2006 DOE HYDROGEN PROGRAM REVIEW
May 16-19, 2006, Washington, DC

Novel Approach to
Non-Precious Metal Catalysts

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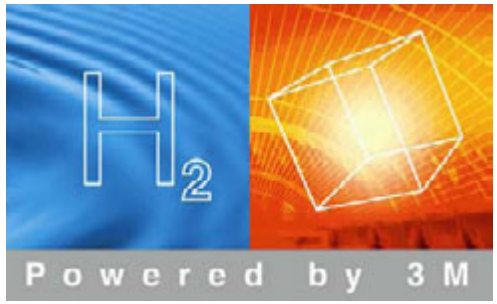
3M Company
May 17, 2006



Project ID#: FC12

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: September 1, 2003
- Project end date: August 31, 2007*
- Percent complete: ~75%

(* Revised end date subject to DOE approval)

Budget

- Total Project funding: $3.6 million
  - DOE: $2.9 million
  - Contractor: $0.7 million
- Funding received in FY05: $897 K
- Projected funding for FY06: $970 K

Barriers

- B. Cost
- C. Electrode Performance

(Technical targets: See next slide)

Partners/Collaborations

- Dalhousie University (subcontractor)
  - Prof. J. Dahn; **High-throughput catalyst synthesis and basic characterization**
- Brookhaven National Lab
  - Dr. X.-Q. Yang and Dr. W.-S. Yoon; **X-Ray Absorption Spectroscopies**
- University of Missouri – Kansas City
  - Prof. D. Wieliczka; **UPS at University of Wisconsin Synchrotron Radiation Center**
- INRS-Energie, Materiaux et Telecommunications
  - Prof. J-P. Dodelet; **EXAFS and UPS characterization of the "model" catalyst**

Objectives

Goal: *Develop new, lower-cost, non-precious metal (NPM) cathode catalysts for replacement of Pt in PEM fuel cells.*

Objectives:

- Reduce dependence on precious metals (Pt).
- Perform as well as conventional precious metal catalysts currently in use in MEA's.
- Cost 50% less compared to a target of 0.2 g Pt/peak kW.
- Demonstrate durability of >2000 hours with <10% power degradation.

Current DOE Targets (from HFCIT Multi-Year R&D Plan):

	Non-Pt Catalyst Activity **per volume** of supported catalyst at 800 $mV_{IR\text{-}free}$
2005	50 A/cm^3
2010	> 130 A/cm^3
2015	300 A/cm^3

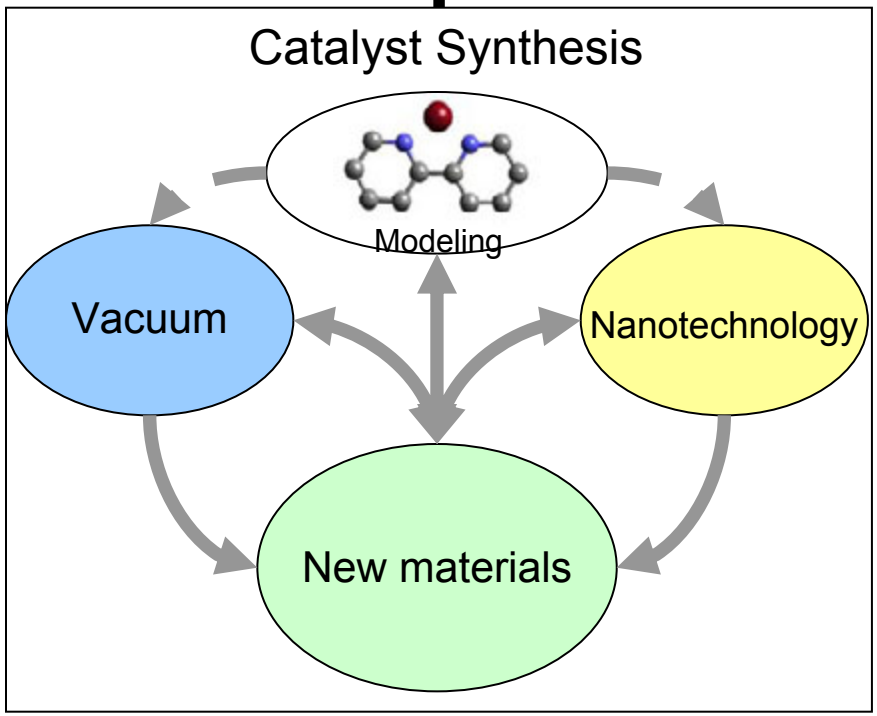
Specific Objectives for 2006:

- Combine most promising precursors, substrates, application procedures, and thermal treatments for best synergetic effects.
- Achieve interim performance milestones.
- Start testing for durability, peroxide (RRDE).
- Expand effort to identify possible active sites (advanced analytical, modeling).

Approach

Physicochemical Characterization

- XPS
- XRF
- SEM
- XRD
- Modeling
- Ellipsometry
- XAS (Brookhaven National Lab)
- SIMS
- UPS



Functional Characterization

- Fuel Cell
  - 50 cm^2 (performance and durability)
  - Segmented
- Gas Diffusion Electrode
- RRDE

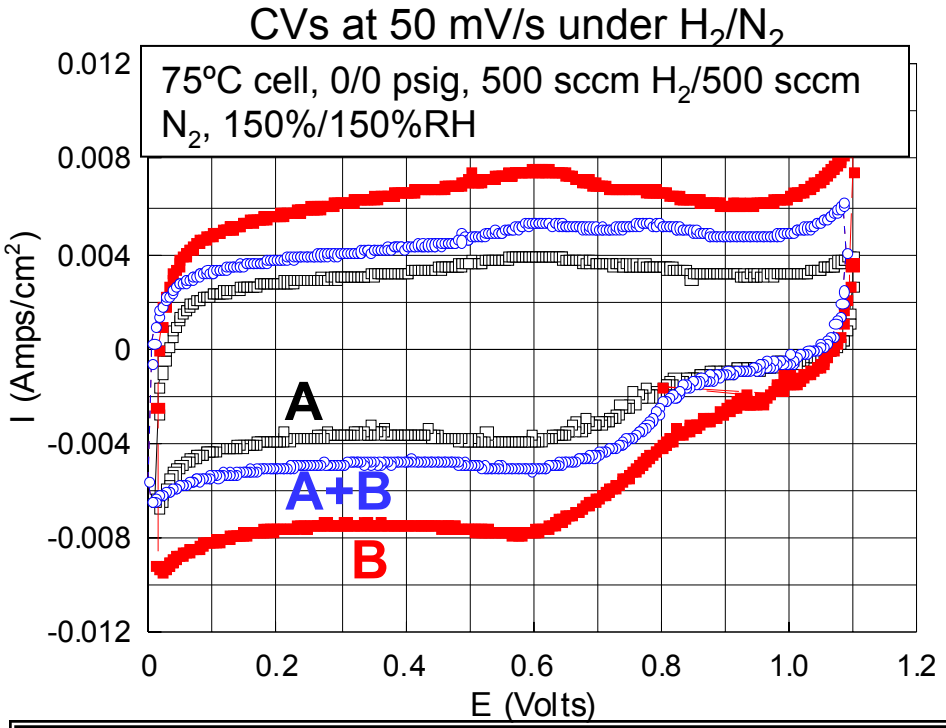
- Catalyst synthesis is carried out via two **complementary and interactive** approaches both readily **scalable** to pilot plant level: **Vacuum Processes** and **Nanotechnology.**
- Extensive physicochemical analytical characterization, including modeling work, is carried out both at 3M and in collaboration with other institutions when appropriate.
- Functional characterization chiefly performed in 50-cm^2 FC; other techniques as required.

