2005 DOE HYDROGEN PROGRAM REVIEW
May 23-26, 2005, Washington, DC

Novel Approach to
Non-Precious Metal Catalysts

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3M Company
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Project ID#: FC14

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: September 1, 2003
- Project end date: August 31, 2006
- Percent complete: ~40
  (consistent with spending)

Budget

- Total Project funding: $3.6 million
  - DOE share: $2.9 million
  - Contracter share: $0.7 million
- Funding received in FY04: $500,000
- Funding for FY05: $700,000

Barriers

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- (Technical targets: See next slide)

Partners

- **Dalhousie University**
  - 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
  - Dr. R. Adzic ***– Exploratory***
- **University of Missouri – Kansas City**
  - Prof. D. Wieliczka; UPS at University of Wisconsin Synchrotron Radiation Center

Project Goal and Objectives

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

DOE Objectives/Targets:

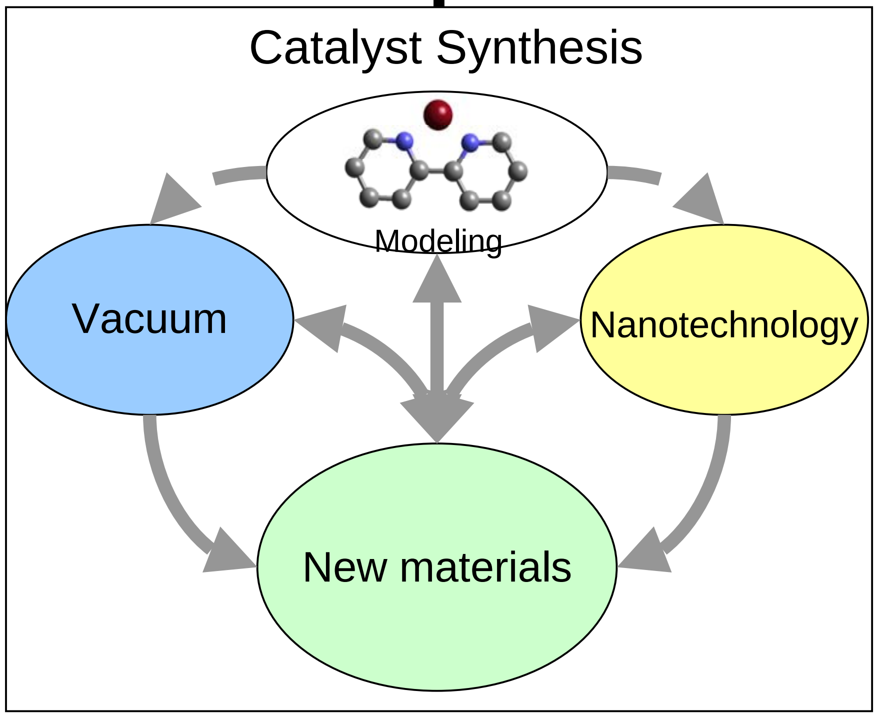
- Reduce dependence on precious metals (Pt).
- Perform as well as conventional precious metal catalysts currently in use in MEA's.
- Cost 50% less compared to a target of 0.2 g Pt/peak kW.
- Demonstrate durability of >2000 hours with <10% power degradation.

Specific Objectives for 2005:

- Synthesize and characterize high catalytically **active sites** for oxygen reduction reaction (ORR) by
  - Introducing new synthetic routes
  - Understanding and overcoming the cause of the high impedance
- Preserve process **compatibility** with **high volume manufacturability**

Approach

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



Functional Characterization
- Fuel Cell
  - 50 cm^2
  - **Segmented**
- **Gas Diffusion Electrode**

- Catalyst synthesis is carried out via two **complementary and interactive** approaches:
  - **Vacuum Processes**: Variety of vacuum processes including mapping via high throughput approach;
  - **Nanotechnology**: Dispersed catalyst on high stability carbon substrate.
- Modeling work is done to guide and verify the synthesis efforts.
- Extensive physicochemical analytical characterization is carried out both at 3M and in collaboration with other institutions when appropriate.
- MEA **fabrication** and 50-cm^2 FC **evaluation** readily **scalable** to pilot plant level.

Technical Accomplishments

Catalyst Synthesis

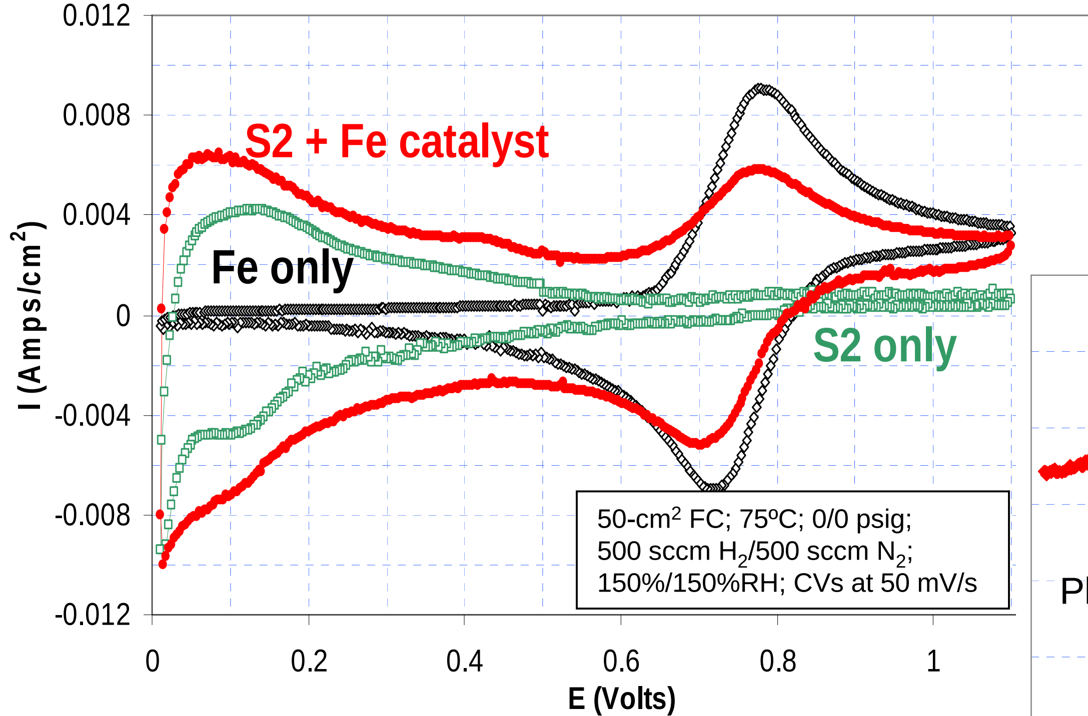
- Broadened space of catalyst synthesis
  - New area: Nanotechnology-based multi-component dispersed catalysts
- Catalytic activity orders of magnitude higher than previously reported on this project *(interim milestone #2 near completion)*

