2007 DOE HYDROGEN PROGRAM REVIEW
May 15 -18, 2007, Washington, DC

Novel Approach to
Non-Precious Metal Catalysts

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3M Company
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Project ID#: FC 4

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Overview

Timeline

- Project start date: September 1, 2003
- Project end date: August 31, 2007
- Percent complete: ~95%

Budget

- Total Project funding: $3.6 million
  - DOE: $2.9 million
  - Contractor: $0.7 million
- Funding received in FY06: $967 K
- Projected funding for FY07: $343 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 $mV_{IR\text{-}free}$
2010	> 130 A/cm^3
2015	300 A/cm^3

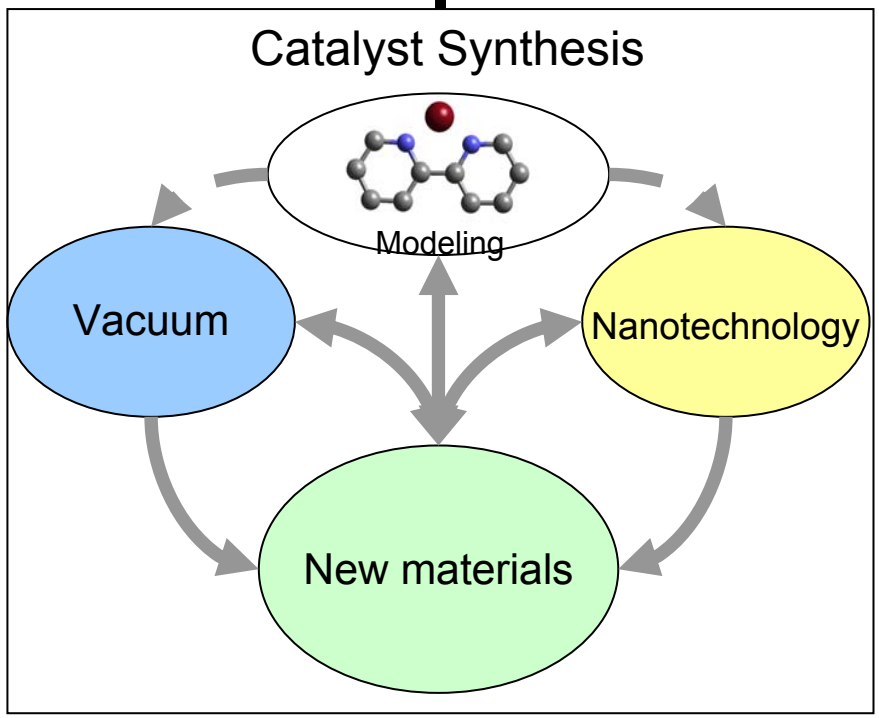
Specific Objectives for 2007 (From last year's *future work* slide, FC#12):

Produce new, better-performing more **durable** catalysts and identify the catalytic sites.

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

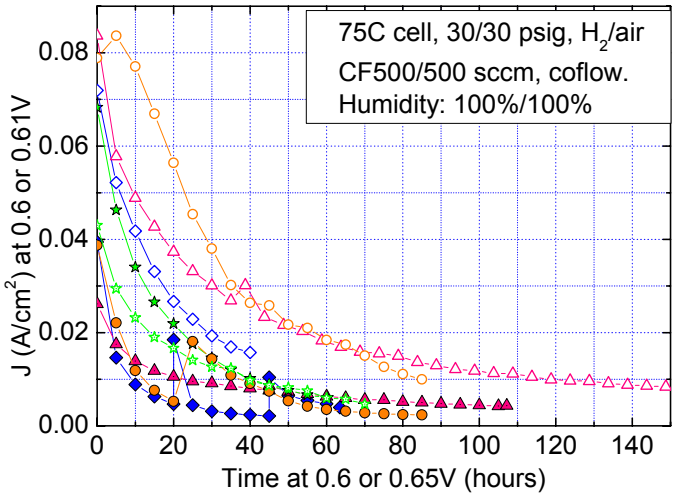
- Catalyst synthesis carried out via two **complementary and interactive** approaches both readily **scalable** to pilot plant level: **Vacuum Processes** and **Nanotechnology.**
- Extensive physicochemical analytical characterization, including modeling work, conducted both at 3M and in collaboration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

Technical Accomplishments

- Achieved durability of over 1,000 hours with practically no irreversible performance losses
  - with ***comparable***, state-of-the-art NPM *catalyst activity* as reported in the literature,
  - tested at 0.65 V under Hydrogen – Air in ***50-cm^2 fuel cell***.
- ***Catalytic activity*** 0.1 A/cm^2 at 0.77 V approached the Interim Milestone #5 (0.1 A/cm^2 at 0.8 V).
- Fabricated higher surface area, thermally stable substrates for use with the ***vacuum approach***. Achieved activity surpassing the best previous result by a *factor of four*.
- Made advances in testing, characterization, and modeling that provide valuable feedback for materials development.

