ElectroCat
Electrocatalysis Consortium

State of the Art of PGM-free Catalyst Activity and Durability

Piotr Zelenay

Los Alamos National Laboratory

Los Alamos NATIONAL LABORATORY

Argonne NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

OAK RIDGE National Laboratory

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

ElectroCat Workshop, Argonne National Laboratory – July 26, 2016

Outline

- **ORR electrocatalyst performance targets for automotive fuel cell applications**
- **Activity and durability of PGM-free catalysts**
- **Durability – main trends**
- **Performance *vs.* cost**
- **Alkaline environments** (as an example of PGM-free catalysts application in systems alternative to low-temperature PEFC)
- **Summary**

PGM-free *vs.* PGM Cathodes: Targeting Competitiveness

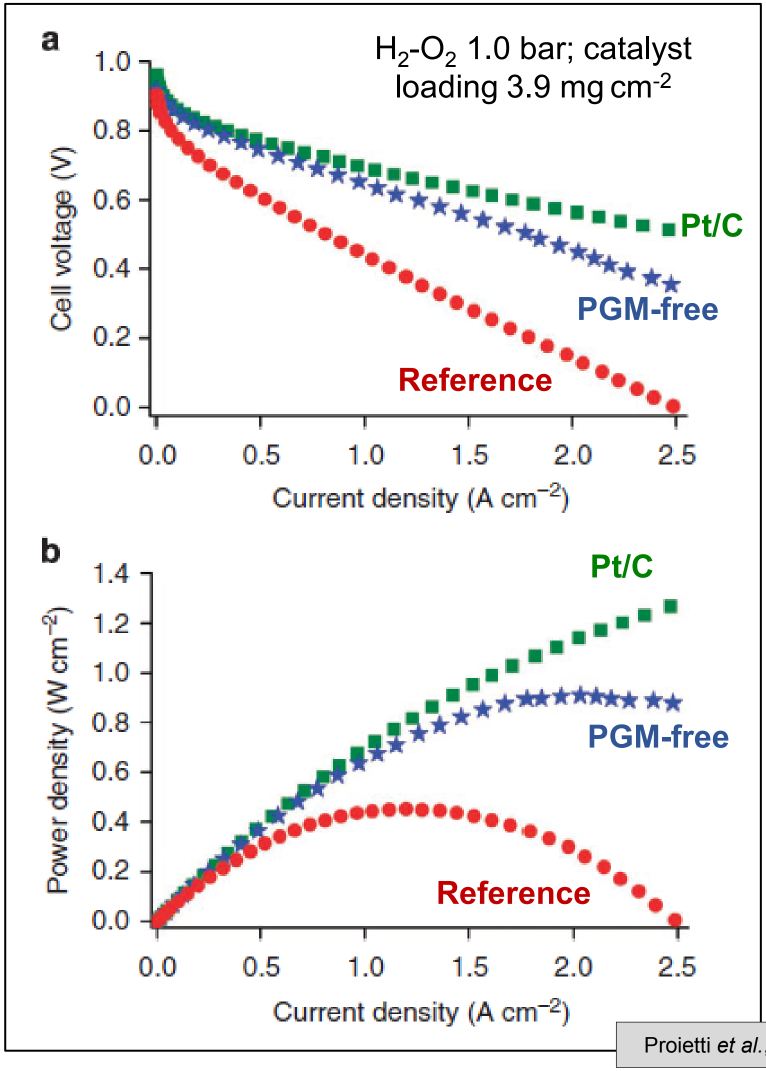
Technical Targets: Electrocatalysts for Transportation Applications			
Characteristic	**Units**	**2015 Status**	**2020 Targets**
Platinum group metal total content (both electrodes)	g/kW (rated, gross) @ 150 kPa (abs)	0.16	0.125
Platinum group metal (PGM) total loading (both electrodes)	mg_{PGM}/cm^2 (electrode area)	0.13	0.125
Mass activity	A/mg_{PGM} @ 0.9 $V_{iR\text{-}free}$	> 0.5	0.44
Loss in initial catalytic activity	% mass activity loss	66	< 40
Loss in performance at 0.8 A/cm^{2*}	mV	13	< 30
Electrocatalyst support stability	% mass activity loss	41	< 40
Loss in performance at 1.5 A/cm^2	mV	65	< 30
PGM-free catalyst activity	**A/cm^2 @ 0.9 $V_{IR\text{-}free}$**	**0.024 A/cm^2**	**> 0.044***

