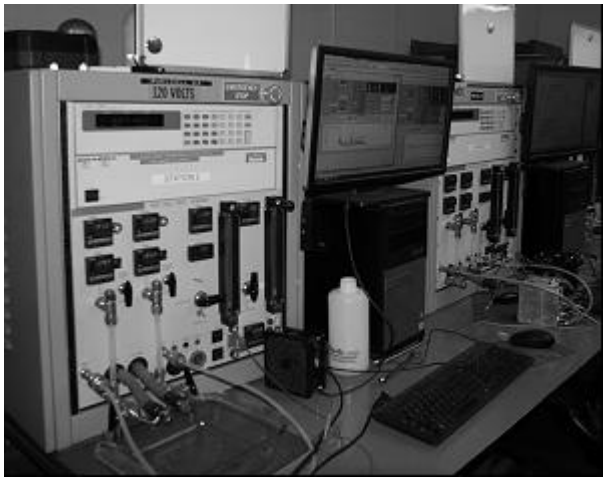
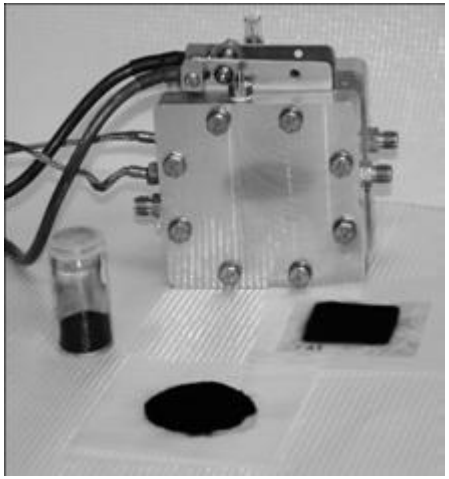
Fuel Cell Seminar & Energy Expositions

PAJARITO POWDER





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 Introduction

PPC founded to:

Create & Manufacture

<u>Affordable</u> Fuel Cell Catalysts

in Commercial Quantities

PPC Introduction

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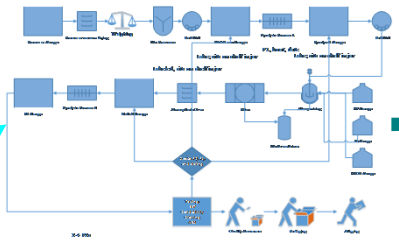

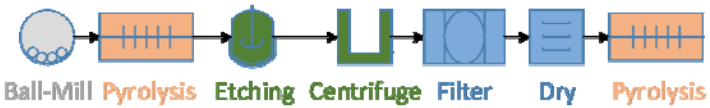

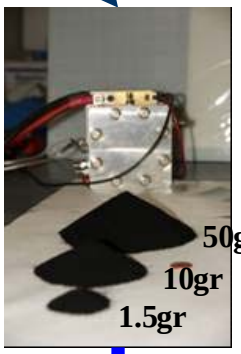

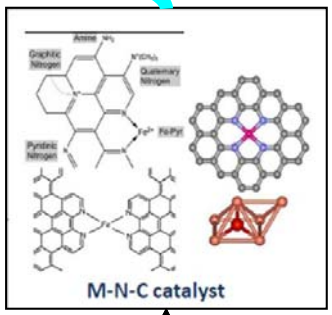

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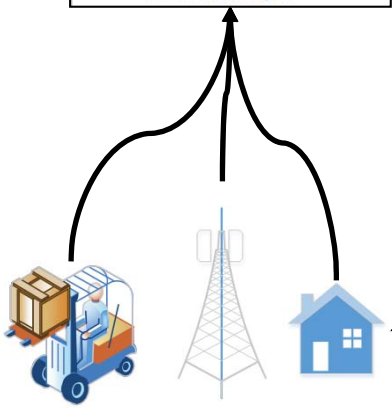
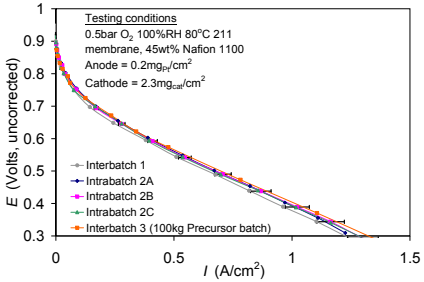
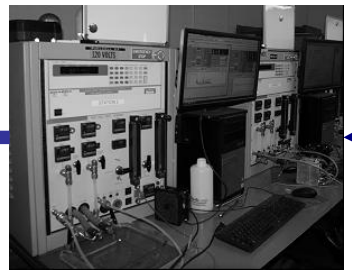
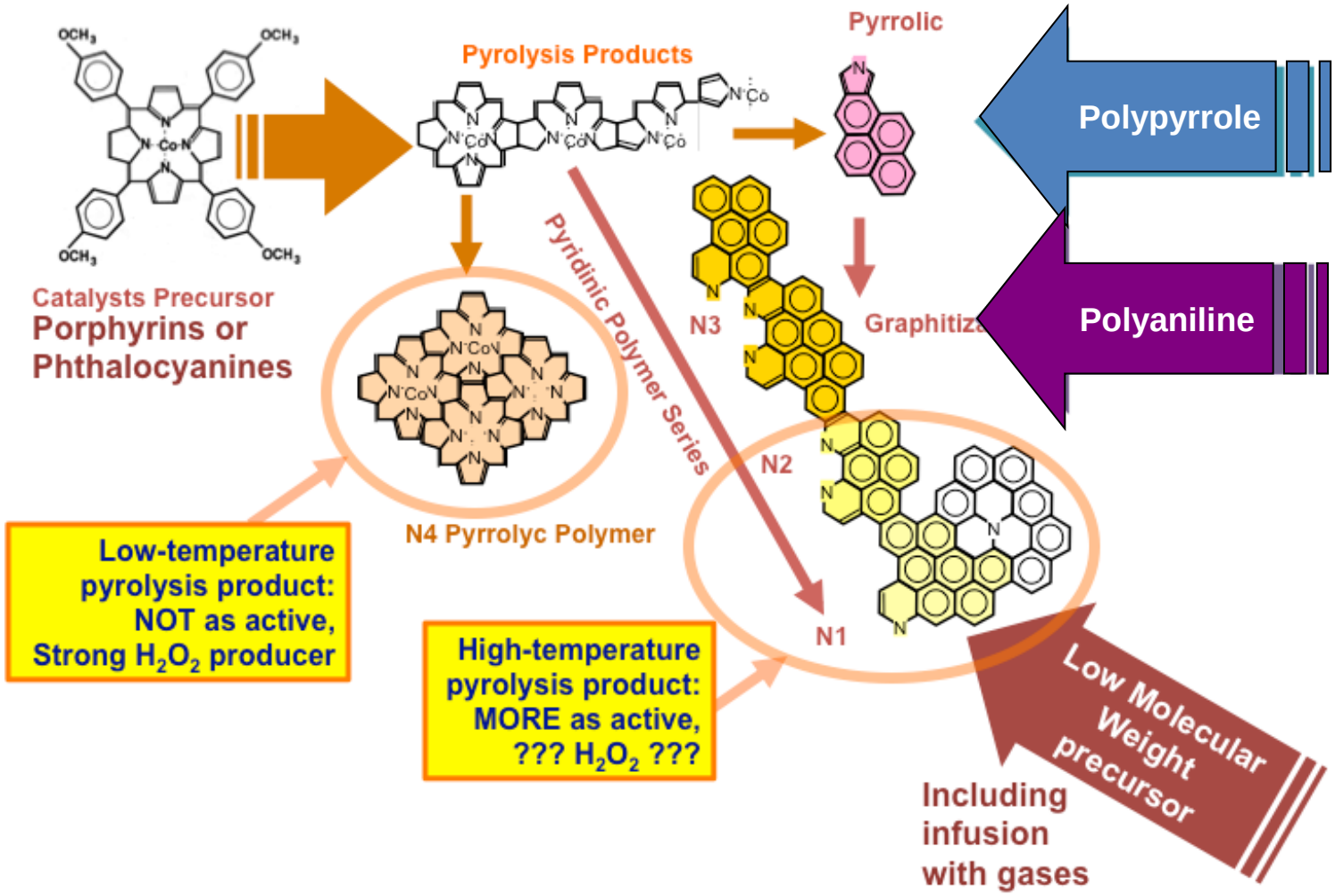