Nanotechnology – Durable Catalyst Support

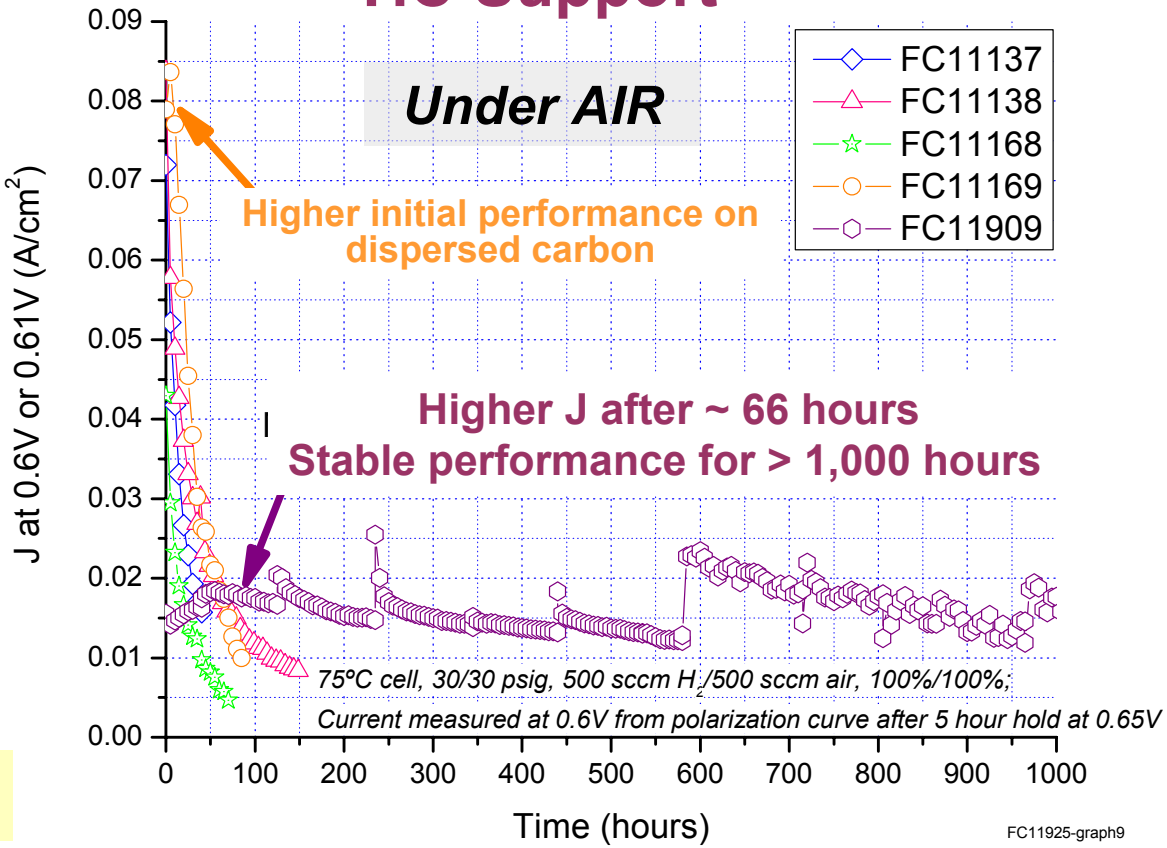
Dispersed Carbon Support



Performance of the catalyst supported on dispersed carbon is initially the best but decays rapidly.

(See Back - up slides for nature of the catalyst)

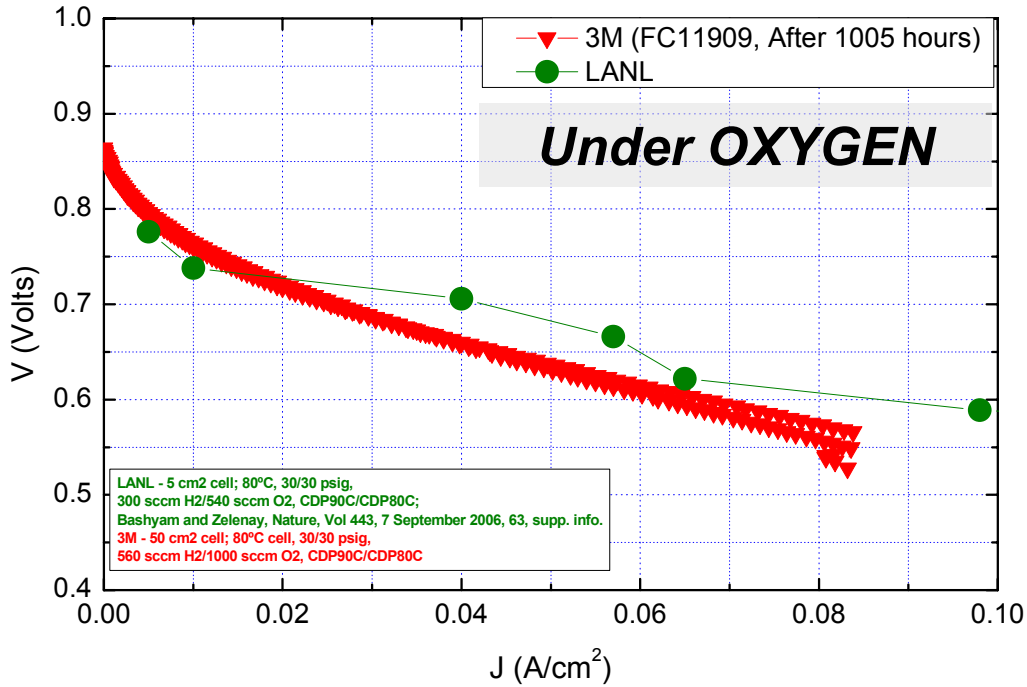
TiC Support



Materials different than dispersed carbon, **conducting** and **electrochemically stable** in fuel cell environment, were introduced as catalyst support. **Performance** of these catalysts is very **stable** and equals the best reported elsewhere. (see next slide)

Durability – Performance Comparison

LANL recently published a paper in ***Nature*** detailing a new catalyst, which shows 100 hrs durability. Under similar test conditions, 3M's catalyst after 1005 hours and LANL's initial performance are comparable.

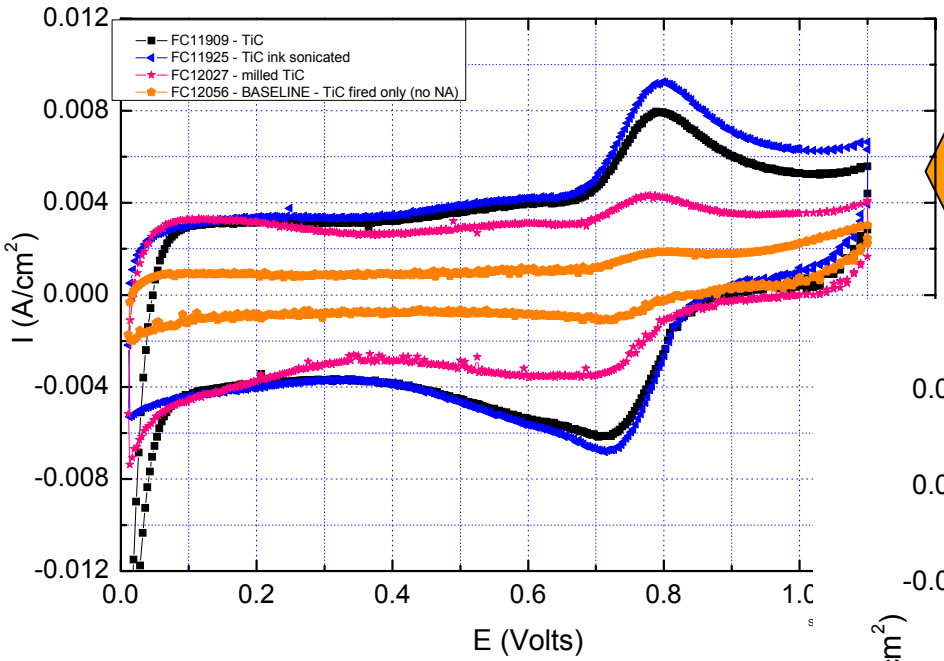


LANL - 5 cm^2 cell; 80ºC, 30/30 psig, 300 sccm H_2/540 sccm O_2, CDP90ºC/CDP80ºC; Bashyam and Zelenay, Nature, Vol 443, 7 September 2006, 63, supp. info.

