2004 DOE HYDROGEN, FUEL CELLS, AND INFRASTRUCTURE
TECHNOLOGIES PROGRAM REVIEW MEETING
May 24-27, 2004, Philadelphia, PA

Novel Approach to
Non-Precious Metal Catalysts

Radoslav T. Atanasoski
3M Company

May 25, 2004

3M/DOE Cooperative Agreement No. DE-FC36-03GO13106

Project Objectives

Overall:

- Demonstrate & develop non-precious metal **NPM cathode catalyst**
  - to **lower cost** **(50 % less vs. target of 0.2 g Pt/peak kW)**
  - to **reduce the dependence** of PEM fuel cell catalysts **on precious metals**
- Additionally**, identify opportunities** for
  - **system cost reduction,** through breakthroughs in key area of the fuel cell, the catalyst
  - application of **cost-effective processes for MEA fabrication**, closely associated with the development of the new catalyst

Sept. 2003 – May 2004:

- Investigate **Fe-N-C as a model** catalytic site
- Test **1- and 2- step synthesis** processes
- **Fabricate** & characterize **MEA's** from initial NPM samples

Budget

($ in millions)

	Total	DOE	Contractor
Total	3.61	2.89	0.72
FY04	1.00	0.80	0.20

Technical Barriers and Targets

- DOE Technical Barriers for Fuel Cell Components
  - O. Stack Material and Manufacturing Cost
  - P. Durability
  - Q. Electrode Performance
- Technical Targets
  - **Performance comparable to platinum** used in current MEAs at a **cost 50% less** compared to a target of **0.2 g Pt/peak kW**
  - **Durability** of greater than **2000 hours** with less than 10% power degradation

Approach

To develop new, ***vacuum deposited****, NPM catalysts, 3M is utilizing:*

- 3M's infrastructure for, and understanding of, catalysts generated by previous and concurrent 3M/DOE cooperative agreements
  - High TM/low Pt catalysts
  - 3M's unique nanostructured thin film substrate
  - Processes compatible with high volume manufacturability
- Recent insights regarding non-Pt based ORR catalysts for PEMFC's
  - Published work regarding ORR catalysts, e.g. Fe-N-C moieties identified by Dodelet (see, e.g., *J. Phys. Chem. B*, 104(2000)11238) *(Designated as "****model catalyst****" in this presentation)*
  - Advances and knowledge regarding vacuum deposited precursors suitable for forming TM catalysts, including a variety of carbon based materials