Catalyst Characterization

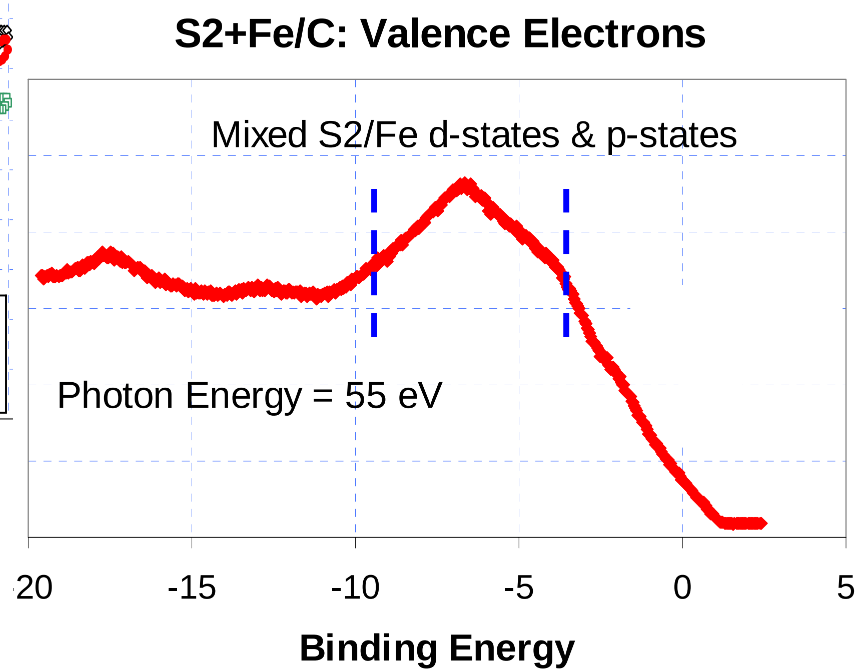
- Insights into catalytic sites based on
  - Modeling: Thermodynamically most favorable CNxFe sites indicated
  - State-of-the-art characterization/analytical techniques
- Progress in addressing and overcoming the catalyst high-impedance issue *(interim milestone #1 completed)*
- Compositional areas of stability and activity of CNxFe space mapped
- New screening methods for catalyst activity

Nanotechnology: Component Characterization

Catalysts based on **Fe** and **Sx as 'matrix/support'** on dispersed carbon have been synthesized. **Electrochemically**, CV for the combination Fe/S2/C catalyst appears as additive of the CVs of the individual components. However,...



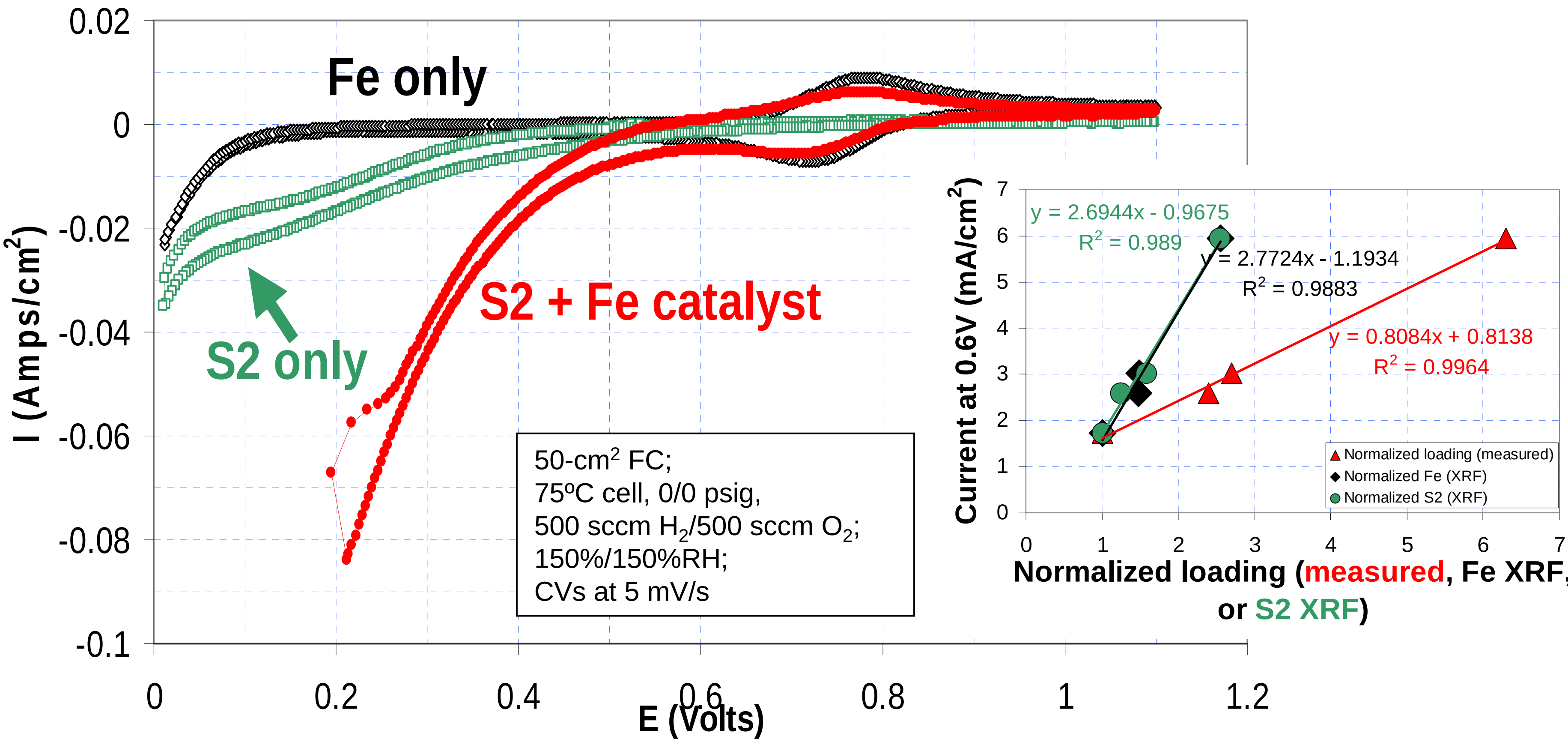
…a closer scrutiny via **UPS** indicates some interaction between the components.



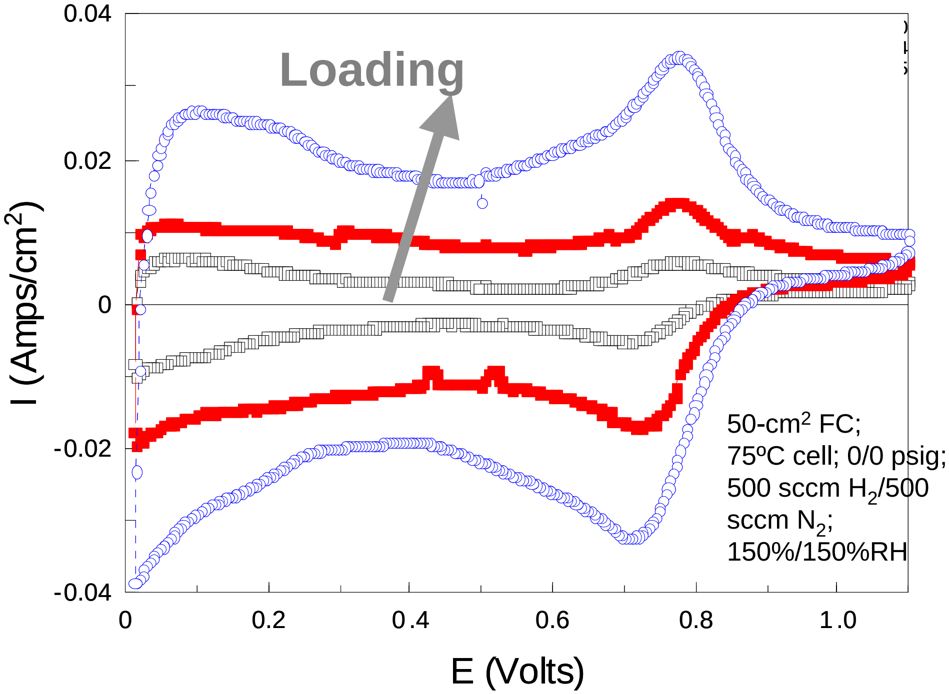
To emphasize catalytic activity, low surface area, high stability carbon was used as support.