*Target is equivalent to PGM catalyst mass activity target of 0.44 A/mg_{PGM} at 0.1 mg_{PGM}/cm^2

PGM-free containing MEAs need to meet DOE performance and durability targets

Activity and Durability of PGM-free Catalysts

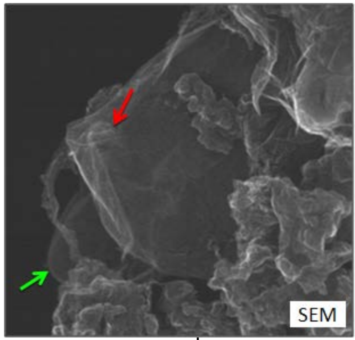
INRS Montreal: ORR Activity of MOF-derived/Fe-based Catalysts



Proietti *et al.*, *Nat. Commun.* **2:416**, 1-9, 2011

High power density, in excess of 0.9 W cm^{-2}, obtained in an H_2-O_2 fuel cell with a Zn-MOF-derived catalyst

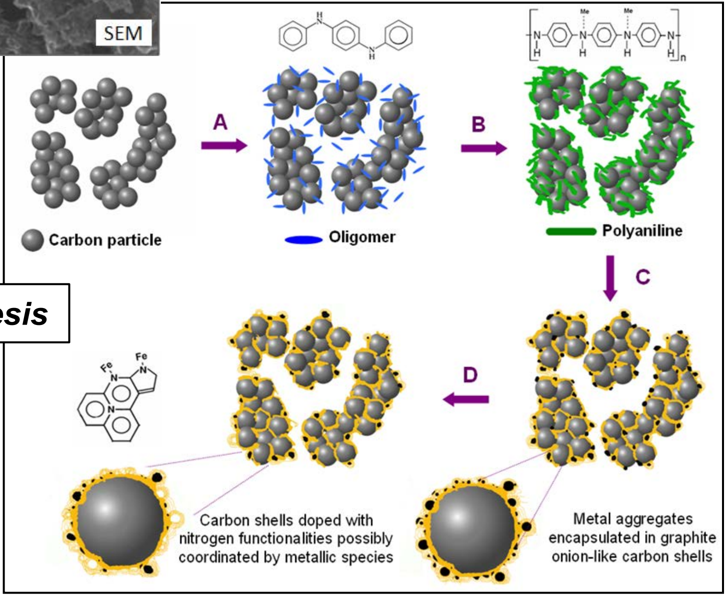
Synthesis of PGM-free Catalysts

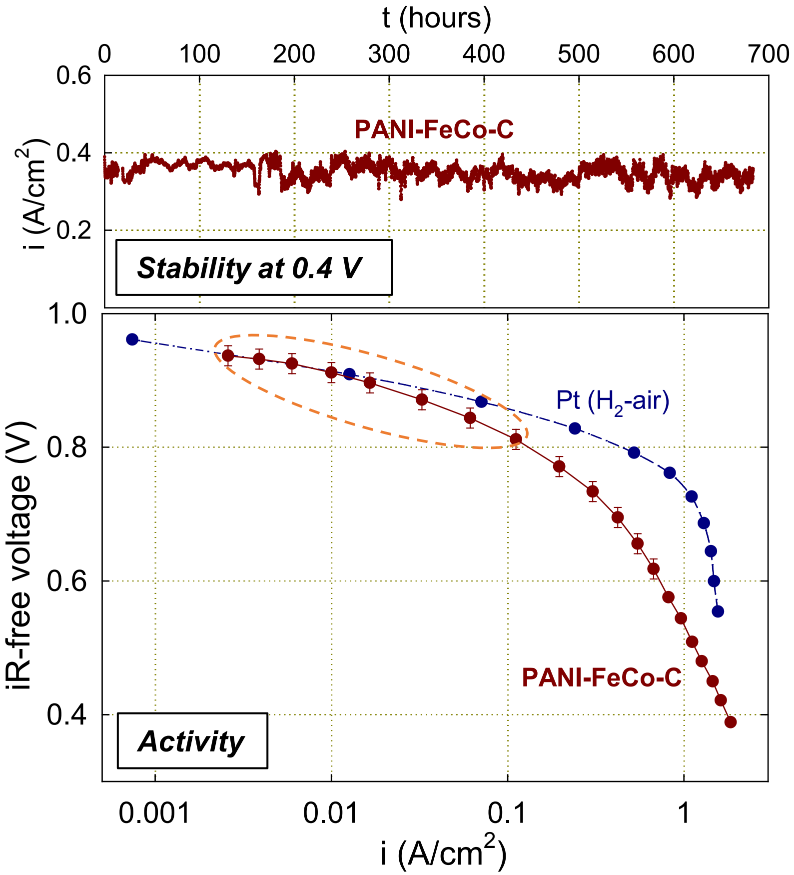


Catalyst SEM: *Layered-graphene sheet marked with green arrow; FeCo- nanoparticle shown with a red arrow.*

G. Wu *et al.*, *Science*, **332**, 443, 2011

The Synthesis

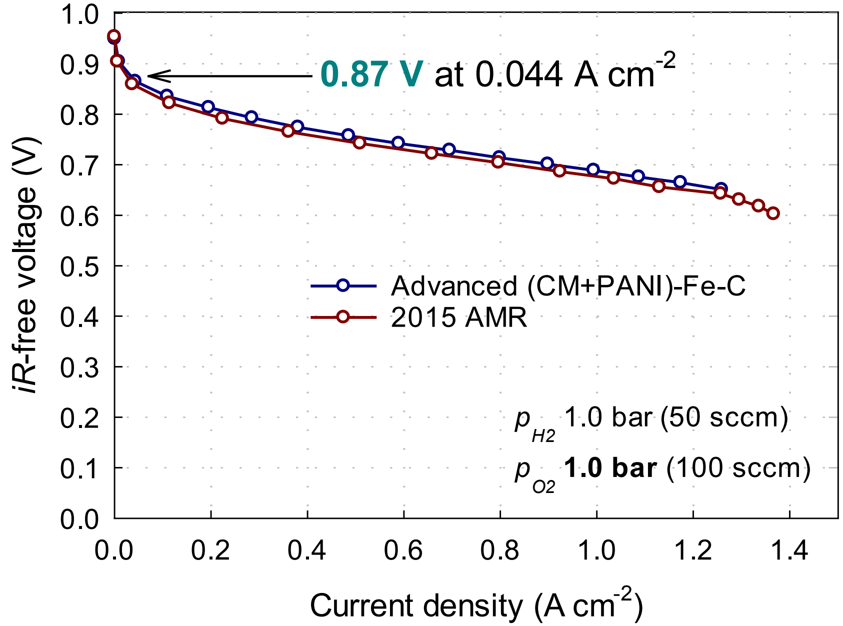




PANI-family of catalysts, combining high activity and selectivity with promising stability and low cost

