2005 DOE Hydrogen, Fuel Cell and Infrastructure Technologies Program Review

Electrocatalyst Supports and Electrode Structures

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FC 5

Project Overview

Electrocatalyst Supports and Electrode Structures

Timeline
- “Started” FY04
- End date not established
- 25% Complete

Barriers
- B. Cost
- C. Electrode Performance
- A. Durability?

Budget
- 100% DOE
- Total FY04 = ~ $400k
- Total FY05 = $800k

Partners
- Radoslav Adzic and co-workers (BNL)
- LANL T-10 and T-12 (Theoretical Physics)
- Karren More (ORNL)

Project Objectives

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

Specific goals:

- Substantially reduce the amount of Pt required.
- Improve Pt catalyst stability/durability (compared to carbon supports).
- Improve electrode manufacturability and performance.

Approach

"Stabilize" Pt catalysts using "interactive" supports

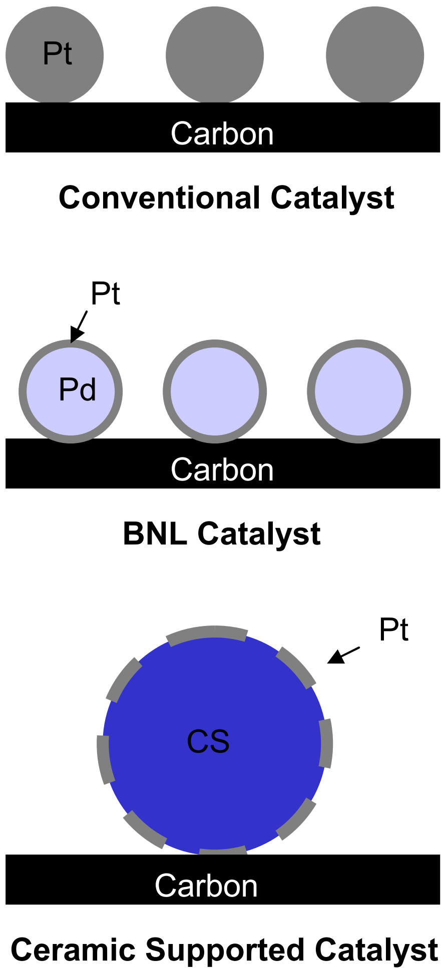
1) Use Group VIII type supports (BNL catalysts).

- Test low Pt-content catalysts for performance and durability

2) Use ceramic supports (CS) that "compensate" the Pt.

- Investigating CS's with unusual properties.
  - Understand CS properties and electrochemistry
  - Prepare materials suitable for FC testing
  - Capitalize on properties for electrode structures.

3) Develop theoretical models to understand support/catalyst interactions.



Technical Targets & Project Milestones

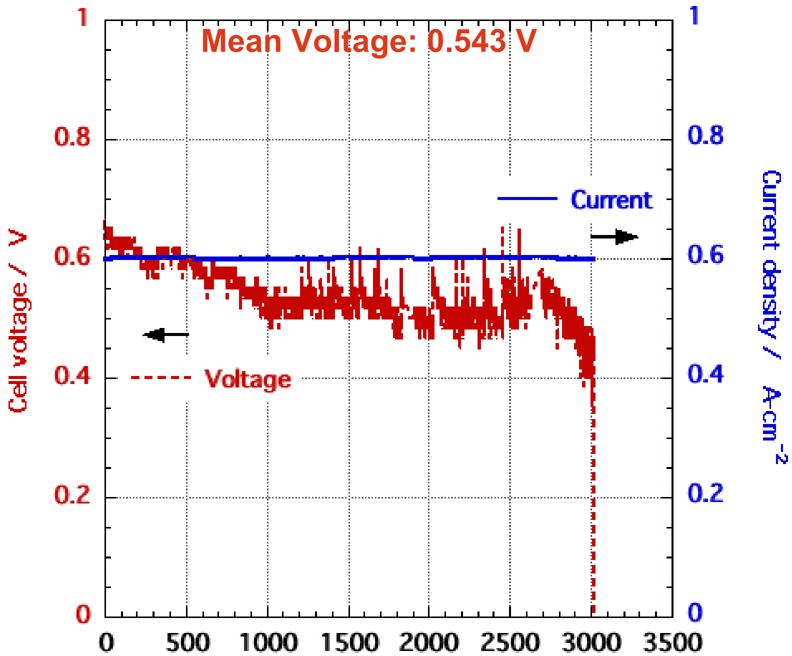
Technical Targets (Tables 3.4.13 & 3.4.14)						
Characteristic	Units	2004 Status		Targets (Stack)		
		Cell	Stack	2005	2010	2015
PGM* Total Content (Electrocatalyst TT)	g/kW (rated)	0.6	1.3	2.67	0.5	0.4
PGM Total Loading (Electrocatalyst TT)	mg PGM/cm^2 electrode area	0.45	0.8	0.7	0.3	0.2
Total Catalyst Loading (MEA TT)	g/kW (rated)	1.1		2.7	0.33	0.2

