg Metals /cm²	Cathode mg Pt /cm²
a	0.22	0.23 Pt	0.23
b	0.18	0.46 Pt-Pd	0.077
c	0.17	0.24 Pt-Pd	0.040

*** Catalyst prepared by R. Adzic et al., Brookhaven National Laboratory**

Low Cost Catalyst Support Materials

✓Objective

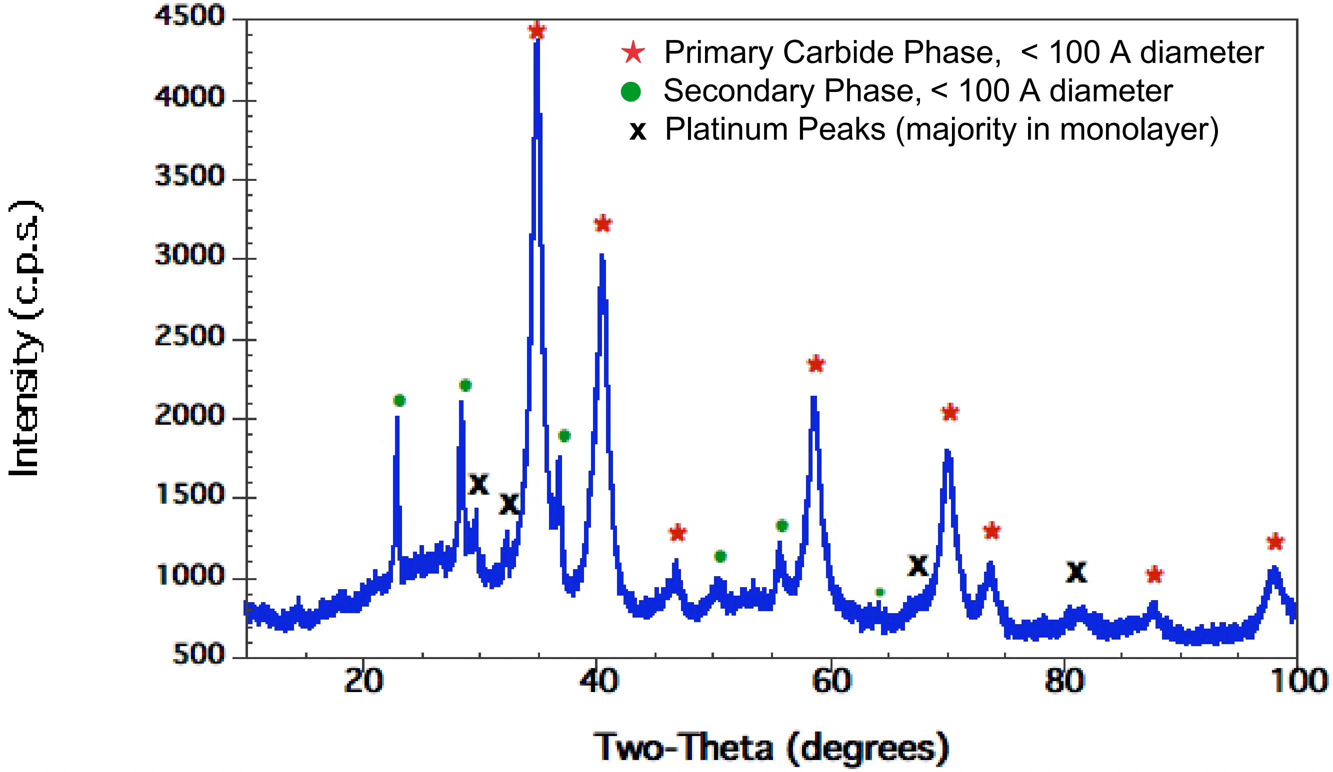
- Develop low-cost, high surface area support materials that "replace" the precious-metal supports (i.e., Adzic and co-workers).
- The support must provide:
  - Electrochemical stability
  - High electronic conductivity
  - Suitable host for platinum
    - Allow stable near-monolayer Pt dispersions.
    - Maintain bulk-like Pt activity.

✓Progress to date

- Produced < 100 Å carbide supports. (some stable in acidic media)
- Produced ~ 100 Å perovskite support.
  - Not stable in acidic media
- Produced ~ 25 Å Pt-Cr crystallites on carbides.
- Achieved Pt monolayers on several supports.

Low Cost Catalyst Support Materials (cont.)