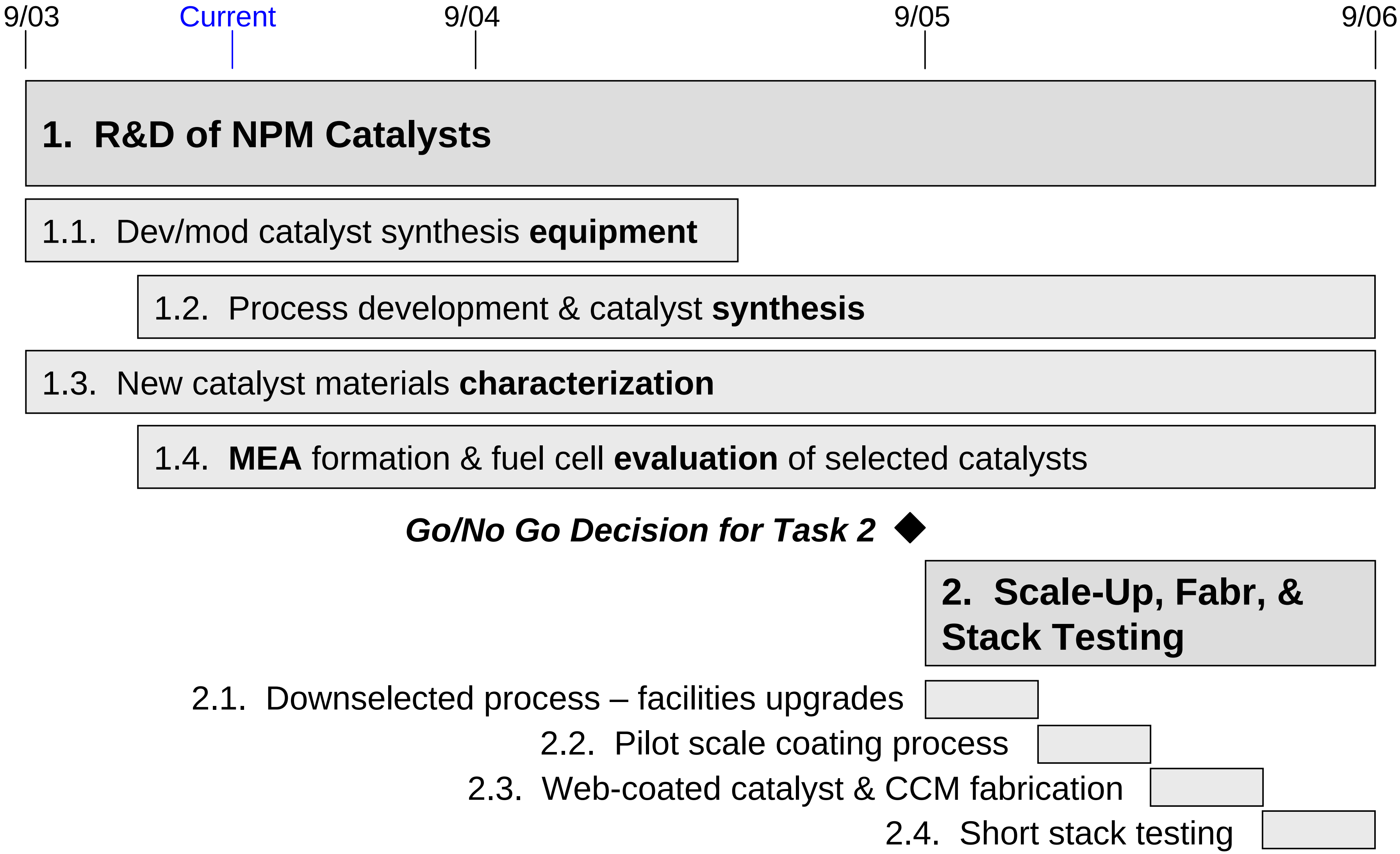
Safety

3M's established procedures regarding safety-related issues include

- Hazard Reviews to ensure compliance with environmental, health, and safety requirements. Required for
  - New or modified facilities, equipment, & processes
  - Fabrication & testing equipment
  - Laboratory & Manufacturing
- New Product Introduction system
  - Risk assessment process in the design and production of products
  - Life Cycle Management process
  - Change Management

No unusual safety issues have been encountered to-date on this project.

