World of Energy Solutions

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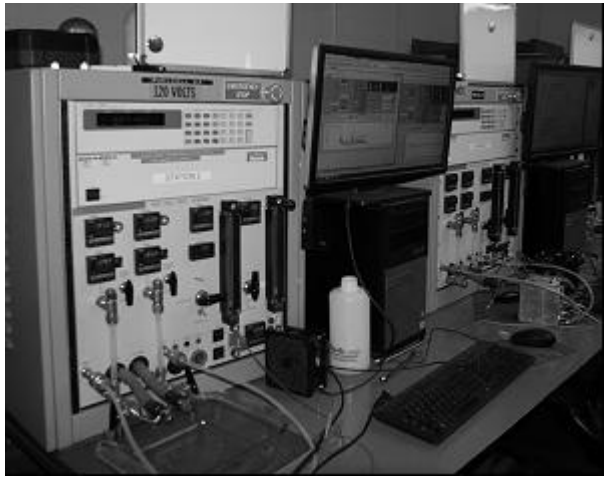

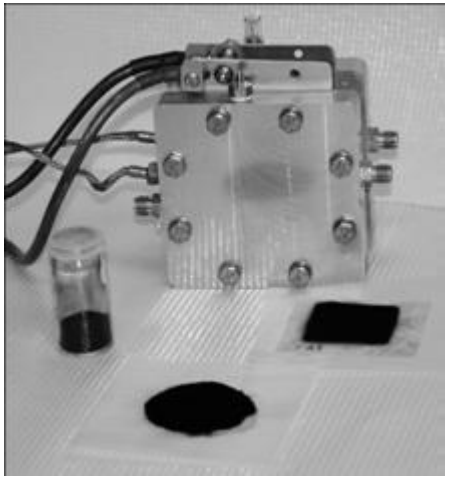

Precious Metal Free Fuel Cell Catalysts, Concepts and Limits

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 Introduction

PPC founded to:

Create & Manufacture

<u>Affordable</u> Fuel Cell Catalysts

in Commercial Quantities

Piotr Zelenay

Los Alamos NATIONAL LABORATORY

PPC Introduction

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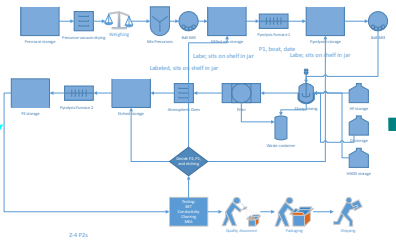

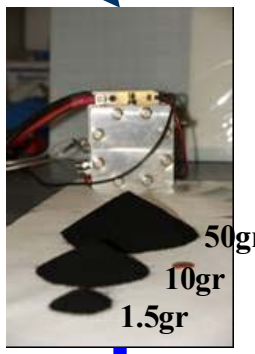

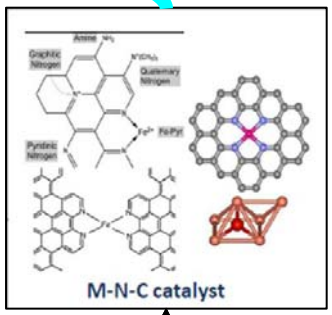

PPC founded to:

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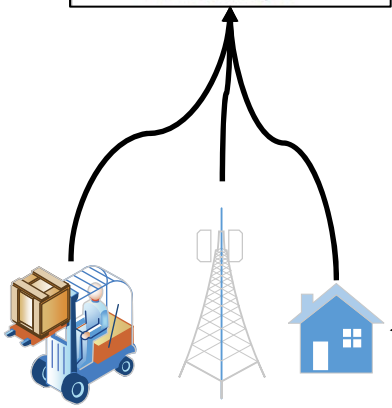

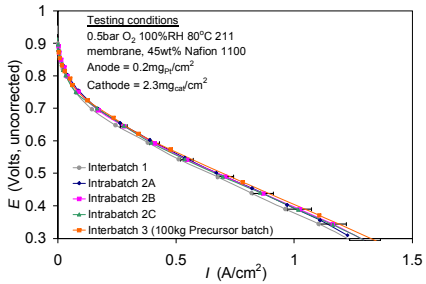

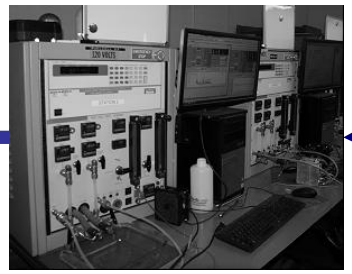

US20080312073A1,WO2012174335A2,WO2013116754A1,WO2012174344A2,WO2014062639A1,WO2014011831A1,WO2014085563A1,WO2014113525A1,

Non-PGM Catalysts

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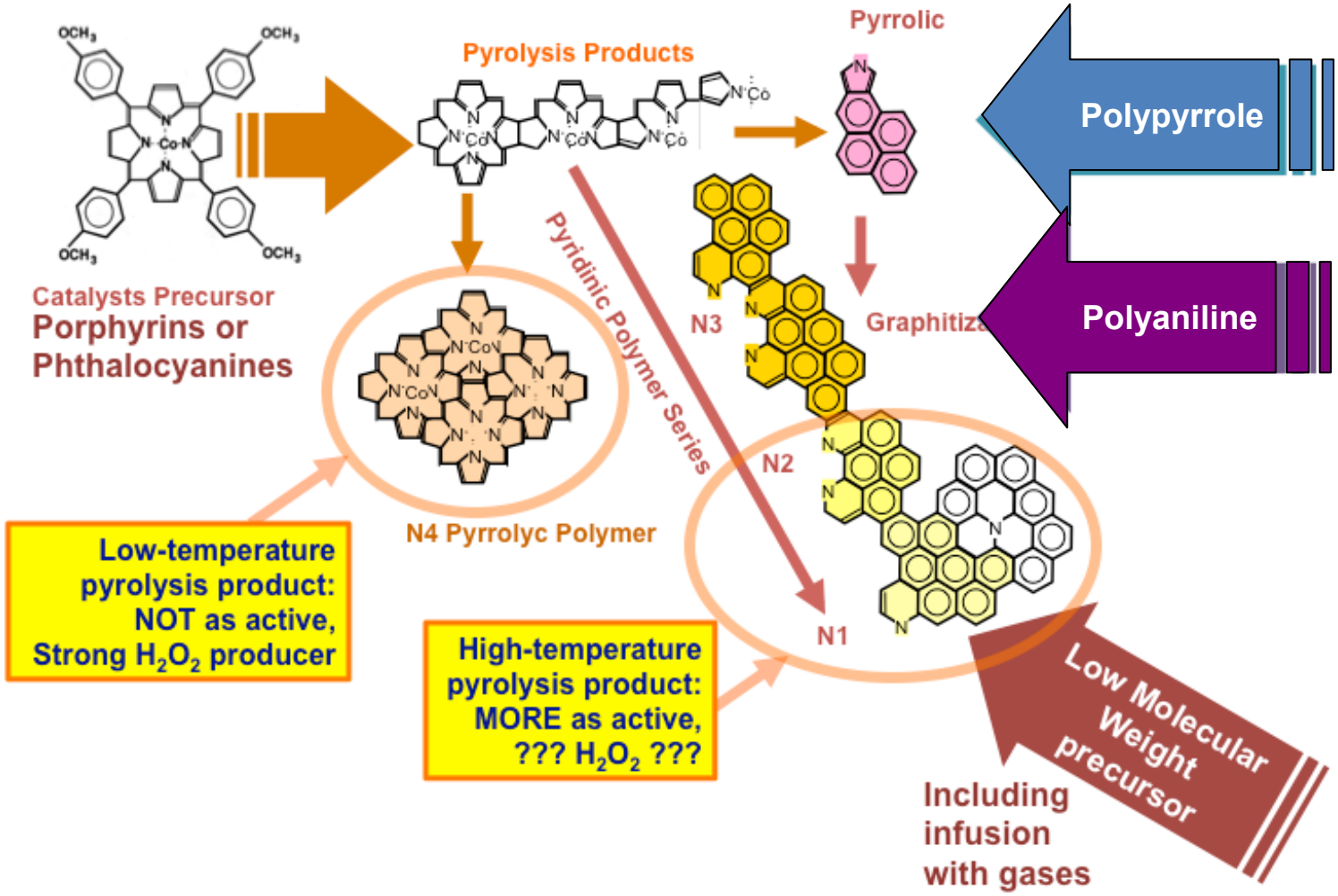

Outline

- 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!

Multifunctional Site/s

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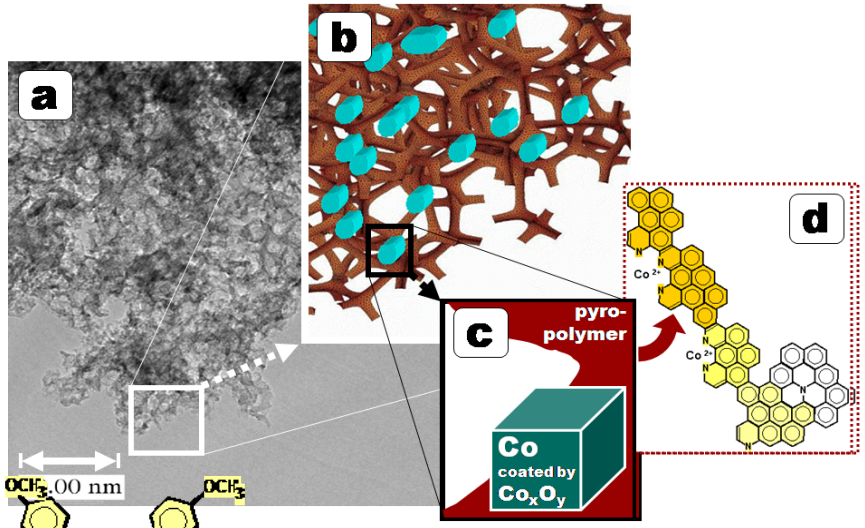
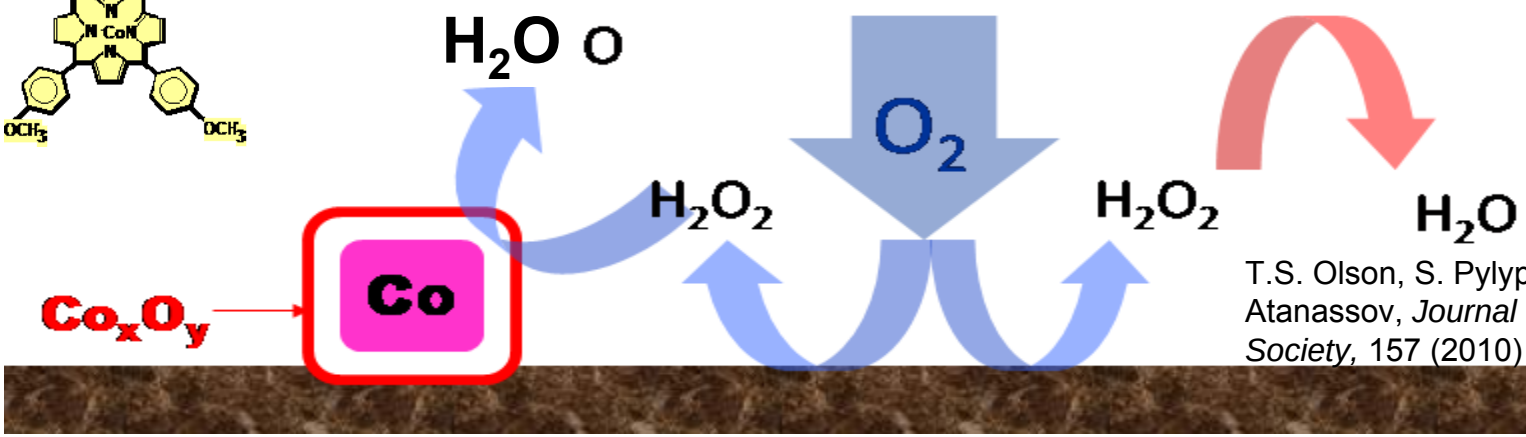


Oxygen Reduction Reaction on Non-PGM Catalysts

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



T.S. Olson, S. Pylypenko, J.E. Fulghum, P. Atanassov, *Journal of the Electrochemical Society,* 157 (2010) B54-B63

DFT: $Fe(N\text{-}C)_4$ Most Likely

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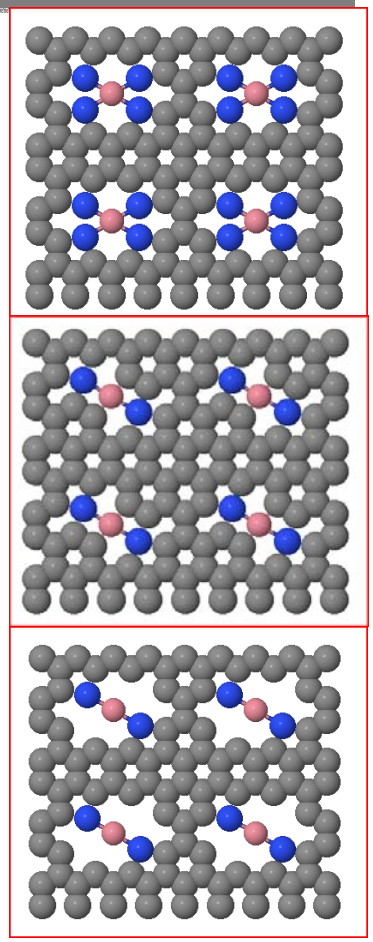
Density-Functional-Theory (DFT).