US20080312073A1,WO2012174335A2,WO2013116754A1,WO2012174344A2,WO2014062639A1,WO2014011831A1,WO2014085563A1,WO2014113525A1,

Non-PGM Catalysts



Outline

- What are non-PGM ORR catalysts?
- **Identifying the active site/s and mechanism**

Active Site Identification

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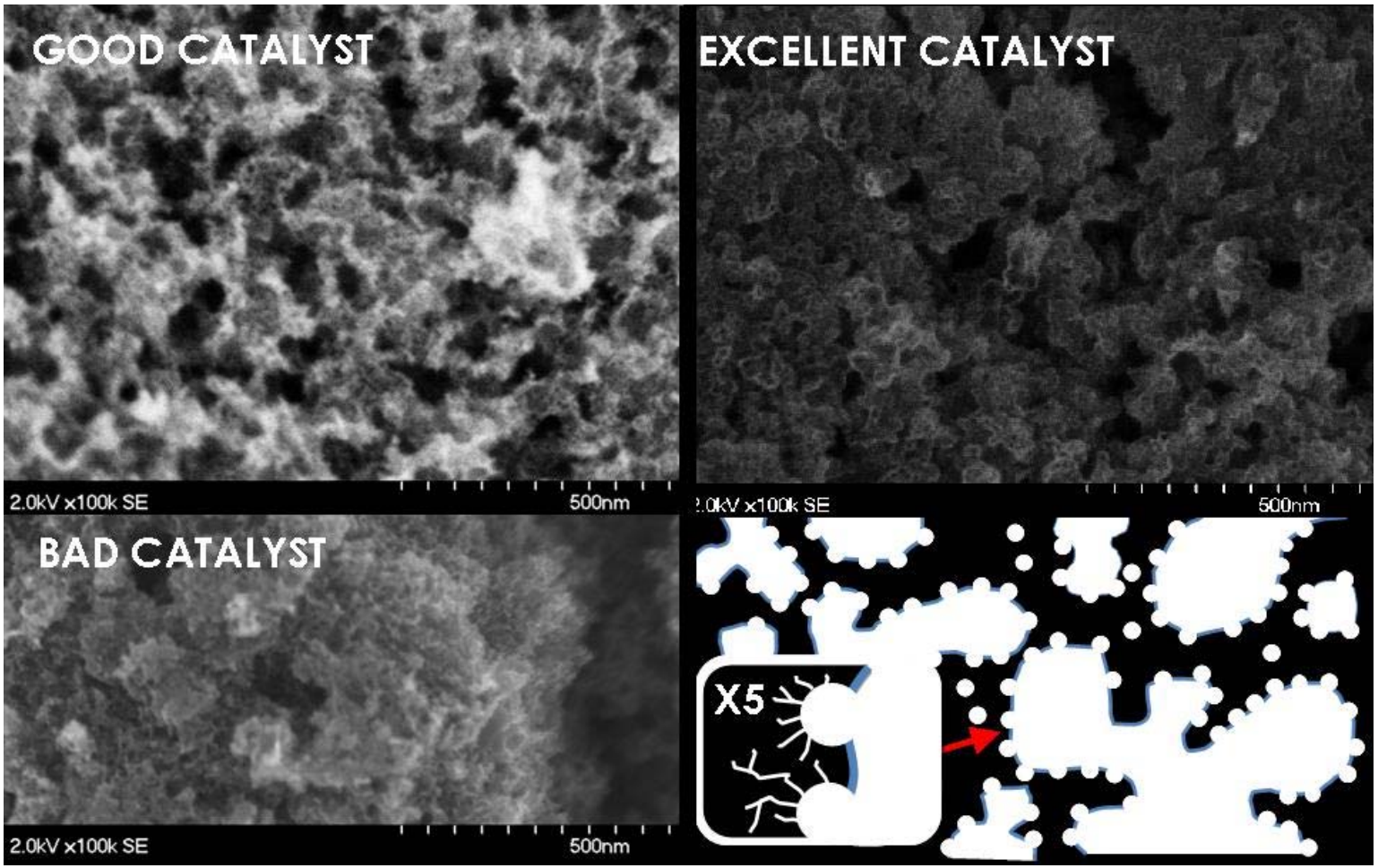
- Electrochemical Analysis
  - Rotating Ring and Rotating Disk Electrode (RRDE and RDE)
- Ab-initio calculations - Density Functional Theory (DFT)
- Multiple chemical species & Activity correlation
  - X-Ray Photoelectron Spectroscopy (XPS)
  - Aberration Corrected Transmission Electron Microscopy (ACTEM)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