*PGM - Platinum group metal

Date	**Milestones for Electrocatalyst Supports and Electrode Structures**
Dec 04	Complete 1000 hr with 0.2 mg Pt/cm^2 at the anode and 0.08 Pt mg Pt/cm^2 (BNL catalyst: 4% Pt-20% Pd) at the cathode
Feb 05	Complete 1000 hr with 0.02 mg Pt/cm^2 (BNL catalyst: 2% Pt-20% Ru) at the anode and 80 µg Pt/cm^2 (BNL catalyst: 4% Pt-20% Pd) at the cathode.
Mar 05	Predict by modeling and successfully synthesize the first versions of “doped” low-cost, stable and high surface area support materials.
Aug 05	Identify the most promising support candidates by testing of electrochemical stability and intrinsic activity.
Sept 05	Test first variations of “new” electrode structures.

Durability of low Pt-content cathode catalysts*

(Dec '04 milestone)



H_2/Air FC
BNL20; N1135,
Constant current test (80 °C)
A: 0.18mgPt/cm^2 (20% Pt-C, ETEK)
C: 0.077mgPt/cm^2 (20% Pd-4%Pt, BNL)
(Total metal at the cathode: 0.45 mg/cm^2)
Stoich: H_2/air= 1.3/2.0

Voltage losses after 2900 hr of testing at constant current (0.6 A/cm^2):

initial V	final V
0.65	0.51

- **Result demonstrates considerable catalyst activity up to 3000 hr**
- **Long-term durability of the Pt-Pd cathode catalyst demonstrated**

Catalyst surface area decrease

Time hr	Q_H mC/cm^2	S_{act} m^{2}Pt/g Pt
0	14.3	88
1413	10.6	65
2027	10.1	62

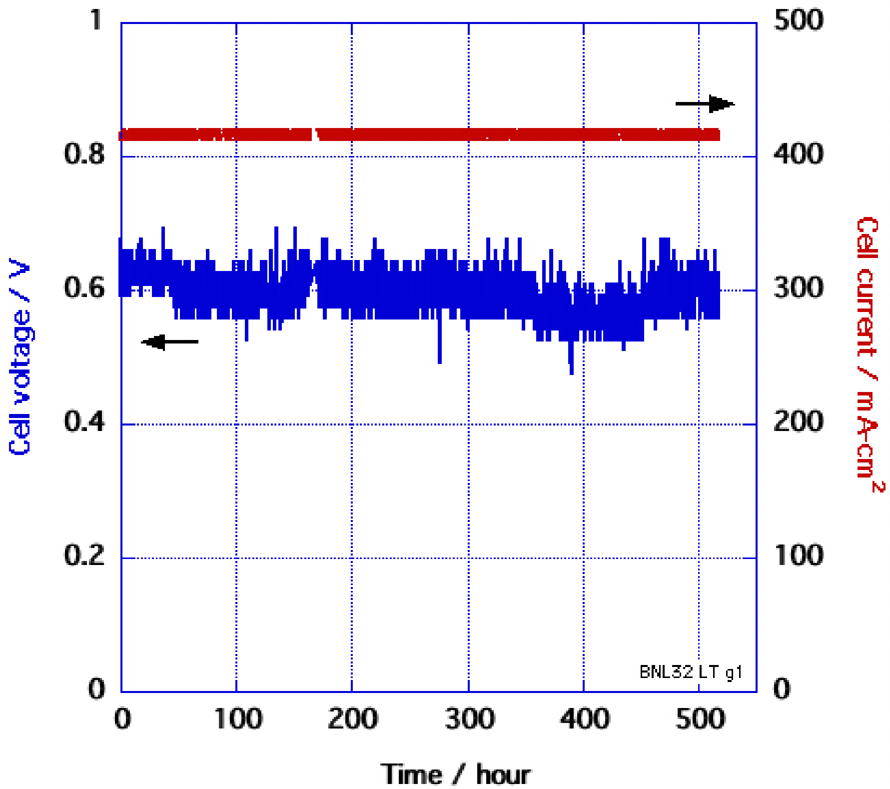
*** Catalysts prepared by R. Adzic et al., Brookhaven National Laboratory**
- BNL presentation Tuesday, May 24 at 1:35 PM (FC 17)

Low-Pt Content Catalysts on both Electrodes *

--- 0.149 mg total Pt /cm² ---

(Feb '05 milestone = 0.1 mg Pt/cm²)

Constant current test (0.4 A/cm²)



Catalyst performance:

0.60 g Pt /kW

3.7 g PGM/kW

'05 Target: 2.67 g PGM/kW

Mean values from curve:
J: 417 mA/cm²,
Voltage: 0.602 V,
Power: 0.251 W/cm²,
Pt Loading: 0.149 mg Pt/cm²

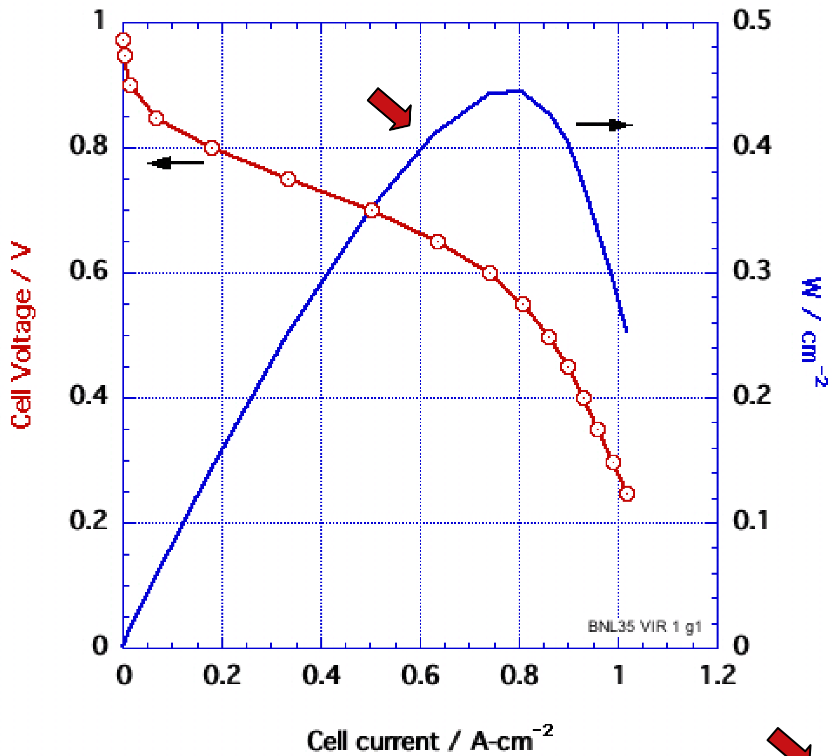
PGM Loading: 0.92 mg/cm²
'05 Target PGM Loading: 0.7 mg/cm²

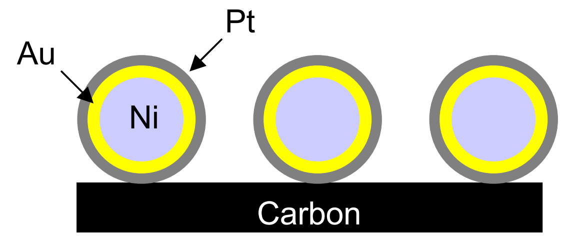
H_2/Air FC
BNL 32 (5 cm2) N1135
A: 0.050 mg Pt/cm² (2 % Pt-20% Ru/C, BNL)
C: 0.099 mg Pt/cm²(6.6 % Pt-18 % Pd/C, BNL)
H_2/air: 1.3/2.0 stoich

*** Catalysts prepared by R. Adzic et al., Brookhaven National Laboratory**
- BNL presentation Tuesday, May 24 at 1:35 PM (FC 17)

Ultra low Pt-content cathode catalysts* (cont'd)

BNL Cathode Catalyst: Pt: 1.44 w%; Au: 2.92 w%; Ni: 8.69 w% (13.0 % total metal/C)





BNL 35 , N1135, 5 cm2
A: 0.077 mg Pt/cm2 (20% Pt/C, ETEK)
C: 0.169 mg Total metals/cm²
(19 µg Pt; 37 µg Au; 0.113 mg Ni/ cm²)

Catalyst performance at 0.6 A/cm²

Composition	g Pt/kW cathode	g Pt+Au/kW cathode	g Pt/kW cell	g Pt+Au/kW cell
Performance	0.05	0.14	0.24	0.33

'05 Target PGM Loading: 0.7 mg/cm²

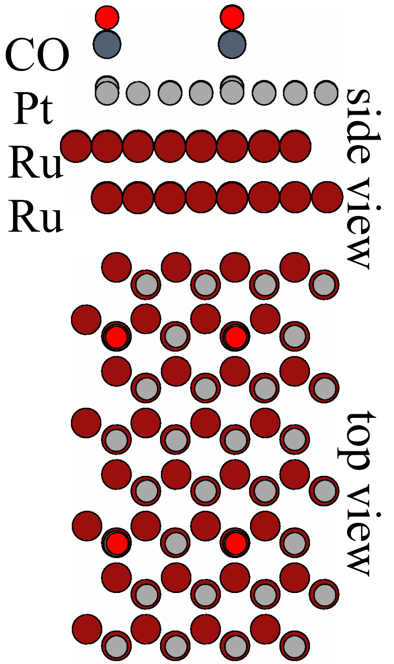
* **Catalysts prepared by R. Adzic et al., Brookhaven National Laboratory**