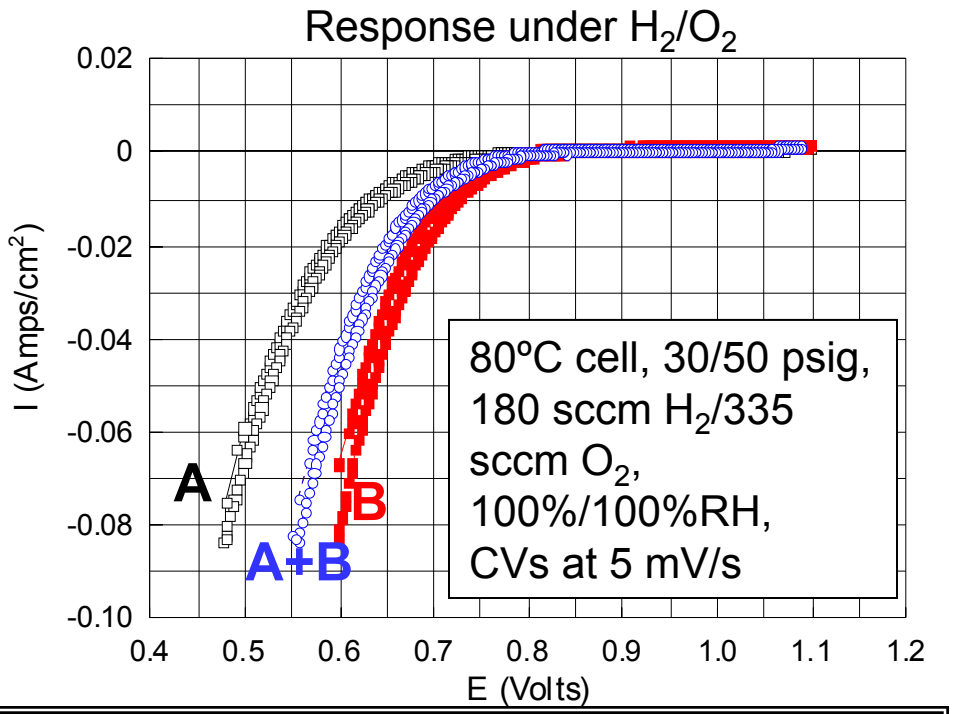
Technical Accomplishments

- Achieved performance exceeding state-of-the-art NPM catalyst activity reported in the literature, with 50-cm^2 samples made by scalable processes.
  - Volumetric current density of 19 A/cm^3 surpasses 2004 status value reported by DOE (8 A/cm^3 at 0.8 V).
  - Met Interim Performance Milestones #2 (0.08 A/cm^2 at 0.6 V) and #3 (0.1 A/cm^2 at 0.7 V).
- Fabricated new higher surface area, thermally stable substrates for use with the vacuum approach. Achieved activity surpassing the best previous result by over an order of magnitude.
  - Integration of the two synthetic approaches is underway.
- Made advances in testing, characterization, and modeling that provide valuable feedback for materials development.
  - Introduced routine durability testing and initiated RRDE studies.
  - Expanded UPS/XAS catalyst characterization to include the “model” catalyst.
  - Modeled catalytic site in more realistic catalyst synthesis environment.

Nanotechnology – New Catalyst Development

- During the past year, approximately 90 nanotechnology samples, falling into several major families, were synthesized and tested.
- The best ORR activity was achieved with precursors **A** & **B**, where **A** & **B** are structurally related isomers.
- The oxygen activity of compounds **A**, **B**, and **a combination of A & B** follow in order of their apparent surface area.

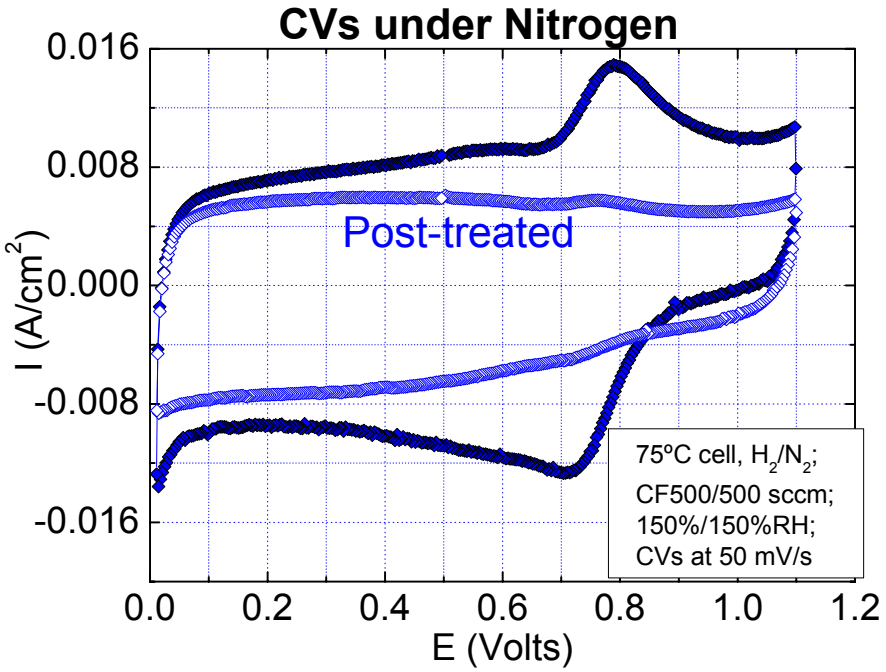


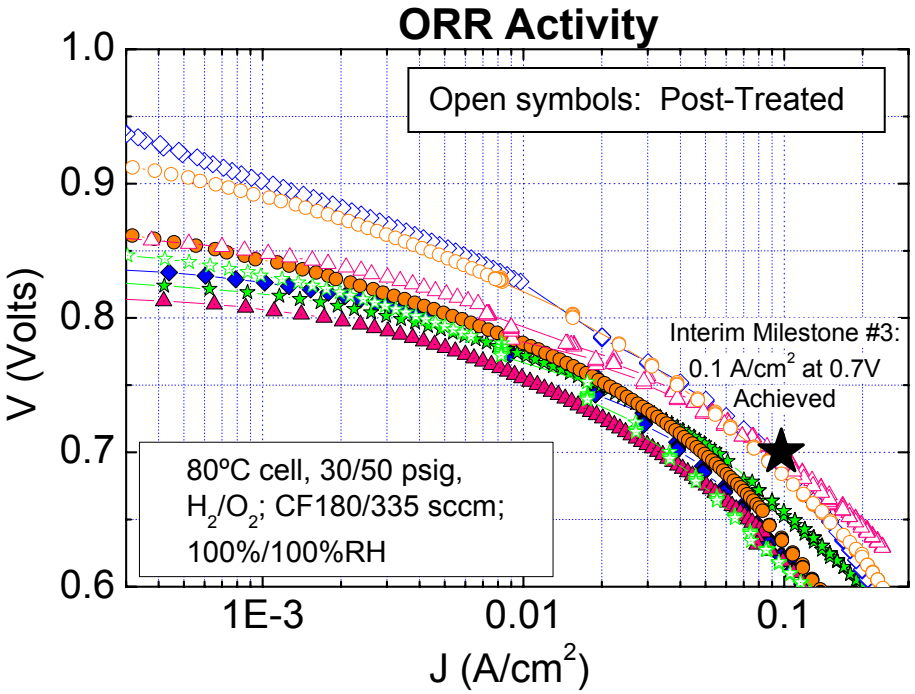


The performance of **compound B** fulfilled Performance Milestone #2: 84 mA/cm^2 at 0.6 V.

Nanotechnology – New Catalyst Development

A family of catalysts focused around **precursor B,** subjected to additional post-treatment, showed the best ORR activity measured on this project to date. Several samples in this family met performance milestone #3 (0.1 A/cm^2 at 0.7 V), indicating a large processing window.