- **Generalized Gradient Approximation (PBE).**
- **3-d periodic boundary conditions.**
- **Plane-waves.**
- **Spin polarized: Co.**
- **PAW-potentials.**
- **Fermi-smearing (σ=0.025 eV)**

Surfaces:

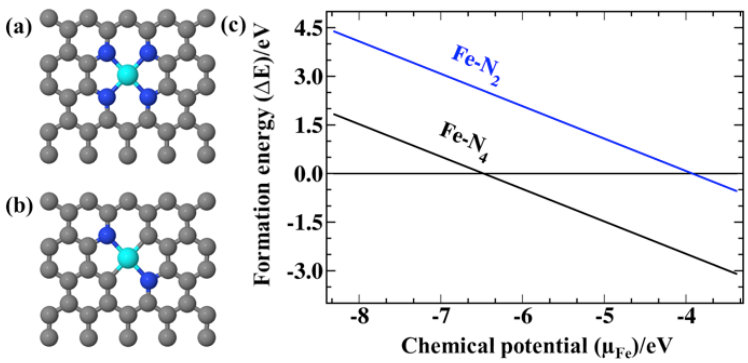
- **Graphene (32 atoms).**
- **14 A vacuum.**
- **Molecule(s) pre-optimized.**
- **Dipol correction.**

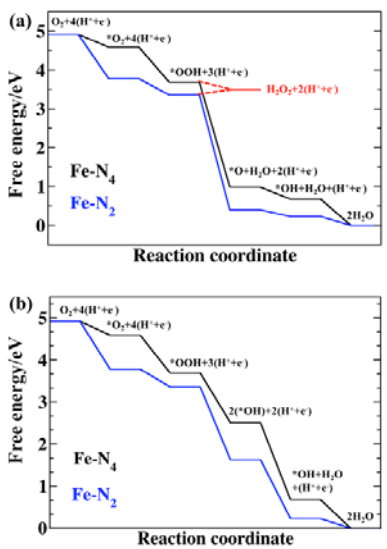


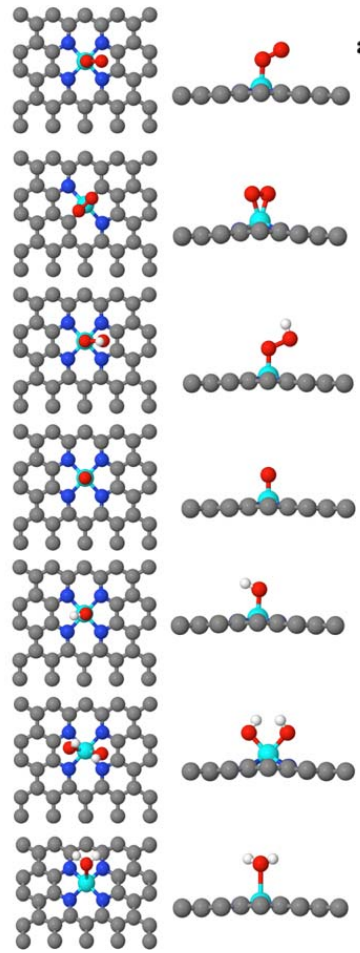
NEW MEXICO STATE UNIVERSITY

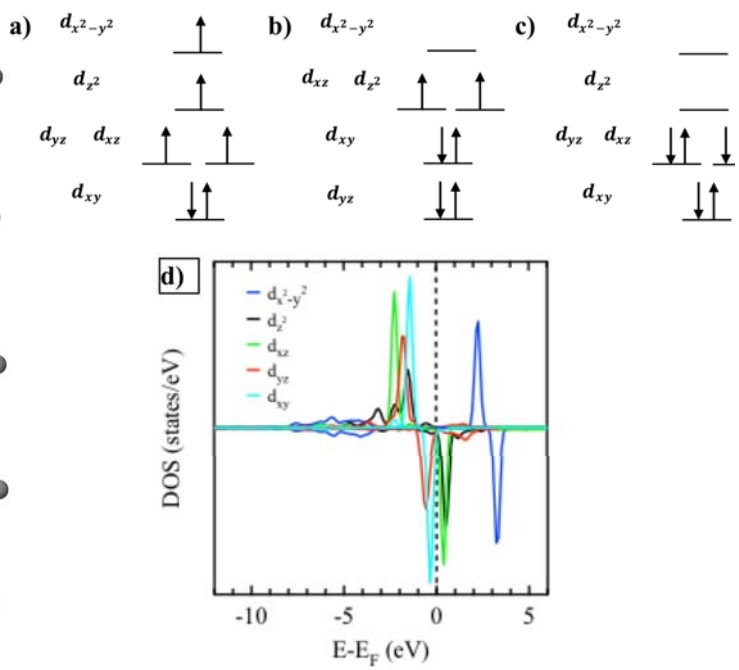
Boris Kiefer

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









Possible electron arrangements in *3d* 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: $Fe(N\text{-}C)_x$ Exist

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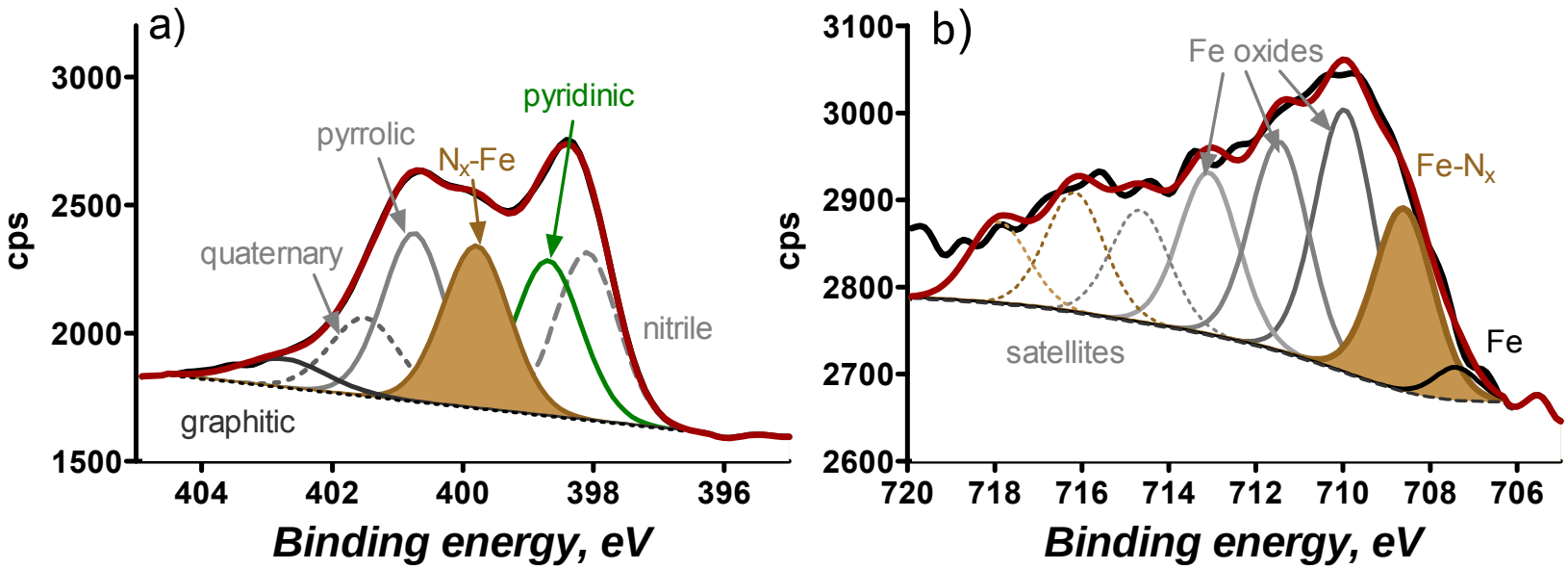
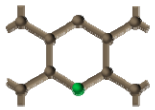
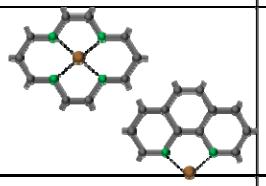
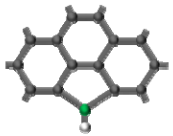
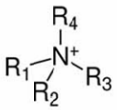
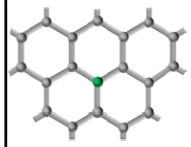


BE, eV	398.5-398.8	399.5-399.8	400.6-400.9	401.5-402	402.5-403
structure					
name	pyridinic	N_x-Me (x=1,2,3,4)	pyrrolic	quaternary	graphitic

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Kateryna Artyushkova

XPS & DFT: Matching

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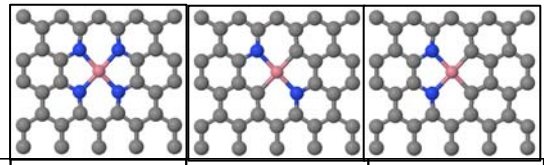
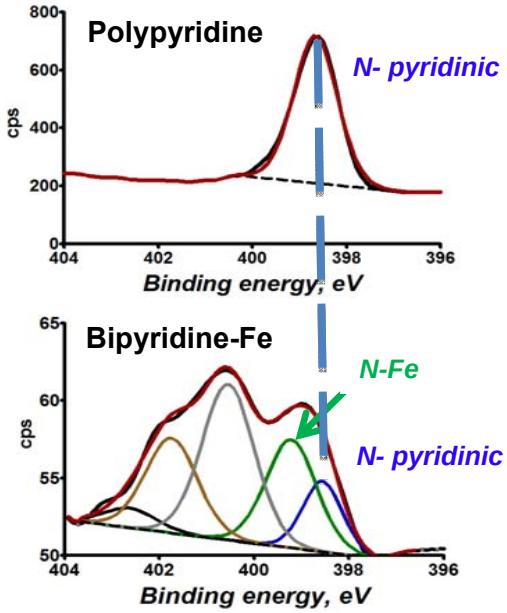
DFT calculations of XPS binding energy shifts