New Initiative: Modeling of Supports

- Atomistic-level modeling that accounts for the electron distributions at the interface should provide insight into support solutions.
- Quantum mechanicers from LANL Theoretical Division (Groups T-10 & T-12) have been engaged (leads: J. Kress & T. Redondo).
    - Methodology: Calcs will use the Vienna Ab Initio Simulation Package (VASP) based on the Generalized Gradient Approximation (GGA). The projector-augmented wave method is used to represent the inner core electrons and the valence electronic wavefunctions are expanded in plane waves.
- FY'05 Work Plan:
    - Model Pt monolayers on Pt, Pd and Ru.
    - Correlate surfaces with ORR activity.

Recent Work w/ Pt Monolayers*

Surface	Surface Energy	E_{ads}(CO)	
Pd(110)	1510 erg/cm^2	1.55 eV	
Pt/Pd(110)	1760 erg/cm^2	1.58 eV	poor
Ru(001)	2530 erg/cm^2	1.78 eV	
Pt/Ru(001)	1640 erg/cm^2	1.22 eV	good



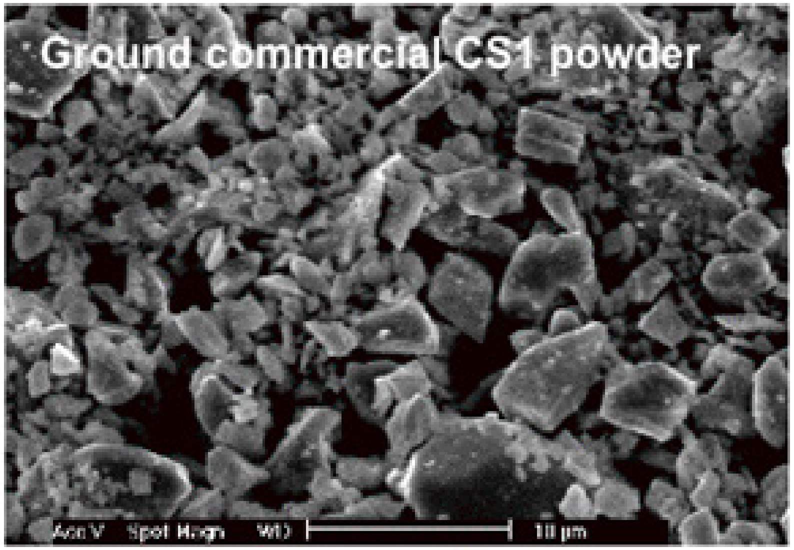
*J. E. Hammerberg, R. Ravelo, T. C. Germann, J. D. Kress, and B. L . Holian, AIP Conference Proceedings, *706*, 565 (2004)

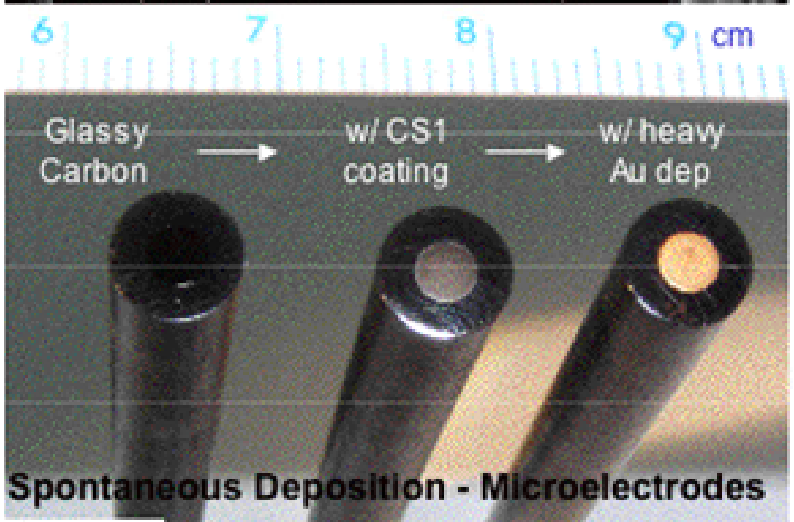
Second Approach: Ceramic Support (CS) Materials

(balance of milestones)

- Objective is to "replace" PGM support (BNL catalysts) with alternatives.
- Alternative supports must be:
  - Low-Cost,
  - Electrochemically Stable,
  - Electronically Conductive,
  - A suitable host for Pt monolayers and nanoparticles.
    - i.e., enable bulk-like activity (unlike carbon).
      - more than just Van-der-Waals interactions.
      - less than total assimilation (unless Group VIII support).
  - Limited Possibilities:
    - Focusing on refractory conductive ceramics.
      - few are electrochemically stable.
        - fewer yet promise to be suitable hosts.