Project Timeline



1. R&D of NPM Catalysts

1.1. Dev/mod catalyst synthesis **equipment**

1.2. Process development & catalyst **synthesis**

1.3. New catalyst materials **characterization**

1.4. **MEA** formation & fuel cell **evaluation** of selected catalysts

Go/No Go Decision for Task 2 ◆

2. Scale-Up, Fabr, & Stack Testing

2.1. Downselected process – facilities upgrades

2.2. Pilot scale coating process

2.3. Web-coated catalyst & CCM fabrication

2.4. Short stack testing

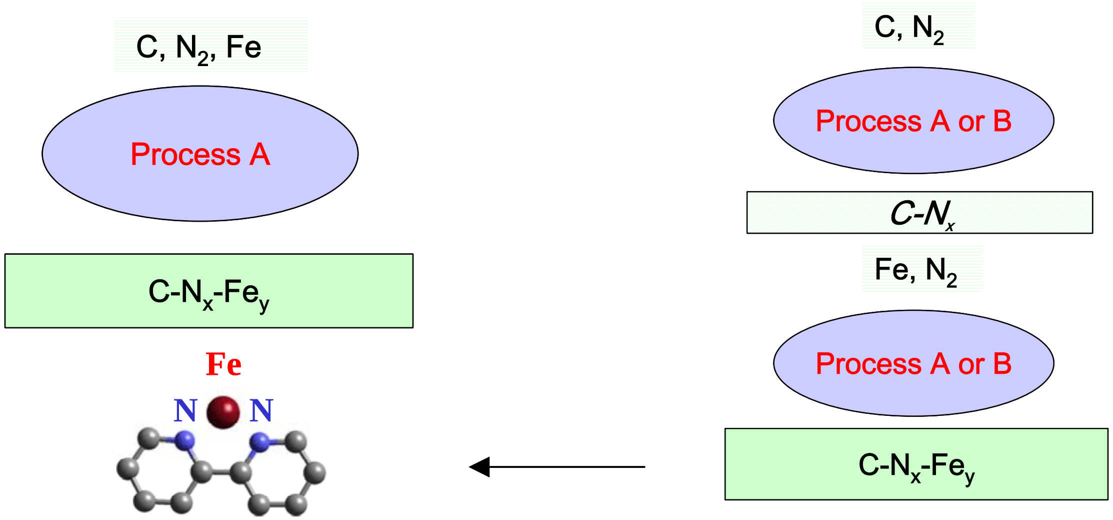
Project Accomplishments

In the initial phase, **reproducing Fe – N – C as a model** catalytic site was attempted. In that regard, we have:

- Produced **highly nitrogenated carbon** by processes compatible with high volume production, mostly in **pyridinic** form.
- Demonstrated **one-step synthesis process** for producing the targeted chemical structure.
- **Formed & characterized 50-cm^2 MEA's** from the new catalyst.
- **Modeled** the incorporation of nitrogen and iron in the graphene layers.

Synthesis & Characterization of NPM Catalyst

Fabricated catalyst materials by 1- and 2-step processes.



C, N_2, Fe

Process A

C-N_x-Fe_y

C, N_2

Process A or B

C-N_x

Fe, N_2

Process A or B

C-N_x-Fe_y

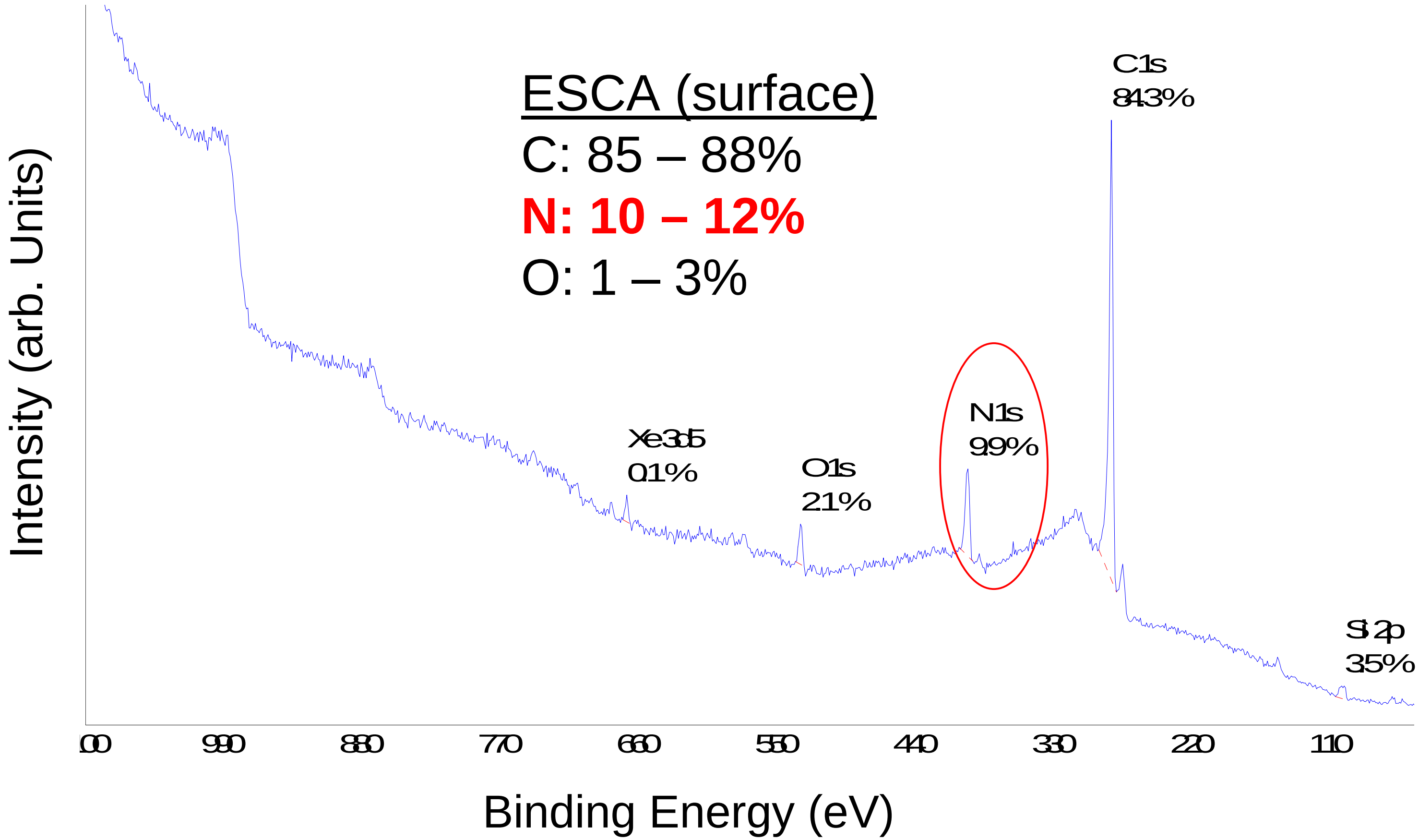
Conducted physicochemical and electrochemical characterization.