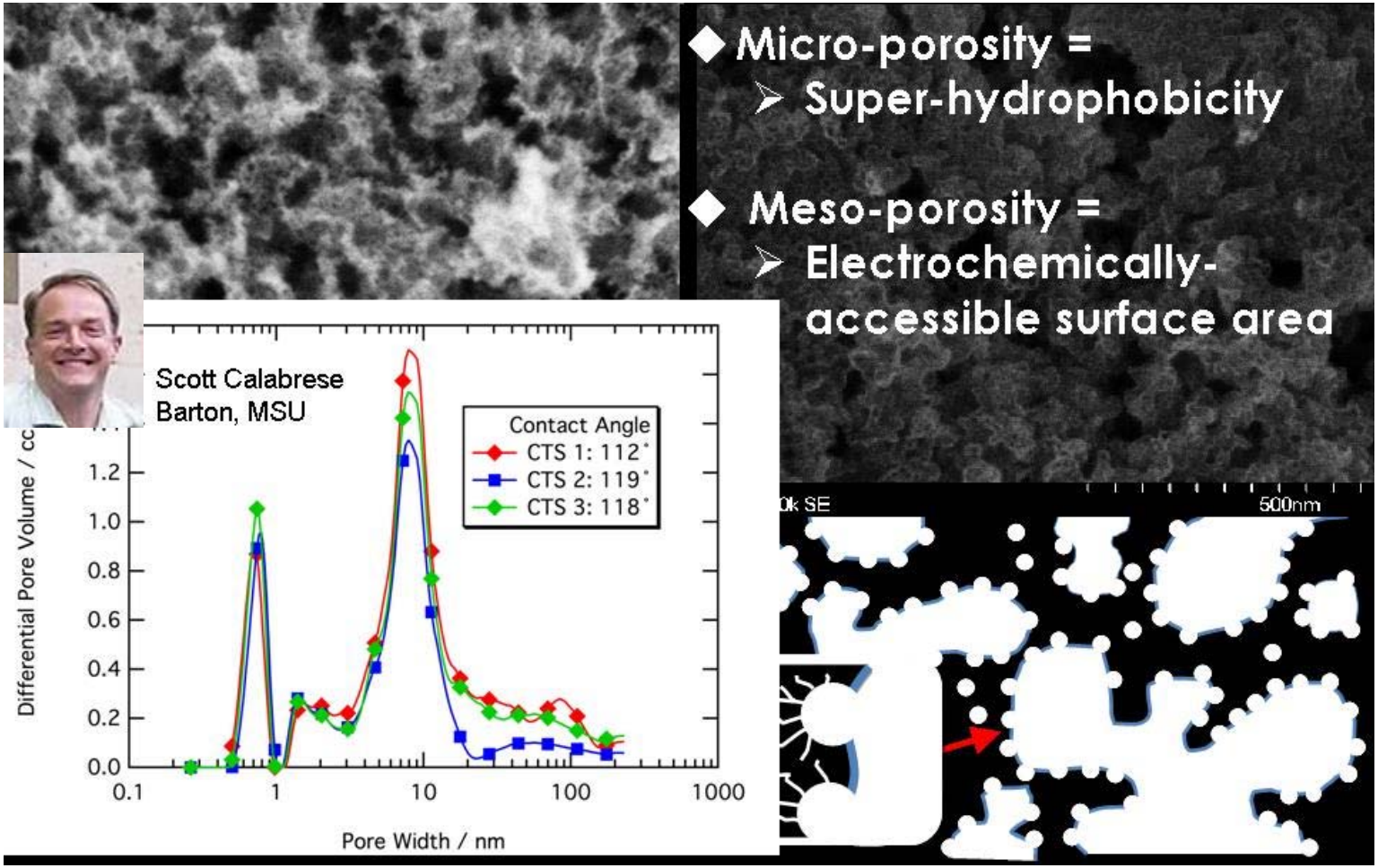
Outline

- What are non-PGM ORR catalysts?
- Identifying the active site/s and mechanism
- **Key morphology**

Pore Structures



Pore Structure Role



Outline

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

Making Non-PGM Catalysts

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- 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

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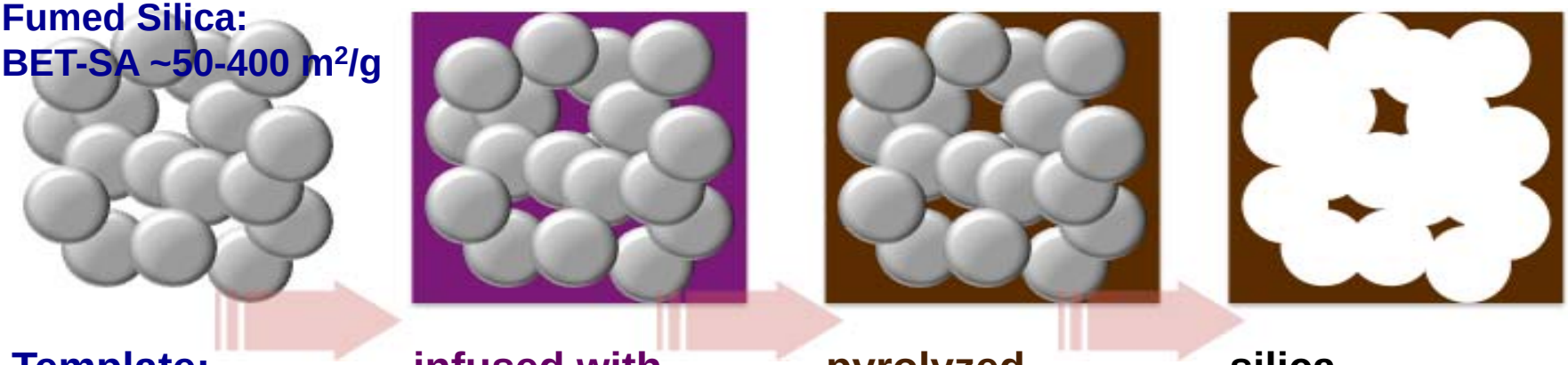
Fumed Silica:
BET-SA ~50-400 m^2/g



