Novel Approach to Non-Precious Metal Catalysts
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3M Company
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This presentation does not contain any proprietary or confidential information
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)

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>DOE</th>
<th>Contractor</th>
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<tbody>
<tr>
<td>Total</td>
<td>3.61</td>
<td>2.89</td>
<td>0.72</td>
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<tr>
<td>FY04</td>
<td>1.00</td>
<td>0.80</td>
<td>0.20</td>
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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
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-cm² 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.

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-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%
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

<table>
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<tr>
<th>Position</th>
<th>Area</th>
<th>Area %</th>
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<tr>
<td>398.50</td>
<td>990</td>
<td>64.7%</td>
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<tr>
<td>400.26</td>
<td>539</td>
<td>35.3%</td>
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Modeling: Nitrogen on Graphite Edge

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

<table>
<thead>
<tr>
<th>Positions of N atoms</th>
<th>Heat of substitution (eV)</th>
<th>Relative Energy (eV)</th>
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</thead>
<tbody>
<tr>
<td>a-b</td>
<td>-2.89</td>
<td>0.0</td>
</tr>
<tr>
<td>a-c</td>
<td>-3.26</td>
<td>-0.37</td>
</tr>
<tr>
<td>a-d (model)</td>
<td>-4.78</td>
<td>-1.89</td>
</tr>
<tr>
<td>a-e</td>
<td>-4.65</td>
<td>-1.76</td>
</tr>
<tr>
<td>a-f</td>
<td>-4.78</td>
<td>-1.89</td>
</tr>
<tr>
<td>g-h (bulk)</td>
<td>1.55</td>
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- 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).

Partial Fe-d Density of States

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

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

Comparison of samples made with and without nitrogen

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

![Graph showing CV at 5 mV/s with Cathode gas: N\textsubscript{2} and Anode gas: H\textsubscript{2}]

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

- Samples made via one-step process

Nitrogen containing sample
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)