3M - 50 cm^2 cell; 80ºC cell, 30/30 psig, 560 sccm H_2/1000 sccm O_2, CDP90ºC/CDP80ºC

Durable Substrate – Surface Area Effect

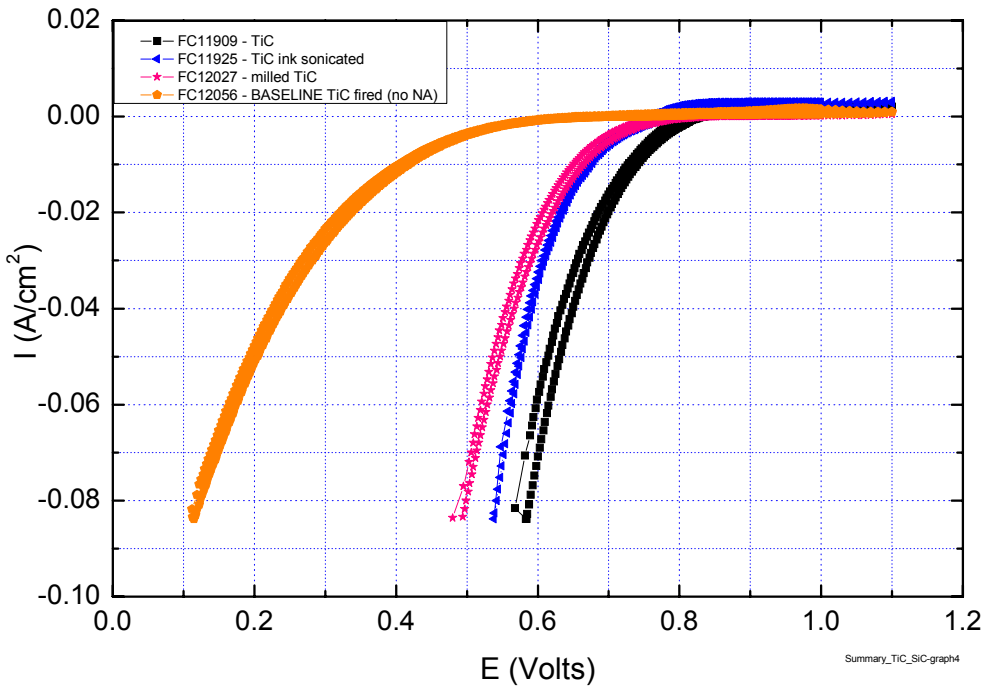
CVs under Nitrogen



The substrate – TiC treated the same way without the catalyst.

The surface area increased by a factor 3 – 4.

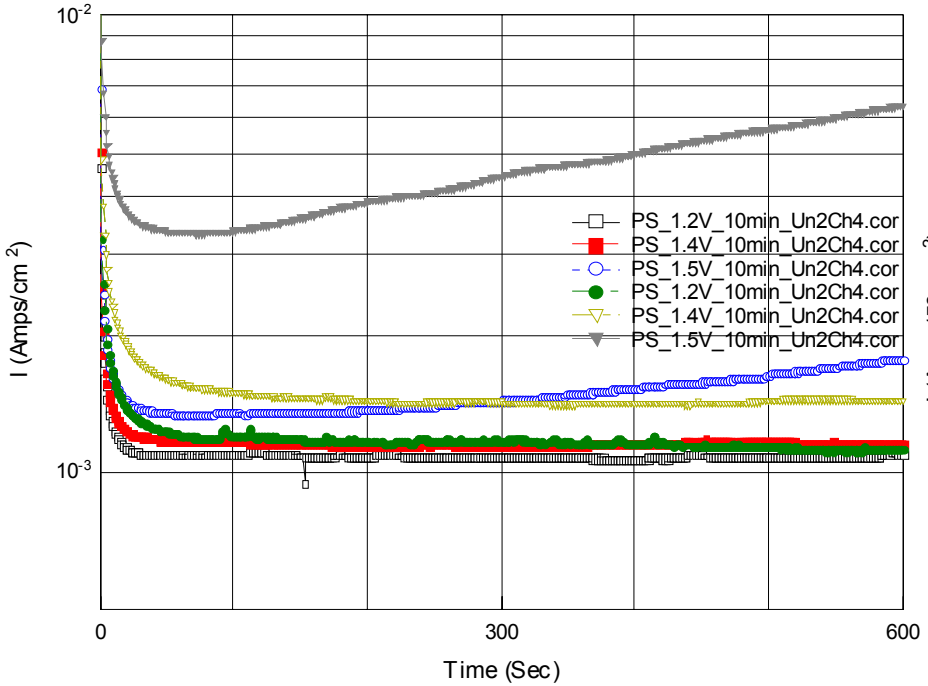
The ORR activity in the presence of the catalyst is orders of magnitude higher.