Template: monodispersed amorphous silica

infused with transition metal salt and N-C precursor

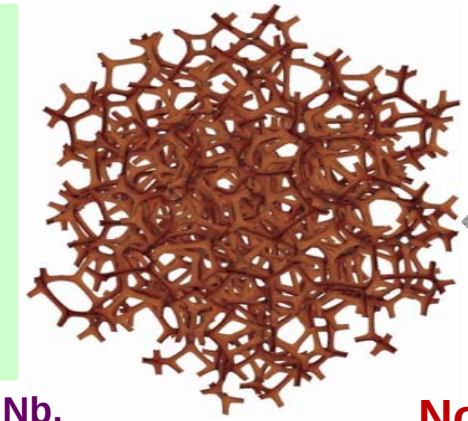
pyrolyzed in inert atmosphere

silica etched by HF and removed

THE UNIVERSITY of NEW MEXICO

Alexey Serov

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



Templated Self-supported Non-PGM Catalyst

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

SSM Catalyst Evolution

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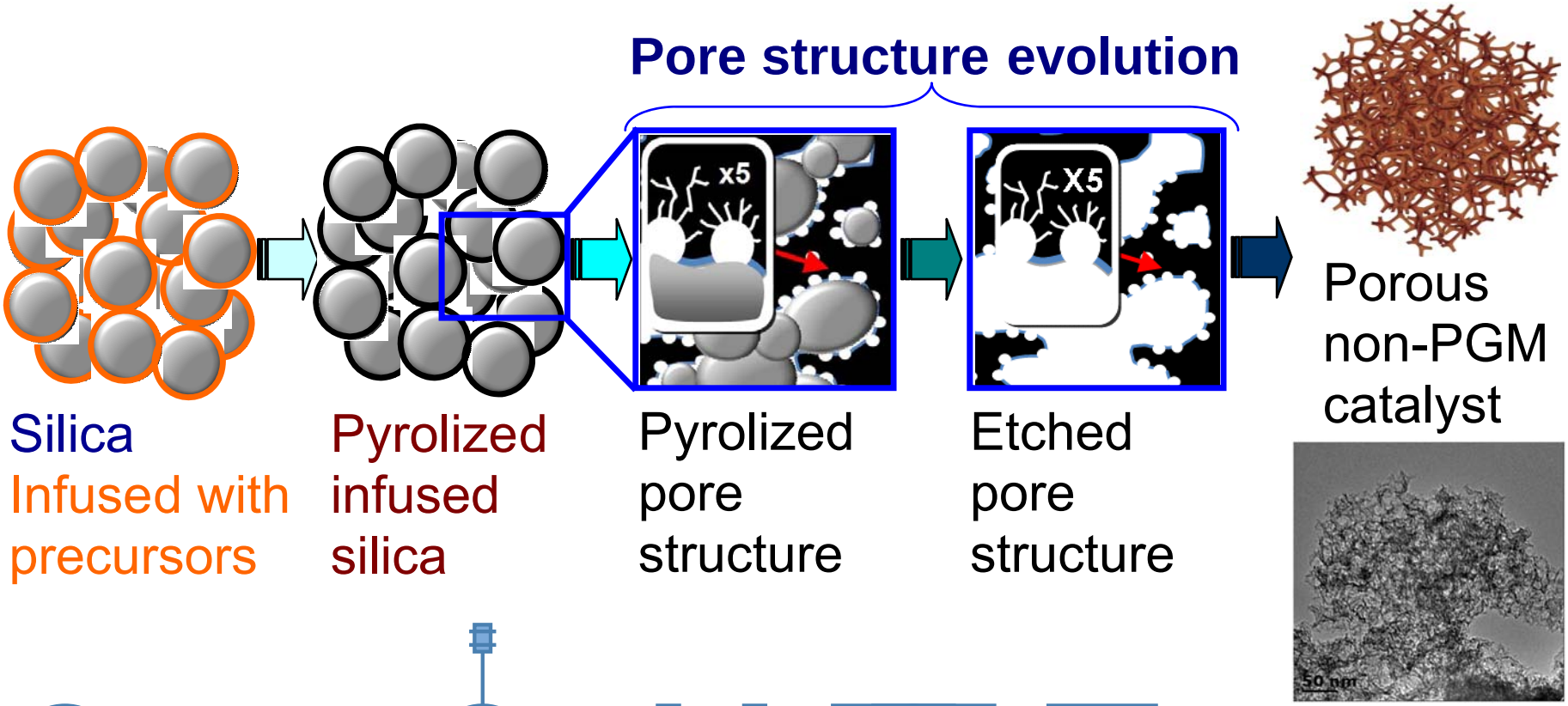

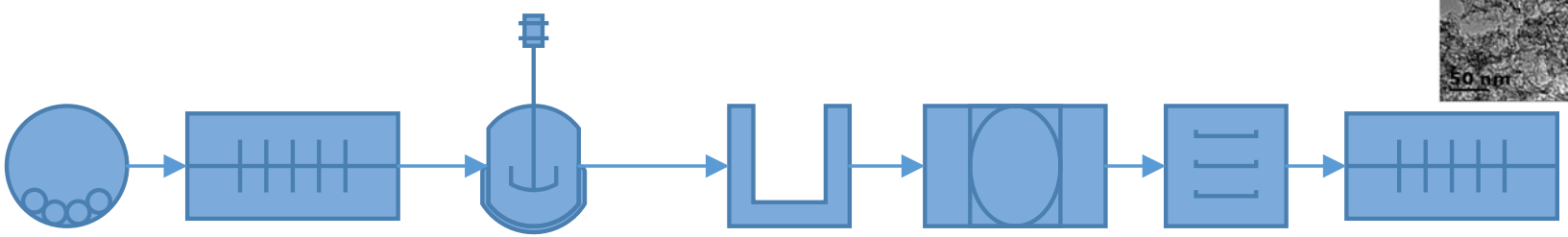

Ball-Mill Pyrolysis Etching Centrifuge Filter Dry Pyrolysis

Iron Nicarbazin Catalyst

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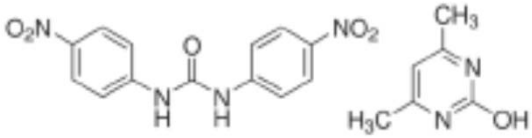
Fe +