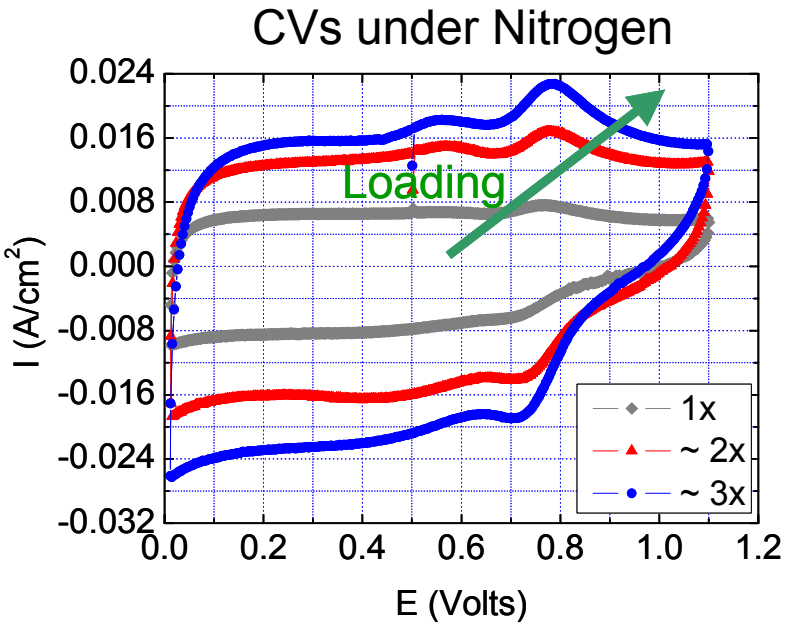


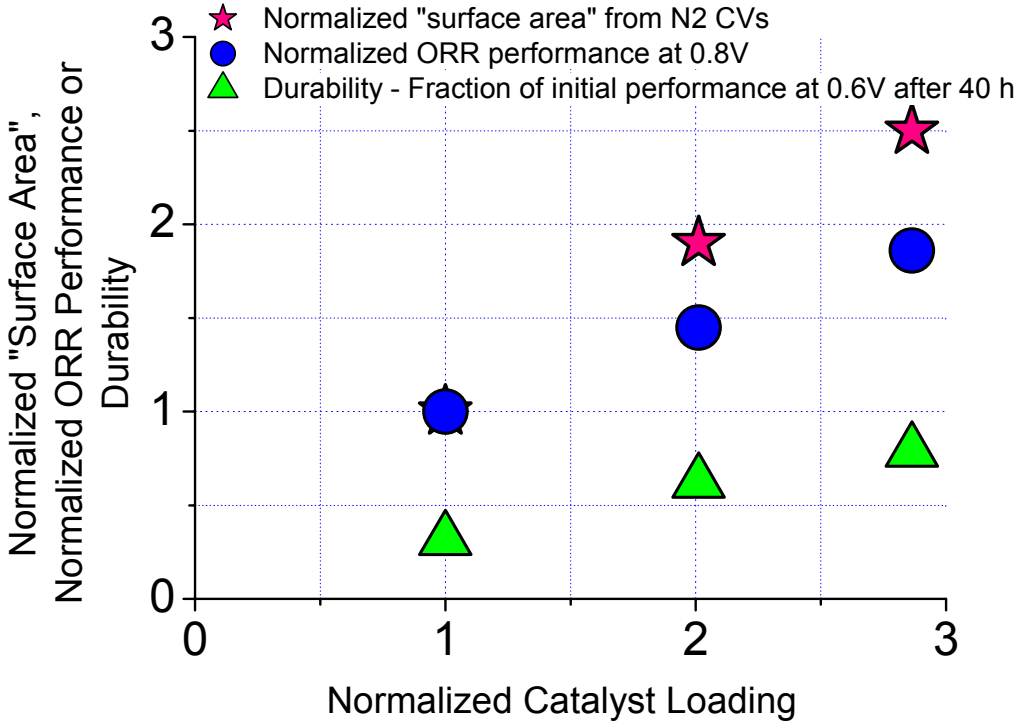


- For post-treated samples, higher ORR activity was produced while lower surface area was measured indicating that the ORR centers of the post-treated sample are more active.
- Best performing catalysts were tested under a variety of test conditions – including air vs. oxygen, gas flow rate, gas pressure, cell temperature, and humidification. The relative performance of the catalysts did not substantially change under these different conditions.

Nanotechnology – Effect of Catalyst Loading

The effect of catalyst loading on performance and durability was examined for the best performing samples.

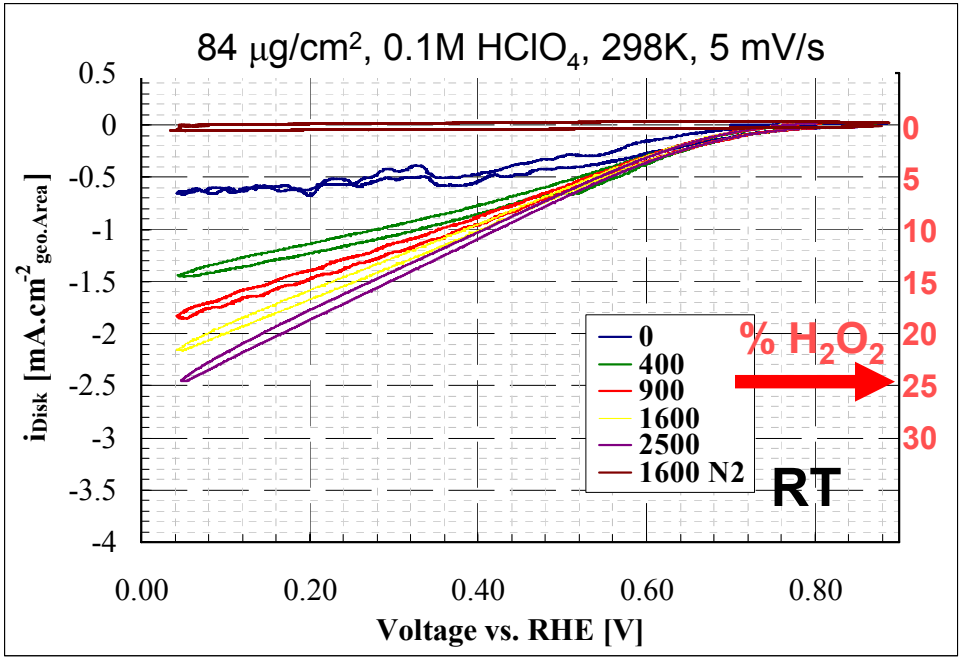


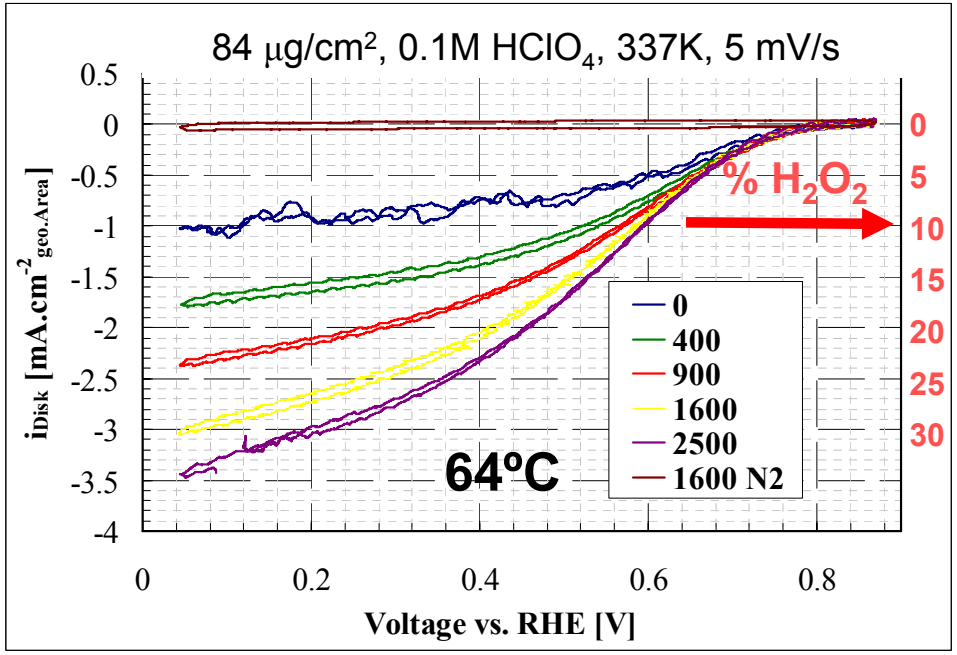


- Evidence of the increased loading is seen in the CVs taken under nitrogen.
- A strong correlation is seen between the catalyst loading and apparent catalyst surface area seen in the N_2 CVs, the ORR performance, and performance durability.
- Durability tests are routinely carried out on all the better performing catalysts.
- Durability testing performed under air—more realistic FC operating condition.
- Majority of decay happens in first 10 hours, after which the performance levels out.