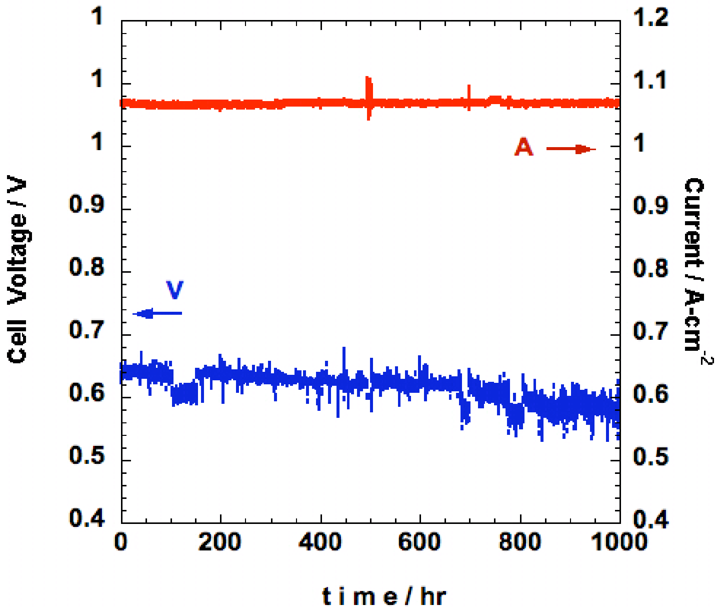
5 wt% Pt on Carbide Support



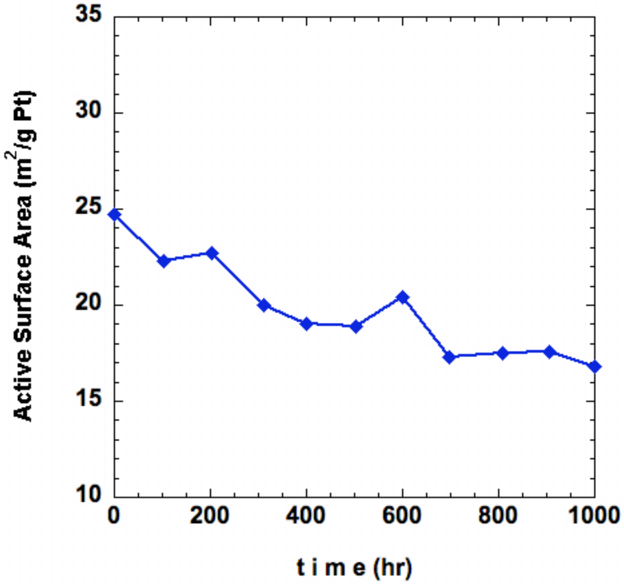
--- **Based on the diminutive size of the Pt peaks, the majority of platinum is noncrystalline (in monolayers).**

--- **Currently testing for activity**

Catalyst Changes After Long-term Operation (1000 hr)