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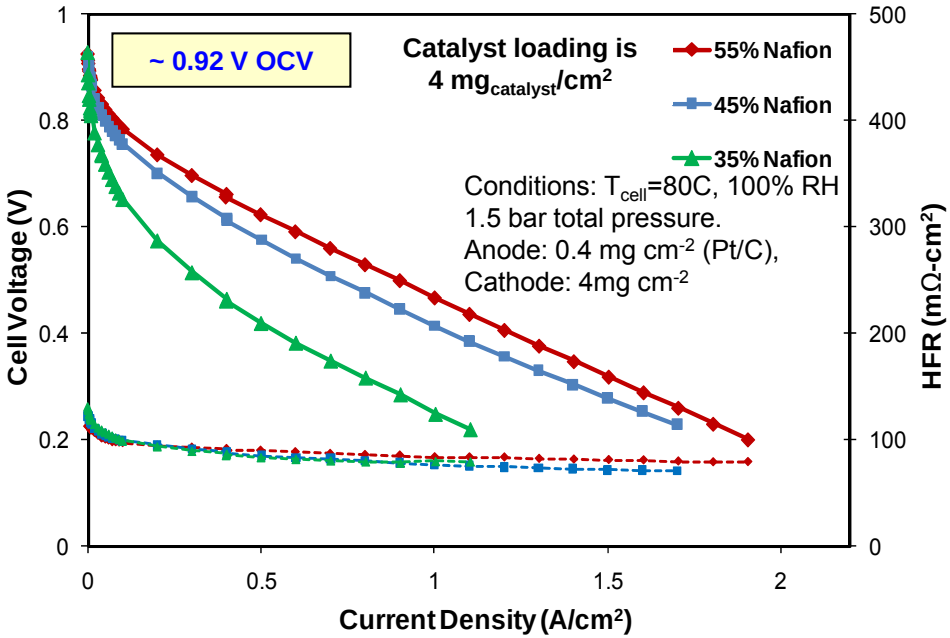
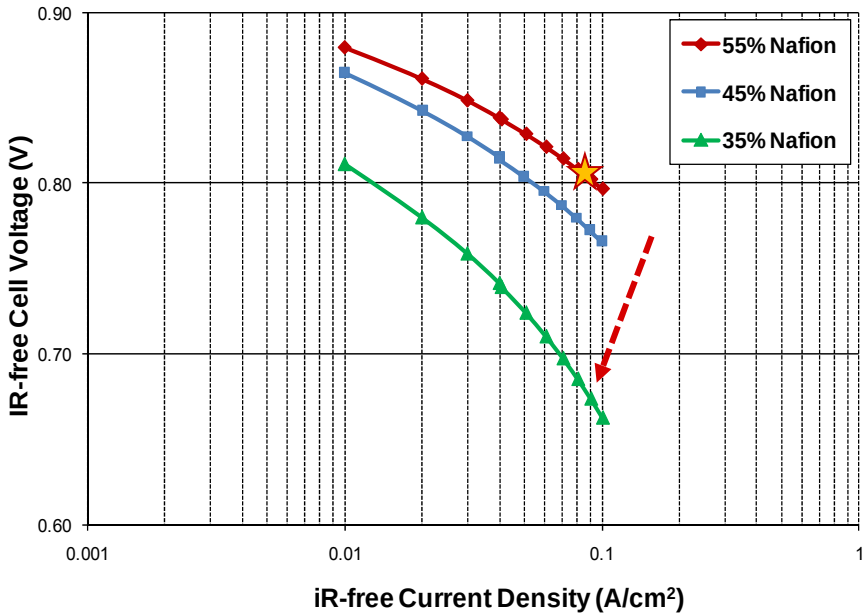
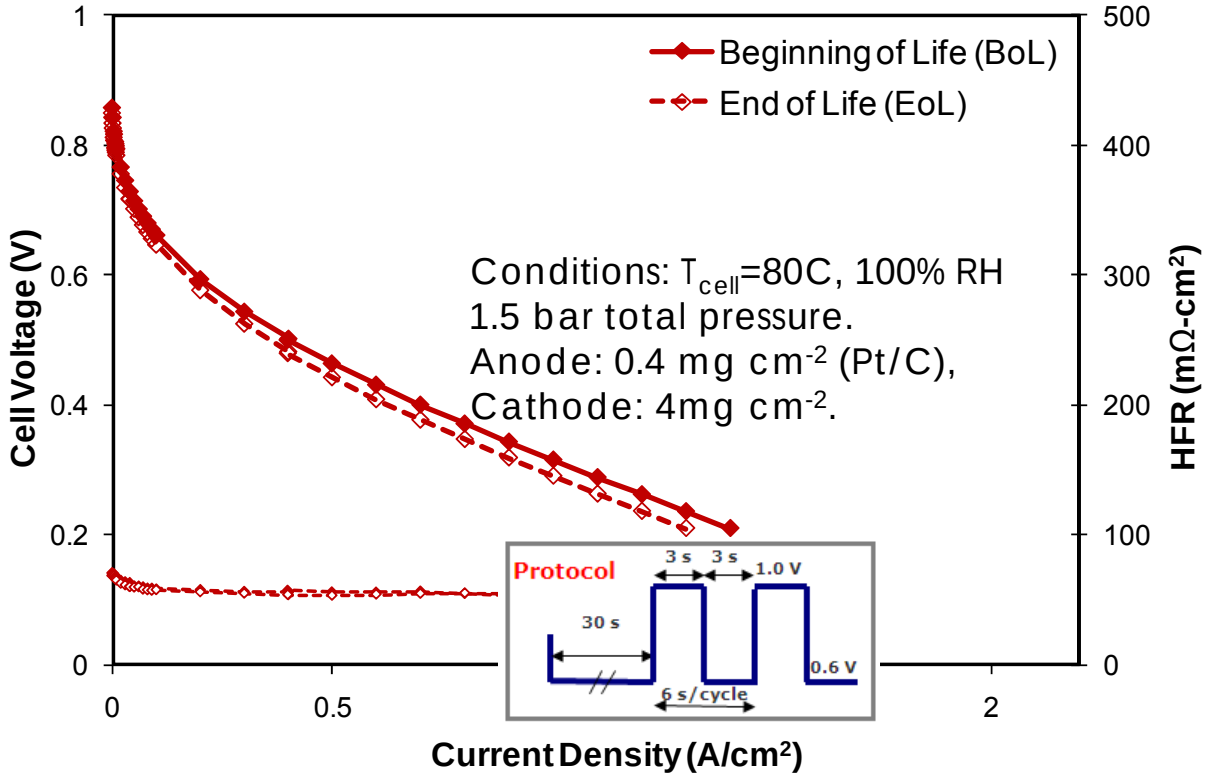




DOE EERE Project ID# FC086 AMR 2013 report, NTCNA testing

Meets DoE target of 100 mA/cm² at $0.8V_{iR\text{-}free}$ in Oxygen

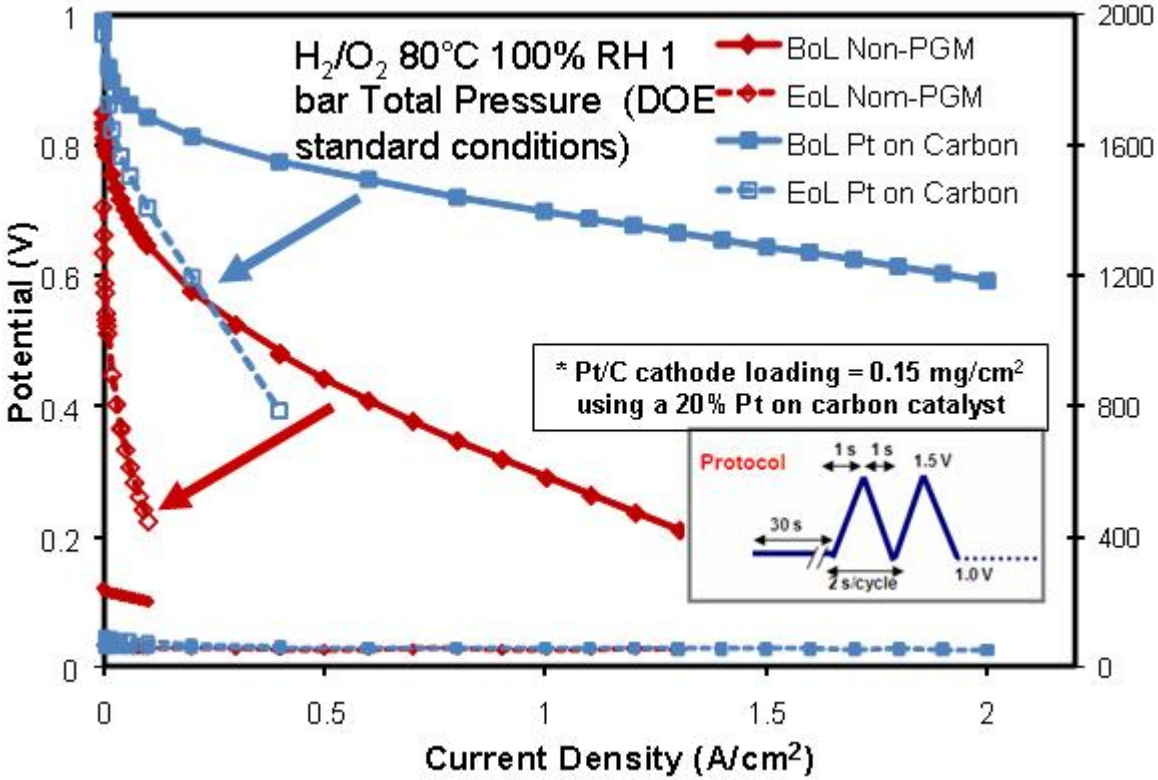
Load cycling AST – Good!