A New Class of Ceramic Support (CS) Materials

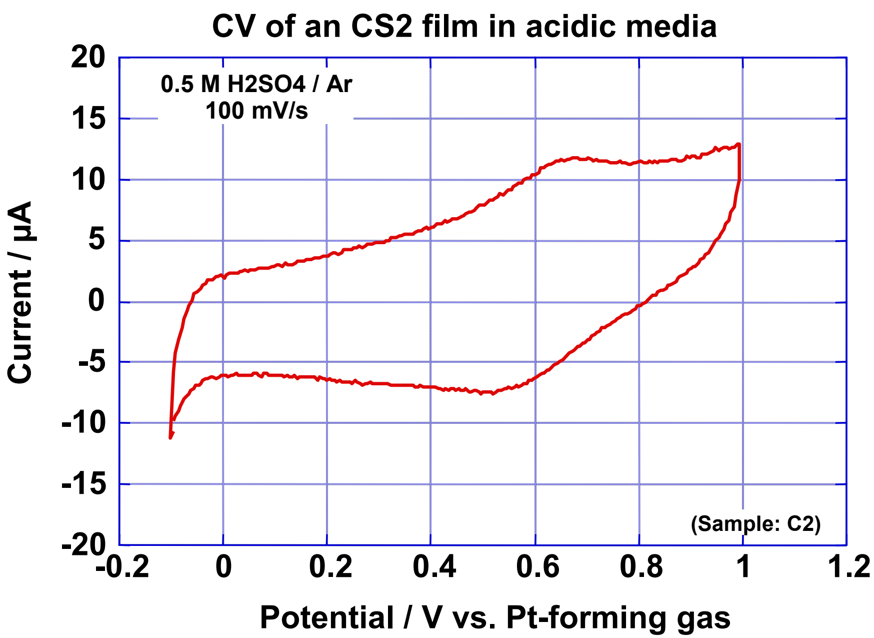




- Certain CS materials support spontaneous deposition.
  - So far have identified three (CS's 1-3) that support deposition.
  - Spontaneously deposits Pt, Pd, Au, Rh, …..
  - Catalyzation process:
    - Add solution.
    - Deposits in seconds.
    - Dry, rinse, or use as is.
- Other Pros:
  - Electrochemically stable
  - "High" dispersions even with low surface area supports.
- Cons:
  - Material availability and sizes