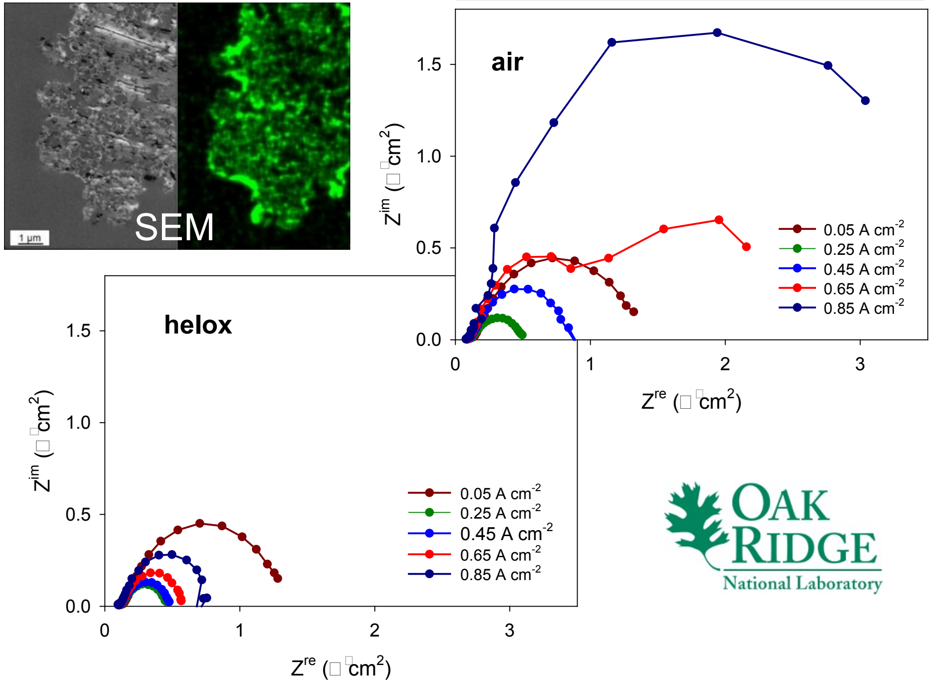
Advanced (CM+PANI)-Fe-C Catalyst

Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 50 sccm, 1.0 bar H_2 partial pressure; Cathode: *ca.* 4.0 mg cm^{-2} O_2, 100 sccm, 1.0 bar O_2 partial pressure; Membrane: Nafion®,117; Cell size: 5 cm^2