Pt cathode active surface area

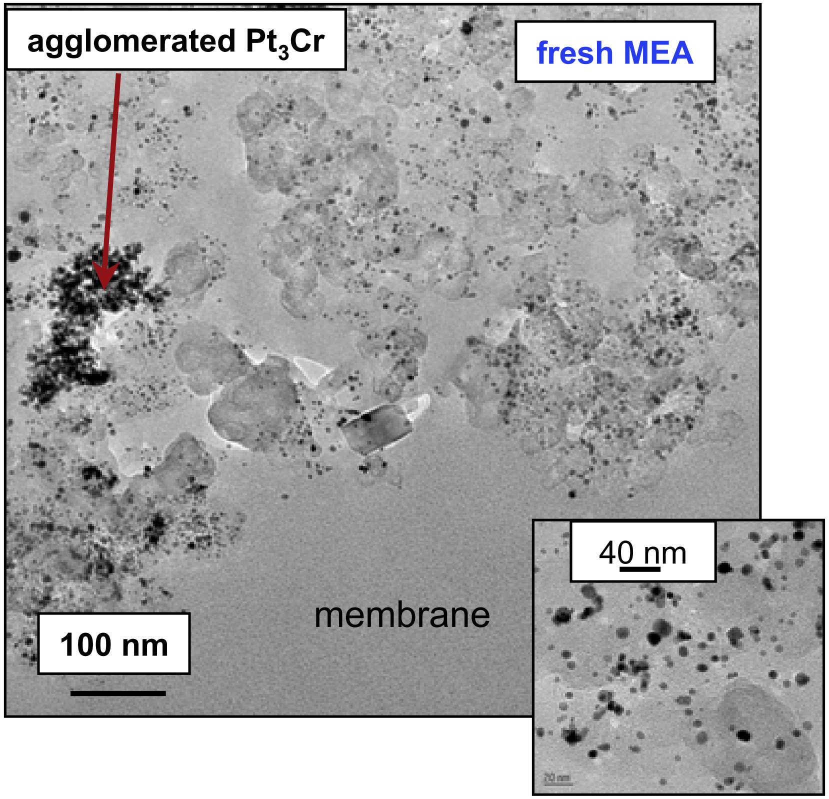


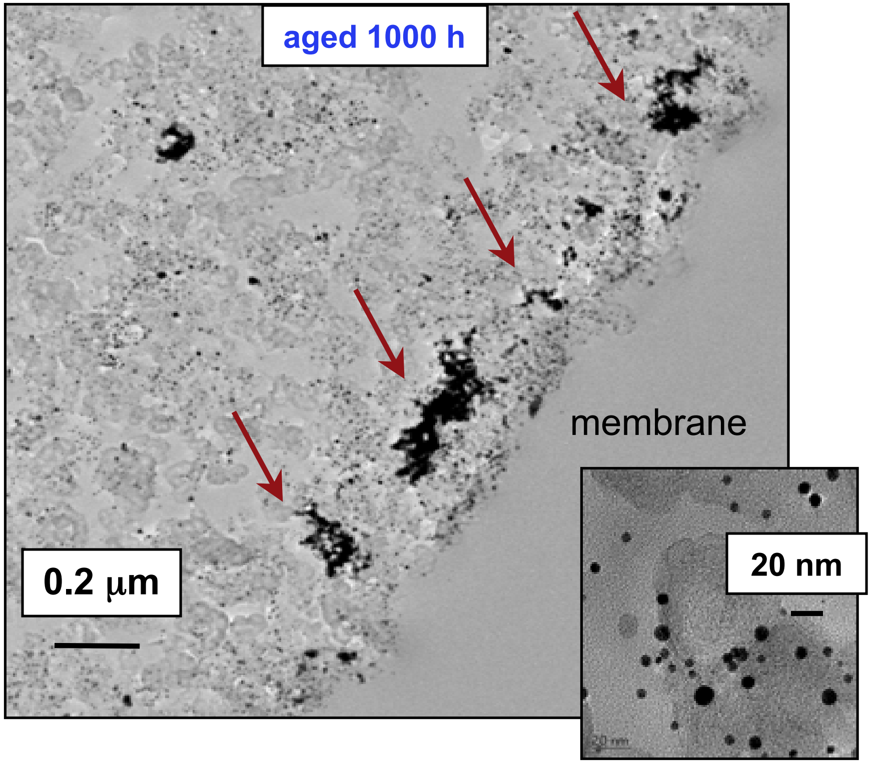
5 cm^2 Cell. Nafion N112. 80 °C
A: 021 mg Pt/cm^2;
C: A: 0.23 mg Pt/cm^2(Pt_3Cr)
Anode/Cathode stoich: 3.6/5.9
Constant current: 1.07 A/cm^2

- **Linear voltage decay rate: 54 µV/hr.**
- **Total voltage drop: 54 mV.**
- **A gradual decreasing in the Pt cathode active surface area was observed: 25 to 17 m^2/g Pt**
- **Pt surface area obtained from H adsorption-desorption charge. (Cyclic Voltammetry).**

Active Pt surface area decreased from 25 to 19 m^2/ g Pt

Cathode Catalyst Changes After Long-term Operation (cont.)