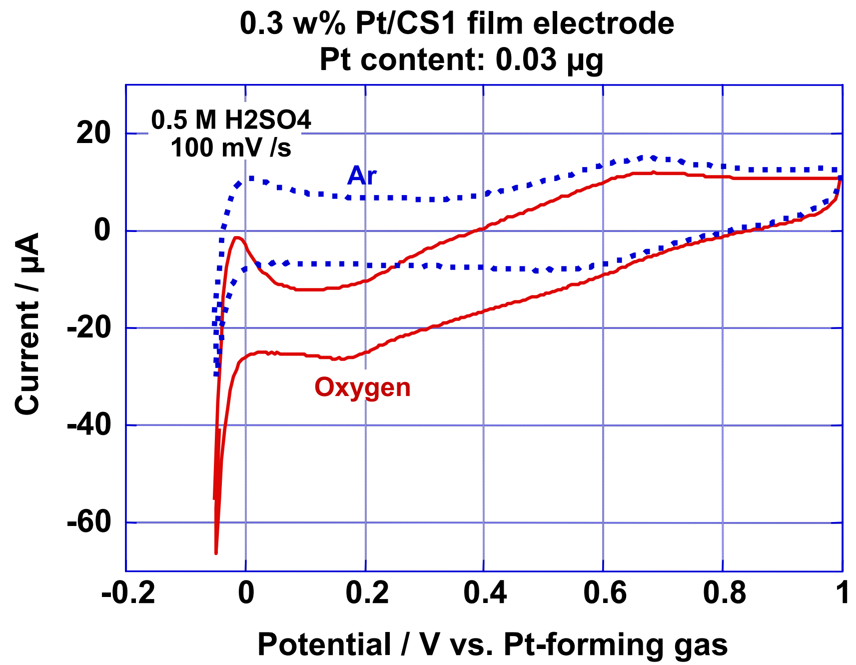
Sample CVs of CS's

Uncatalyzed CS2



--- Unusual CV for a Ceramic

Pt catalyzed CS1

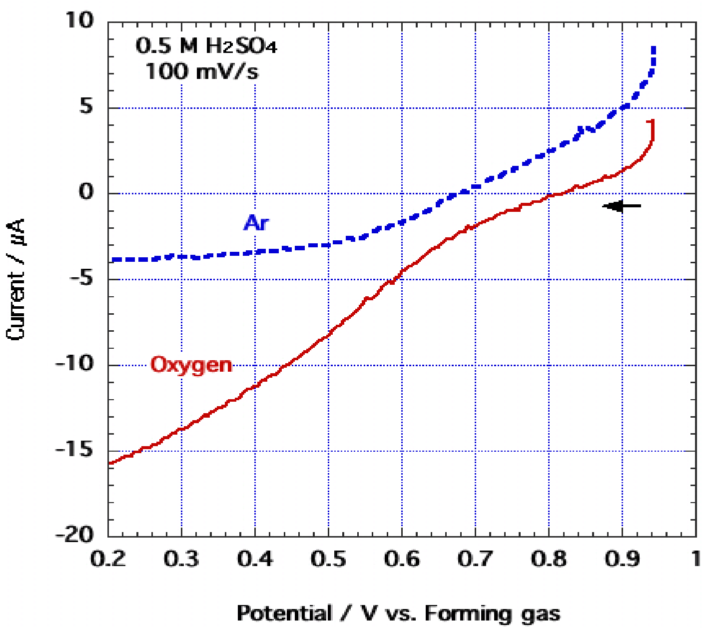


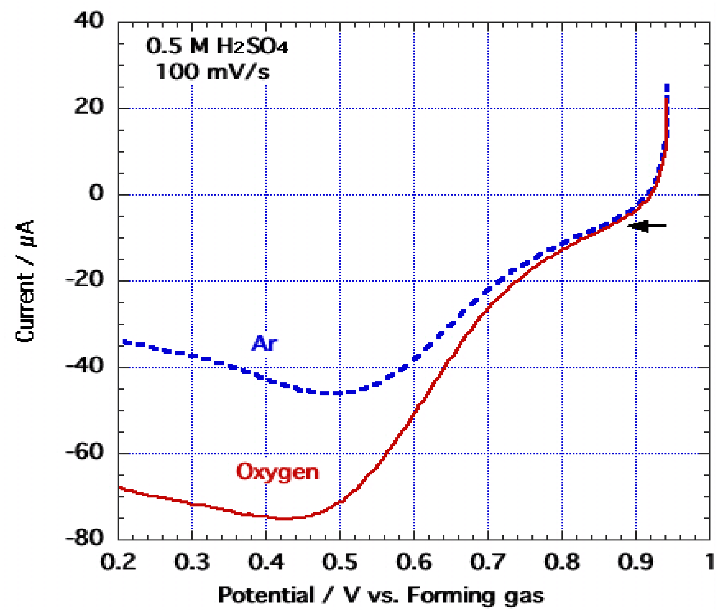
--- Off-set due to ORR superposition on baseline (Ar) scan.

Linear Sweep Voltammetry of CS films containing spontaneously deposited Pt

Comparison of CS1 & CS2 results

Maximum Pt content in each case: 0.4 µg.
Pt diameter: ~ 5 nm (from XRD)



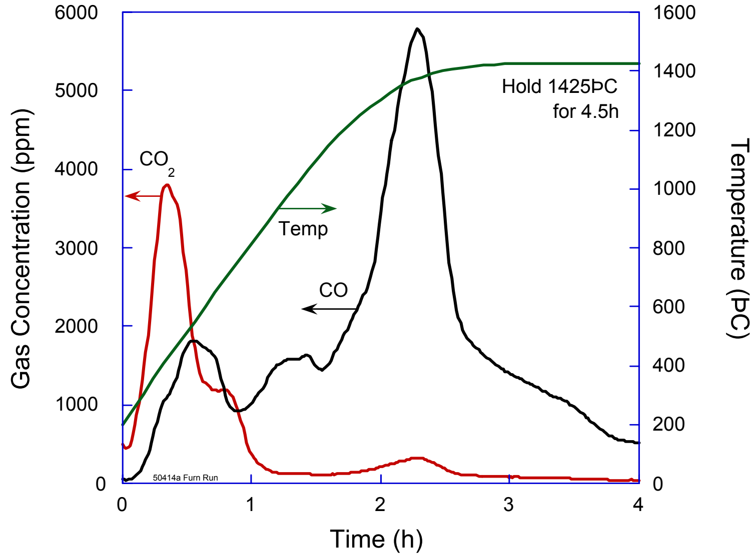


- Qualitative results, rotating-ring disk electrode (RRDE) experiments will be used to quantify ORR performance.
- Higher surface area CS's are needed to attain higher Pt dispersions and useful FC supports.
- Commercial CS3 powders are too impure for testing.

