Precious Metal Free Fuel Cell Catalysts, Concepts and Limits

Barr Halevi, Pajarito Powder LLC
Outline

• What are non-PGM ORR catalysts?
• Identifying the active site/s and mechanism
• Key morphology
• Making deployable non-PGM catalysts
• Successes
• Challenges
PPC founded to:
Create & Manufacture
Affordable Fuel Cell Catalysts
in Commercial Quantities

Piotr Zelenay
PPC founded to: Create & Manufacture Affordable Fuel Cell Catalysts in Commercial Quantities
Non-PGM Catalysts

Catalysts Precursor: Porphyrins or Phthalocyanines

Low-temperature pyrolysis product: NOT as active, Strong H₂O₂ producer

High-temperature pyrolysis product: MORE as active, ??? H₂O₂ ???

Polypyrrole

Polyaniline

Including infusion with gases

Low Molecular Weight precursor
Outline

• What are non-PGM ORR catalysts?
• Identifying the active site/s and mechanism
Active Site Identification

• Electrochemical Analysis
  – Rotating Ring and Rotating Disk Electrode (RRDE and RDE)
• Ab-initio calculations - Density Functional Theory (DFT)
• Multiple chemical species & Activity correlation
  – X-Ray Photoelectron Spectroscopy (XPS)
  – Aberration Corrected Transmission Electron Electron Microscopy (ACTEM)
  – Raman Spectroscopy
  – Mössbauer Spectroscopy
  – $\Delta \mu$ X-Ray Absorption Spectroscopy ($\Delta$XAS)
    – Electrochemical XAS (e-XAS)
• Good statistical analysis and correlation of all of the above!
Oxygen Reduction Reaction on Non-PGM Catalysts

- Bi(+) -functional Mechanism
- Two(+) types of Active Sites

Multifunctional Site/s

DFT: Fe(N-C)$_4$ Most Likely

Density-Functional-Theory (DFT).
- Generalized Gradient Approximation (PBE).
- 3-d periodic boundary conditions.
- Plane-waves.
- Spin polarized: Co.
- PAW-potentials.
- Fermi-smearing ($\sigma = 0.025$ eV)

Surfaces:
- Graphene (32 atoms).
- 14 Å vacuum.
- Molecule(s) pre-optimized.
- Dipol correction.

Boris Kiefer
DFT: Fe(N-C)$_4$ Most Likely

Possible electron arrangements in 3$d$ orbitals of Fe$^{+2}$ in Fe-N$_4$ sites: a) high spin, b) intermediate spin, and c) low spin states, and d) electronic density of states (DOS) of Fe in graphitic Fe-N$_4$ sites.

S. Kattel, P. Atanassov and B. Kiefer, PCCP 13800-13806
XPS: Fe(N-C)_x Exist

<table>
<thead>
<tr>
<th>BE, eV</th>
<th>398.5-398.8</th>
<th>399.5-399.8</th>
<th>400.6-400.9</th>
<th>401.5-402</th>
<th>402.5-403</th>
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<tbody>
<tr>
<td>structure</td>
<td><img src="image1" alt="Pyridinic" /></td>
<td><img src="image2" alt="Pyrrolic" /></td>
<td><img src="image3" alt="Quaternary" /></td>
<td><img src="image4" alt="Graphitic" /></td>
<td></td>
</tr>
<tr>
<td>name</td>
<td>pyridinic</td>
<td>N_x-Me (x=1,2,3,4)</td>
<td>pyrrolic</td>
<td>quaternary</td>
<td>graphitic</td>
</tr>
</tbody>
</table>

Kateryna Artyushkova
Both Me-N$_2$ and Me-N$_4$ centers are present but their relative amount changes upon exposure to oxidizing atmosphere –stabilization of N$_4$ centers.

ACTEM – Fe/N Sites Exist

ACTEM images proves Nitrogen & Iron single sites in graphene

Gerd Duscher  
Matt Chisholm
The relative content of D1 or D2 is high, demonstrating the successful integration of the majority of the iron in FeNₓCᵧ molecular sites during pyrolysis.

The existence of Fe-N coordinations by Mössbauer spectra, (doublets) is also supported by the Fe-N binding energy in XPS at 399.6 eV.