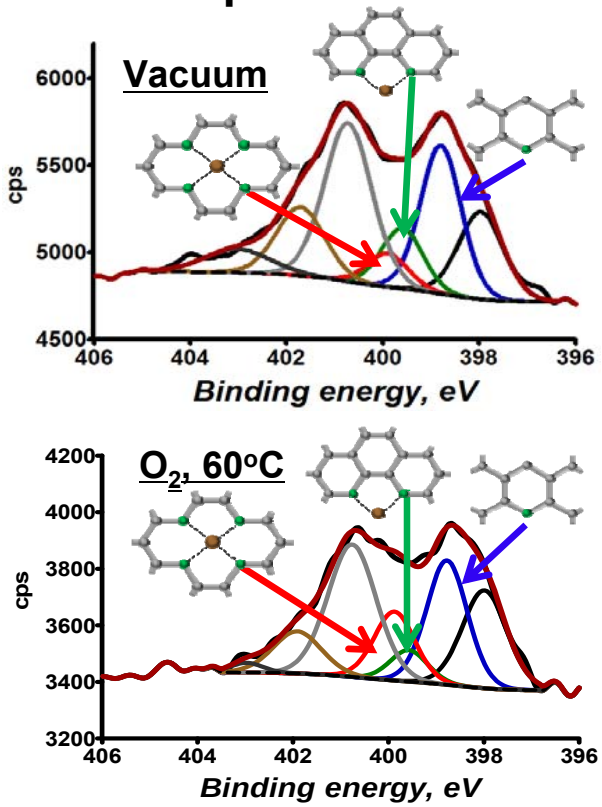


	$Me-N_4$	$Me-N_2$	$Me-N_2$
theory	+1.1 eV	0.8 eV	1.0 eV
experiment	+0.9-1.1 eV		



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

Ambient pressure XPS



K. Artyushkova, B. Kiefer, B. Halevi, A. Knop-Gericke, R. Schlogl and P. Atanassov, *Chem. Comm,* 49 (2013) 2539 – 2541

ACTEM – Fe/N Sites Exist

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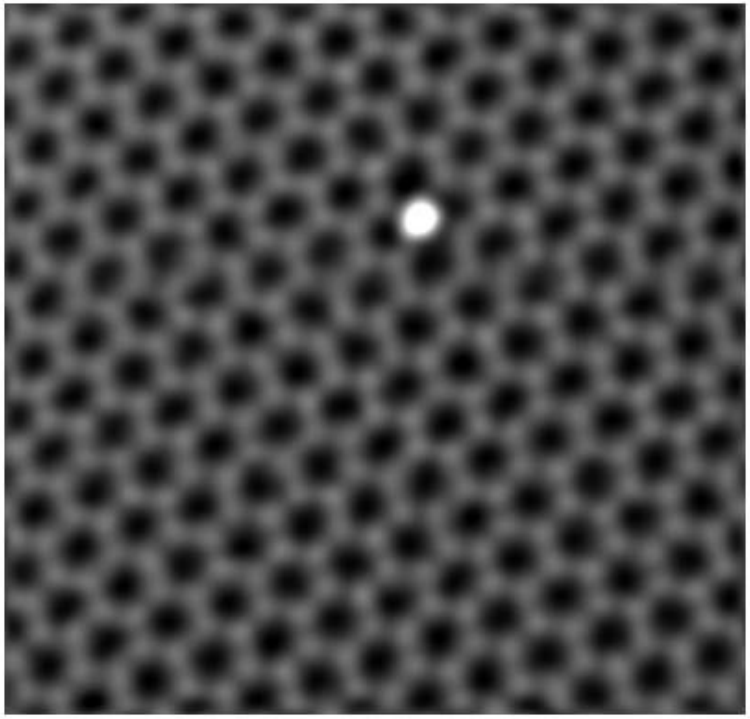
ACTEM images proves Nitrogen & Iron single sites in graphene

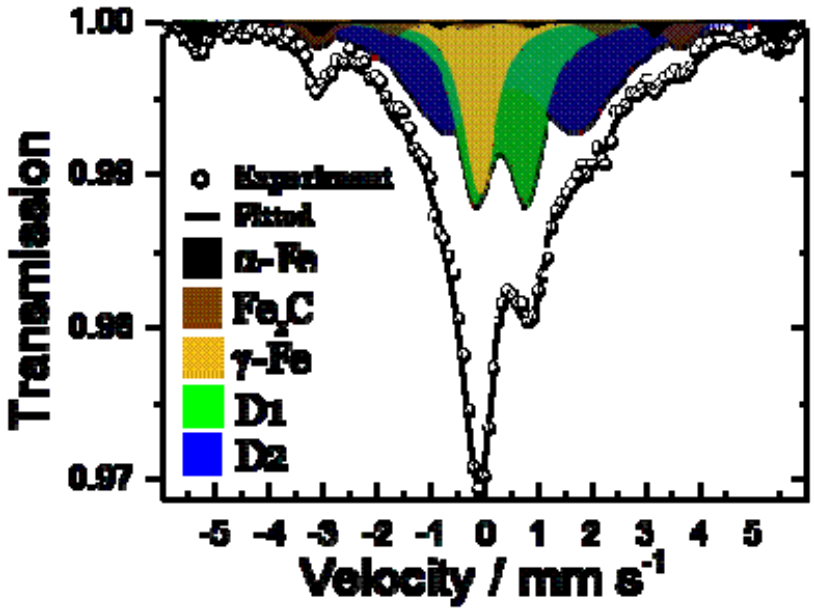
Gerd Duscher



Matt Chisholm

OAK RIDGE National Laboratory

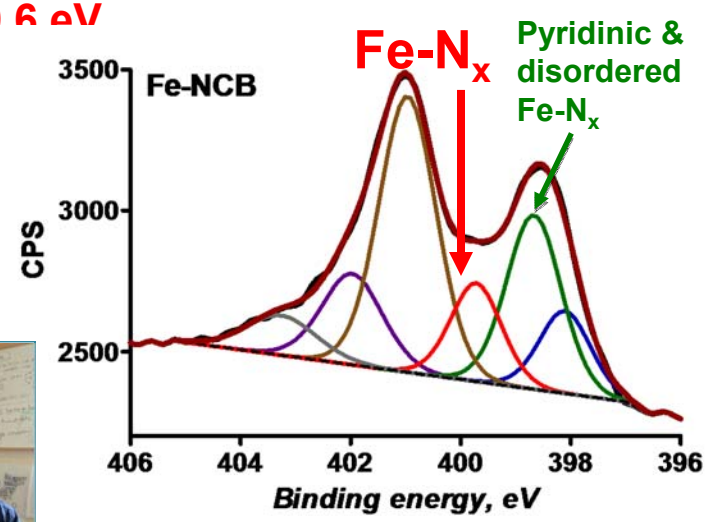
Mössbauer: $Fe(N\text{-}C)_4$



Component (assignment)	IS	QS	H	LW	Relative absorption area
	mm·s^{-1}	mm·s^{-1}	Tesla	mm·s^{-1}	%
α-Fe	0.04	-	33.5	0.37	4
Fe_xC	0.29	-	20.2	0.62	8
Param. or γ-Fe	- 0.07	-	-	0.67	14
D1 ($Fe^{II}N_4$ LS)	0.33	0.98	-	0.80	30
D2 ($Fe^{II}N_4$ MS)	0.51	2.34	-	1.83	44

The relative content of D1 or D2 is high, demonstrating the successful integration of the majority of the iron in FeN_xC_y 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



Frederic Jaouen, U Montpellier

ΔXAS – $Fe(N\text{-}C)_x$ & Fe-Fe

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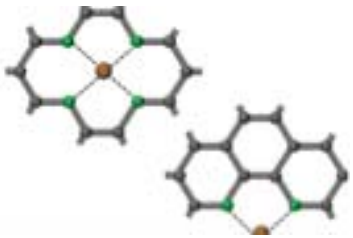
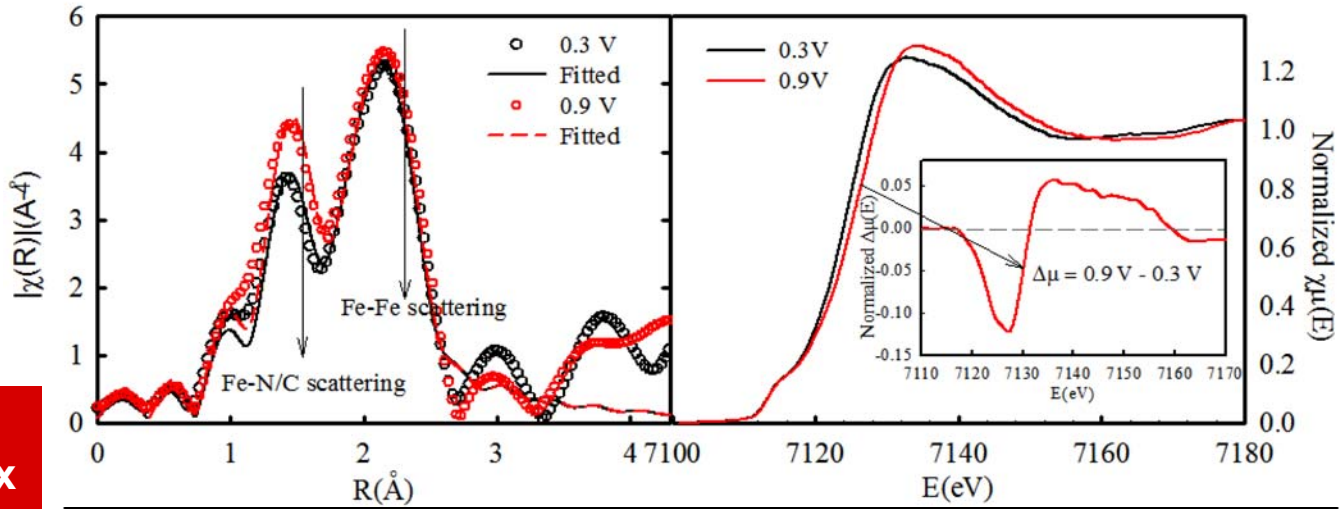


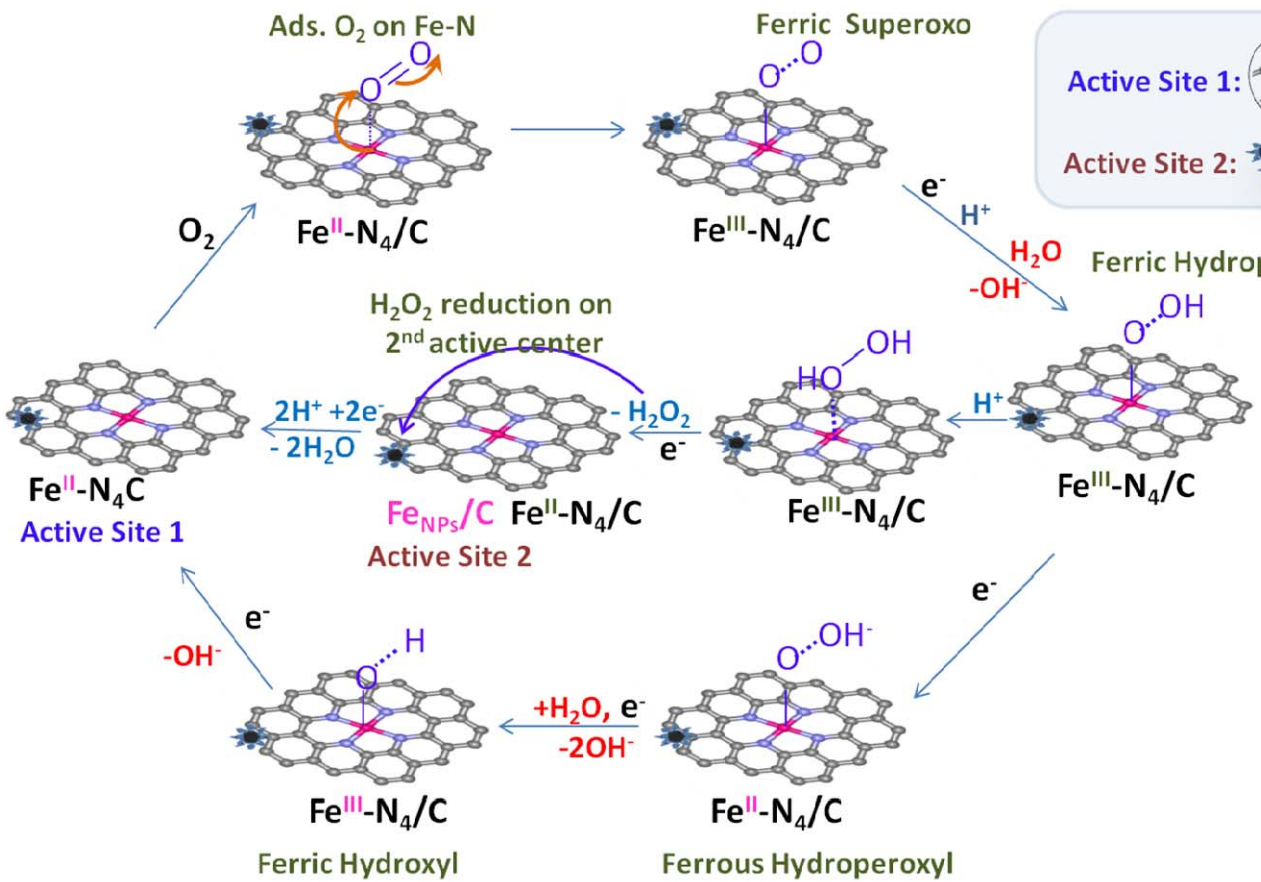


Fe^{2+}-N_4 active site at 0.3 V undergoes redox transition to a penta-coordinated (H)O–Fe^{3+}–N_4 at 0.90 V

	Fe-C/N/O path				Fe-Fe path			
Potential	CN	R (Å)	σ^2 (Å^2)×10^{-3}	E_0 (eV)	CN	R (Å)	σ^2 (Å^2)×10^{-3}	E_0 (eV)
0.3 V	3.6(7)	2.02(2)	9(3)	-5(1)	1.2(3)	2.51(1)	9(3)	-5(1)
0.9 V	4.0(8)	2.01(2)	4(2)	-6(2)	1.3(3)	2.52(1)	4(2)	-6(2)

Sanjeev Mukerjee

eXAS – mechanism?