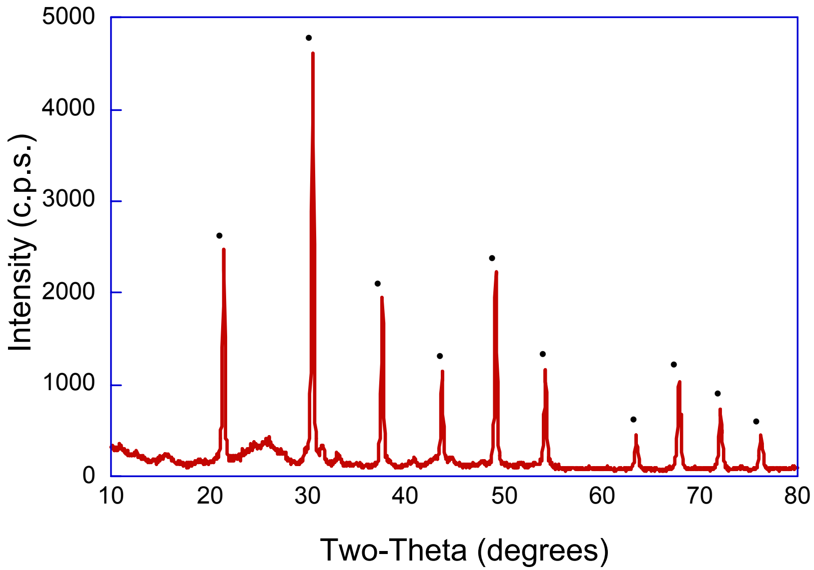
Synthesis of High Purity, High-Surface Area CS3

low-cost materials and process

HT Furnace Synthesis

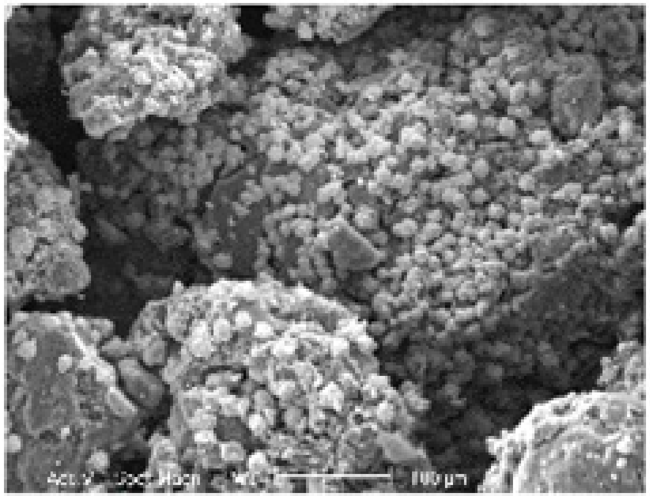


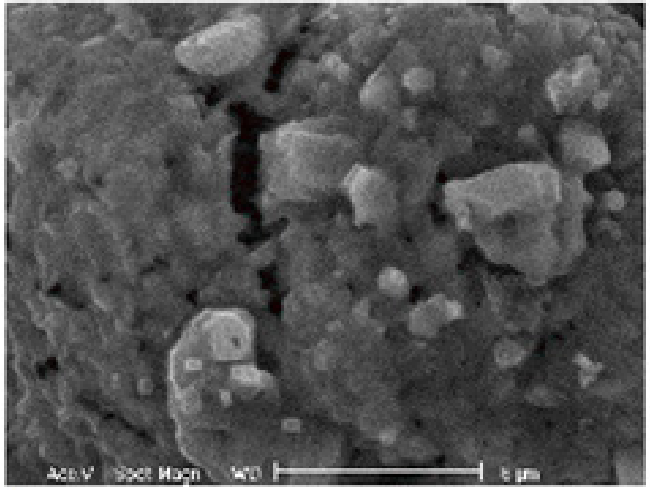
XRD of CS3 product



- ***~ 50 wt% CS3 on carbon.***
- ***< 1000 Å average diameter CS3 crystallites (vol. weighted).***
- ***Precursor is critical - otherwise no or minimal yield of desired material.***
- ***Source materials < $1/g.***
- ***First "success" - much yet to do wrt particle size.***