Nanotechnology – RRDE Measurements

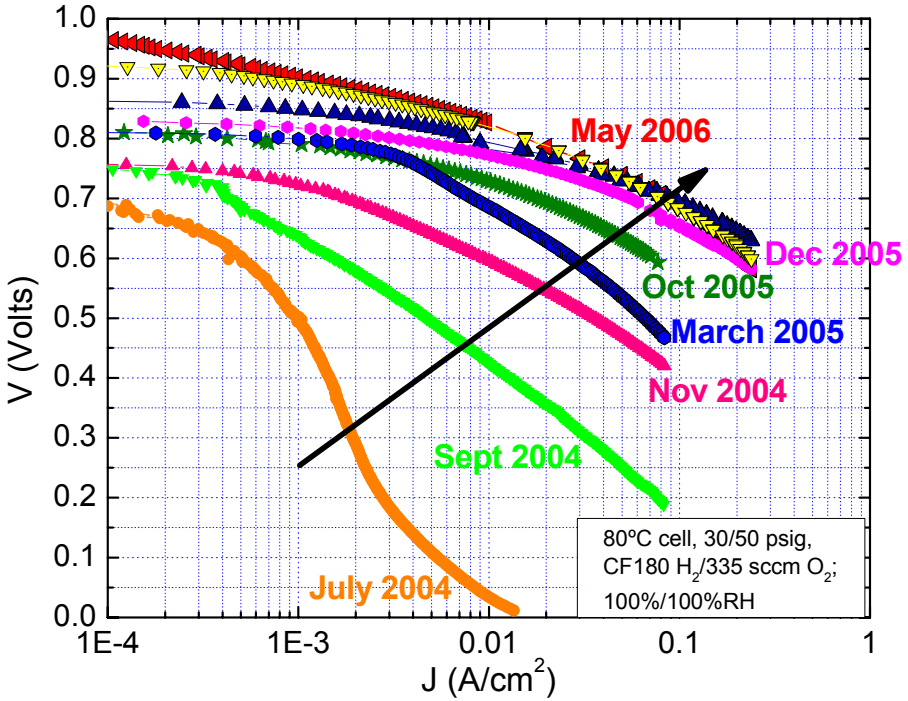
As planned, RRDE studies were carried out on catalysts that showed the best performance in a 50-cm^2 fuel cell.

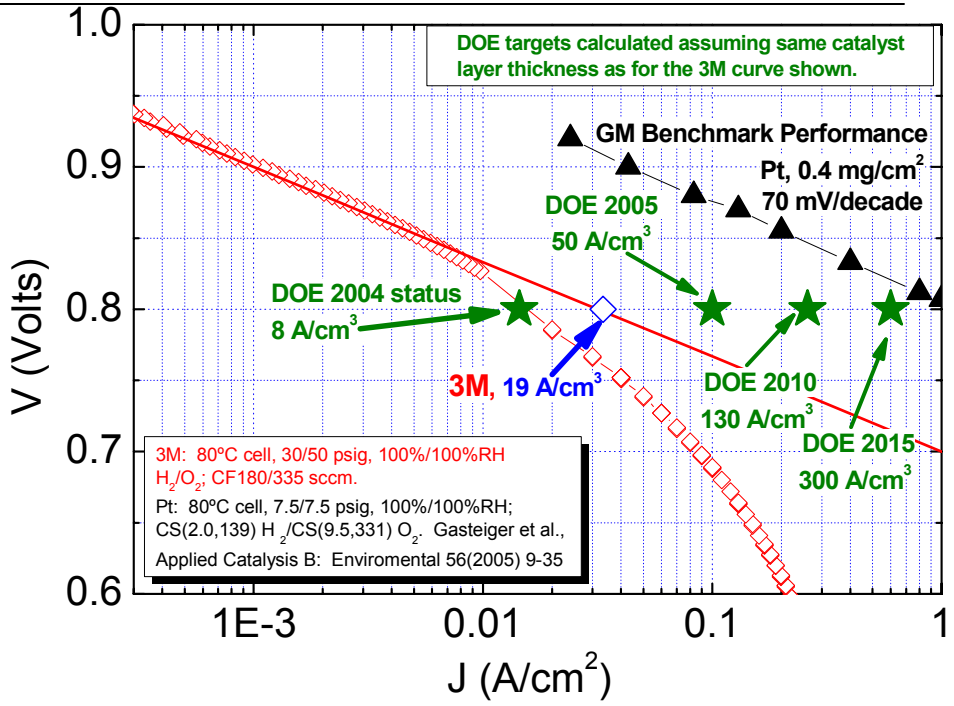




RRDE measurements on Catalyst **B** show a large dependence of the ORR kinetics on the temperature. As a consequence, the peroxide production falls from 25% at RT to only 10% at 64ºC. The corresponding number of electrons exchanged increases from 3.5 to 3.8.

Nanotechnology – Progression and Comparison to DOE Targets





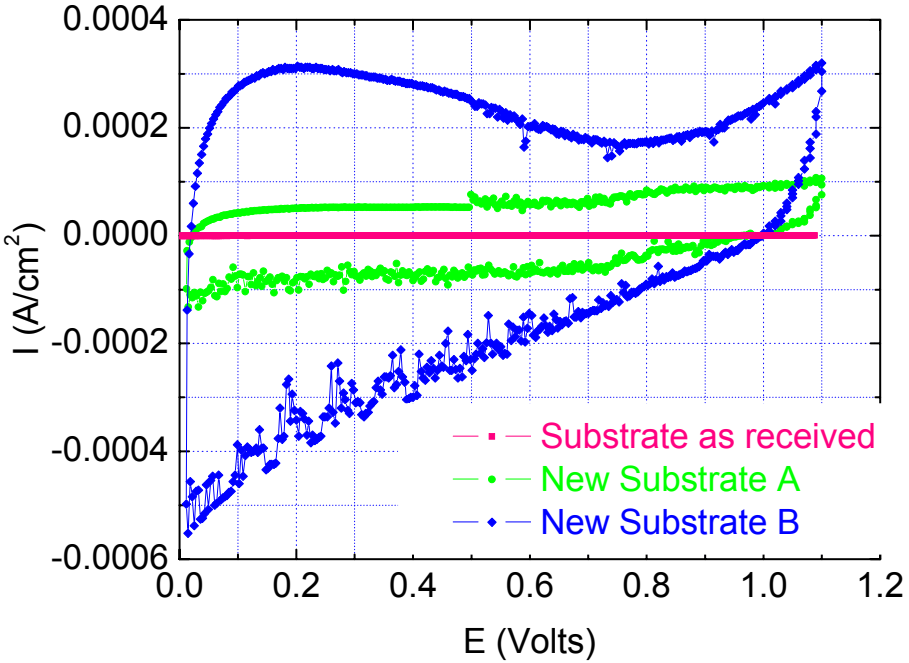
- The best performing catalysts from classes of materials and/or processes are presented above.
- From the beginning of the effort, ORR activity measured on nanotechnology samples has improved substantially (three orders of magnitude at 0.7 V) and is among the best reported in the literature when tested in a real fuel cell.