Oxygen Reduction Reaction on Non-PGM Catalysts

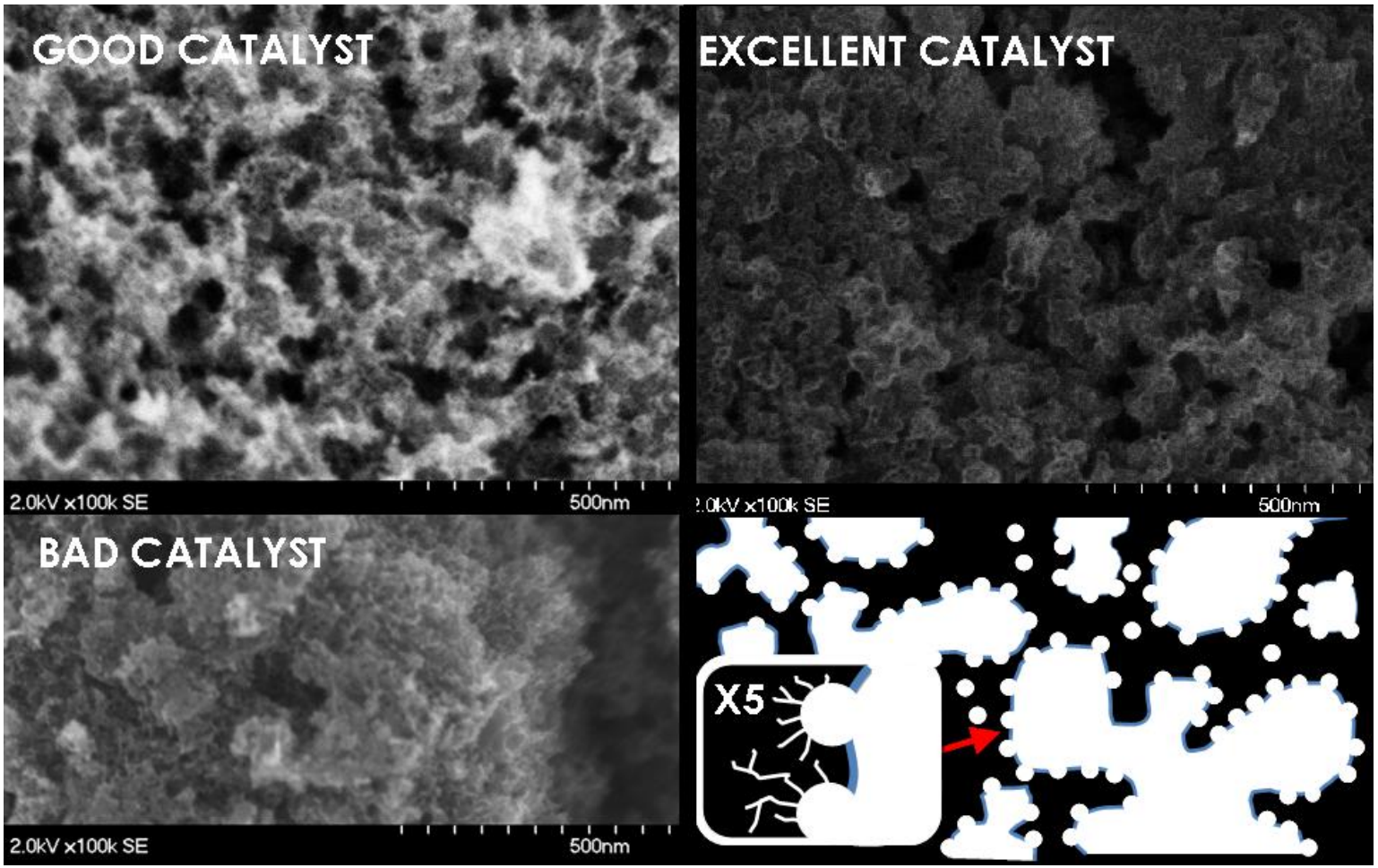
- Bi(+?) -functional Mechanism
- Two(+?) types of Active Sites

U. Tylus, Q. Jia, K. Strickland, N. Ramaswamy, A. Serov, P. Atanassov and S. Mukerjee, *J. Phys. Chem. C*, 118 (2014) 8999-9008

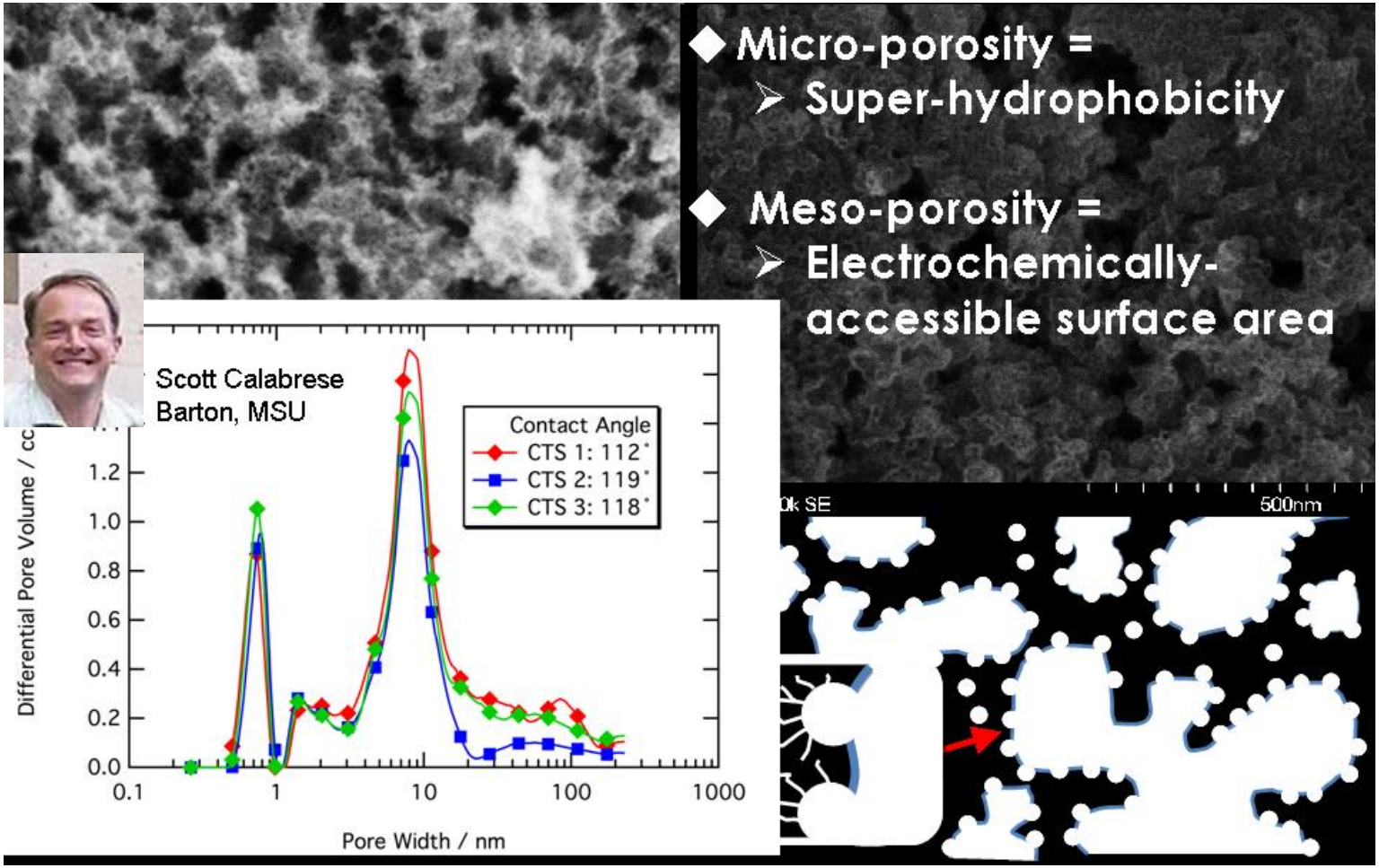
Outline

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

Pore Structures

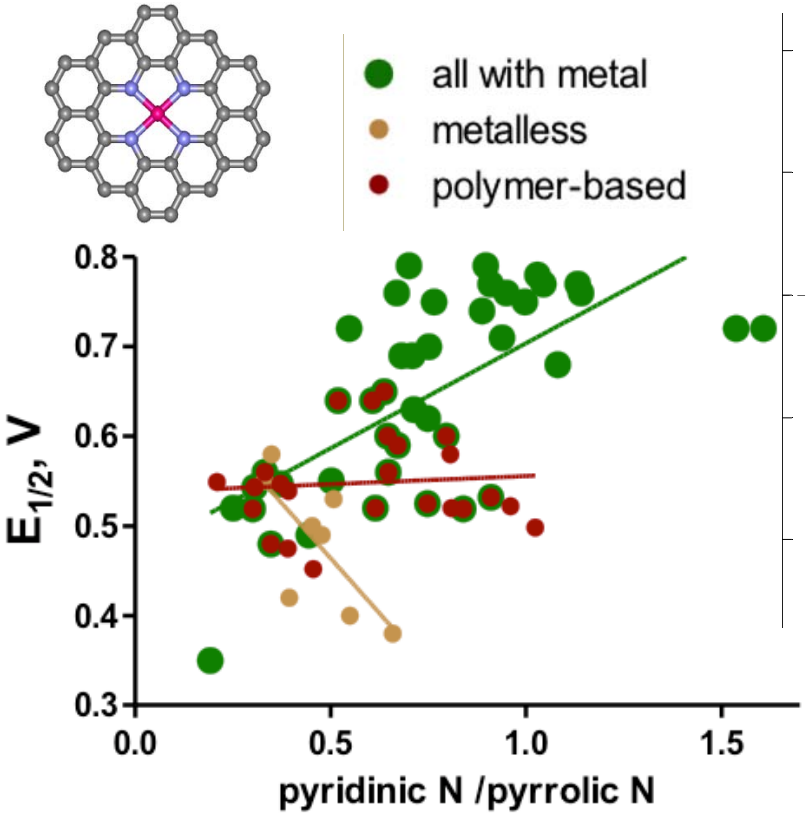


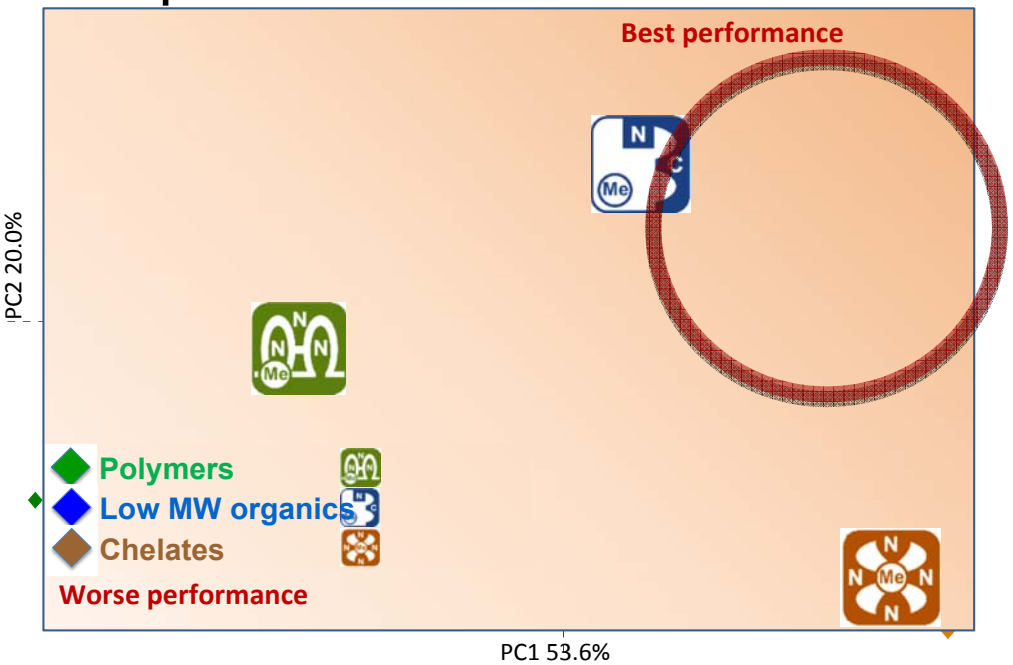
Pore Structure Role



Different Active Sites

Structure-to-Property Relationships





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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