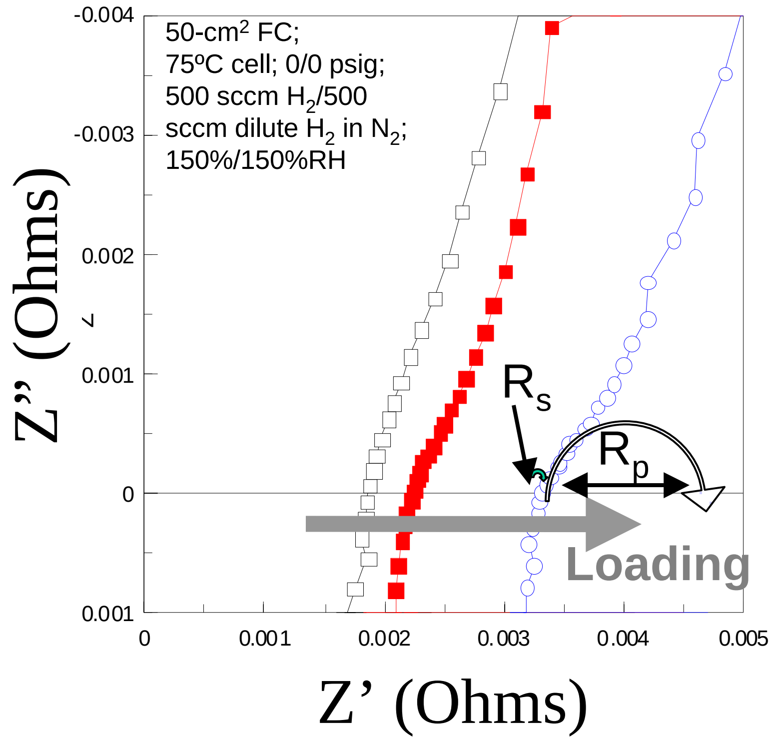
Nanotechnology: ORR Component Synergism

- While CV baselines are additive, the **oxygen performance is enhanced** relative to the addition of the two single component oxygen response curves when a combination S2 and Fe catalyst is used. This points to a possible synergy between S2 and Fe.
- Increases in the S2 + Fe catalyst loading, determined both by weight basis (before testing) and XRF measurements (after test), result in a linear increase in current at 0.6 V.



Nanotechnology: Catalyst Loading Effect





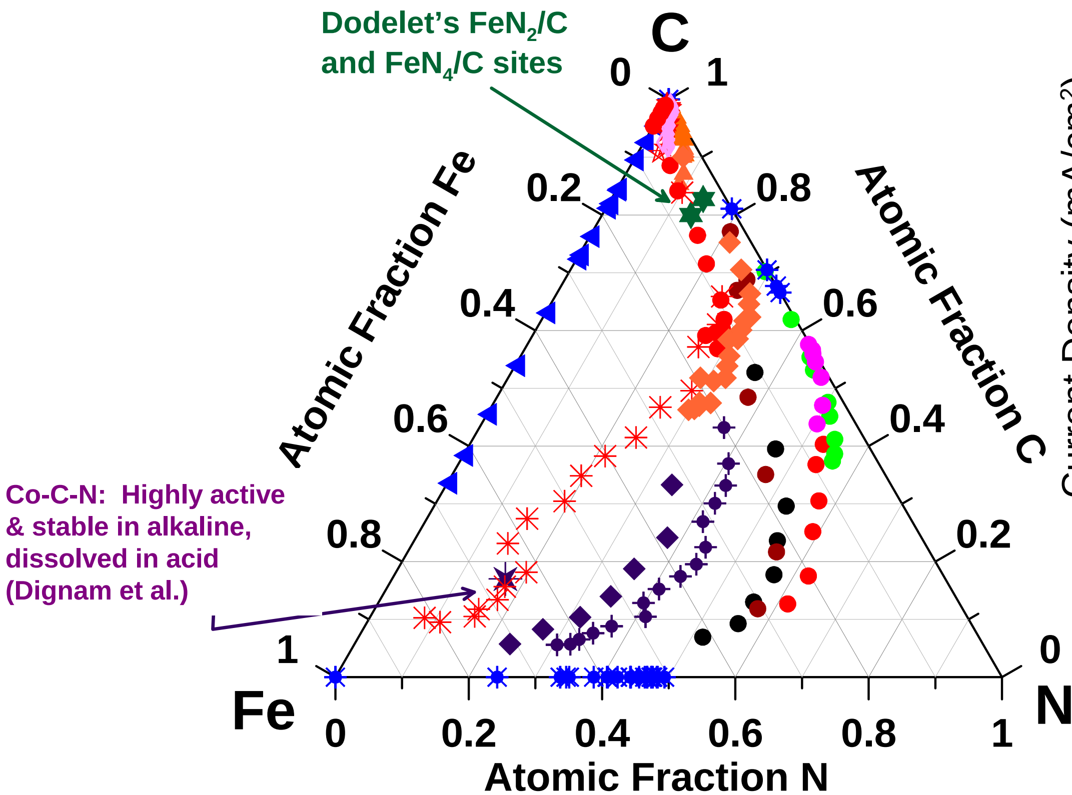
The effect of catalyst loading can be seen both in the increase in the relative magnitude of the CVs (taken under nitrogen) and in the change in impedance (under hydrogen). With more catalyst, the ohmic resistance, Rs, increases, while the polarization resistance, Rp, decreases.

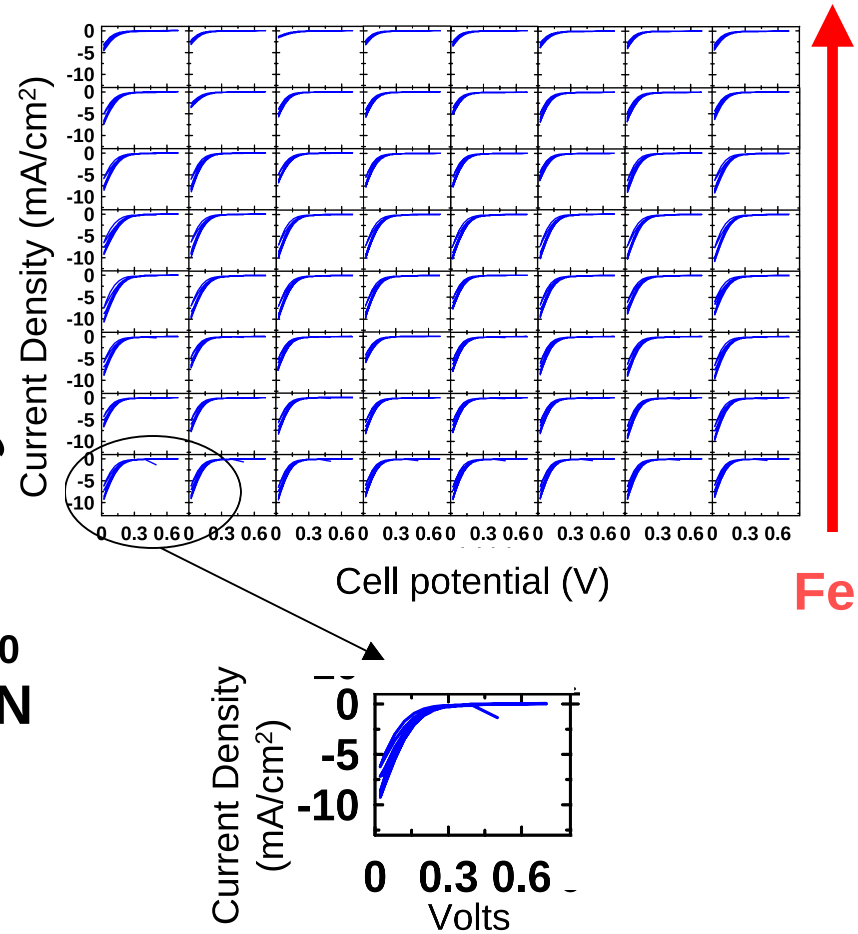
Normalized Loading	Rs ($ohm*cm^2$)	Rp ($ohm*cm^2$)
1	0.095	0.27
2.67	0.115	0.09
5.25	0.170	0.06

Vacuum Processes: The CNxFe Space

Multiple series of CNxFe compositions were produced (Dalhousie University).