- Performance of best 3M nanotechnology sample has a Tafel slope similar to Pt allowing for direct comparison of activity in the kinetic region.
- Volumetric current density exceeds state-of-the-art value reported by DOE (8 A/cm^3 at 0.8 V).
- Ink formulation and coating optimization could provide gains in volumetric activity.

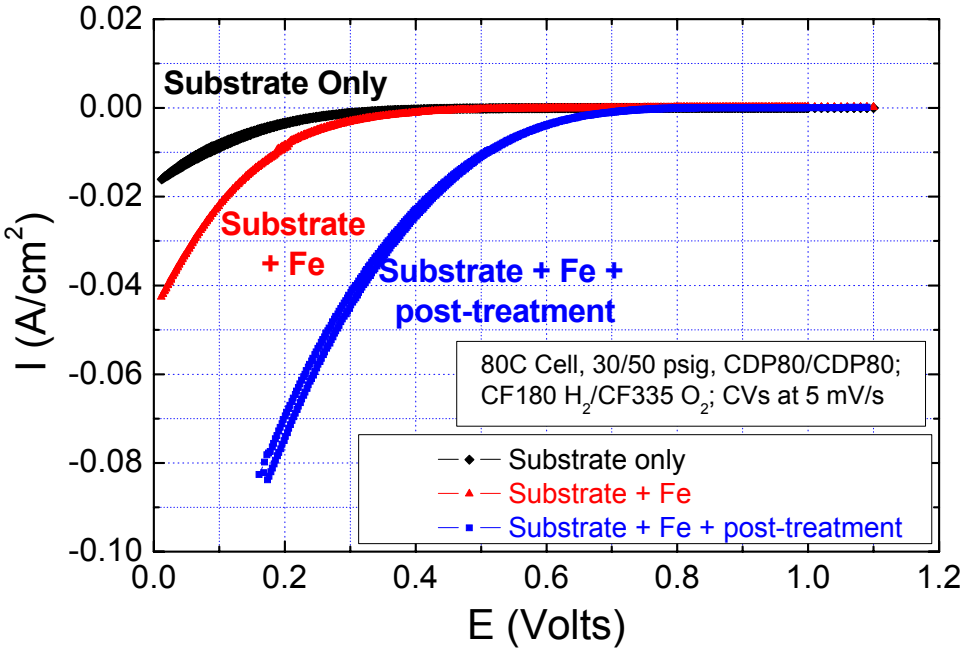
Vacuum Processes – New Substrates

New higher surface area, thermally stable substrates (developed at 3M expense, utilizing 3M proprietary technology) were introduced.

CVs under nitrogen of the new "uncatalyzed" substrates show a huge **increase in surface area**



ORR activity new substrate A only, new substrate A with vacuum deposited Fe catalyst, and the post-treated catalyst.

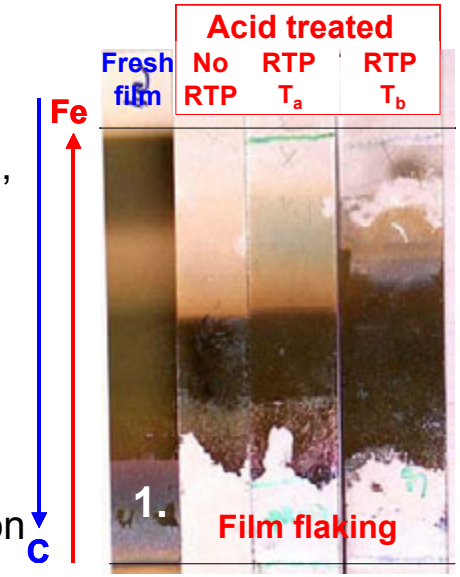


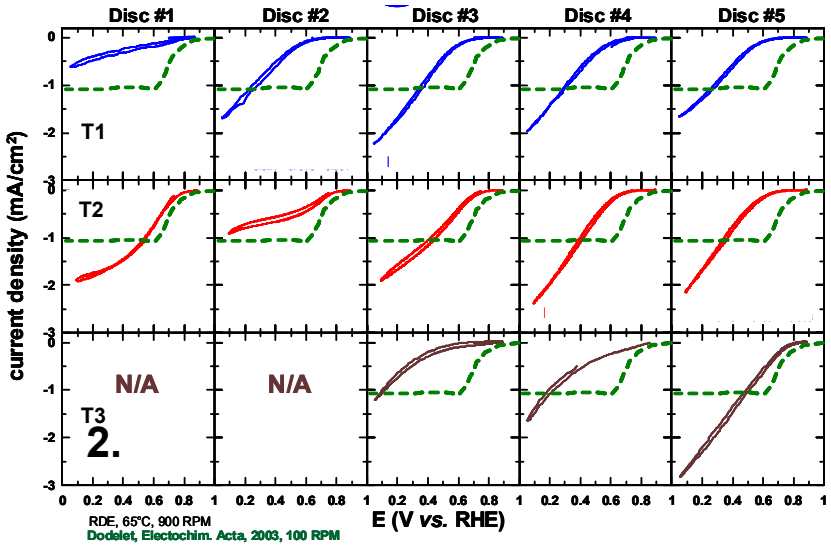
- **Performance of post-treated sample is significantly better than any previous result from the vacuum approach.**
- Best performance result shown above is with substrate A. Higher surface area substrate B may provide further gains.

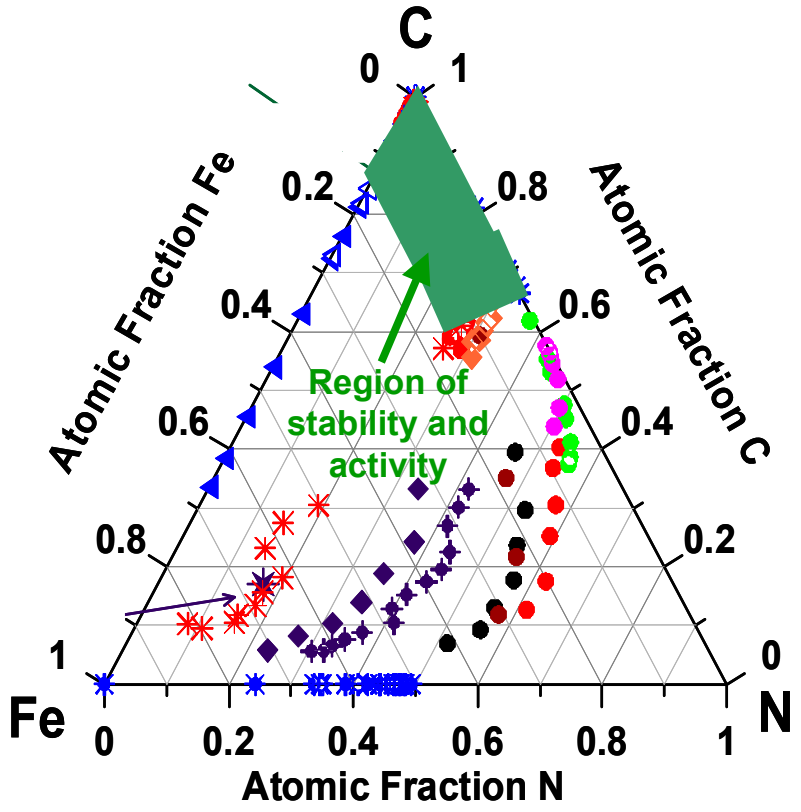
Vacuum Processes – Catalyst Stability and Activity

(Dalhousie University)

- Using combinatorial sputtering, range of compositions on a single glass slide were prepared, thermally treated in rapid thermal processor (RTP), and immersed in 0.5 M H_2SO_4 for 7 days to determine stability.
- Stable compositions were produced on glassy carbon disks and tested by RDE.