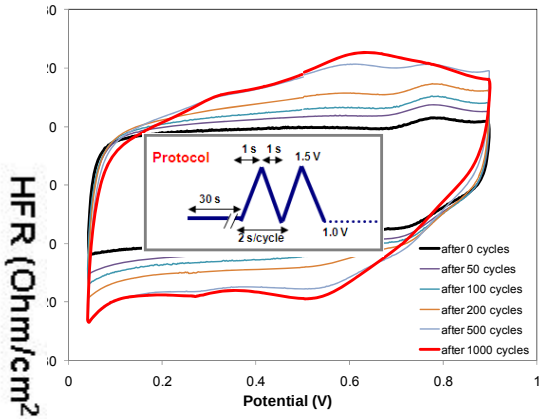
DOE EERE Project ID# FC086 AMR 2103 report, NTCNA testing

Minimal change in performance is observed after 10,000 potential cycles (load cycling) from 0.6 to 1.0V.

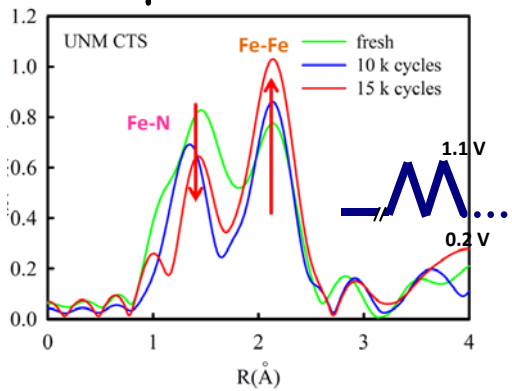
Start/Stop AST – Good!



ECSA



Δμ EXAFS



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

Durability under start/stop similar to Pt/C

Outline

- What are non-PGM ORR catalysts?
- Identifying the active site/s and mechanism
- Key morphology
- **Making deployable non-PGM catalysts**

Scale-up process

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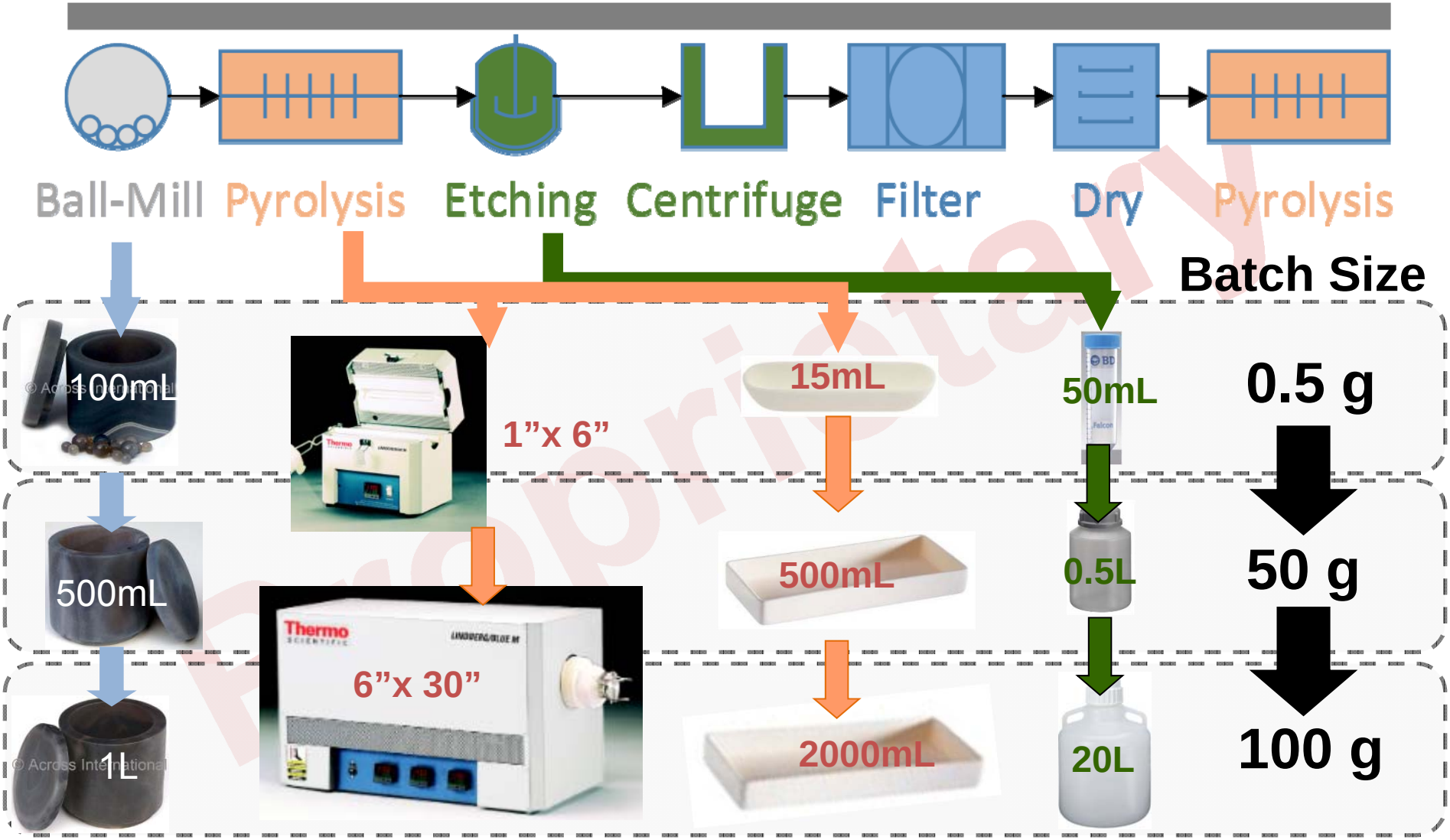