Stability is tested in liquid acid and activity in 64-channel fuel cell (for acid soak protocol, see J. Electrochem. Soc., **152** (1) A61-A72 (2005)).





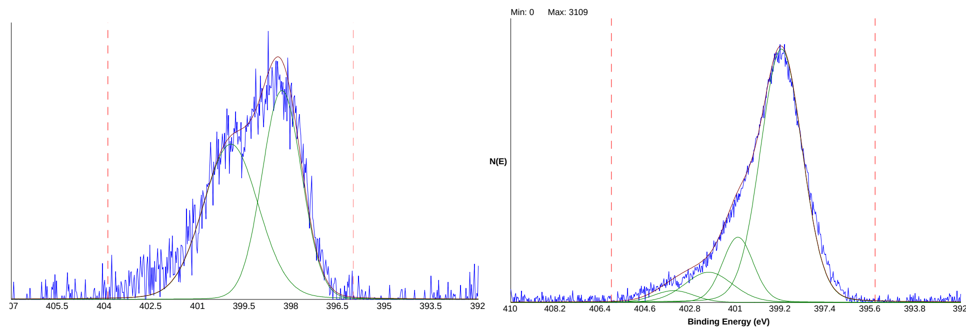
FeN system as a baseline was completed first (manuscript submitted)

Vacuum Processes: Effect of Iron on Nitrogen in CNxFe

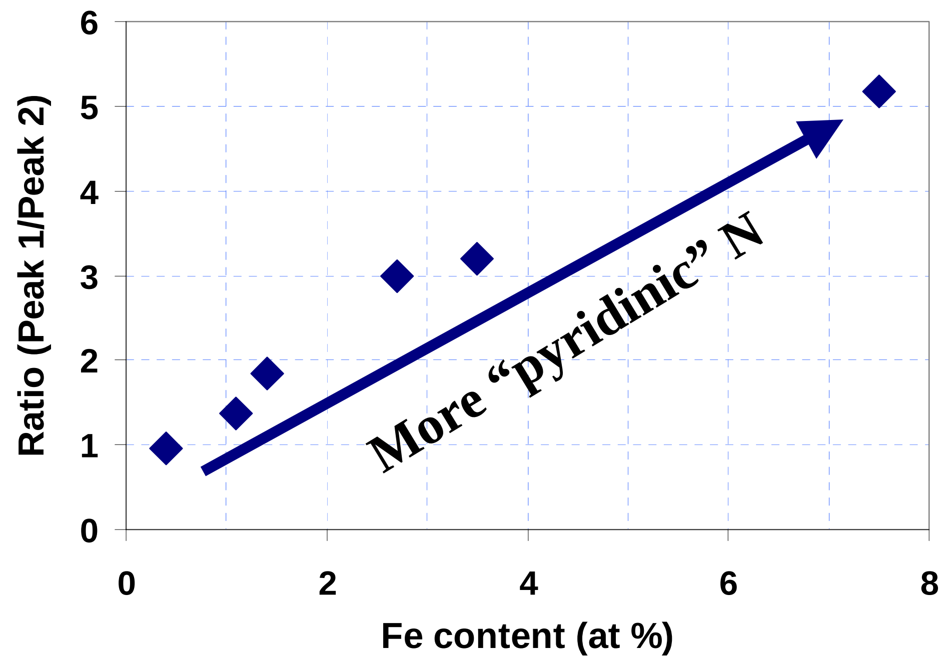
Addition of iron to nitrogenated-carbon alters the chemical environment of the nitrogen atoms.

- NPM catalyst literature - ESCA spectra of N1s core at 398.5 eV labeled as "pyridinic"
- However, no direct evidence of surface terminated nitrogen that is sp^2-bonded to carbon has been provided.
- Alternatively, nitrogen substituted into an sp^3-bonded carbon environment can also give a 398.5 eV N1s binding energy component.
- ESCA of N1s does not give unique material fingerprint for ORR catalytic tendency.
- In spite of a strong 398.5 eV component, no substantial activity in our material was found.

C-Nx (~15%N) C-Nx:Fe(7%)

