Deployment of Non-Platinum Catalysts for PEM Fuel Cells

Alexey Serov, Pajarito Powder LLC and UNM Teams
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*
PPC founded to: Create & Manufacture Affordable Fuel Cell Catalysts in Commercial Quantities
Non-PGM Catalysts

Catalysts Precursor
Porphydrins or Phthalocyanines

Pyrolysis Products

Low-temperature pyrolysis product:
NOT as active, Strong H$_2$O$_2$ producer

High-temperature pyrolysis product:
MORE as active, ??? H$_2$O$_2$ ???

Including infusion with gases

Polypyrrole
Pyrrolic
Polyaniline

Pyridinic Polymer Series

N4 Pyrrolyc Polymer

N1
N2
N3

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 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!
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• What are non-PGM ORR catalysts?
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• Key morphology
Pore Structures

GOOD CATALYST

EXCELLENT CATALYST

BAD CATALYST

X5
Pore Structure Role

- **Micro-porosity =**
  - Super-hydrophobicity

- **Meso-porosity =**
  - Electrochemically-accessible surface area

![Pore structure image](image_url)
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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
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

Alexey Serov

Templated Self-supported Non-PGM Catalyst
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

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Iron Nicarbazin Catalyst

Catalyst loading is 4 mg_{catalyst}/cm^2

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}

Meets DoE target of 100 mA/cm^2 at 0.8V_{ir-free} in Oxygen

DOE EERE Project ID# FC086 AMR 2013 report, NTCNA testing
Load cycling AST – Good!

Conditions: $T_{\text{cell}} = 80\,^\circ\text{C}$, 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)**

\[ \Delta \mu \text{ EXAFS} \]

Durability under start/stop similar to Pt/C

**ECSA**

**DOE EERE Project ID# FC086 AMR 2103 report, NTCNA testing**
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Scale-up process

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

Batch Size

- 100mL
- 500mL
- 1L
- 1" x 6"
- 6" x 30"
- 2000mL
- 500mL
- 15mL
- 50mL
- 0.5L
- 20L
- 0.5 g
- 50 g
- 100 g
50+ Grams Scale-Up

**Testing conditions**
- 0.5 bar O₂, 100% RH, 80°C, 211 membrane, 45 wt% Nafion 1100
- Anode = 0.2 mg Pt/cm²
- Cathode = 2.3 mg cat/cm²

**RDE**
- 1600 RPM, O₂
- A @ 10 mV/s
- B @ 10 mV/s
- C @ 10 mV/s

**5% I error bars**

**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
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

A. Serov, M. Padilla, A.J. Roy, P. Atanassov, T. Sakamoto, K.
PPC Capabilities

• Multiple non-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
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• 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
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Questions?

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