50+ Grams Scale-Up

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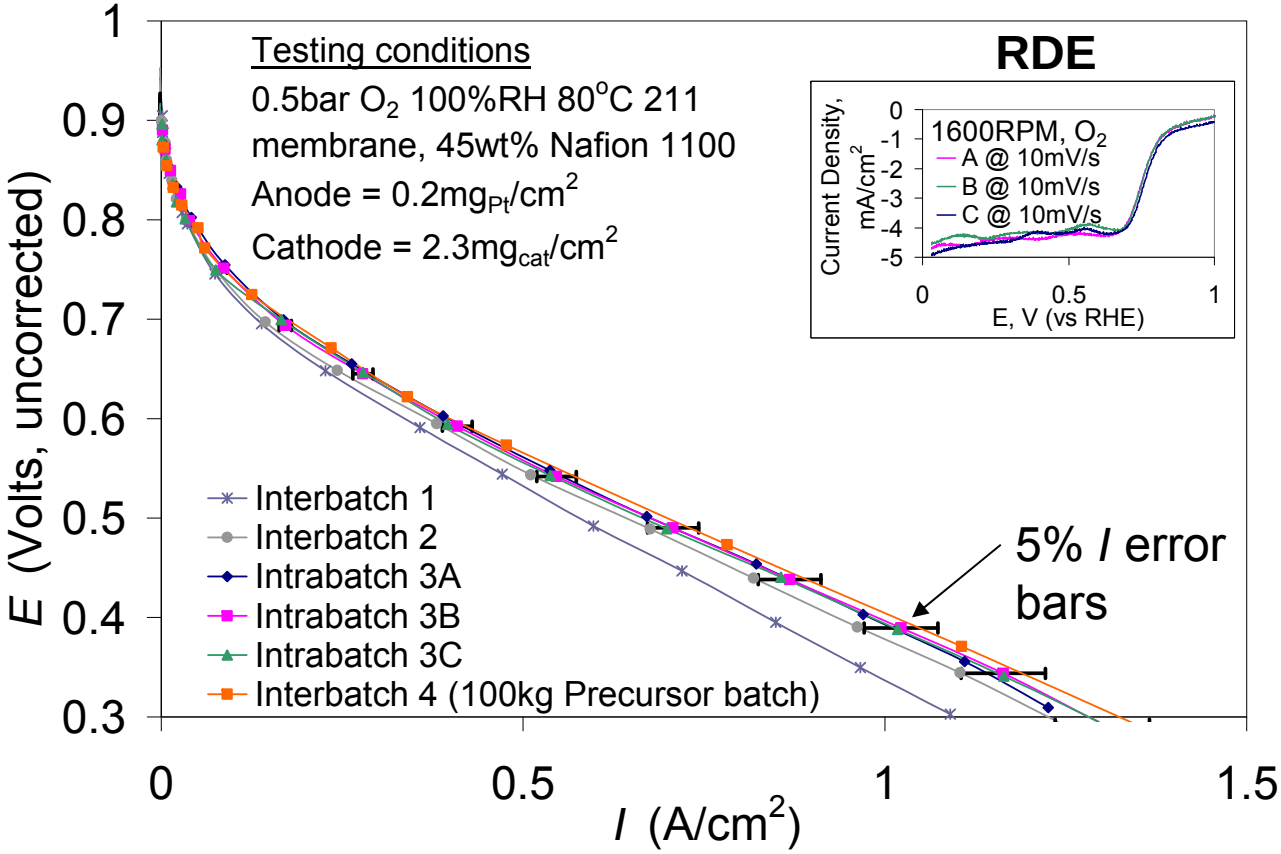
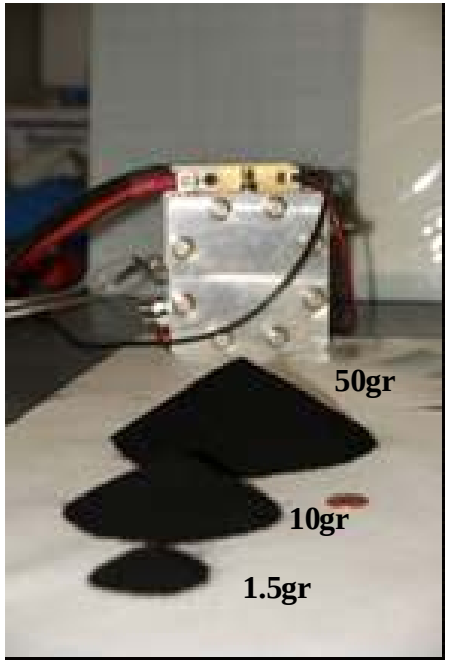