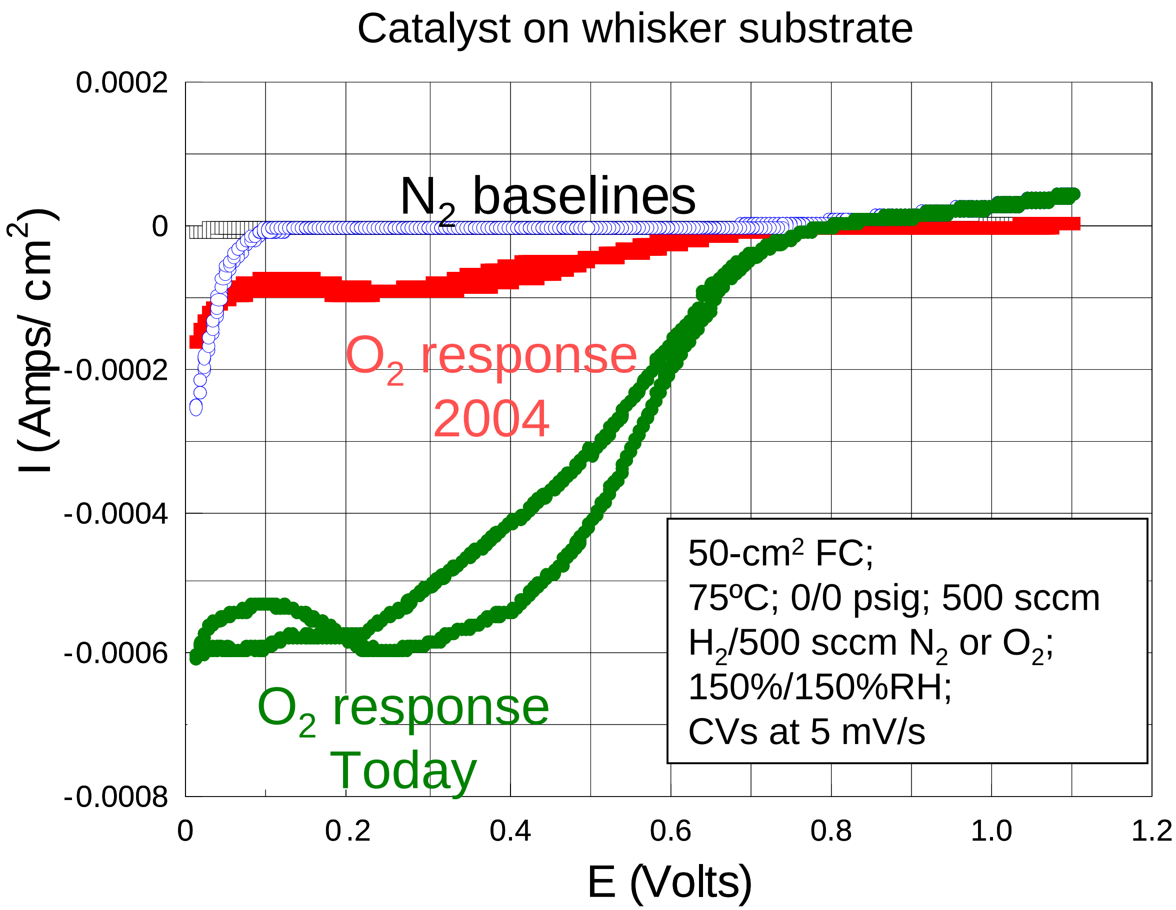


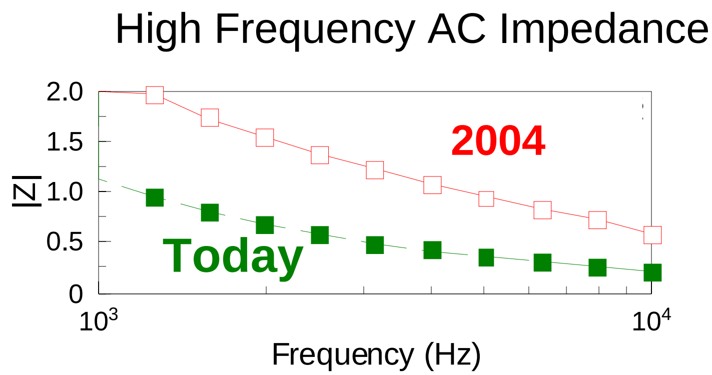
N1s Component Ratio



Vacuum Processes: Fuel Cell Characterization

Sample made via vacuum synthesis showed an ORR catalytic activity an **order of magnitude** greater than the previous best result.

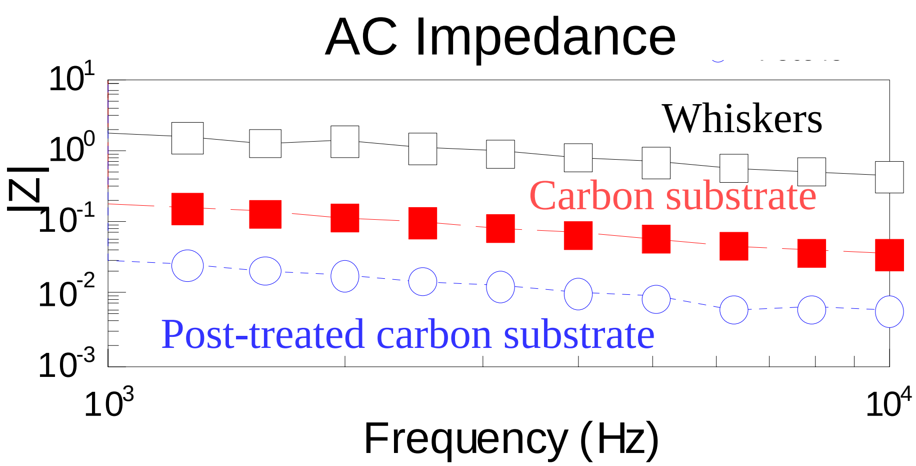


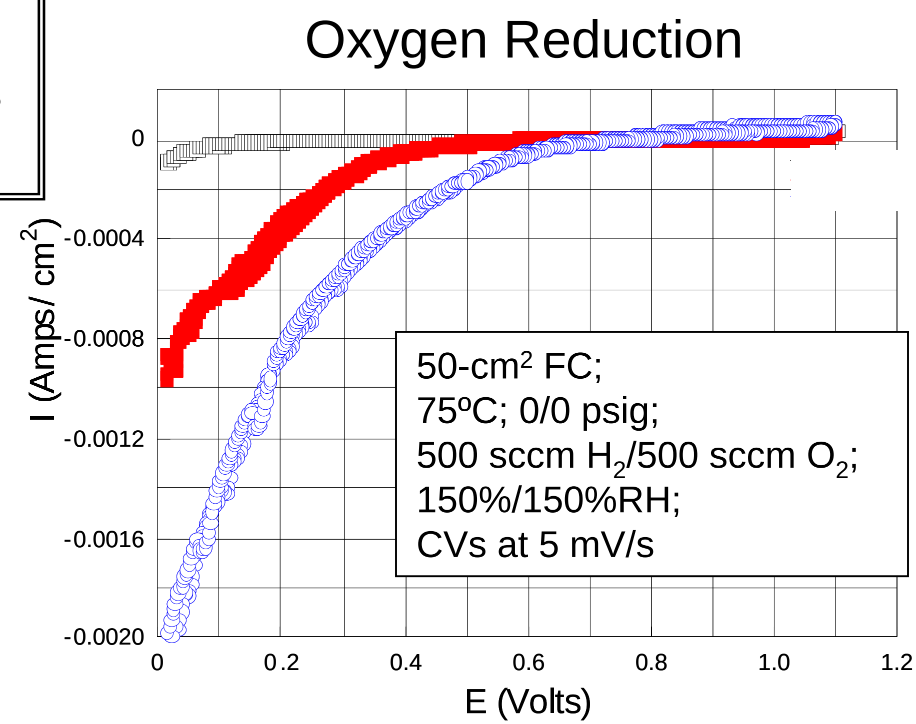


Impedance improved by a factor of 2.5; however, remains high.

Vacuum Processes: Catalyst Impedance

Post-treatment reduces impedance (interim milestone #1) and improves oxygen response.





- Impedance values of catalyst depend on the type of substrate.
- Certain post-process treatments of the coated carbon substrate decrease the impedance even more.

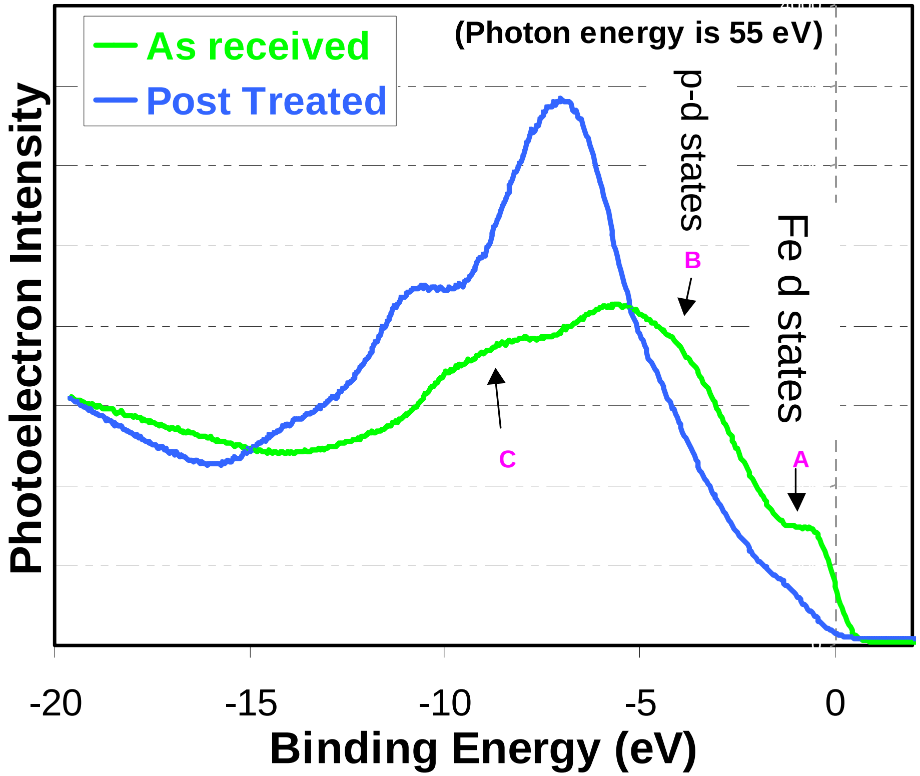
Oxygen response increases as the impedance decreases. However, the decrease in impedance cannot fully account for the increase in activity.