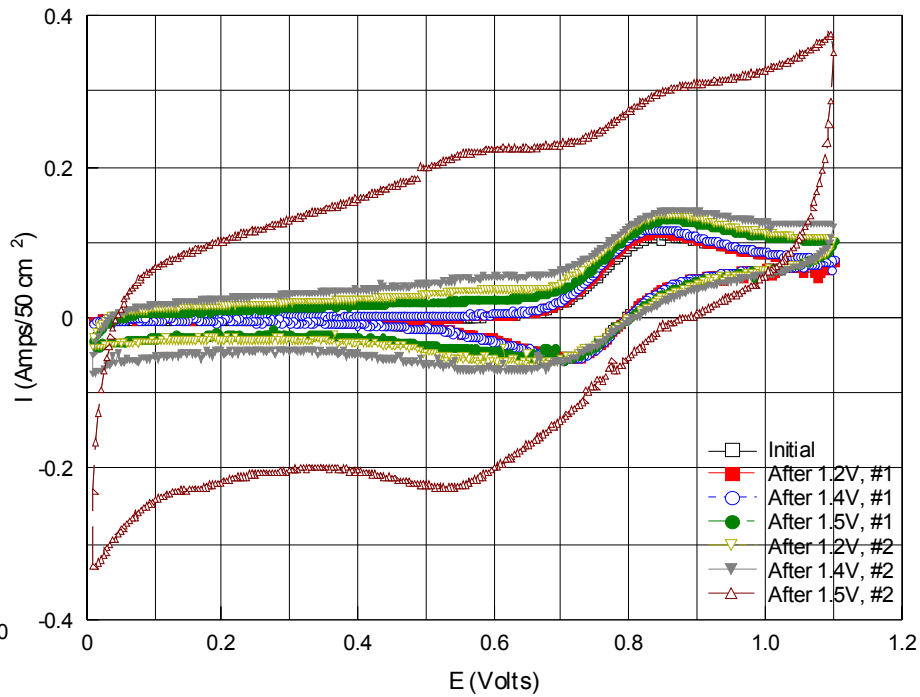


Durable Substrate – Voltage Stability

PS held at **1.2V, 1.4V**, and **1.5V** for **10 minutes**; then repeated (**1.2V, 1.4V, 1.5V**); 75ºC, **N_2**, 132%/132%RH.

N_2 CVs (50 mV/s) – **Initial, After 1.2V, 1.4V, and 1.5V for 10 min and after additional 10 min** at **1.2V, 1.4V,** and **1.5V**



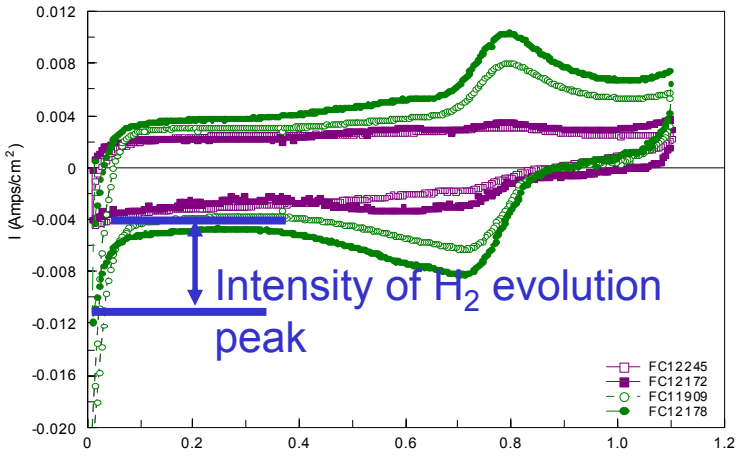


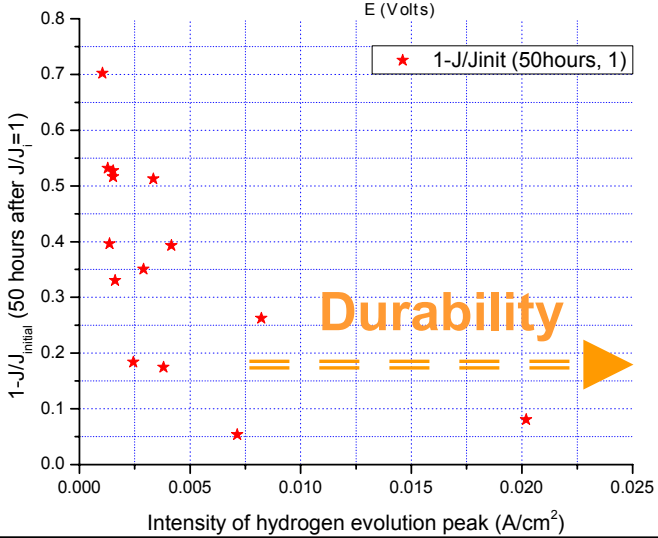
The new substrate material – **TiSi** – is **stable up to 1.4 V**. Only after second exposure at 1.5 V, for a total of 20 minutes, considerable surface area effect is observed.

Durability – Other Catalyst Properties

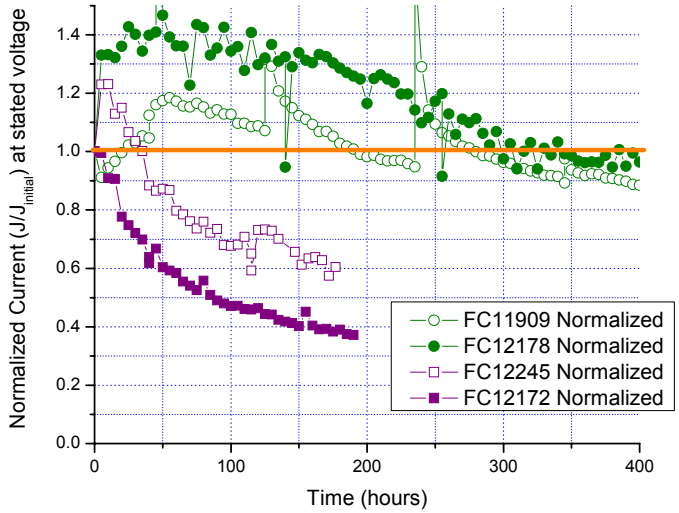
Larger hydrogen evolution peak (in the N_2 CVs) showed **greater durability**.

N_2 CVs (50 mV/s)