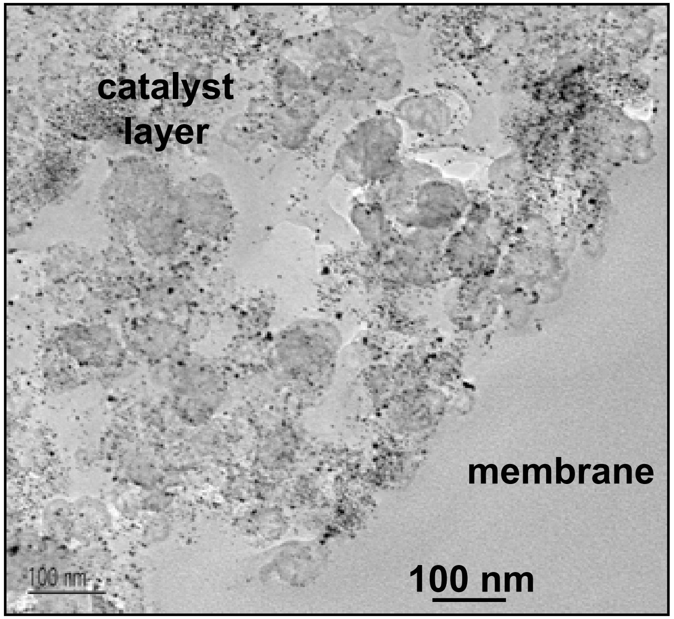
Fresh MEA
- **Pt_3Cr particle size ~ 4-12 nm**
- **Inhomogeneous dispersion of catalyst**

- **Aging for 1000 hr results in Pt_3Cr-enrichment at membrane/cathode interface.**
- **Pt_3Cr particle coarsening and sintering observed**

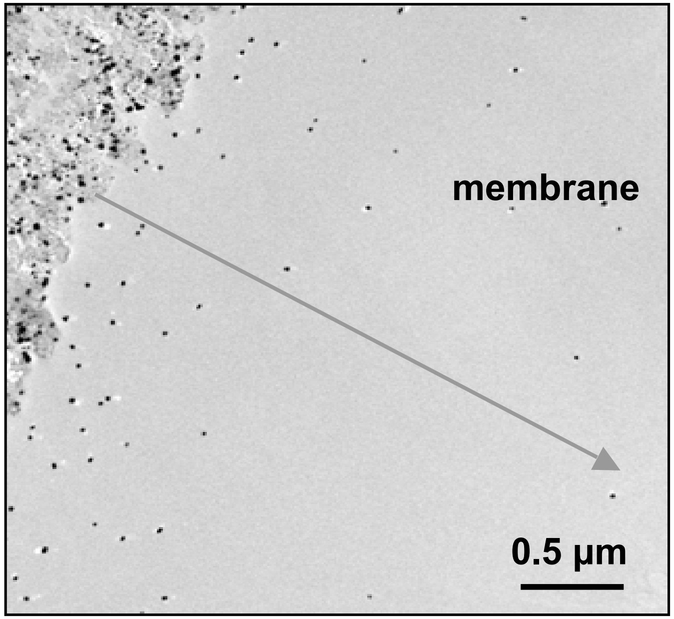
Images taken by Karren More, ORNL

Anode Catalyst Changes After Long-term Operation (cont.)

Fresh MEA



MEA after 1000 hr



5 cm^2 cell at 80 ^oC
A: 0.22 mg Pt/cm^2
C: 0.23 mg Pt_3Cr/cm^2
Constant current: 1.07 A/cm^2

- **Extensive particle coarsening and redistribution observed after aging.**
- **Particle coarsening at the anode/membrane interface.**
- **Pt particles dispersed ~3 μm into the membrane (arrow)**

Images taken by Karren More, ORNL

Ruthenium Migration (Crossover)