- Materials Fabricated
  - **43** substrate coatings (12 carbon, 28 C-N_x)
  - **13** C-N_x-Fe_y catalyst materials via Process A, one-step synthesis
  - **30** TM catalyst synthesis via Process B, two-step
- Physicochemical Characterization
  - ESCA analysis on 43 samples, 140 spectra
  - XRF: 28 samples, 39 spectra
- Electrochemical Characterization
  - over **50 fuel cells**

$C\text{-}N_x$ Precursor: Nitrogen Content

High nitrogen content necessary, but not sufficient, for high surface density catalyst sites.

- Achieved 5 times higher N content than in the model catalyst.



ESCA (surface)

C: 85 – 88%

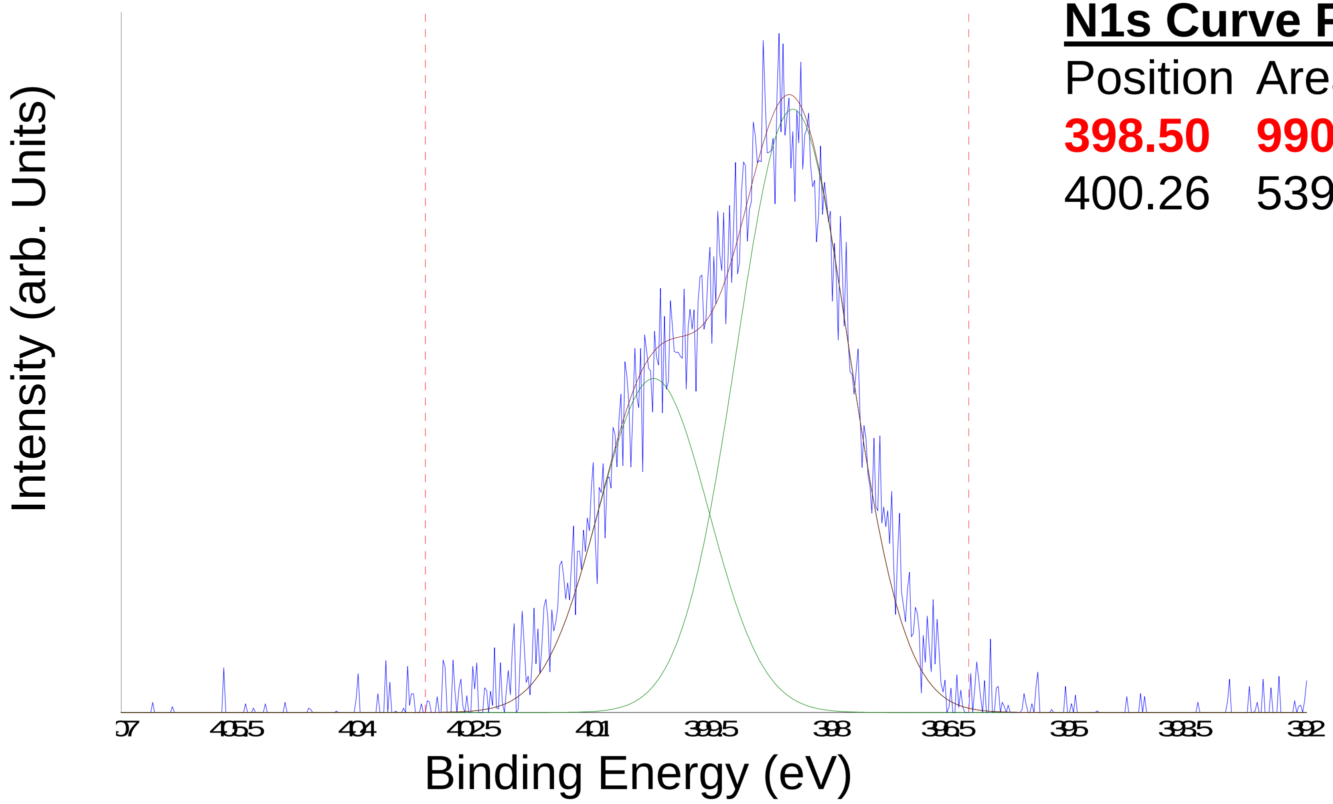
N: 10 – 12%

O: 1 – 3%

Percentage of Pyridinic Nitrogen in Fe-N-C

To form high catalytic activity sites, nitrogen must be in pyridinic form.

- Achieved 15 – 20 % higher pyridinic N than in model catalyst.