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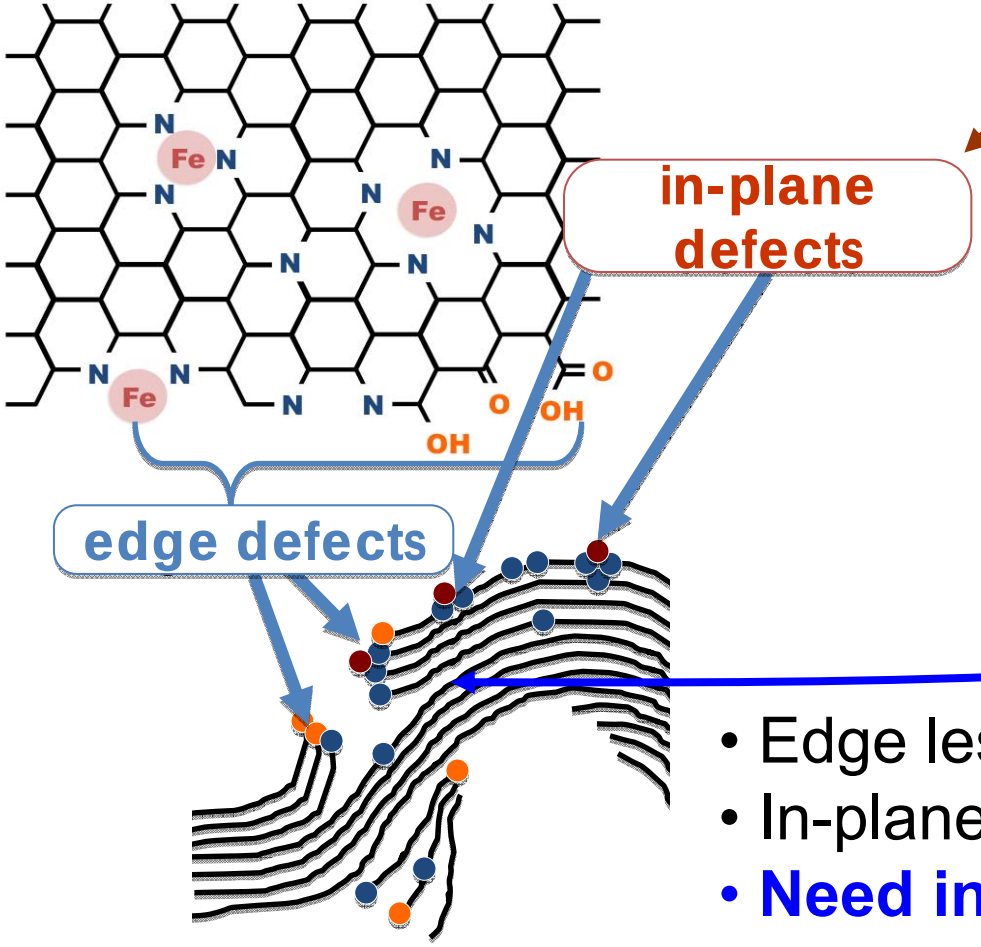
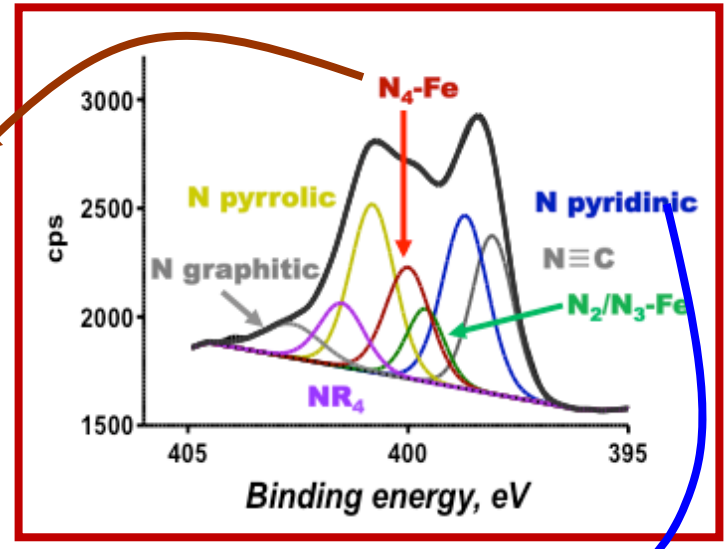
- Multiple ways to make non-PGM catalysts
  - Need to bring precursors together on nano-scale then react them to make active sites
  - Some processes are very complex with iterations of mixing, cooking, pyrolysis, etching.
  - Commonality:
    - Similar precursors
      - M/N/C compounds (ex: cyanamide)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

Different Active Sites





- Edge less stable, more active
- In-plane more stable, less active
- **Need in-plane for stable/durable catalysts!**

Sacrificial Support Method

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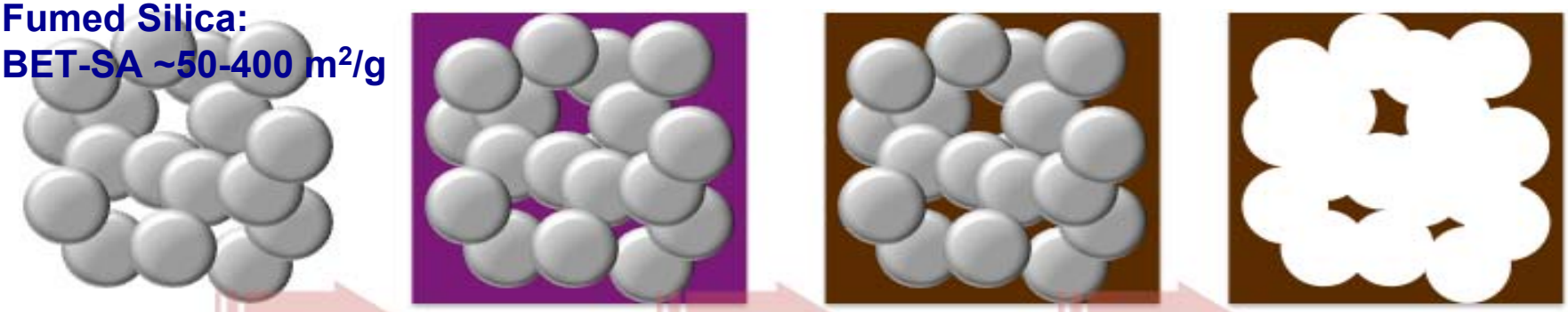
Fumed Silica:
BET-SA ~50-400 m^2/g



Template: monodispersed amorphous silica

infused with transition metal salt and N-C precursor

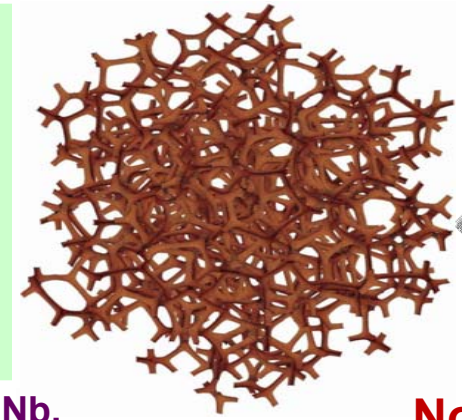
pyrolyzed in inert atmosphere

silica etched by HF and removed

Alexey Serov

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

SSM Catalyst Evolution

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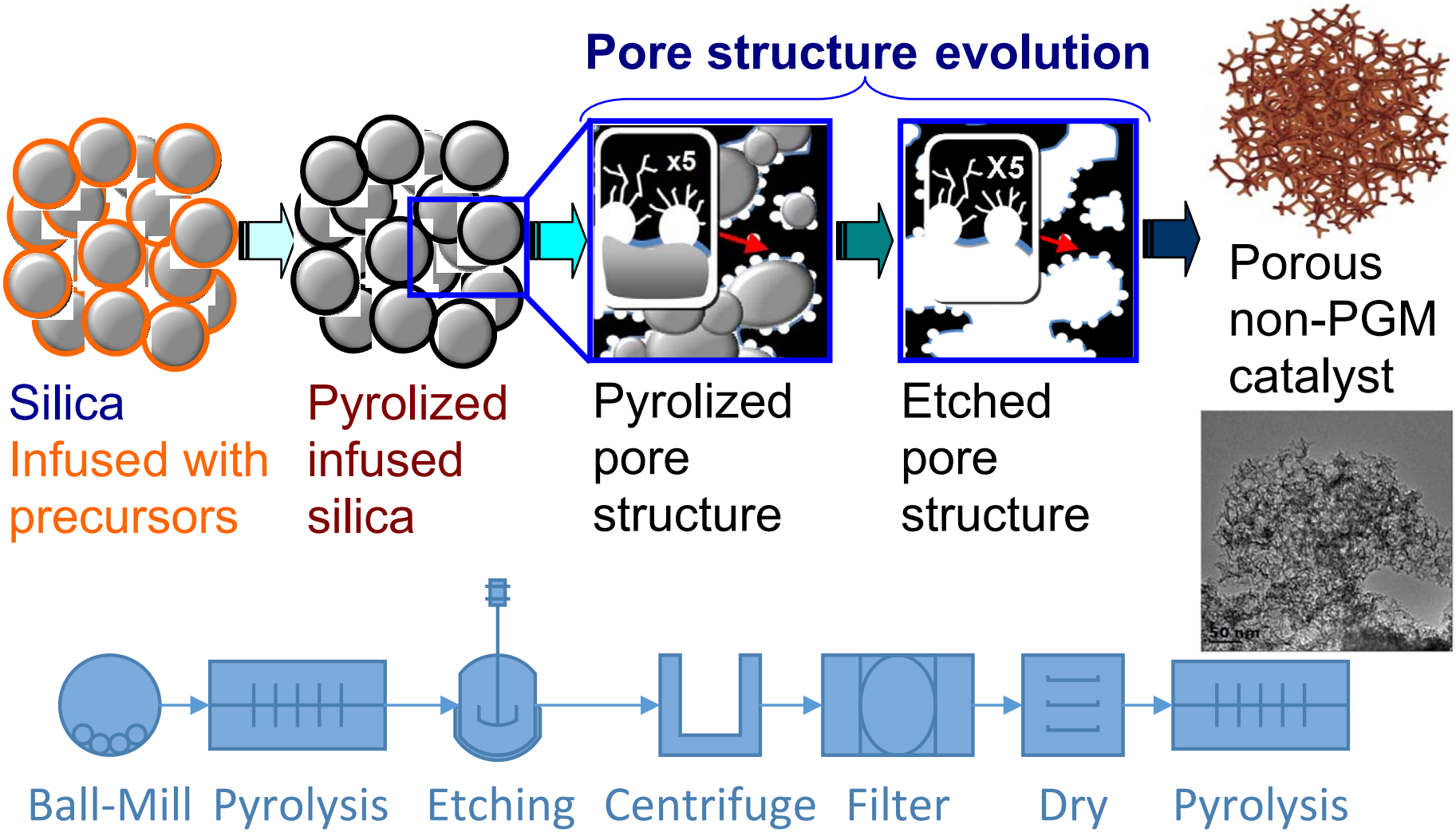
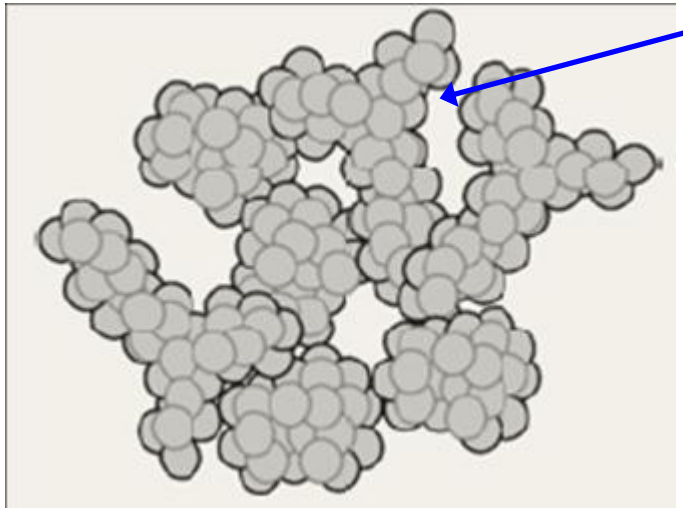
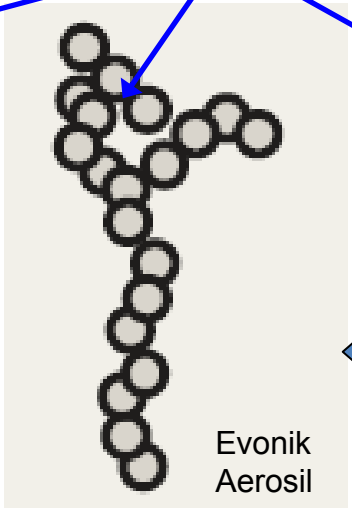