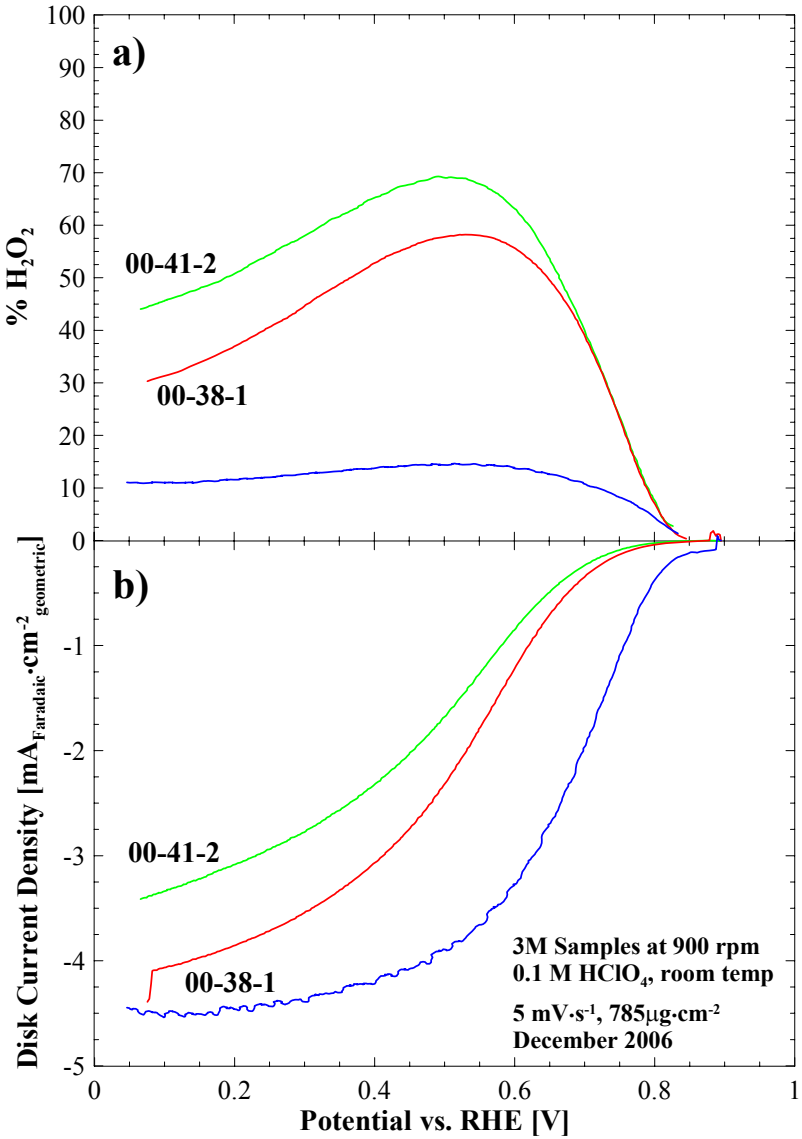


Normalized durability current



This may **point to surface properties** of the catalyst that are ***essential for durability.***

Durability – Peroxide Content

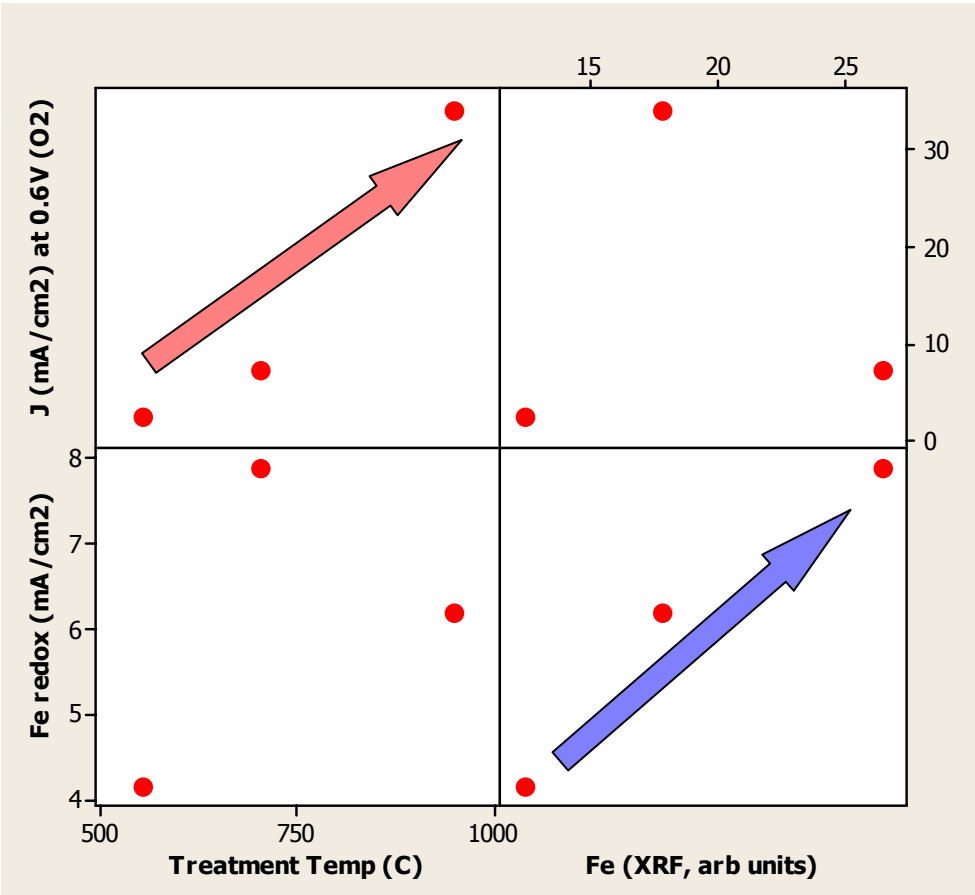


RRDE studies performed on three different catalysts at Dalhousie University.

- Peroxide emission of best performing catalyst on TiC substrate is relatively low (< 10%).
- Same peroxide content on the same catalyst made on carbon substrate did not result in durable product.

Thermal Treatment – The Role of Iron

Thermal treatments to 550ºC, 700ºC, and 900ºC in ammonia were performed on three aliquots of the same catalyst batch.



- Performance increases with thermal treatment temperature, NOT THE AMOUNT OF IRON.

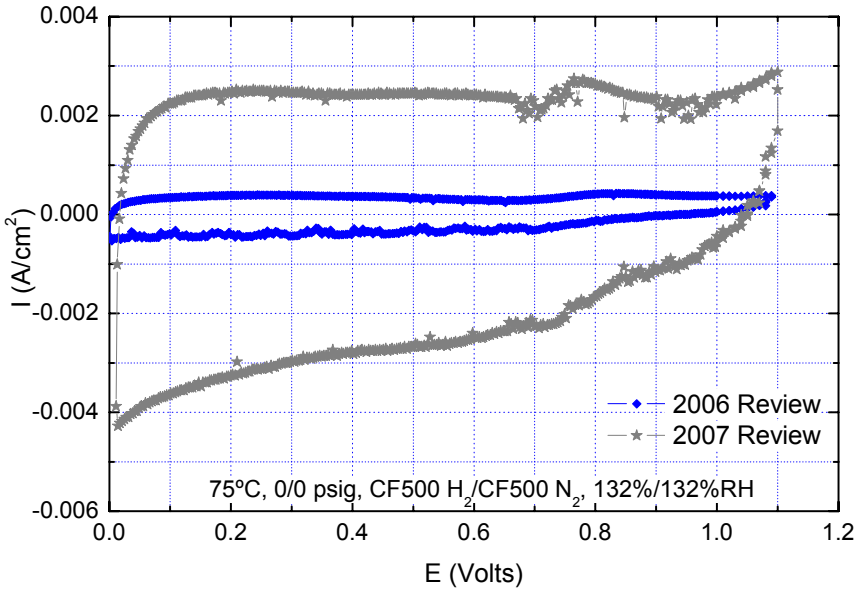
- Nearly 1:1 correspondence of Fe content measured via XRF *vs* the intensity of the Fe redox in the N_2 CVs.