<table>
<thead>
<tr>
<th>Component (assignment)</th>
<th>IS (mm·s⁻¹)</th>
<th>QS (mm·s⁻¹)</th>
<th>H (Tesla)</th>
<th>LW (mm·s⁻¹)</th>
<th>Relative absorption area (%)</th>
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</thead>
<tbody>
<tr>
<td>α-Fe</td>
<td>0.04</td>
<td>-</td>
<td>33.5</td>
<td>0.37</td>
<td>4</td>
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<tr>
<td>Fe₅C</td>
<td>0.29</td>
<td>-</td>
<td>20.2</td>
<td>0.62</td>
<td>8</td>
</tr>
<tr>
<td>Param. or γ-Fe</td>
<td>-0.07</td>
<td>-</td>
<td>-</td>
<td>0.67</td>
<td>14</td>
</tr>
<tr>
<td>D1 (Fe⁷N₄ LS)</td>
<td>0.33</td>
<td>0.98</td>
<td>-</td>
<td>0.80</td>
<td>30</td>
</tr>
<tr>
<td>D2 (Fe⁶N₄ MS)</td>
<td>0.51</td>
<td>2.34</td>
<td>-</td>
<td>1.83</td>
<td>44</td>
</tr>
</tbody>
</table>
Fe$^{2+}$-$N_4$ active site at 0.3 V undergoes redox transition to a penta-coordinated (H)O–Fe$^{3+}$–$N_4$ at 0.90 V.

<table>
<thead>
<tr>
<th>Potential</th>
<th>CN</th>
<th>R  (Å)</th>
<th>$\sigma^2 (\text{Å}^2) \times 10^3$</th>
<th>$E_0$ (eV)</th>
<th>CN</th>
<th>R  (Å)</th>
<th>$\sigma^2 (\text{Å}^2) \times 10^3$</th>
<th>$E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 V</td>
<td>3.6(7)</td>
<td>2.02(2)</td>
<td>9(3)</td>
<td>-5(1)</td>
<td>1.2(3)</td>
<td>2.51(1)</td>
<td>9(3)</td>
<td>-5(1)</td>
</tr>
<tr>
<td>0.9 V</td>
<td>4.0(8)</td>
<td>2.01(2)</td>
<td>4(2)</td>
<td>-6(2)</td>
<td>1.3(3)</td>
<td>2.52(1)</td>
<td>4(2)</td>
<td>-6(2)</td>
</tr>
</tbody>
</table>
eXAS – mechanism?

Oxygen Reduction Reaction on Non-PGM Catalysts
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• What are non-PGM ORR catalysts?
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Pore Structures

GOOD CATALYST

EXCELLENT CATALYST

BAD CATALYST

X5
Pore Structure Role

- Micro-porosity =
  - Super-hydrophobicity

- Meso-porosity =
  - Electrochemically-accessible surface area
Different Active Sites

Structure-to-Property Relationships

- Polymers
- Low MW organics
- Chelates
- Worse performance

**E_{1/2}, V**

pyridinic N/pyrrolic N

PC1 53.6%

PC2 20.0%

Best performance

Worse performance

Kateryna Artyushkova
Outline

• What are non-PGM ORR catalysts?
• Identifying the active site/s and mechanism
• Key morphology
• Making non-PGM catalysts
Making Non-PGM Catalysts

• Multiple ways to make non-PGM catalysts
  – Need to bring precursors together on nano-scale then react them to make active sites
  – Some processes are very complex with iterations of mixing, cooking, pyrolysis, etching.
  – Commonality:
    • Similar precursors
      – M/N/C compounds (ex: cyanamide) & Metal salts +N/C compounds
    • Mixing
    • Pyrolysis at 800-950C
    • Etch excess metal particles
Different Active Sites

- Edge defects
- In-plane defects

• Edge less stable, more active
• In-plane more stable, less active
• Need in-plane for stable/durable catalysts!
Sacrificial Support Method

Fumed Silica: BET-SA ~50-400 m²/g

Template: monodispersed amorphous silica
infused with transition metal salt and N-C precursor
pyrolyzed in inert atmosphere
silica etched by HF and removed

N-C Precursor: 1,4-Phenylenediamine 3-Hydroxytyramine 4-Aminoantipyrine Diethanolamine N-Hydroxysuccinimide Phenanthroline Carbendazime

Metals: Ce, Zr, V, Ti, Ta, Nb, W, Mo, Fe, Ru, Co, Ni, Cu

Templated Self-supported Non-PGM Catalyst

Alexey Serov
SSM Catalyst Evolution

Silica Infused with precursors

Pyrolized infused silica

Pyrolized pore structure

Etched pore structure

Porous non-PGM catalyst

Ball-Mill Pyrolysis Etching Centrifuge Filter Dry Pyrolysis

October 8, 2014

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Precipitated Silica: Sponge-like

Fumed Silica: Sponge-like

Typical Pt/C

Sacrificial support allows for pore size tailoring to match current Pt/C catalysts
Iron Nicarbazin Catalyst

Fe +

Catalyst loading is 4 mg catalyst/cm²

~ 0.92 V OCV

Conditions: T<sub>cell</sub>=80°C, 100% RH, 1.5 bar total pressure. Anode: 0.4 mg cm⁻² (Pt/C), Cathode: 4 mg cm⁻²

Meets DoE target of 100 mA/cm² at 0.8V<sub>irr-free</sub> in Oxygen

DOE EERE Project ID# FC086 AMR 2103 report, NTCNA testing
Load cycling AST – Good!