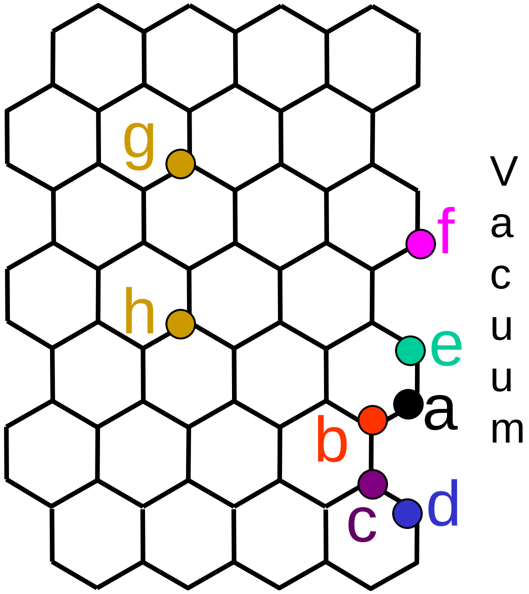


N1s Curve Fit Summary

Position	Area	Area %
398.50	**990**	**64.7%**
400.26	539	35.3%

Modeling: Nitrogen on Graphite Edge

Heat of formation from the reaction: $N_2 + C_x \rightarrow C_{(x-2)}N_2 + 2C_{(\text{graphite})}$



Positions of N atoms	Heat of substitution (eV)	Relative Energy (eV)
a-b	**-2.89**	**0.0**
a-c	**-3.26**	**-0.37**
a-d (model)	**-4.78**	**-1.89**
a-e	**-4.65**	**-1.76**
a-f	**-4.78**	**-1.89**

g-h (bulk)	**1.55**	**---**

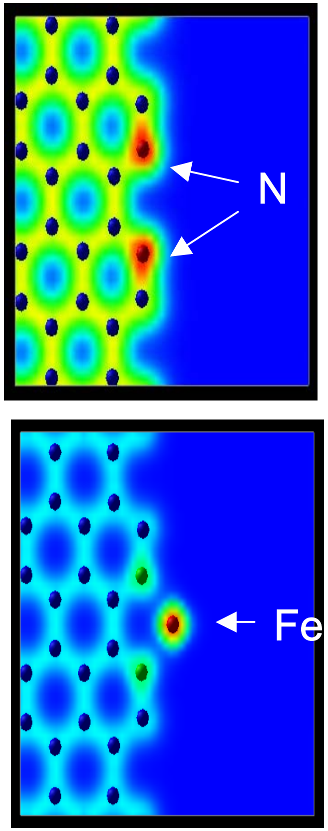
- Substituting carbon for nitrogen in the graphene edges is thermodynamically favorable, especially if two N atoms are far apart.
- Substitution in the bulk is unfavorable.

Model Catalyst Calculations: Fe-N_2-C

Incorporation of **2 N atoms in pyridinic sites** on the edge of a graphene sheet (upper).