Characterization of Synthesized CS3



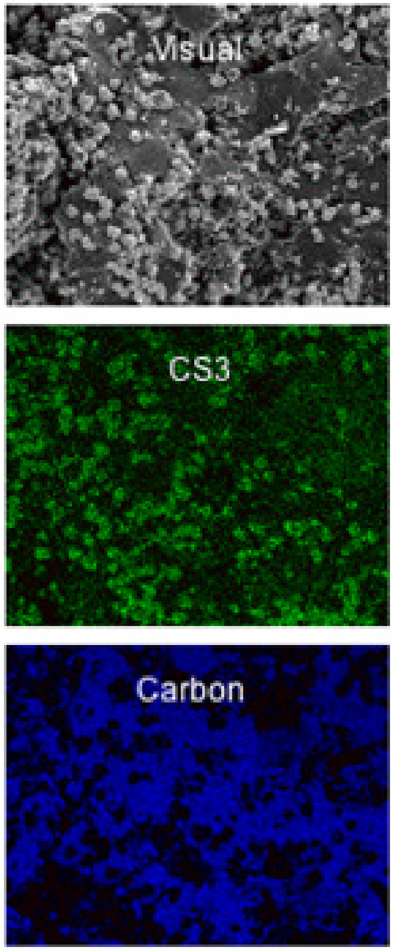


SEMs

- Sample appears to consist of ~ 10 micron crystalline agglomerates on a >> 100 micron substrate

Elemental Mapping →

- Indicates that the agglomerates are CS3 rich and the substrate is a carbon rich mixture containing CS3.
- "majority" of CS3 in the substrate?



Responses to ‘04 Reviewers’ Comments

- “Results are measurements on BNL catalysts - approaches to making improvements are scarce” (edited).
  - LANL “support” effort modest and just started up in ‘04.
  - Majority of “reportable” results were on BNL catalysts. Did not reflect total LANL effort.
- “Inadequate staffing/resources to pursue new materials development. Progress and ability to relate properties to scale-up will be lacking” (ed.).
  - New personnel on board that excel in materials development.
  - Good track record in developing technologies adopted by industry.
- “Efforts on low-cost catalyst support materials may not be most effective use of time by this group.” “Less focus on new materials development.”
  - New materials development very important for success of FCs.
  - Low-cost supports are actually an interesting scientific challenge - drives to the heart of what constitutes an active surface.

Why investigate new Supports?

- Possibly provides another tool (like alloying) to improve Pt performance
  - Manipulating metal-support interactions may improve:
    - *Dispersion & Utilization*
    - *Activity of highly dispersed particles*
    - *Durability*

Accomplishments and Milestone Progress

- Demonstrated long-term performances of low Pt-content (BNL) catalysts.
- Discovered ceramics that support spontaneous deposition (in addition to providing low-cost, conductivity, electrochemical stability, etc.).

Date	Milestone	Status
Dec 04	Complete 1000 hr with 0.2 mg Pt/cm^2 at the anode and 0.08 Pt mg Pt/cm^2 (BNL catalyst: 4% Pt-20% Pd) at the cathode	Completed 3000 hr
Feb 05	Complete 1000 hr with 0.02 mg Pt/cm^2 (BNL catalyst: 2% Pt-20% Ru) at the anode and 80 μg Pt/cm^2 (BNL catalyst: 4% Pt-20% Pd) at the cathode.	In progress (500 hr)
Mar 05	Predict by modeling and successfully synthesize the first versions of "doped" low-cost, stable and high surface area support materials.	"Half"Done (new direction)
Aug 05	Identify the most promising support candidates by testing of electrochemical stability and intrinsic activity.	Mostly Complete
Sep 05	Test first variations of "new" electrode structures.	Developing

Future Work

- Remainder of FY'05.
  - Continue FC testing of BNL catalysts.
    - Study particle size changes after long term operation.
  - Develop quantum mechanical models.
  - Screen other CS's for "activity."
  - Understand spontaneous deposition process.
  - Synthesize high-purity, high-surface area CS's.
  - Attain and test high Pt dispersions on CS's.
    - Quantify ORR performance using RRDE's.
  - Attempt first new electrode structures / processes.
- FY'06.
  - Continue optimizing CS materials and CS based catalysts.
  - Fuel cell testing of BNL and CS-based catalysts.
  - Develop advantageous CS-based electrode structures.
  - Expand theoretical models to CS's, etc.
  - Study catalyst surface characteristics and changes using X-ray absorption techniques (S. Conradson).

Publications

1. K. Sasaki, J. X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R. R. Adzic, Ultra-low platinum content fuel cell anode electrocatalyst with a long-term performance stability; *Electrochim. Acta*, **49**, 3873 (2004).

2. K. Sasaki, M. Vukmirovic, F. Uribe and R. Adzic, Ultra-low Pt Loadings Electrocatalysts forH_2/Co and Metahanol Oxidation. 206th Meeting of The Electrochemical Society. Hawaii, Oct. 2004. Abstract No.1502.

3. F. A. Uribe, T. Rockward, J. A. Valerio and R. R. Adzic, “Performance of PEMFC Electrodes Containing Low-Pt Loadings”. 206th Meeting of The Electrochemical Society. Hawaii, Oct. 2004. Abstract No. 1857.

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)