- Most Fe remains on the sample treated to 700^{O}C.

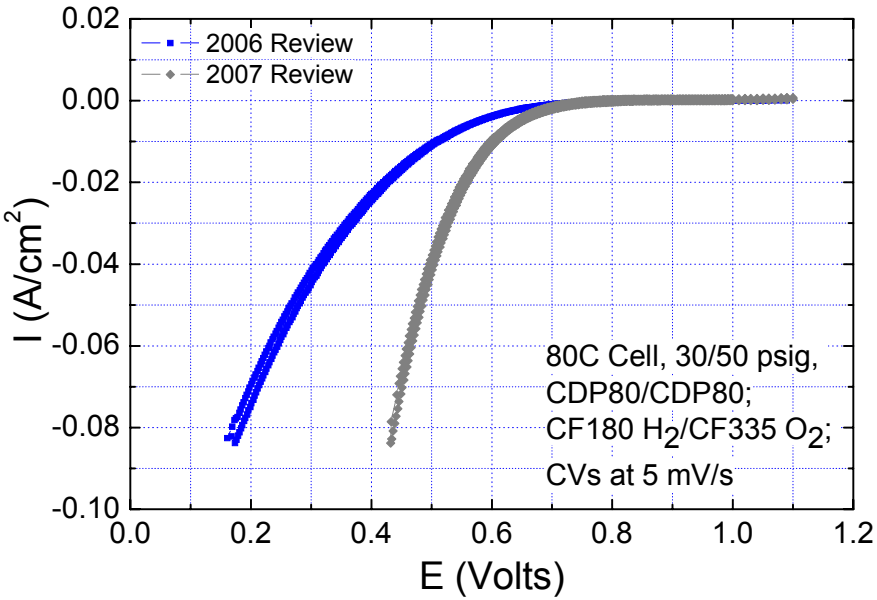
Vacuum Processes – New Substrates

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

CVs under nitrogen of the new substrate show a large **increase in surface area**



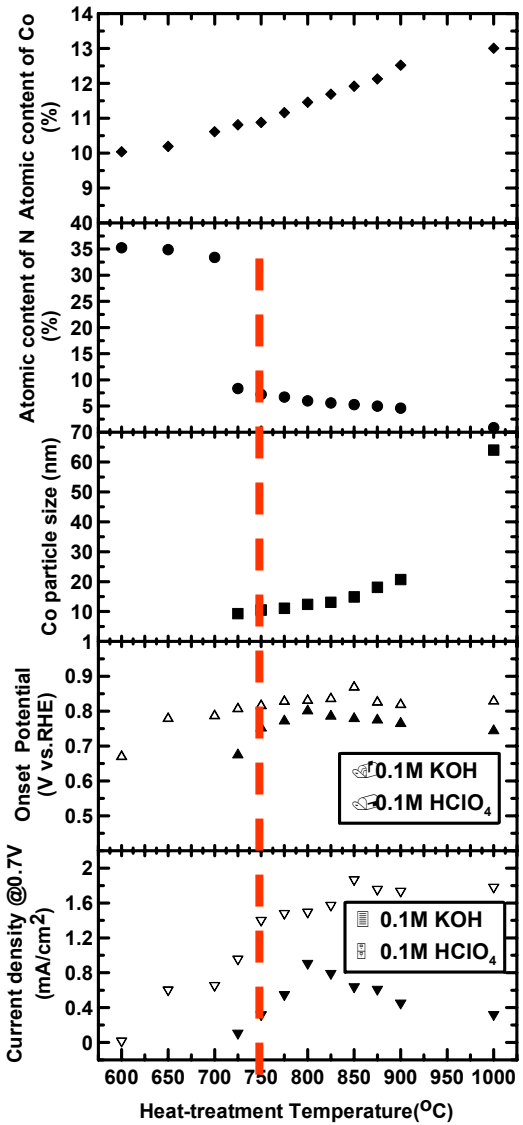
ORR activity of the new substrate with vacuum deposited Fe catalyst



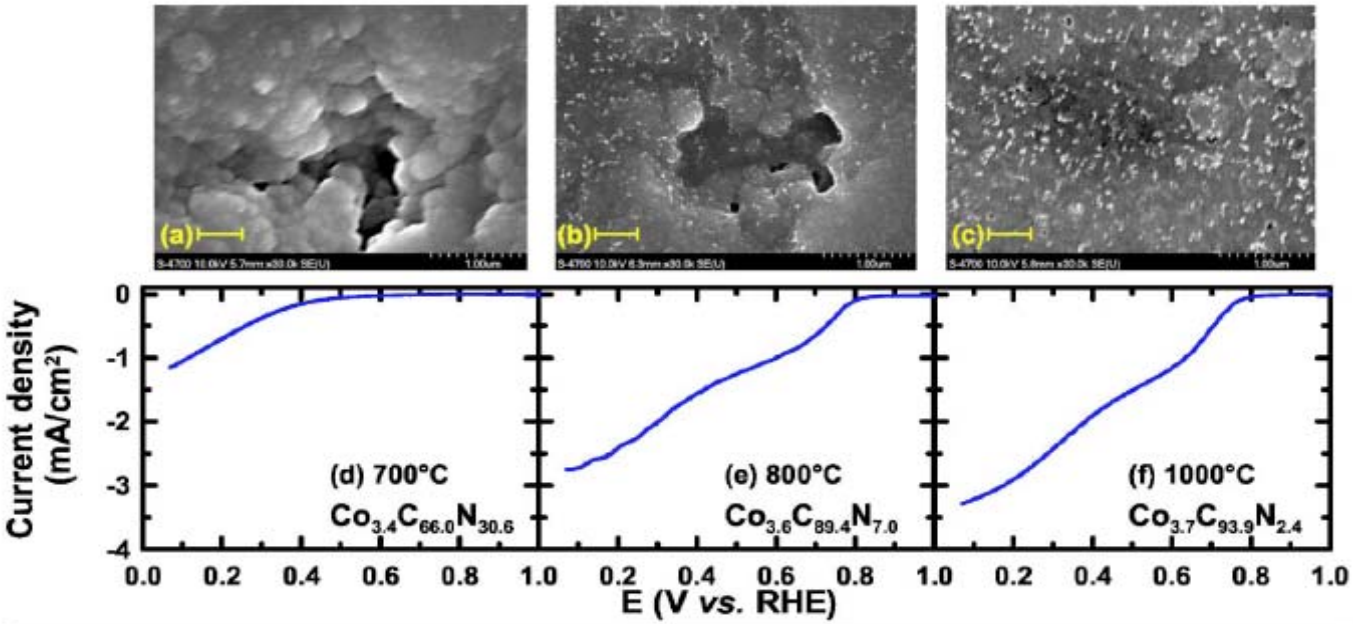
- **Performance of the new catalyst is significantly better than the best 2006 results from the vacuum approach.**