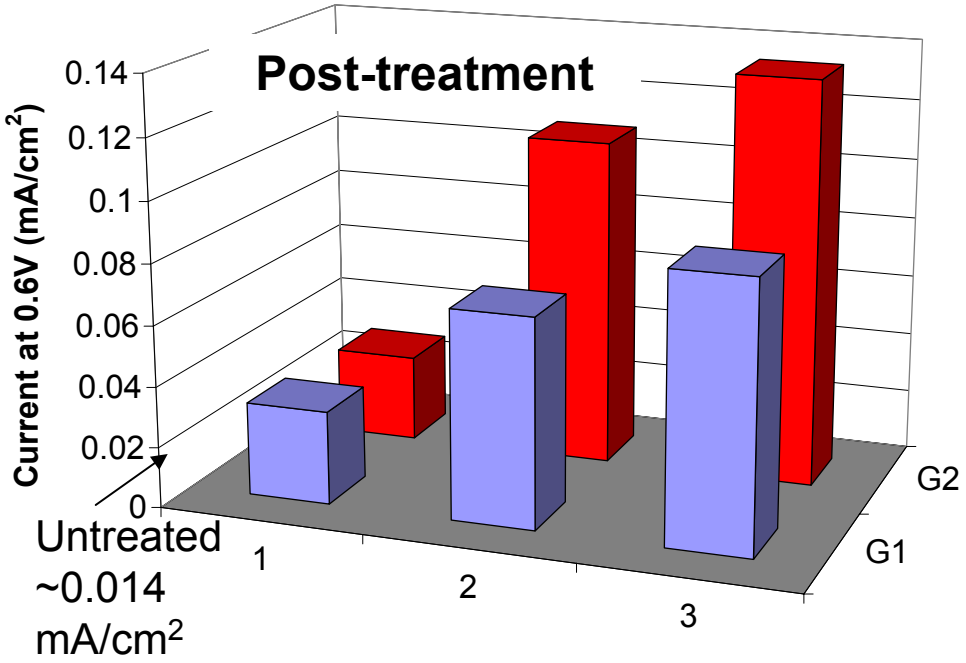


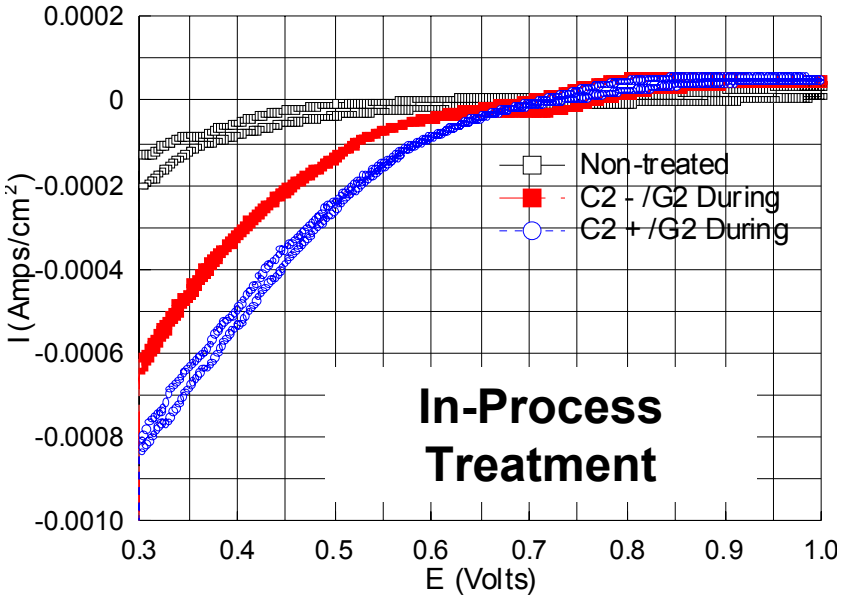


From these tests, the area of stability and activity of vacuum-deposited Fe (or Co) -C-N materials has been determined.

Vacuum – Post- and In-Process Treatment

Motivated by the achievement of Milestone #1 (eliminate large impedance), a series of samples from a single Process A CNxFe coating run were thermally treated at three different conditions in two different nitrogenous gases.

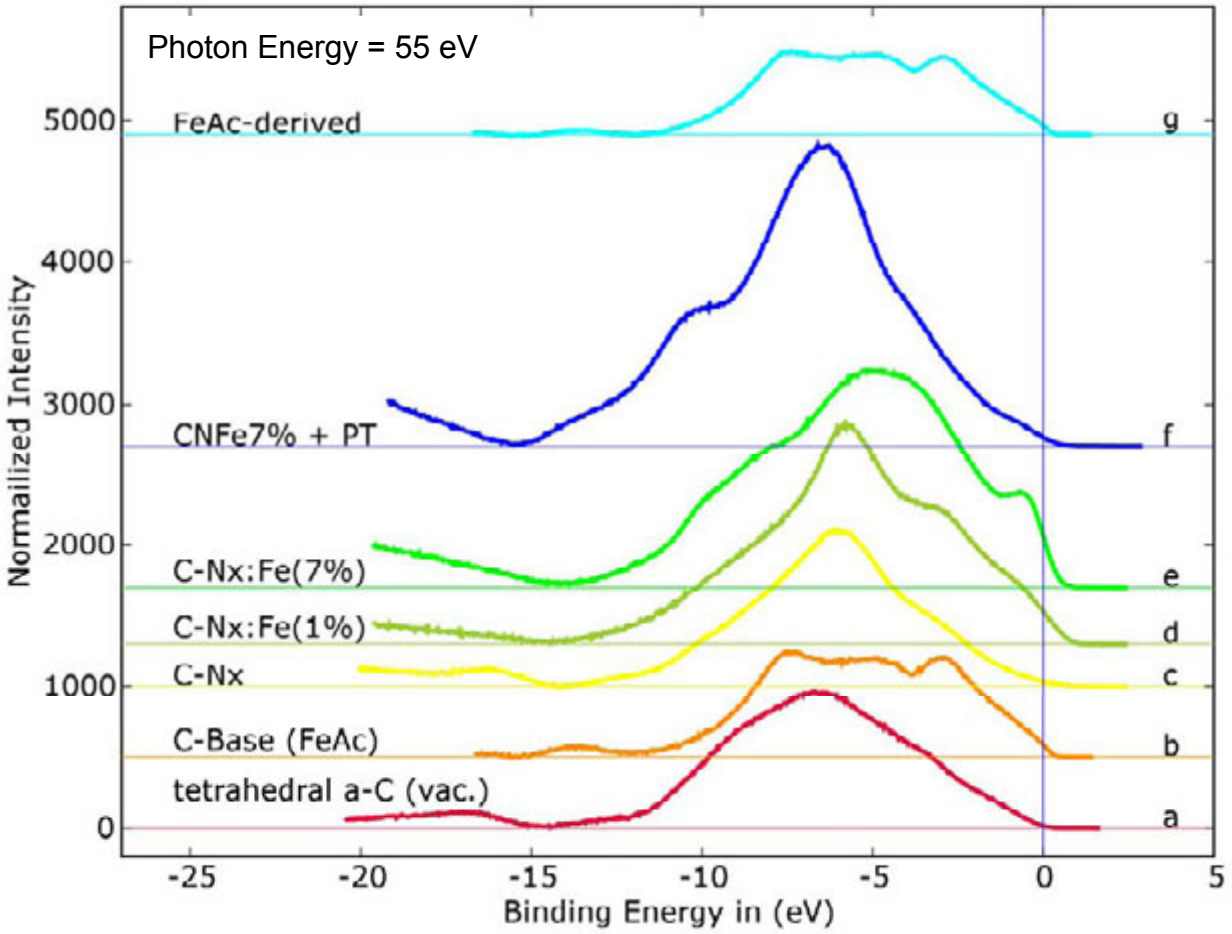




Equipment modifications were made for thermal treatment of the catalyst during the vacuum deposition process. Samples deposited in this fashion give **performance of similar magnitude to samples post-treated under equivalent conditions**. In-process treatment conditions were identified that reduce impedance and increase performance.