Proprietary



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

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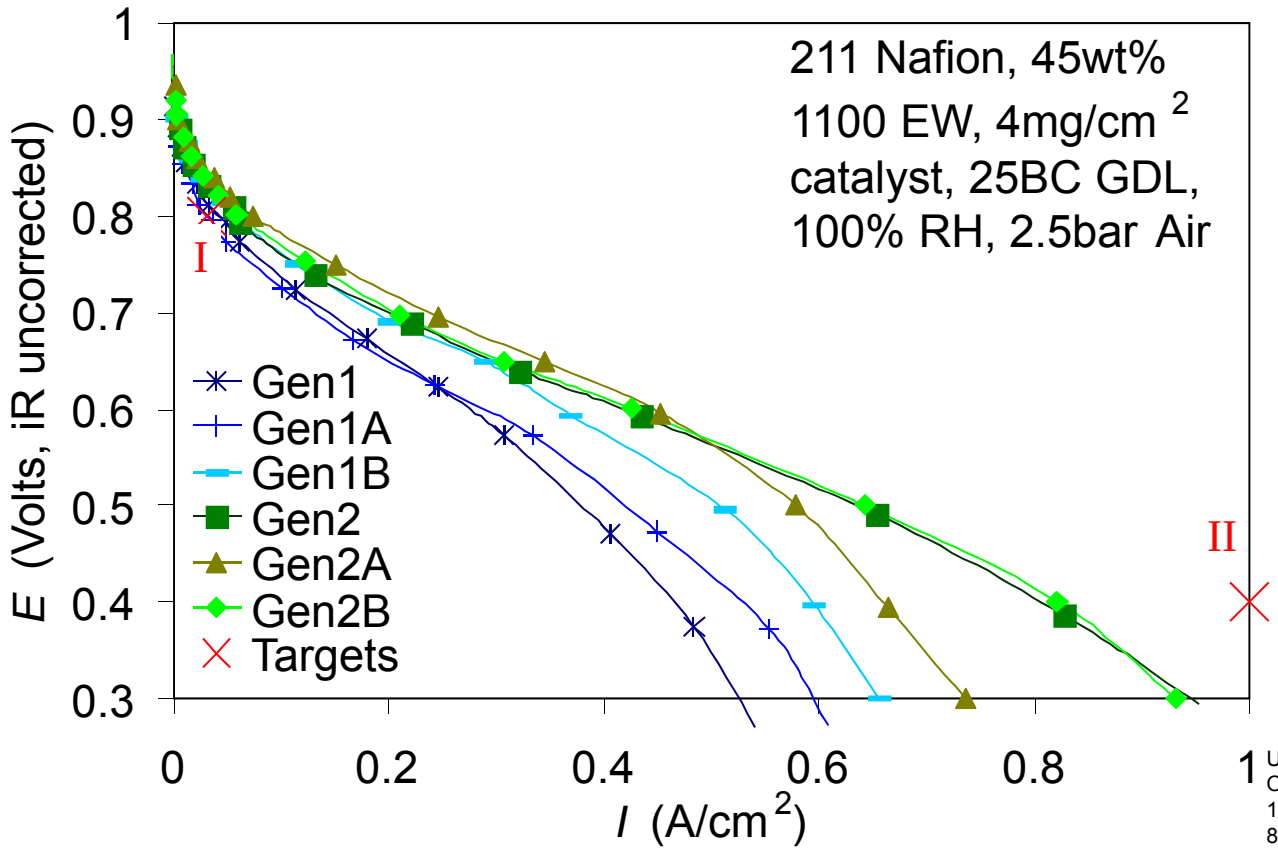
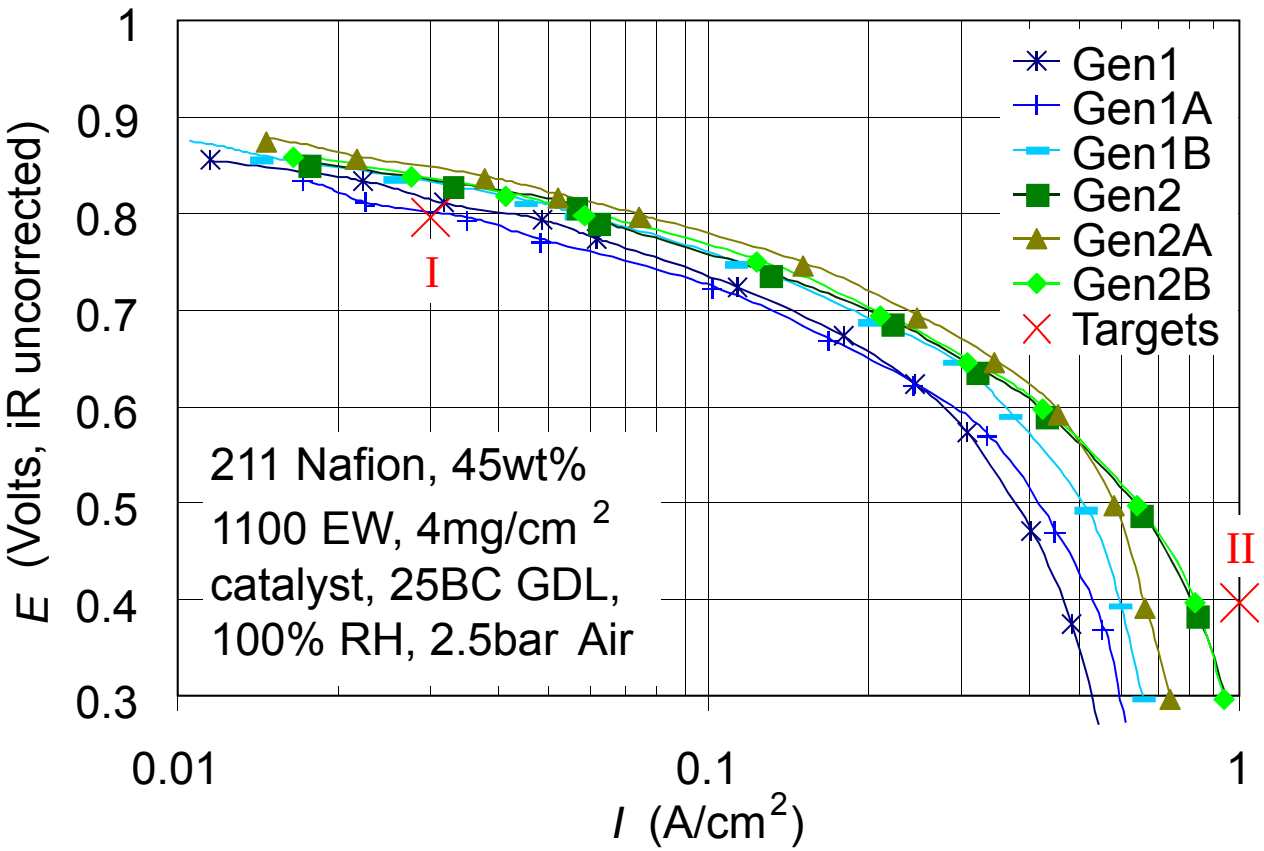
Proprietary



US20080312073A1,WO2012174335A2,WO2013116754A1,WO2012174344A2,WO2014062639A1,WO2014011831A1,WO2014085563A1,WO2014113525A1,

Catalyst formulation leading to MEA performance improvements
DoE Target I met, <u>without iR correction</u> – 60% improvement towards target II

Improved formulation



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Catalyst formulation leading to MEA performance improvements
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Outline

- What are non-PGM ORR catalysts?
- Identifying the active site/s and mechanism
- Key morphology
- Making deployable non-PGM catalysts
- **Successes**

Non-PGM ORR catalysts

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- 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

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

Precious Metal Free Fuel Cell Electric Vehicle

FC 凸 (DEKO: Convex) DECK

43rd Tokyo Motor Show

A. Serov, M. Padilla, A.J. Roy, P. Atanassov, T. Sakamoto, K.
***Angewandte Chemie Intern. Ed.*, (2014) DOI: 10.1002/anie.201404734**

PPC Capabilities

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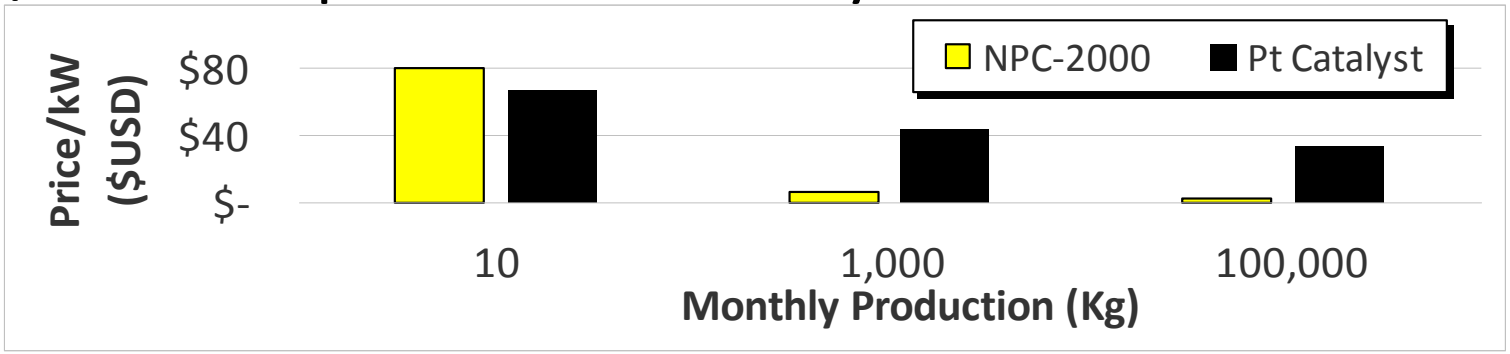
- Multiple non-PGM catalyst production methods and formulations scaled to 25-100gr
- Fixed Product Line (200gr/day capacity)
  - ***NPC-2000 & 1000:*** non-platinum, drop-in fuel cell catalysts with different performance/price points
  - ***PHC-3000:*** Ultra low loaded platinum content catalyst for higher performance
- Custom Catalyst Design
- Contract Manufacturing

Outline

- What are non-PGM ORR catalysts?
- Identifying the active site/s and mechanism
- Key morphology
- Making deployable non-PGM catalysts
- 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
- US Department of Energy, EERE Program
- 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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