Vacuum Processes – Thermal Treatment

Nitrogen Loss



Heterogeneity



The loss of nitrogen is accompanied by a transition from homogeneity to heterogeneity in the material structure which is reflected on ORR activity as measured by RDE. (**Dalhousie University**)

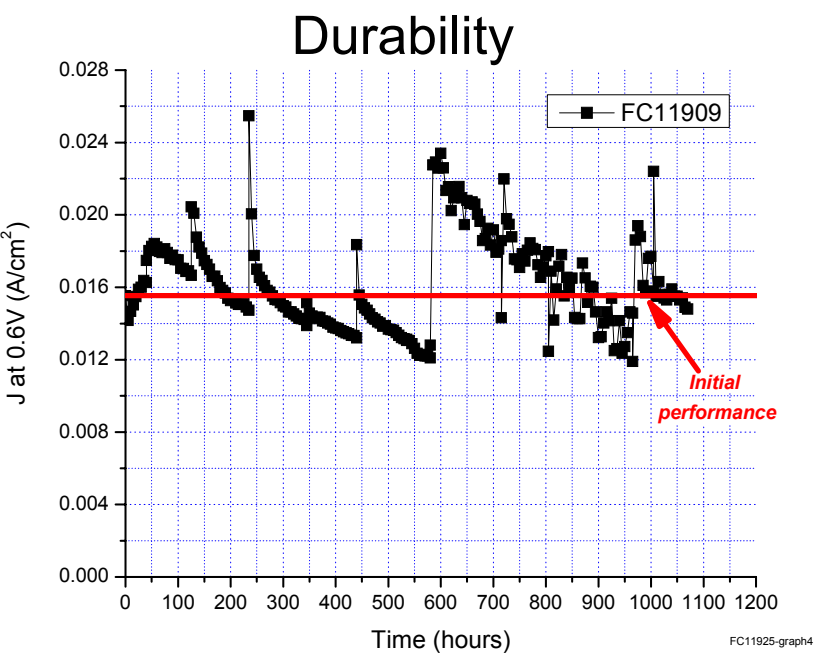
E. B. Easton, R. Yang, A. Bonakdarpour, and J. R. Dahn*, *Electrochem. and Solid-State Lett.*, **10** 1 B6-B10 2007

Future Work

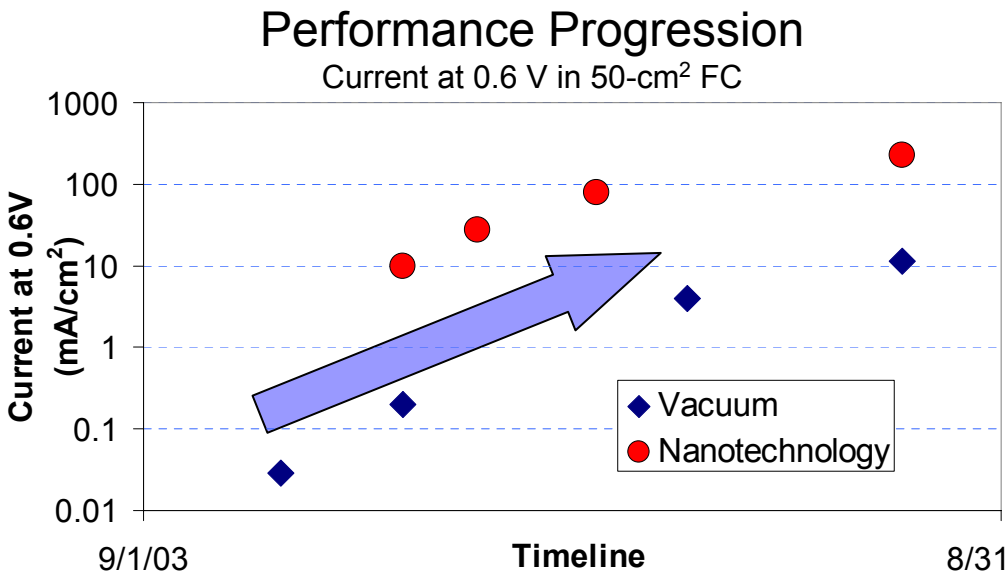
Remainder of project:

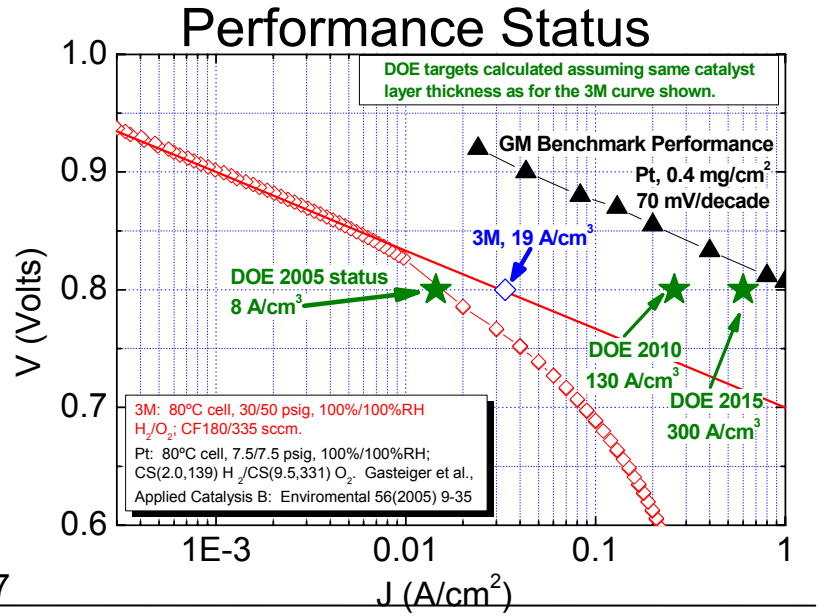
- Fulfill reporting obligations, most notably the Final report.
- Prepare manuscripts for publication and conference presentations.
- Explore further the area of more durable catalysts substrates and identify the catalytic sites (**will continue after completion of the Project**).