Characterization – UPS – 3M Vacuum Deposited vs. Model Catalyst (Dodelet)

Photoelectron Spectra – valence e^- density of states



- FeAc-derived catalyst provided by Prof. J-P. Dodelet
- UPS data produced in collaboration with Prof. D. Wieliczka, U of Missouri-Kansas City at the U of Wisconsin Synchrotron Radiation Center

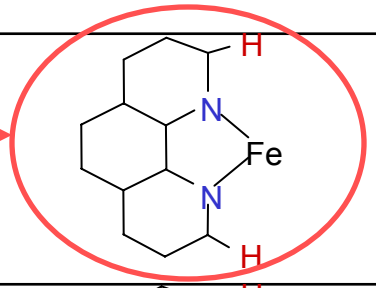
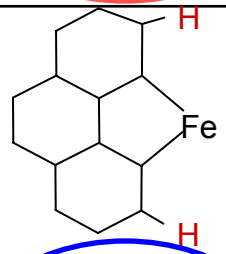
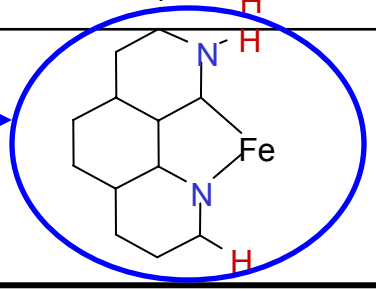
- Electron structure differs in vacuum deposited vs. iron acetate derived catalyst.
- Fe in iron acetate (FeAc) derived catalyst is low and difficult to detect. The spectra of the FeAc catalyst (g) is similar to the starting carbon powder (b).
- Post treatment alters electron structure (f). Fe states near the Fermi level are reduced.

Modeling – Effect of Hydrogen

The relative energy of the several C-N-Fe compounds was calculated both in the presence and absence of hydrogen.

Lowest energy with hydrogen present

Lowest energy in the absence of hydrogen

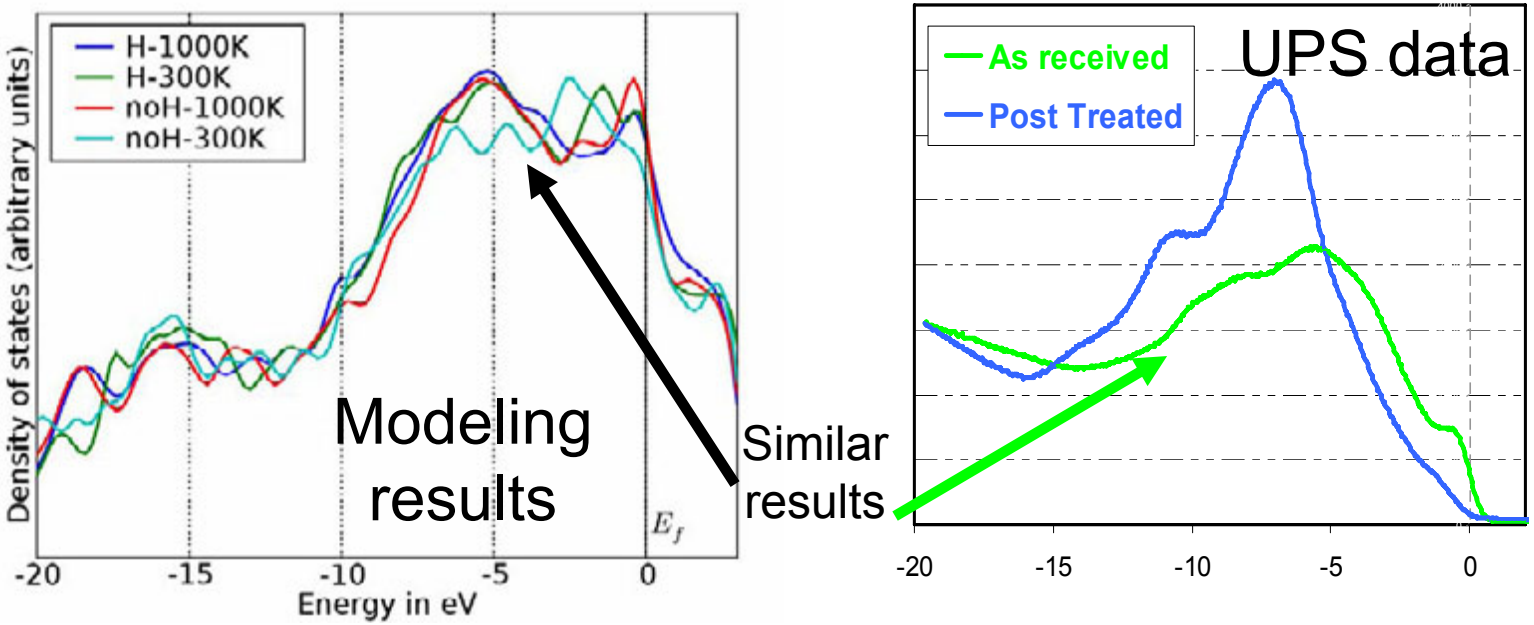
Structures	Relative Energy (eV) with hydrogen (without hydrogen)
	0.0 (0.0)
	+2.01 (-0.12)
	+0.33 (-0.99)

The presence or absence of hydrogen affects the lowest energy binding site of Fe on nitrided graphene edge. With hydrogen, the Dodelet "model" catalyst is the lowest in energy. The results of this study have been published in *J. Phys. Chem. B*[*]

[*] M. Jain, et al., *J. Phys. Chem. B,* 110 (2006) 4179-4185

Modeling – Amorphous Structures

- Examined amorphous structures formed by a liquid quench method using *ab initio* molecular dynamics (VASP). Structures formed by liquid-quenching are known to be similar to the ones obtained using vacuum deposition processes*.
- Considered Fe in CN_x disordered systems formed during the vacuum deposition processes.



- While the overall density-of-state curves calculated via modeling look similar, there are differences in the states around the Fermi level depending on the presence or absence of hydrogen and the quench temperature.
- Both the high and low temperature quench compare well with as-received experimental data. High temperature quench does not match with the experimental post-treated.

* A. R. Merchant, et al., Phys Rev B, **65**, 024208 (2002)

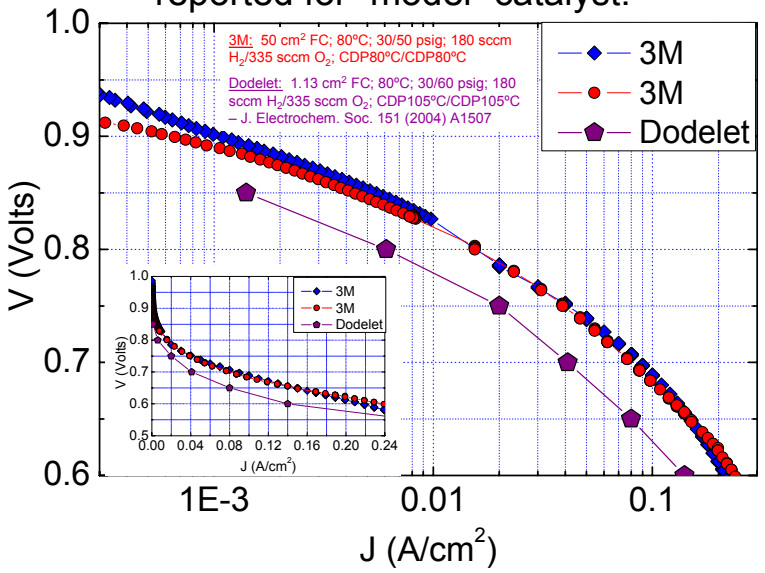
Future Work

Remainder of project: Produce new, better-performing more durable catalysts and identify the catalytic sites.