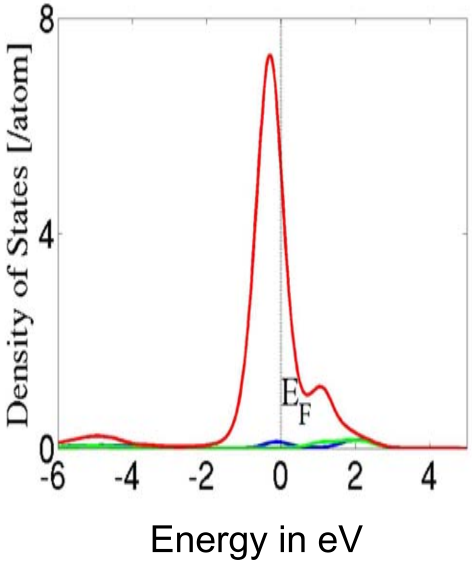
Iron appears to **be in Fe^{++}** and injects charge into the support (lower).

Electron charge distribution



1. VASP (Vienna Ab-initio Simulation Package)
2. Plane waves for electron wavefunction.
3. Projector Augmented Waves (PAW)
4. PBE exchange correlation functional

Partial **Fe-d** Density of States

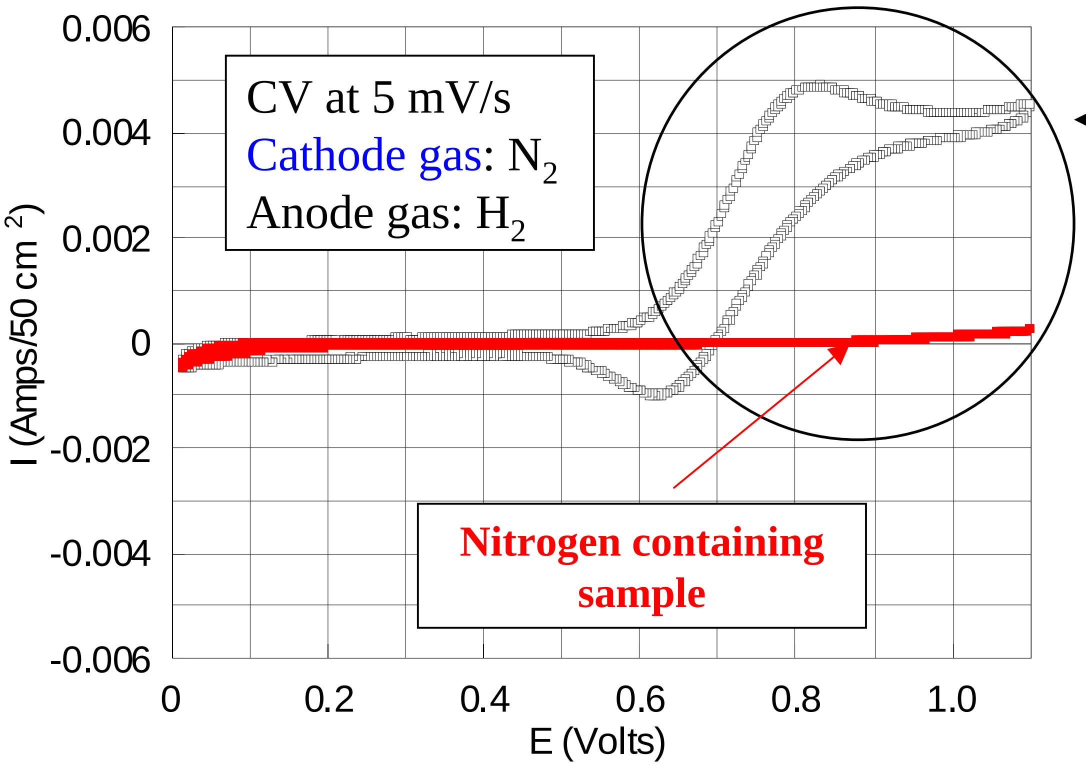


Fe-d states are close to Fermi level and may be **available for catalytic activity**.

Electrochemical Characterization: Stability Evaluation

Comparison of samples made **with** and **without nitrogen**

- CV's indicate **films made with nitrogen are more stable**.