SSM Pore Structure

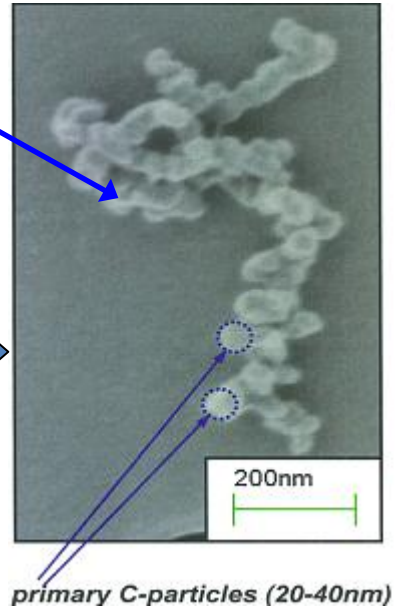
Primary particle size:
10-40nm



Precipitated Silica:
Sponge-like



Fumed Silica:
Sponge-like



Typical Pt/C

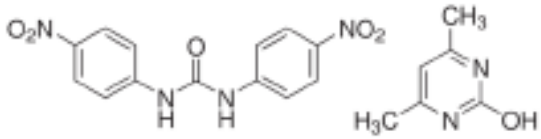
Sacrificial support allows for pore size tailoring to match current Pt/C catalysts

ECS PEFC SHORT COURSE 2013,
SFO (T.J. Schmidt & H.A. Gasteiger)

Iron Nicarbazin Catalyst

PAJARITO POWDER

Fe +



NISSAN R&D AMERICAS

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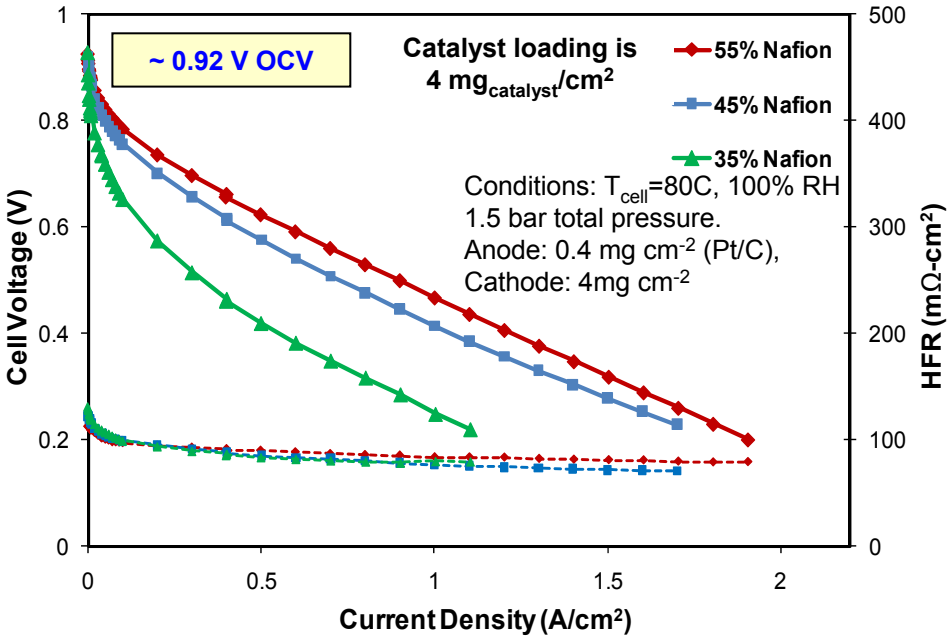
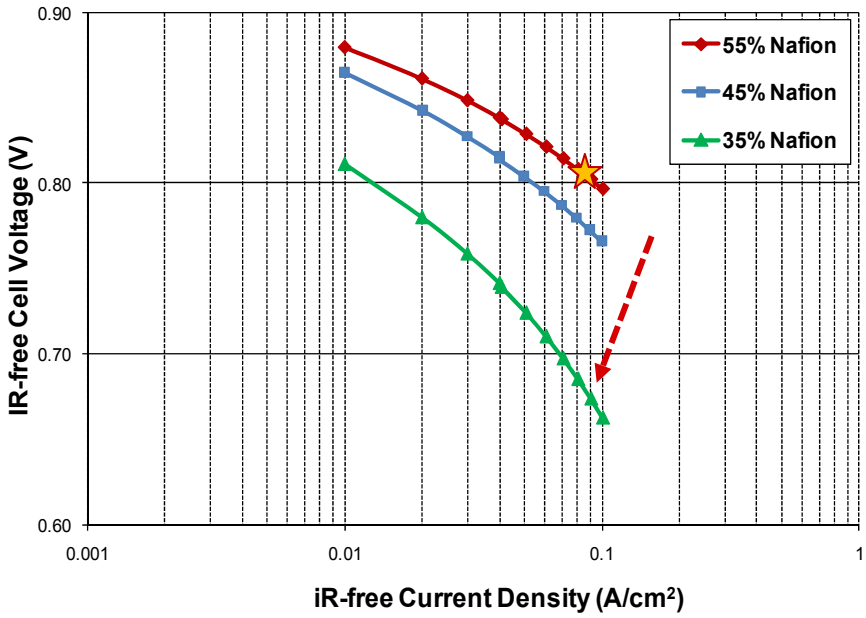
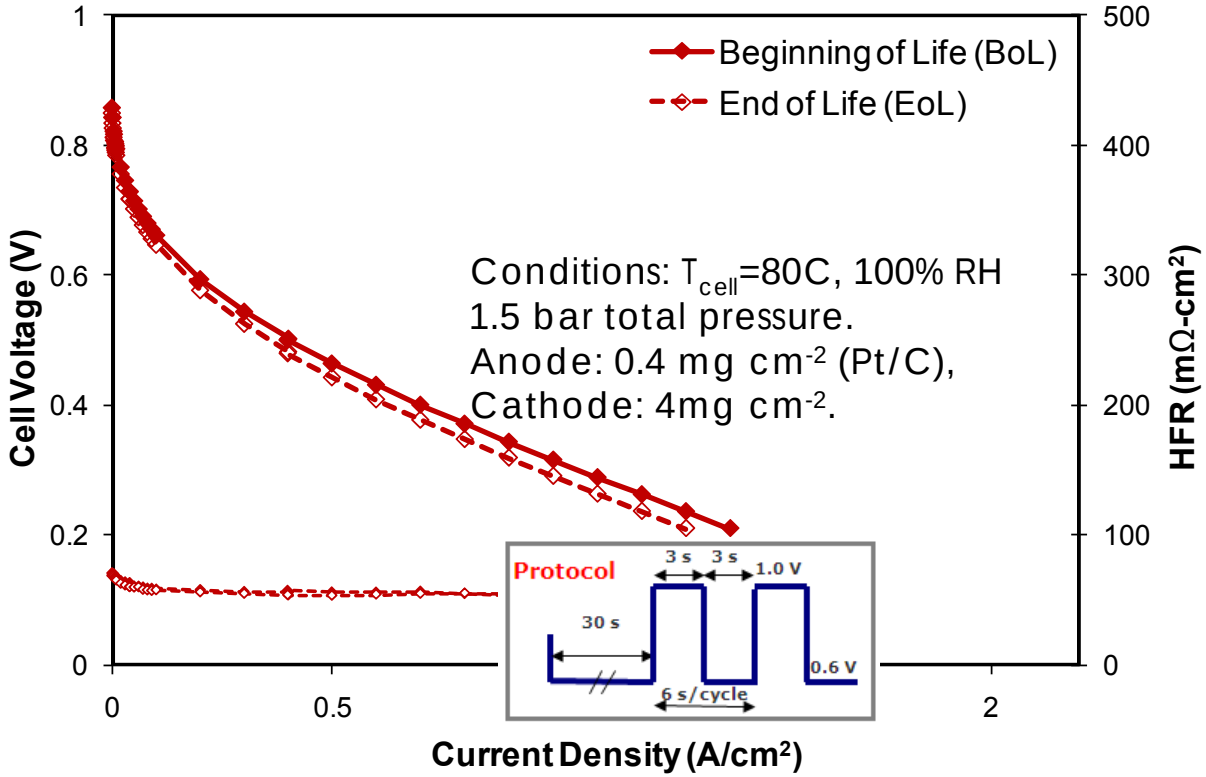




DOE EERE Project ID# FC086 AMR 2103 report, NTCNA testing

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

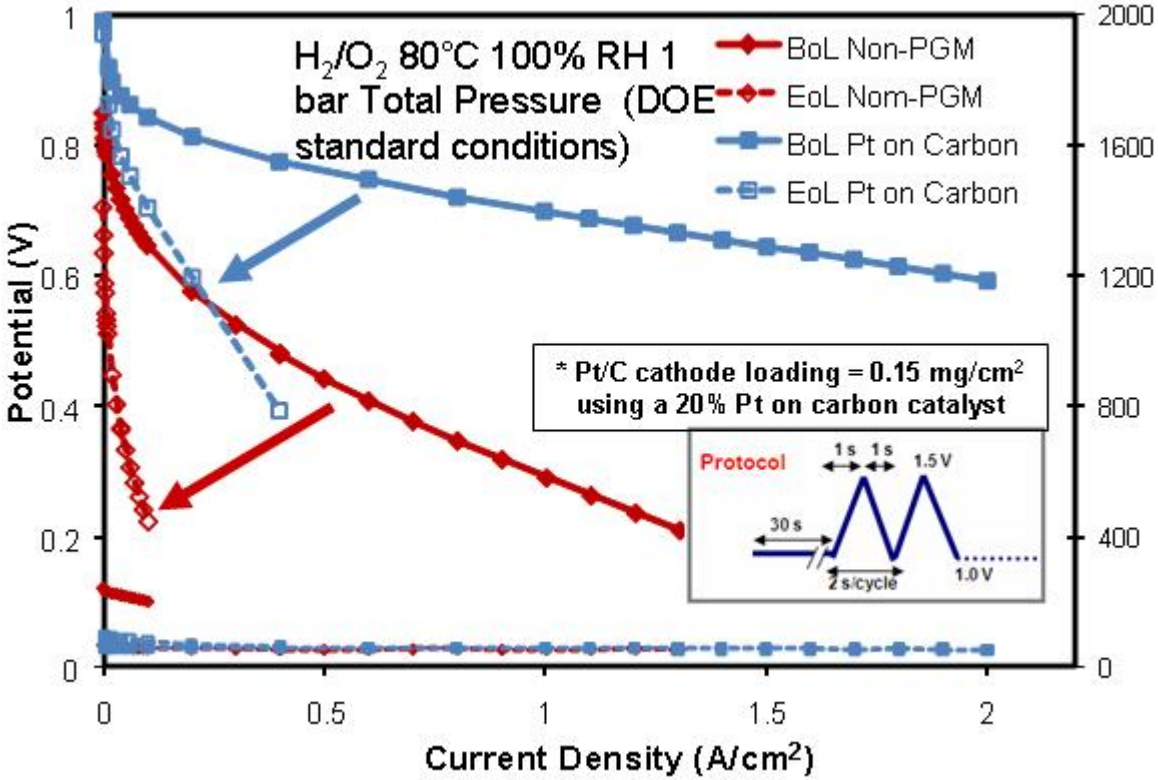
Load cycling AST – Good!