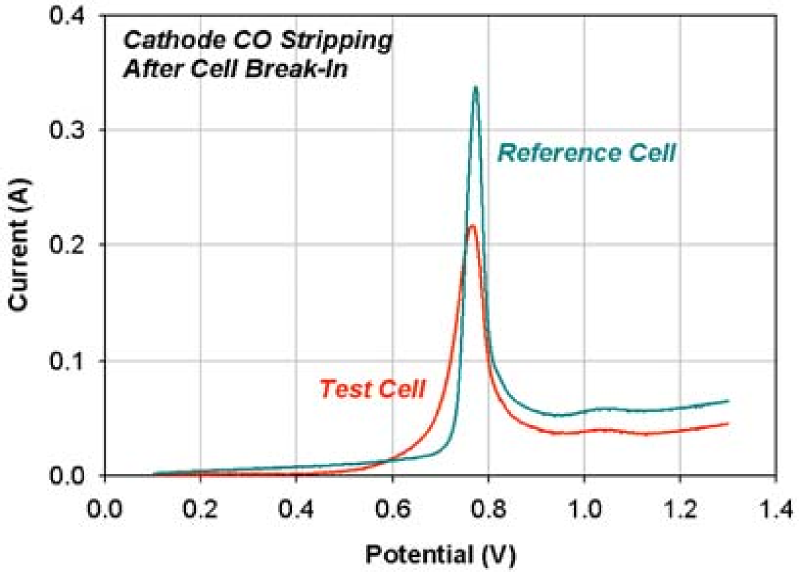
CO-Stripping & Cell Performance Data

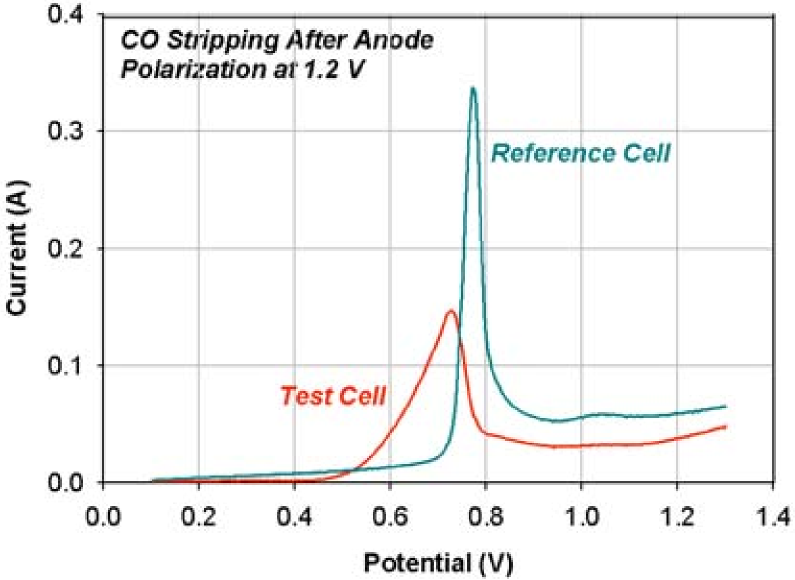
- **Ru migration (crossover) through Nafion™ membranes recently identified at LANL as *performance durability issue* in DMFCs**
- **Potential impact on PEM cathode performance:**
  - ✓ *Blocking of active catalyst sites for oxygen reduction*
  - ✓ *Lowering activity of Pt catalyst due to formation of a binary Pt-Ru catalyst (alloyed or two-phase)*
- **Focus of the present study:**
  - ✓ *Degree of Ru release from the Pt-Ru/C PEM anode*
  - ✓ *Effect of Ru deposition on the cathode performance*
- **Experimental:**

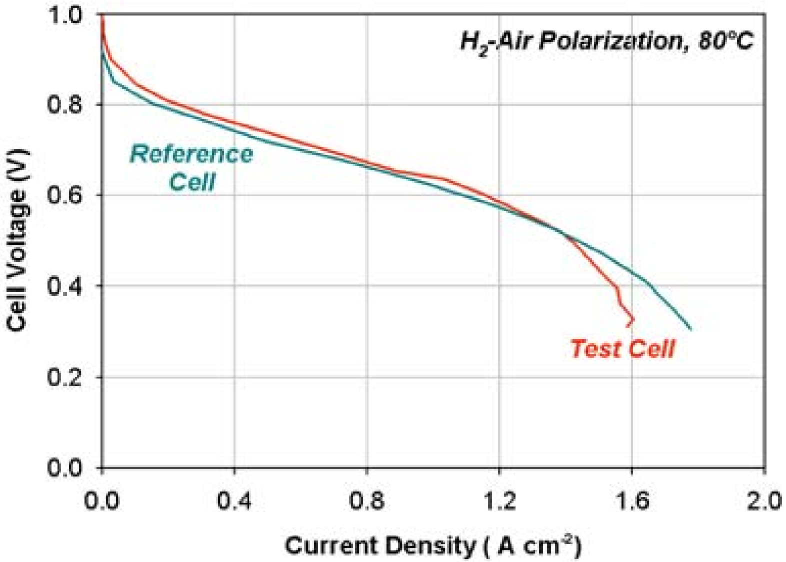
Cell	Anode	Cathode	Membrane
Test 5 cm^2 area	54 wt% 2:3 Pt-Ru/C 0.2 mg Pt cm^{-2}	20 wt% Pt/C 0.2 mg Pt cm^{-2}	Nafion 112
Reference 5 cm^2 area	20 wt% Pt/C 0.2 mg Pt cm^{-2}	20 wt% Pt/C 0.2 mg Pt cm^{-2}	Nafion 112