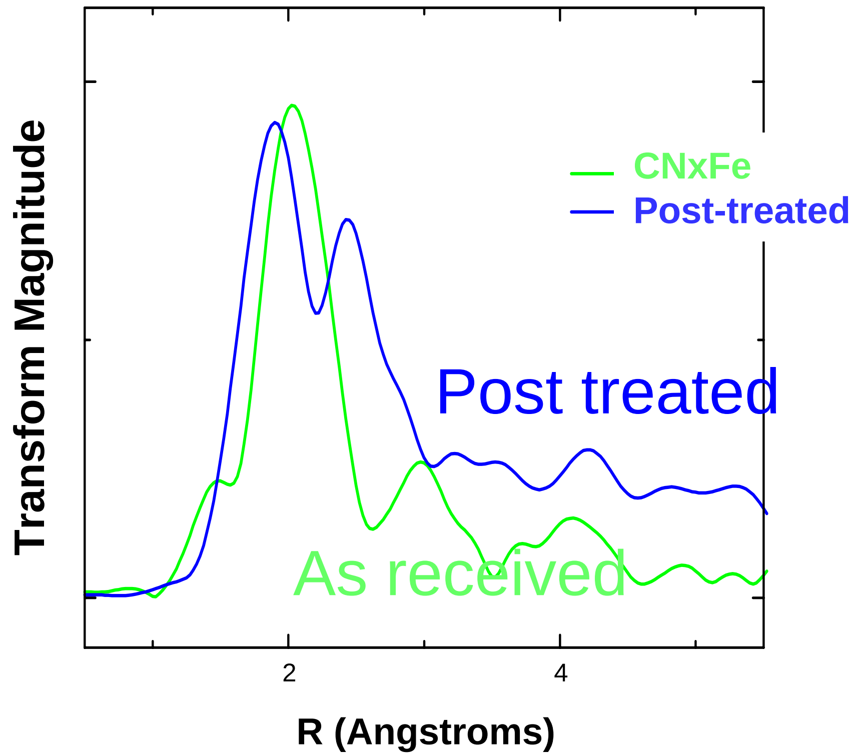
UPS & EXAFS: Post-Treatment Effects

Synchrotron UPS and EXAFS reveal electronic and structural changes from post-treatment of the catalyst.

- Valence e-structure significantly modified by post-treatment.
- Fe d-state intensity at Fermi level is reduced.

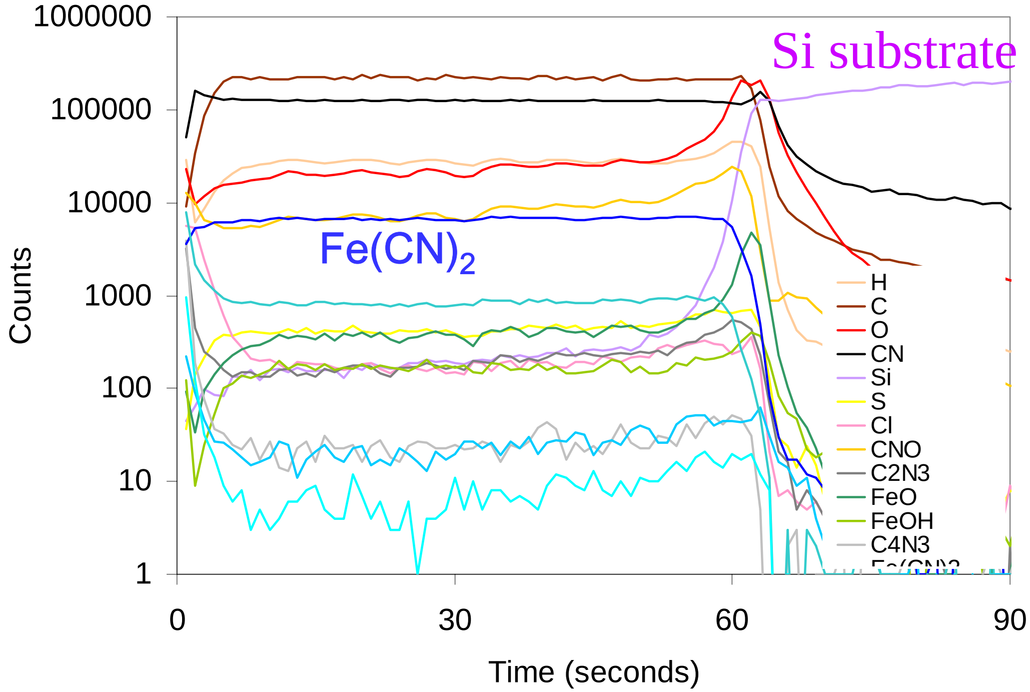
- Fe nearest neighbor distance decreases ~0.15 Å
- Increased atomic order



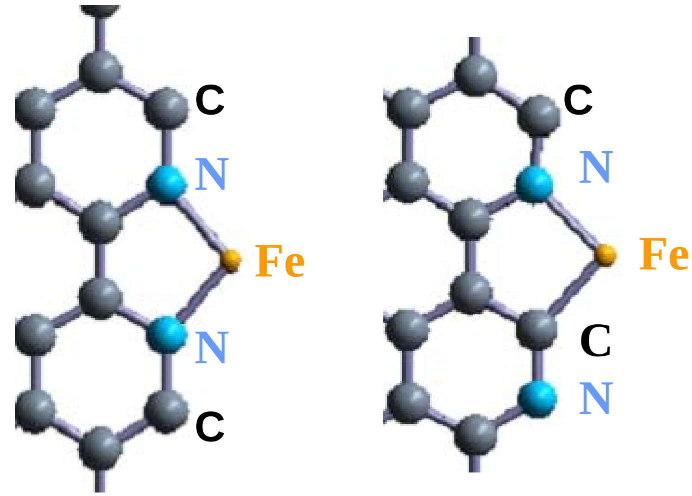


SIMS Characterization and Modeling

SIMS Characterization



The Models



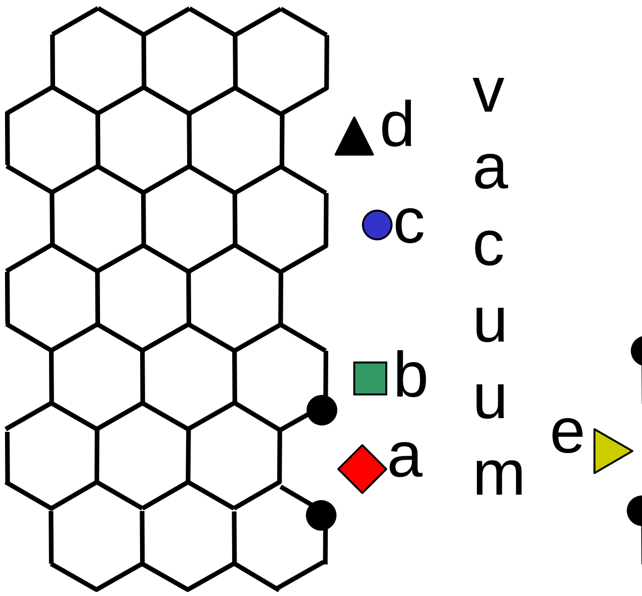
Model catalyst (Dodelet)