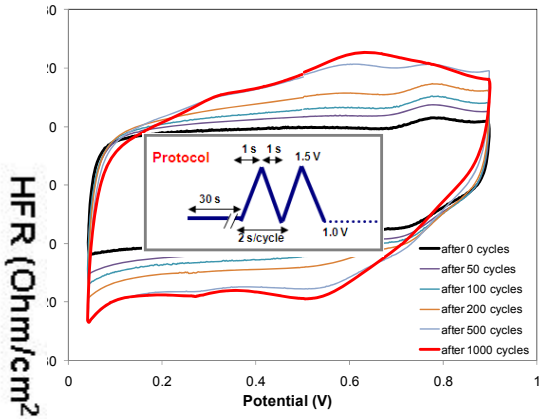
DOE EERE Project ID# FC086 AMR 2103 report, NTCNA testing

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

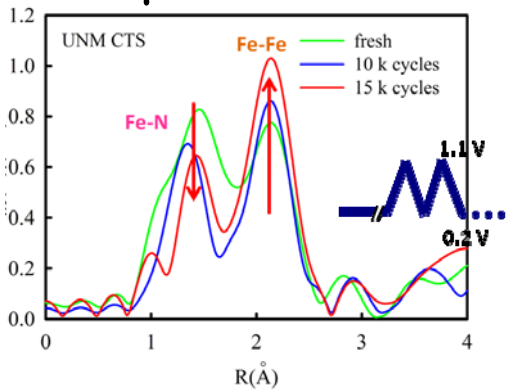
Start/Stop AST – Good!



ECSA



Δμ EXAFS



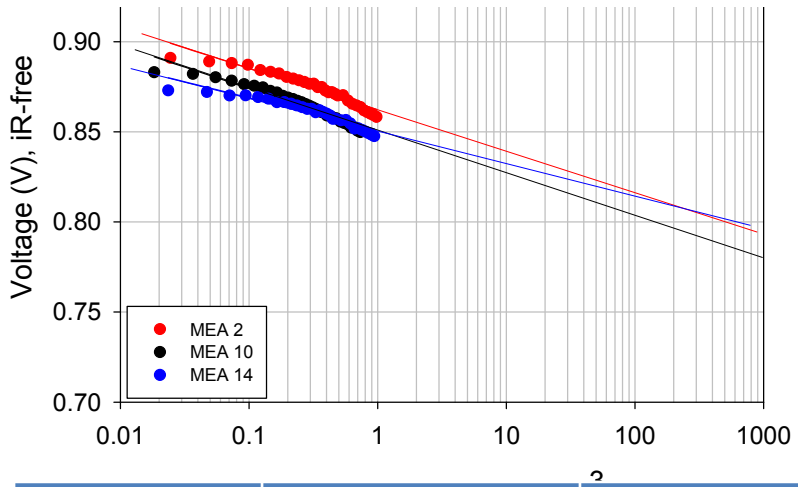
DOE EERE Project ID# FC086 AMR 2103 report, NTCNA testing

Durability under start/stop similar to Pt/C

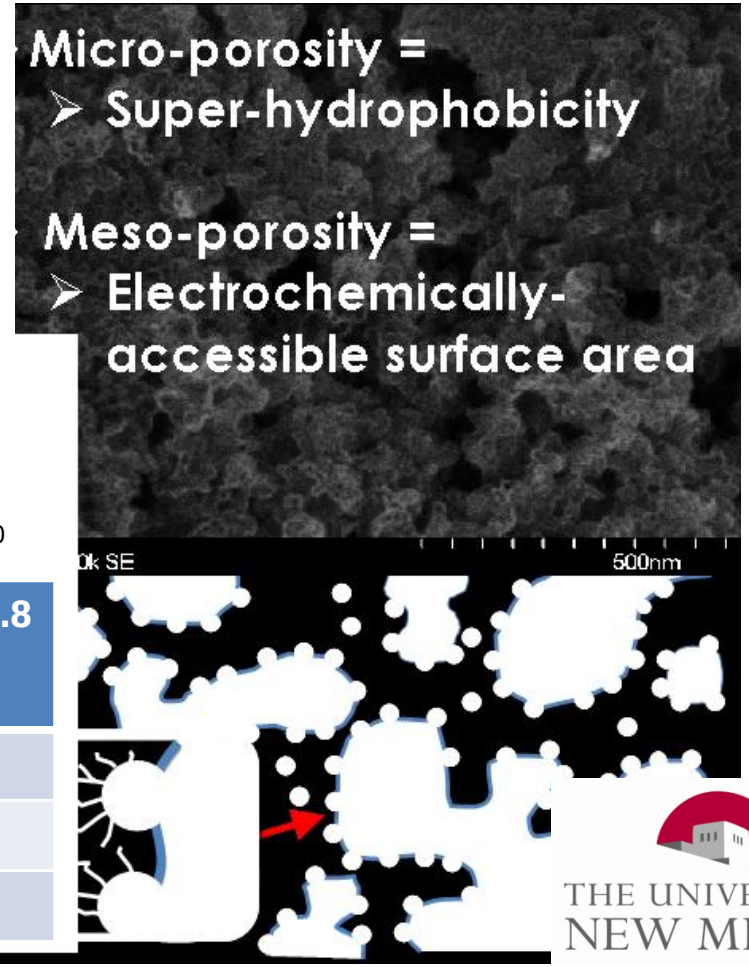
Volumetric Projection

PAJARITO POWDER

Sanjeev Mukerjee, NEU



Sample	mV @ 200 A/cm³	A/cm³ @ 0.8 V (iR free)
MEA 2	809	400
MEA 10	796	150
MEA 14	810	400



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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**

Scale-up process

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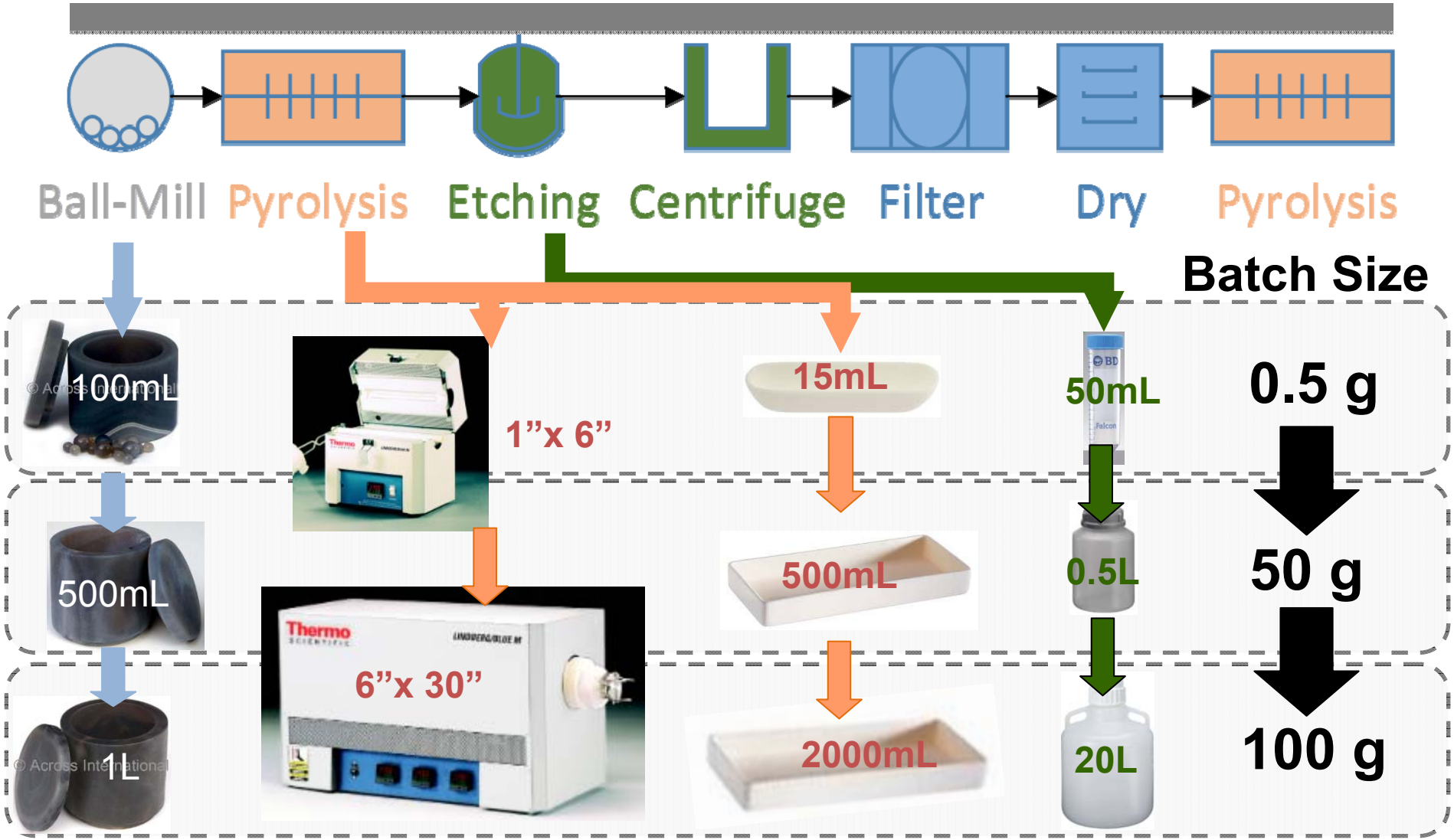