CV at 5 mV/s
Cathode gas: N_2
Anode gas: H_2

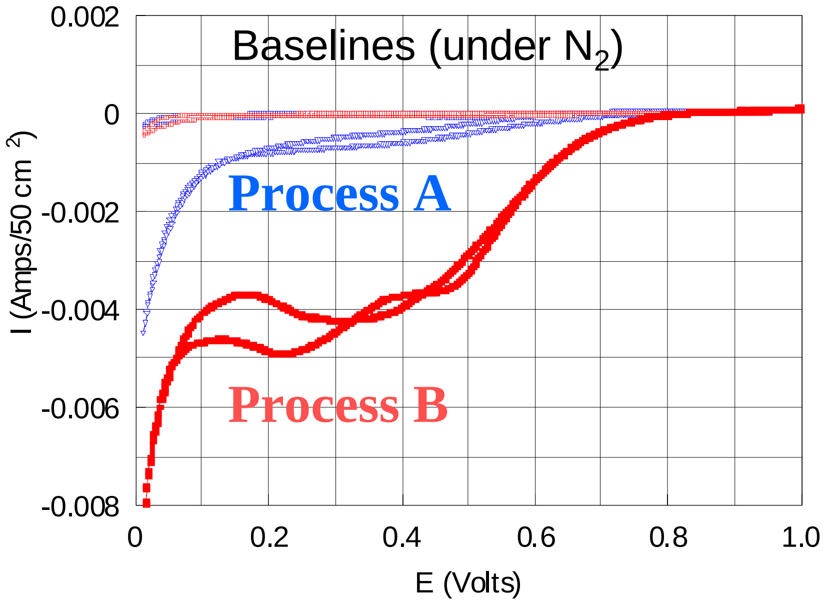
Nitrogen containing sample

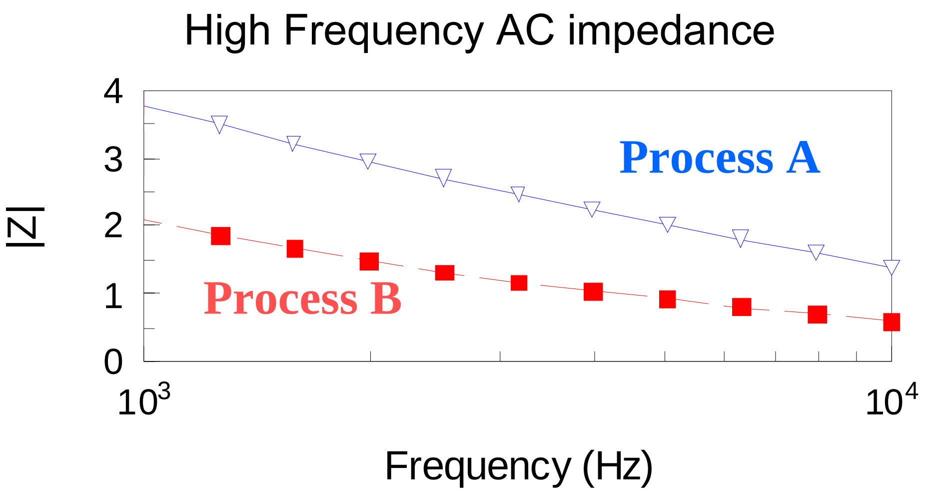
Anodic current as evidence of less stable nature of coating – **nitrogen-free sample**

Samples made via one-step process

Electrochemical Characterization: Oxygen Response

Comparison of samples made by **one-step** (Process A) or by depositing TM on nitrogenated carbon from (Process B)





- TM coated on N-C exhibits better activity and lower impedance than one-step sample without losing stability.
- All the building blocks for the model catalyst are in place, but electrochemical activity remains to be improved.

Future Plans

- Assess appropriateness of nitrogenated carbon precursor for transformation into catalyst.
  - Thermal application of TM to achieve TM – N – C model catalyst
- Identify the nature of the most active sites.
  - Intensify and expand the use of physicochemical methods (XPS, XRF, etc.).
- Continue modeling leading to promising NPMC systems.
- Explore boundaries of the NPMC space.
  - Broaden the range of process variations and key synthesis parameters.
  - Use of fast screening methods (subcontract with Jeff Dahn)