Summary



- In 2007, a **major breakthrough in durability** was achieved.
- **Overall,** the project established **new synthetic approaches** and opened **new avenues** for further development in the NPMC world.
- Strong interactive advanced characterization and modeling complement the synthetic effort.
- Strong, fully-integrated collaborations supplement 3M expertise and lead to fundamental understanding of catalyst.
- **12** publications, presentations, and three invited lectures.
- **Today, 3M's catalysts are among the best performing and most durable NPMC tested in a real fuel cell.**

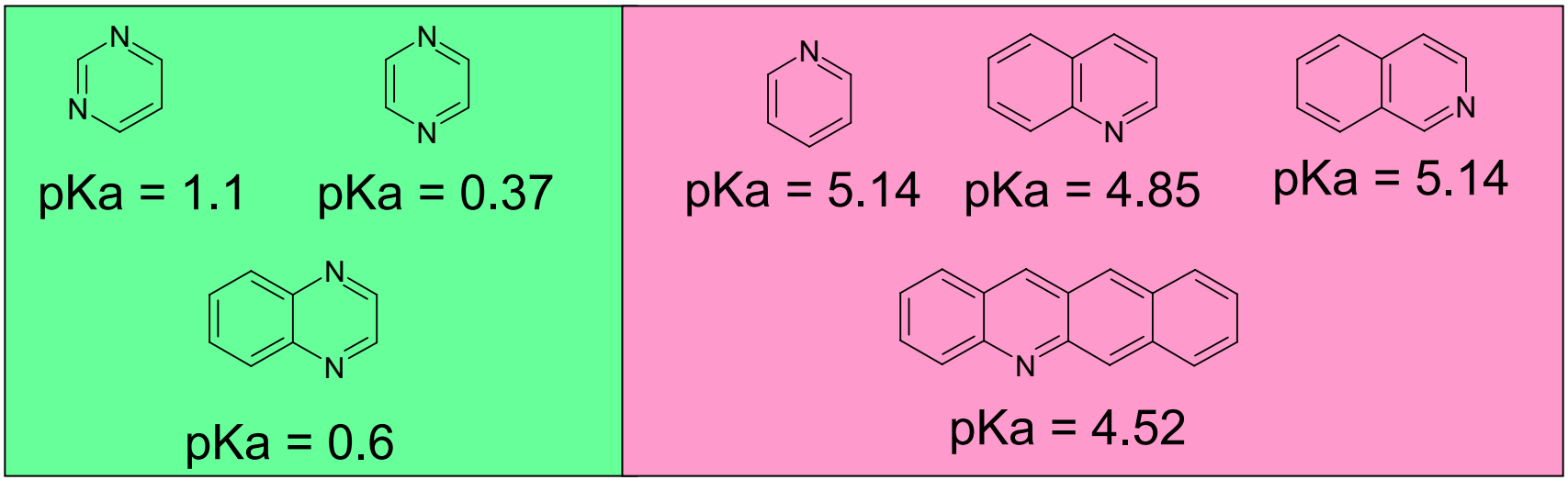




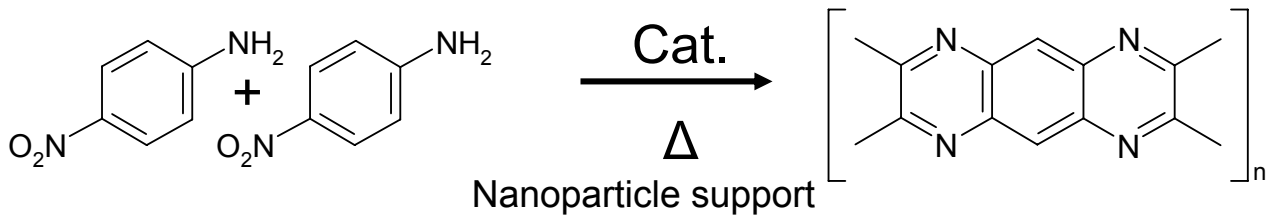
Highly Nitrogenated Carbon – HNC – for Acidic FC

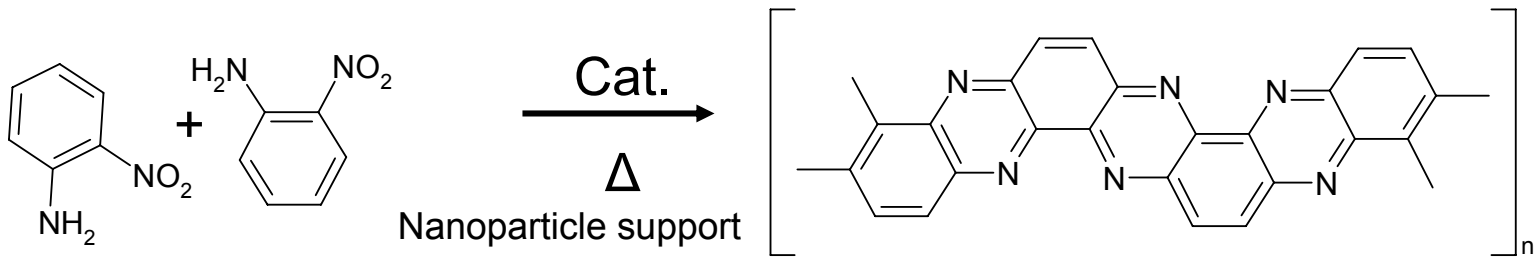
Catalyst activity depends on the content and the **basicity** of the N sites:

- Requires low basicity of nitrogen sites
- "Pyridinic" – higher basicity
- "Pyrazinic" – lower basicity
- Model compounds (Literature values):



Thermal Polymerization to Form New HNC





(One possible configuration)

- When iron or cobalt are present, metal is retained as bonded to nitrogen
- Further thermal processing increases conductivity
- Metal cation is used to retain active nitrogen sites (template)
- Metal can be removed with retention/enhancement of activity
- Can titrate sites to examine nitrogen density and basicity
- Supported on nanoparticle support for high surface area