50+ Grams Scale-Up

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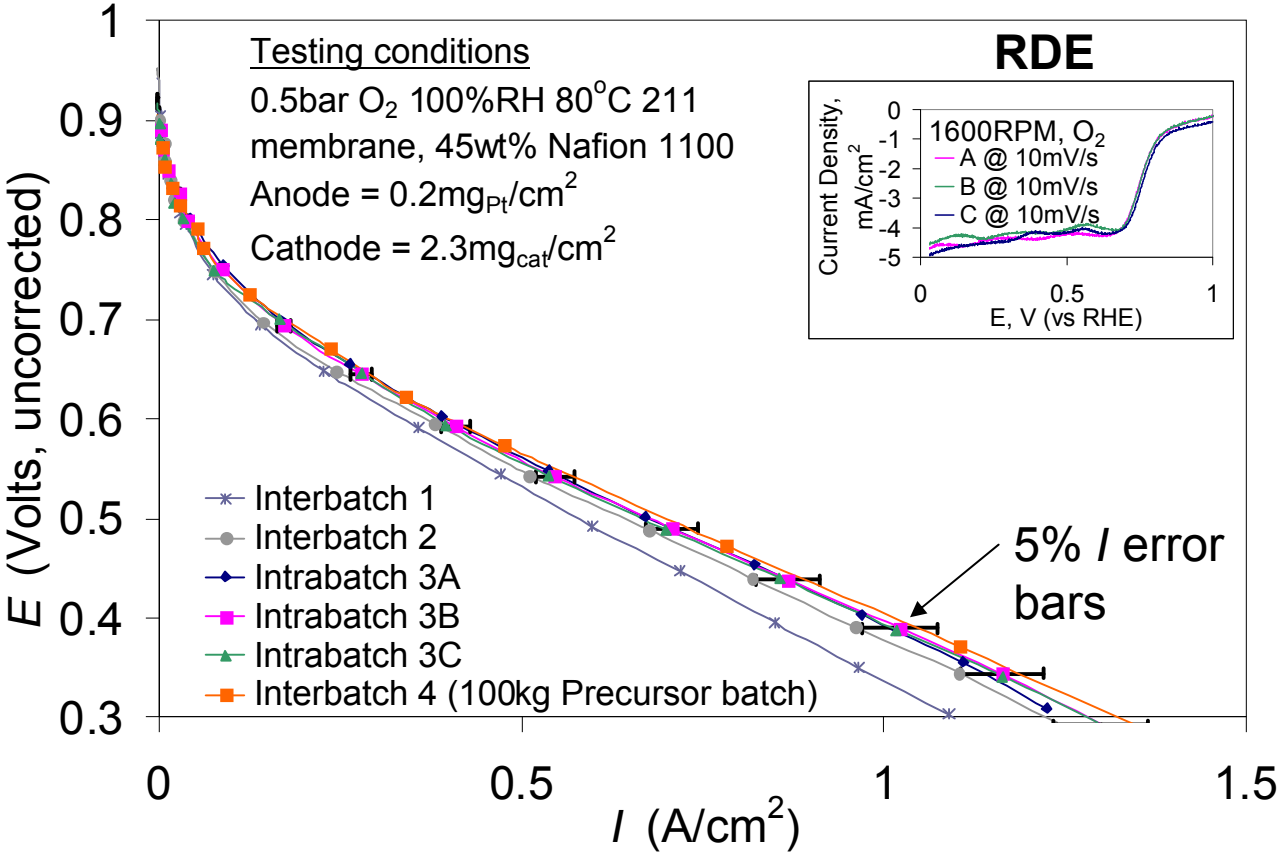
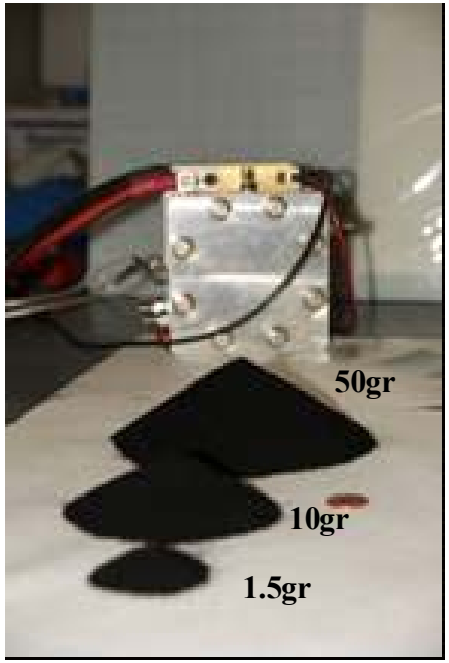


Proprietary



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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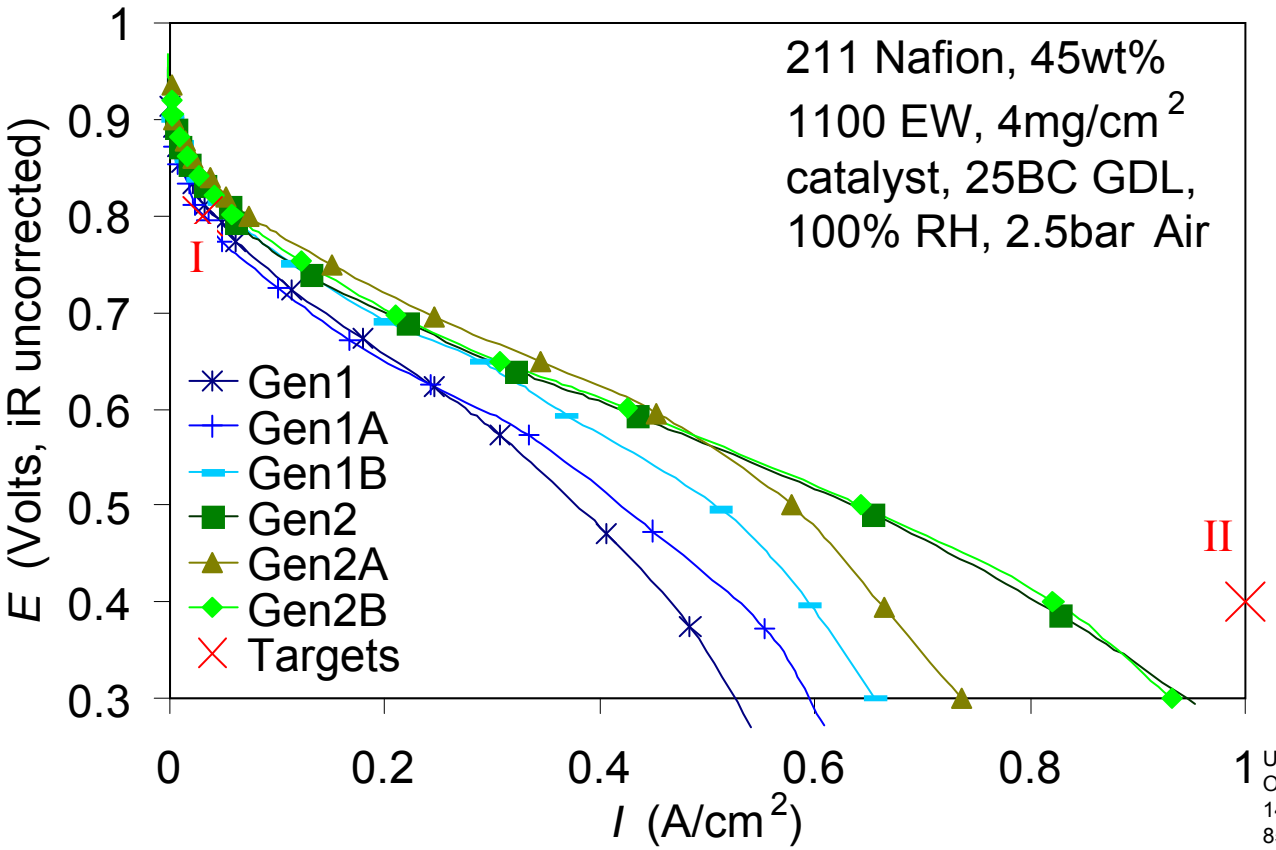
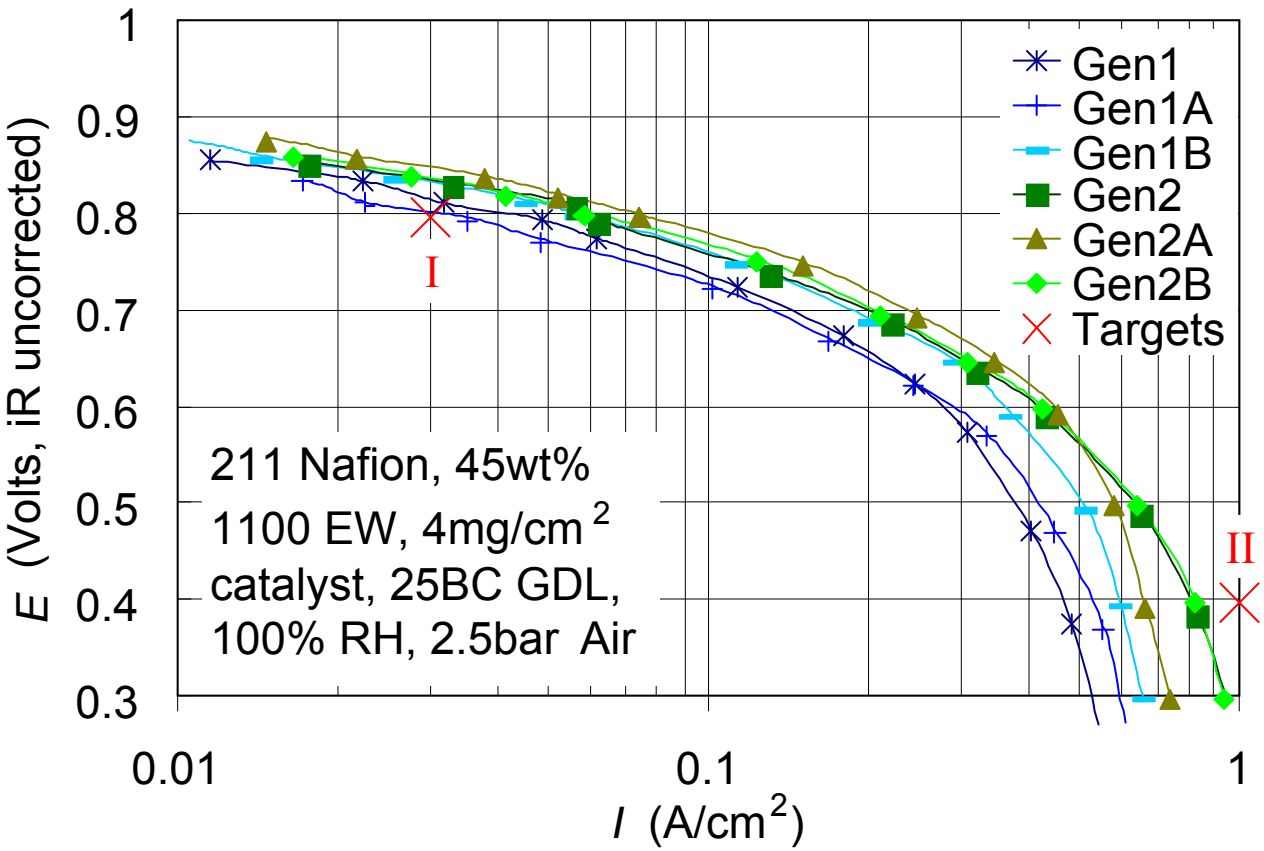
Proprietary



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



Proprietary

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

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

PAJARITO POWDER

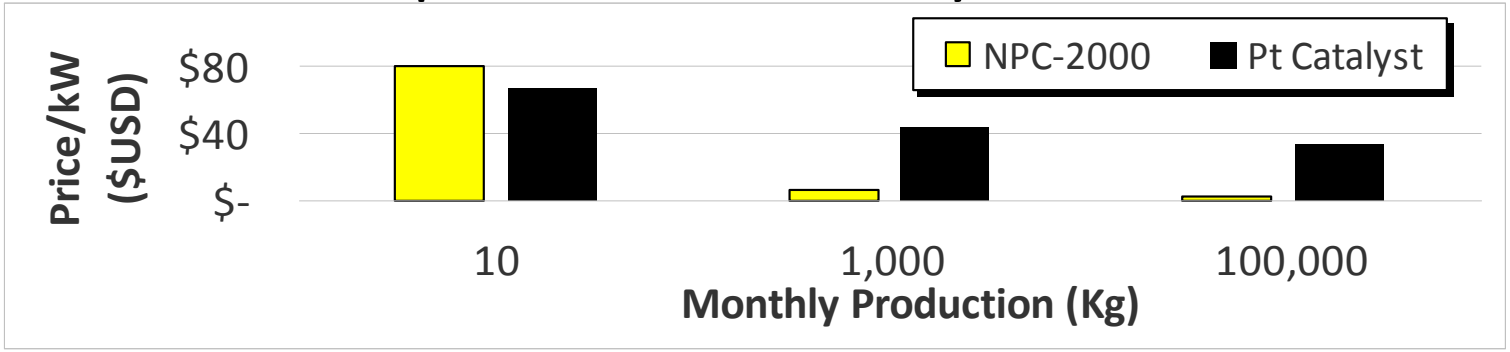
- Multiple no-PGM catalyst production methods and formulations scaled to 25-100gr
- Fixed Product Line (200gr/day capacity)
  - ***NPC-2000 & 1000:*** non-platinum, drop-in fuel cell catalysts with different performance/price points
  - ***PHC-3000:*** Ultra low loaded platinum content catalyst for higher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

Outline

- 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, Energy Efficiency and Renewable Energy Program
- University of New Mexico
  - Profs. Plamen Atanassov, Alexey Serov, and Kateryna Artyushkova
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  - 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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