Ruthenium Migration (Crossover)

CO-Stripping & Cell Performance Data







- ***Ru migration detected in PEM fuel cells operating with Pt-Ru/C anode***
- ***CO-stripping indicates Ru coverage at the cathode surface below ~10%***
- ***No impact on cell performance observed at short operating times***
- ***Longer-times & high anode potential accelerate Ru migration***

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 cm^2 cells tested in several laboratories

  Round Robin Testing Participants:
  - *LANL (1st: Nov 2003, 5th: June 2004)*
  - *Teledyne (2nd: Dec 2003 - Feb 2004)*
  - *Greenlight Power Technologies (3rd: March-April 2004)*
  - *Electrochem Technologies (4th: May 2004)*

* Data Collection and Report: LANL

* Presentations: *FC Seminar, Miami, FL , Nov. 2003*
  FC Seminar, San Antonio, TX , 2004 (abstract submitted)

Technical Accomplishments and Progress

Summary

1. *Showed negative and irreversible effects of low SO_2 and H_2S levels on FC performance, and demonstrated that filtration is an effective alternative for mitigating this problem.*
2. *Demonstrated long-term stability (up to 1000 hr) of low Pt-content (Pt-Ru BNL) catalysts.*
3. *Quantified NaCl negative effect on FC performance. Its presence decreases the ionomer conductivity and increases GDL hydrophilicity.*
4. *Achieved significant performance with low Pt-content cathode catalyst.*
5. *Produced low-cost and small particle (<100 Å) materials for supporting Pt monolayers.*
6. *Showed that extensive Pt particle ripening and redistribution occurs at the anode catalyst layer-membrane interface, after long term performance (1000 hr).*
7. *Observed Ru-migration from anode to cathode under operating FC conditions.*
8. *Actively participated in the USFCC by developing and performing the "Single Cell Testing Protocol".*
9. *Completed all the milestones planned to date.*

Selected Comments From Last Year Review

1. **Need to find solution or mitigating means to SO_2 problem.**
   We show here that the use of commercial SO_2 filters is an option available for solving this problem. Other strategies are being considered.

2. **Quantification of problems with contaminants not that useful.**
   Our presentations on the "effect of air impurities on FC performance" have been welcomed by FC researchers and developers. The scientific literature on this subject is poor.

3. **We need analysis and conclusions from data that can be used to advance technology, i.e. single test protocol does not develop fundamental understanding of catalyst and electrode operation.**
   USFCC (Materials & Components Working Group) proposed the participation of LANL in this activity. There is ample agreement that "a standard procedure" for single cell testing is necessary for the evaluation of new materials and components. Our participation in this activity is supported by DOE within this project.

Future Work

1. Study the dependence of SO_2 poisoning on operating cell voltage.
2. Determine maximum SO_2 tolerance without special air filter.
3. Explore strategies for SO_2 cleaning (de-poisoning) under operation.
4. Study the effect of other air impurities on FC performance.
5. Evaluate stability of low Pt-content catalysts in long term tests.
6. Test cell with BNL catalysts at both electrodes.
7. Measure metal contents in the BNL catalysts by XRF imaging before and after testing in fuel cells.
6. Continue formulation of new high surface-area catalyst supports to improve Pt utilization.
7. Test Ru migration during long-term operation.
8. Participate in USFCC activities: Single Cell Testing Protocol (5th set of measurements in the Round Robin testing, data collection and analysis)

Project Safety

Management Safety Controls

- **Hazard Control Plan (HCP):** ***Hazard based safety review.***
- **Integrated Work Document (IWD): Task** ***based safety review.***
- **Integrated Safety Management (ISM).**

Define work → Analyze hazards → Develop controls → Perform work → Ensure performance

Engineering Controls

- **Hydrogen room sensors.**
- **H_2 sensor interlocked with solenoid valve will shut off H_2 supply into the room.**
- **H_2 sensor alarms at 10% LEL, closes valve at 20% LEL.**
- **In the process of replacing tube trailers with on-demand H_2 generators.**

Safety Related Lessons

Only 1 reportable safety incident in more than 20 years (2001): ***Excessive power from an FC operating on pure O_2 partially burned wire insulation in a test station.***

**** Power limits were set to shut off the test stations if exceeded.***

**** Currently, operation with pure O_2 is only permitted if the experiment is being attended.***

**** Related controls were included in the HCP.***