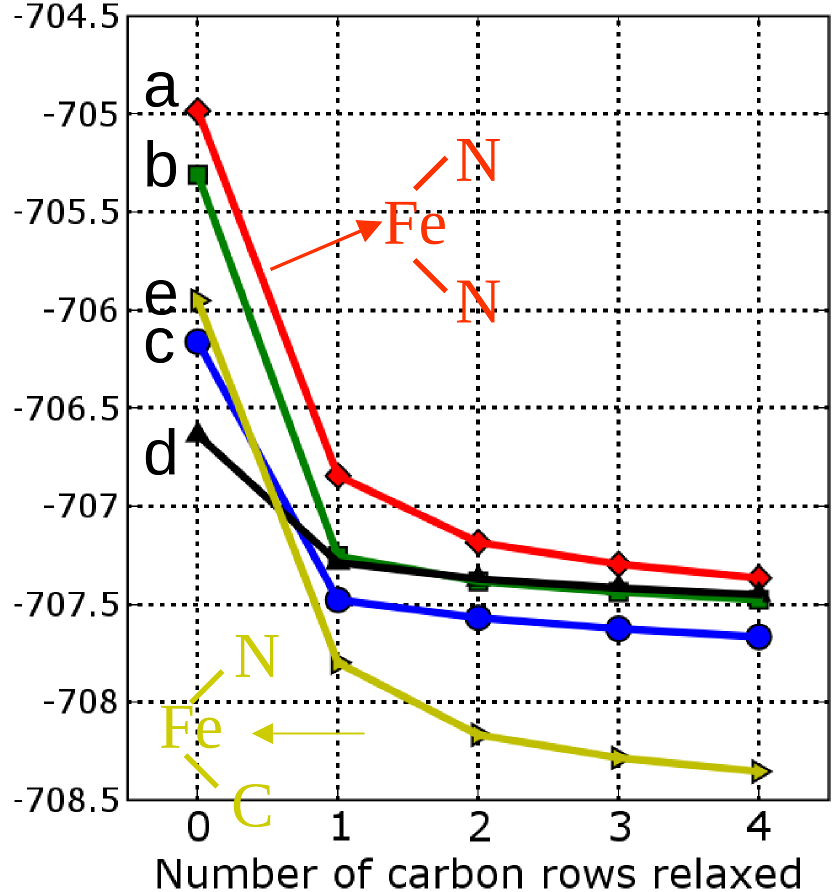
Lower in energy by 0.99 eV (*ab initio*)

- SIMS characterization showed the coating is uniform throughout the sample. Several samples gave reproducible results.
- Fragments indicating CN_2Fe structures **have not** been detected.

- Modeling work indicates that literature-proposed CN-Fe-**NC** catalyst structure is not the lowest in energy. The structure depicted on the right, where Fe is connected to one nitrogen and one carbon, CN-Fe-**CN**, is lower.

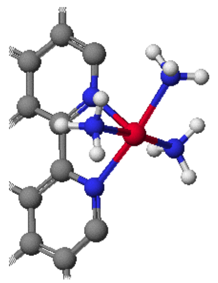
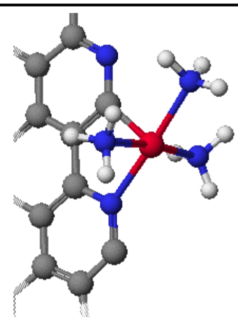
Modeling: Iron – Nitrogen Substitution





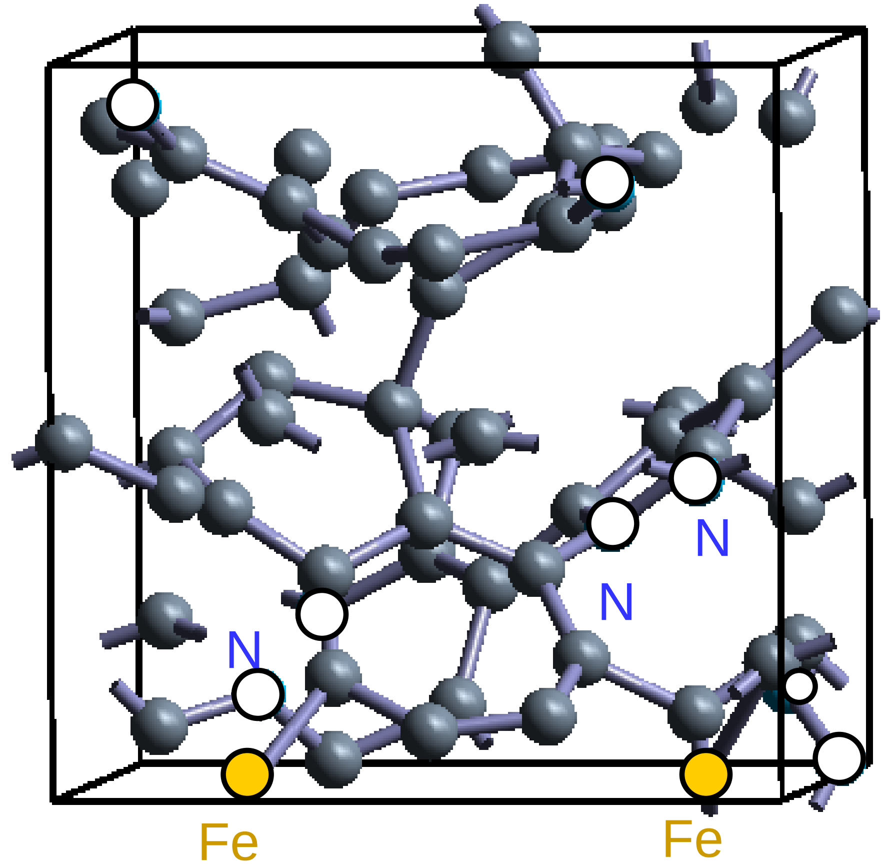
Relaxation does not make a big difference for relative stability of only N substituted on the edge of graphene sheet. For **Fe substituted** sheets, it not only **changes the magnitude** of relative energies, but **also the order**.

Modeling: Fe Coordination and Effect of Disorder

	FeN_2C_4 with 3 NH_3 ligands
N-Fe-N	
C-Fe-N	
Relative Energy	-1.72 eV

Completing the Fe coordination does not change the relative energetics.