**Conditions:** $T_{cell} = 80^\circ C$, 100% RH, 1.5 bar total pressure.
Anode: 0.4 mg cm$^{-2}$ (Pt/C),
Cathode: 4mg cm$^{-2}$.

Minimal change in performance is observed after 10,000 potential cycles (load cycling) from 0.6 to 1.0V.
Start/Stop AST – Good!

**H₂/O₂ 80°C 100% RH 1 bar Total Pressure (DOE standard conditions)**

*Pt/C cathode loading = 0.15 mg/cm² using a 20% Pt on carbon catalyst

**Start/Stop AST – Good!**

**Durability under start/stop similar to Pt/C**

DOE EERE Project ID# FC086 AMR 2103 report, NTCNA testing
Volumetric Projection

Sanjeev Mukerjee, NEU

<table>
<thead>
<tr>
<th>Sample</th>
<th>mV @200 A/cm³</th>
<th>A/cm³ @0.8 V (iR free)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA 2</td>
<td>809</td>
<td>400</td>
</tr>
<tr>
<td>MEA 10</td>
<td>796</td>
<td>150</td>
</tr>
<tr>
<td>MEA 14</td>
<td>810</td>
<td>400</td>
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Micro-porosity =
- Super-hydrophobicity

Meso-porosity =
- Electrochemically-accessible surface area

MEU-SEM 500nm
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Scale-up process

Ball-Mill → Pyrolysis → Etching → Centrifuge → Filter → Dry → Pyrolysis

Batch Size

0.5 g
50 g
100 g

Scale-up process
Testing conditions
0.5bar O₂ 100%RH 80°C 211 membrane, 45wt% Nafion 1100
Anode = 0.2mgPt/cm²
Cathode = 2.3mgcat/cm²

Improved inter-batch variability illustrated by Samples 1, 2, 3 and 4
Improved intra-batch variability (<5% @0.4V) illustrated by GDEs made from Sample 3
Improved performance for different sources of precursors, see Sample 4
**Improved formulation**

Catalyst formulation leading to MEA performance improvements

DoE Target I met, without iR correction – 60% improvement towards target II

211 Nafion, 45wt%
1100 EW, 4mg/cm² catalyst, 25BC GDL, 100% RH, 2.5bar Air

**Graph:**

- **Axes:**
  - Y-axis: $E$ (Volts, iR uncorrected)
  - X-axis: $I$ (A/cm²)

- **Lines:**
  - Gen1
  - Gen1A
  - Gen1B
  - Gen2
  - Gen2A
  - Gen2B
  - Targets

- **Notes:**
  - Improved formulation
Improved formulation

Catalyst formulation leading to MEA performance improvements
DoE Target I met, without iR correction – 60% improvement towards target II
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Non-PGM ORR catalysts

- Characterization techniques developed
- Mostly likely active site/s identified
- Iterative approach to synthesis
  - Key factors hypothesized
  - Catalysts made
  - Catalysts characterized
    - Correct surface chemistry
    - Porosity
  - Key factors identified
Commercialization

Precious Metal Free Fuel Cell Electric Vehicle

FC ⚔️ (DEKO: Convex) DECK

43rd Tokyo Motor Show


B. Pivovar, Alkaline Membrane Fuel Cell Workshop Final Report
NREL/BK-5600-54297
PPC Capabilities

- Multiple no-PGM catalyst production methods and formulations scaled to 25-100gr
- Fixed Product Line (200gr/day capacity)
  - **NPC-2000 & 1000**: non-platinum, drop-in fuel cell catalysts with different performance/price points
  - **PHC-3000**: Ultra low loaded platinum content catalyst for higher performance
- Custom Catalyst Design
- Contract Manufacturing
Outline

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- Successes
- Challenges and Limits
Limits

- Pt/C activity per gram likely unachievable
- BUT, Cost/Performance parity exists today
  - $/kW to improve dramatically at scale

- Additional work is needed
  - Electrode must be re-optimized for non-PGM
  - Additional durability and stability testing
Thanks

- Verge Fund
- University of New Mexico
  - Profs. Plamen Atanassov, Alexey Serov, and Kateryna Artyushkova
- New Mexico State University
  - Prof. Boris Kiefer
- Northeastern University
  - Prof. Sanjeev Mukerjee and several students
- Michigan State University
  - Prof. Scott Calabrese Barton and Nate Leonard
- Los Alamos National Laboratory
  - Drs. Piotr Zelenay, Hoon Chung, and Gang Wu
- Nissan technical Center North America
  - Drs. Nilesh Dale, Ellazar Niangar, and Taehee Han
Questions?

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