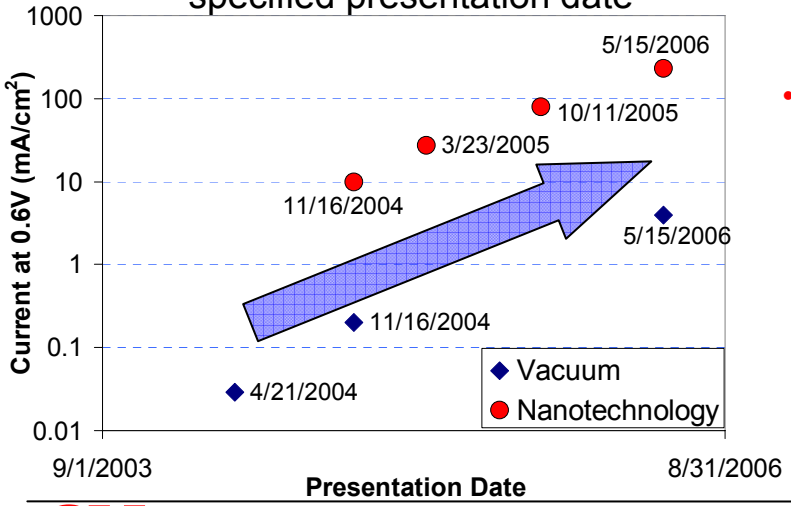
- Direct the synthetic effort towards achieving Milestone #5 performance (0.1 A/cm^2 at 0.8 V in 50-cm^2 fuel cell, which is equal to the DOE 2005 volumetric activity target).
- Combine the two synthetic processes to achieve more active and durable catalysts.
- In the nanotechnology area, combine the most promising precursors, appropriately pretreated substrates, application procedures, and thermal treatment processes for best synergetic effects.
- In the vacuum processes, aided by advanced characterization, modeling and process parameters from the nanotechnology area, exploit the new, higher surface area substrates to make more active catalysts.
- On the fundamental level, identify with more certainty the possible active sites via modeling based on advanced experimental studies of the catalyst.
- For best performing catalysts, continue to test durability in fuel cell operation, peroxide (RRDE, fluoride), etc.

Summary

Performance of 3M NPMC surpasses results reported for "model" catalyst.



Current at 0.6 V measured in 50-cm² FC on specified presentation date



- Project is aimed at developing new, high catalytic activity non-precious metal catalysts to replace Pt and lower the cost of PEM fuel cells.
- Volumetric current density exceeds state-of-the art value for NPM catalysts reported by DOE.
- Current response has improved an order of magnitude in the past year on both vacuum and nanotechnology approaches. Interim performance milestones achieved.
- New test methods implemented, including rotating-ring disk and durability testing.
- Strong interactive advanced characterization and modeling complement the synthetic effort.
- Strong, fully-integrated collaborations supplement 3M expertise and lead to fundamental understanding of catalyst.
- Ten publications and presentations, including three invited lectures and two published papers. Three patent applications.
- **Today, 3M's catalysts are among the best performing NPMC tested in a real fuel cell.**

Non-Pt Catalyst Activity per volume of supported catalyst at 800 $mV_{IR\text{-}free}$ (A/cm^3)			
3M		DOE	
Measured	Tafel-Slope Extrapolated	2004 Status	2005 Target
8	19	8	50

Back-up Slides

Response to Reviewers' Comments

Majority of comments from reviewers were positive and in line with planned activities and achieved results.

- *"Outstanding and comprehensive approach covering all aspects of catalyst discovery: theory, synthesis/experiment, and reduction to practice."*
- *"Significant progress has been achieved in improving initial activity levels."*
- *"Excellent collaboration with university partners and clear indication of what they are contributing to project."*
- *"Technology transfer is inherent to the project, since 3M is ultimately capable of commercializing the technology if technical and economic viability is proven."*

Reviewers' comments specific to future work covered activities that were already planned.

- *"Catalyst activity is still low, despite improvements, relative to both the Dodelet results on similar materials as these and to platinum."* – Performance has improved and now exceeds the best results reported in the literature (Dodelet). Future work is primarily focused on further improvements to catalytic activity as planned.
- *"Needs stronger durability component." "Incorporate RRDE measurements to check for peroxide."* – Initially, performance was too low to merit resource-intensive tasks such as durability testing and RRDE. The focus was on improving catalytic activity. Now that catalytic activity has improved, durability studies are routinely performed at 3M and RRDE measurements (Dalhousie University) have begun.

Other comments included:

- *"No real evidence that the synthesis process is scaleable at low cost"* – From the onset of a new synthetic route, only scaleable and economical processes are being considered based on similar 3M manufacturing experience.

Publications and Presentations

1. E. B. Easton, T. Buhrmester, J. R. Dahn, “Preparation and Characterization of Sputtered Fe(1-x) N(x) Films,” *Thin Solid Films,* 493 (2005) 60 – 66.
2. M. Jain, S.-H. Chou, A. Siedle, “In Search for Structure of Active Site in Iron-Based Oxygen Reduction Electrocatalysts,” *J. Phys. Chem. B* **,** 110 (2006) 4179-4185.
3. R. Atanasoski, “Recent Advances in the 3M MEA Technology for PEMFC: The Catalysts,” Departmental Seminar, Chemical Engineering Department, Univ. of South Carolina, Columbia, SC, April 21, 2005.
4. 2005 DOE Hydrogen Program Review - Washington, DC - May 23 - 26, 2005.
5. VII.C.9 - Non-Precious Metal Catalysts, DOE Hydrogen Program FY 2005 Progress Report, p. 289.
6. E. B. Easton, D. A. Stevens, T. Buhrmester, D.G. O'Neill, R.T. Atanasoski and J. R. Dahn, “A Study of Vacuum Deposited Fe-C-N Based Catalysts For Oxygen Reduction,” 208th Meeting of The Electrochemical Society, Los Angeles, CA, Oct. 16 - 21, 2005.
7. M. Jain, “Non-Precious Metal Catalysts for PEM Fuel Cells” *(Invited),* Workshop on Computational Materials and Molecular Electronics,” Austin, TX, Oct. 20 – 22, 2005.
8. R. Atanasoski, “Recent Advances in the 3M MEA Technology for PEMFC: The Catalysts: Low Platinum and Non-Precious Metal Catalysts” *(Invited)*, Keynote Lecture at the International Conference on " New Proton Conducting Membranes and Electrodes for PEMFCs," in Honor of Prof. G. Alberti, Assisi, Italy, Oct. 22-26, 2005.
9. D. G. O'Neill, A. Schmoeckel, G. Vernstrom, D. O'Brien, M. Jain, R. Atanasoski, E. B. Easton, T. Buhrmester, J. Dahn and D. Wieliczka, “Vacuum Deposited Non-Precious Metal Catalysts for PEM Fuel Cells” (*Invited*), MRS Meeting, SESSION A3: Fuel Cells, Electrodes and Solid Oxide Fuel Cells, Boston, Nov. 28 – Dec. 02, 2005.
10. M. Jain, S.-H. Chou, A. Siedle and D. G. O'Neill, “Theoretical Modeling of Non-Precious Metal Catalysts for PEM Fuel Cells,” MRS Meeting, SESSION A3: Fuel Cells, Electrodes and Solid Oxide Fuel Cells, Boston, Nov. 28 –

Critical Assumptions and Issues

Non-precious metal catalyst (NPMC) technology is in an early R&D phase. The two most critical issues in its development continue to be activity and durability.

- Activity must be addressed first to develop candidate materials and demonstrate that they have the potential for meeting fuel cell performance targets.
- Improving durability is equally challenging and must be focused on materials that have proven their potential for catalytic activity, but it cannot be assumed that the target durability is achievable for a given material.

Unlike platinum, progress and experience in one NPMC system, as a rule, do not apply to others.

- Much larger and more in-depth effort is needed in many areas and directions in order to find a candidate NPMC material that can replace Pt.
- Under this project, the vacuum and nanotechnology experimental approaches along with advanced characterization and modeling have been used synergistically to make greater progress than could have been achieved with any one alone. However, significant additional work in all these areas is required to realize the goals for a commercializable NPMC system.