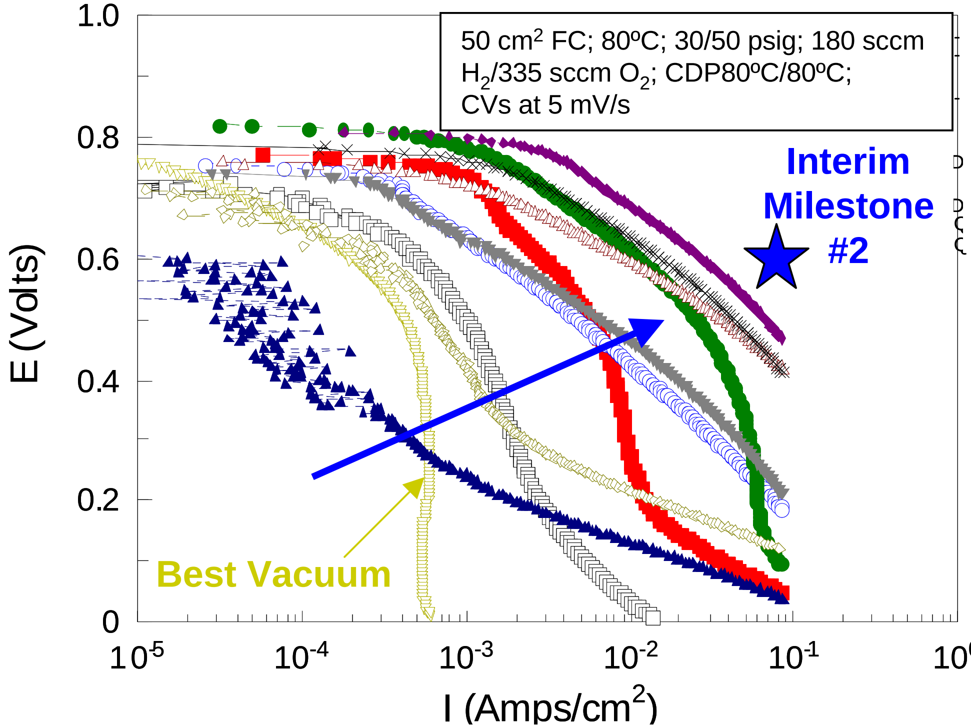
(manuscript submitted)



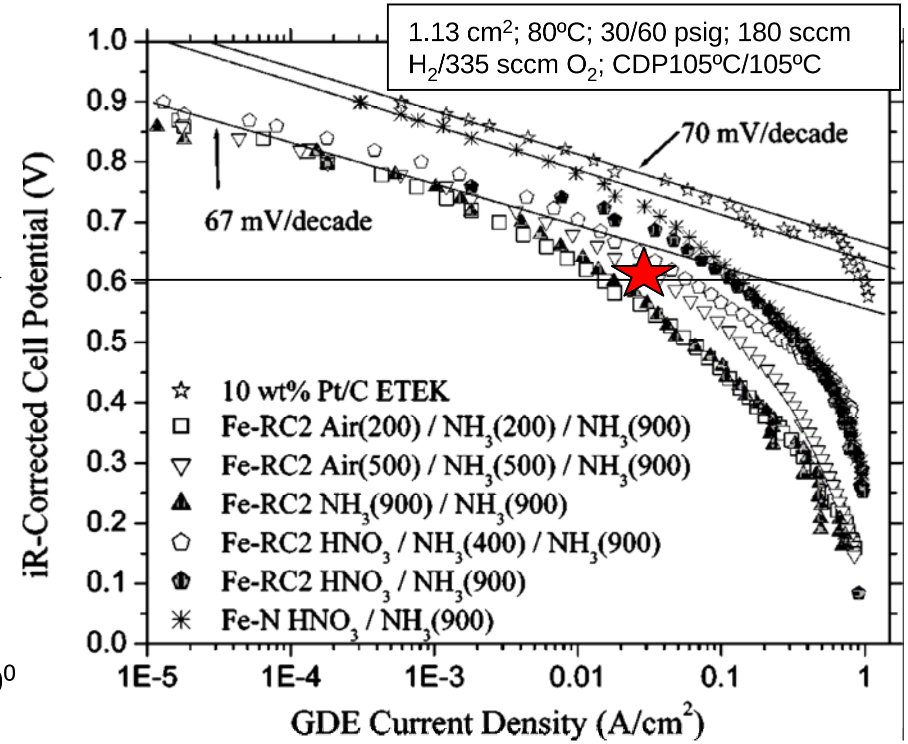
Considering disordered systems generated using *ab initio* molecular dynamics.

Summary of Accomplishments

Catalytic activity has progressed during this reporting period and now can be compared with data reported elsewhere.



This Project: Selected from over 120 50-cm² FCs.



Dodelet, J. Electrochem. Soc., 151 (2004) A1507

★ 3M present status

Summary (continued)

- The tremendous activity during the past year has produced an extremely large number of catalyst samples synthesized, screened, characterized, and fully tested. This resulted in improved catalyst performance and is reflected in the quality and quantity of materials characterized by state-of-the-art techniques.
- The Project has been greatly aided and expanded by the introduction of nanoparticle-based catalysts.
- The modeling and characterization work has produced some unexpected results that could provide a lead to the synthetic effort, common to both the vacuum- and the nanoparticle-based processes.
- The origin of the high coating impedance has been well understood and the catalysts' stability region has been mapped.
- Task oriented, interactive collaboration with Universities and National Labs has been established.
- Two manuscripts and one patent application have been submitted.

Response to Reviewer's Comments

1. Technology Transfer/Collaboration
   - Collaboration: Interactive and fruitful collaborations have been established with universities and national labs.
   - Transfer: Approach emphasizes ease of technology transfer to product commercialization.
     - Processes used for catalyst synthesis are amenable to scale-up.
     - Produced catalyst in quantities sufficient for 2-kW stacks as proved by making multiple MEA's for 50-cm^2 fuel cell testing.
2. Planning/Milestones
   - Besides the decision for scale-up, interim milestones have been established.
3. Initial Performance/Activity Needs Improvement
   - Performance improved orders of magnitude. Root causes of high impedance understood and ways for overcoming it are being implemented.

Future Work

Remainder of fiscal 2005

- Direct the synthetic effort towards achieving Milestone #2 performance.
- Implement the most recent findings by combining the two synthetic processes to eliminate the impedance issue and achieve a synergetic effect.

2006

- In the nanotechnology area, combine the most promising nanoparticle precursors, appropriately pretreated substrates, application procedures, and thermal treatment processes for best synergetic effects.
- In the vacuum processes, utilize the advanced instrumental techniques and the modeling effort for process parameter changes and the nanotechnology accomplishments for the best synergetic effects between the two synthesis paths.
- On the fundamental level, point out with more certainty the possible active sites via modeling. Continue and expand the effort to experimentally confirm/identify the nature of the new ORR catalysts.
- For best performing catalysts, test stability, peroxide (RRDE, fluoride), etc.
- Downselect the catalyst for scale-up and 1- to 2-kW stack testing by 3/06.

Publications and Presentations

Publications:

1. E.B. Easton, T. Buhrmester, J.R. Dahn:
   "Preparation and Characterization of Sputtered Fe(1 – x) N(x) Films",
   submitted to *Thin Solid Films*
2. M. Jain, S.-H. Chou, A. Siedle:
   "Structure of FeN_2C_4 Moiety from Quantum Mechanic Study",
   submitted to *J. Electrochem. Soc*.

Presentations:

1. R. Atanasoski:
   "Recent Advances in the 3M MEA Technology for PEMFC: The Catalysts",
   Departmental Seminar, Chemical Engineering Department, Univ. of South Carolina, Columbia, SC, 21 April 2005

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Accidental H_2 release in cylinder closet leading to ignition from:
  - H_2 line or manifold breach
  - Accident during replacement of cylinders

Hydrogen Safety

Our approach to deal with this hazard is:

- Design
  - Hydrogen cylinder closet and gas distribution system adhere to codes.
  - Reduction in number of cylinders in the closet
  - 2-step regulators (less susceptible to failure and designed to fail closed)
  - H_2 sensors in all labs and cylinder closet, alarm system
  - Automatic shut-off of H_2 gas supply if sensors detect H_2 release
- Procedures
  - SOP's for cylinder changing, alarm responses, test station operation
  - Cylinder changing restricted to highly trained personnel
  - Regular maintenance checks – sensors, leak check of valves, etc.
- Installing H_2 Generator (in non-inhabited mechanical room) to significantly reduce total volume of H_2 in facility