Fluorine mapping

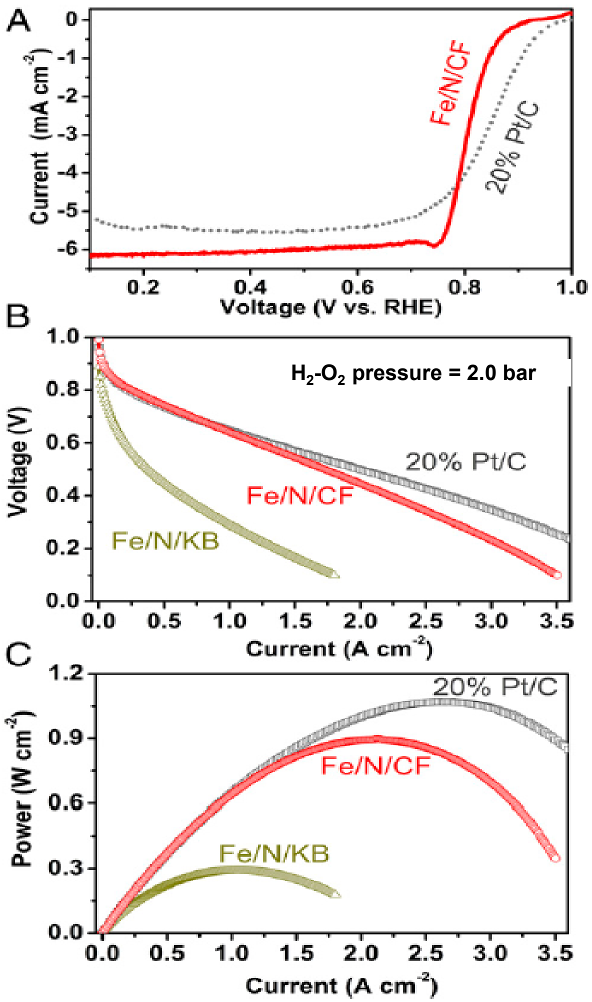
Impedance spectroscopy



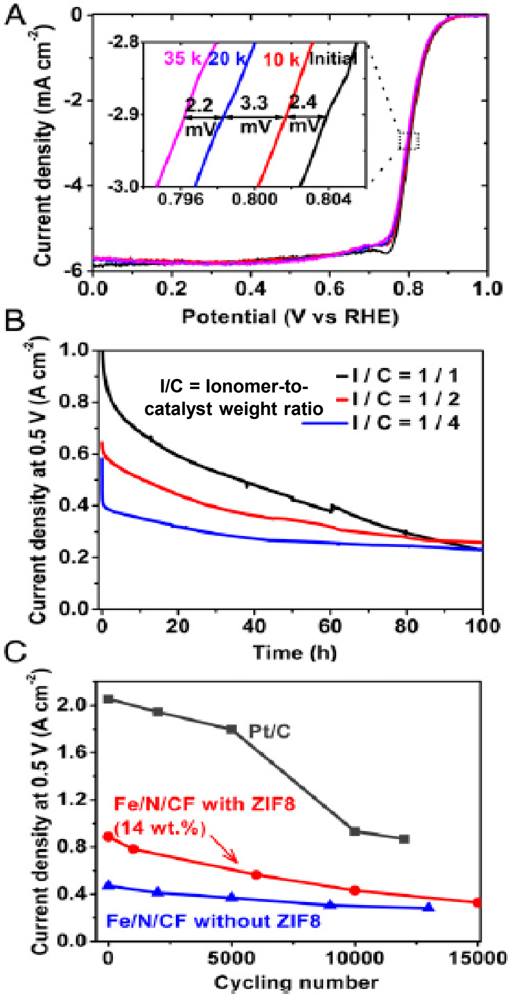
- Improved ORR activity achieved through modifications to (CM+PANI)-Fe-C catalyst synthesis and improvements in electrode design, enhancing O_2 transport within the catalyst layer
- 0.044 A cm^{-2} reached at **0.87 V** (*iR*-free) in the H_2-O_2 fuel cell test

ANL MOF-derived Catalyst in Carbon Nanofibrous Network

Activity



Durability



0.6 – 1.0 V cycling at 50 mV s^{-1} in Ar-purged electrolyte

constant voltage test at 0.5 V

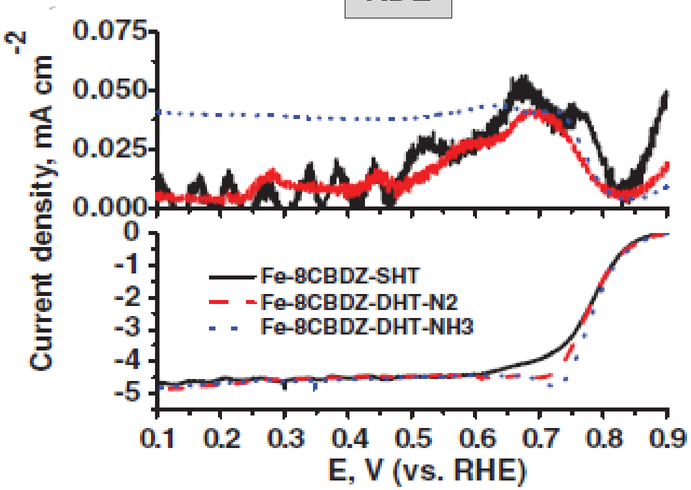
0.6 – 1.0 V cycling at 50 mV s^{-1} under N_2

Shui *et al.*, *Proc Natl Acad Sci*, **112**, 10629, 2015

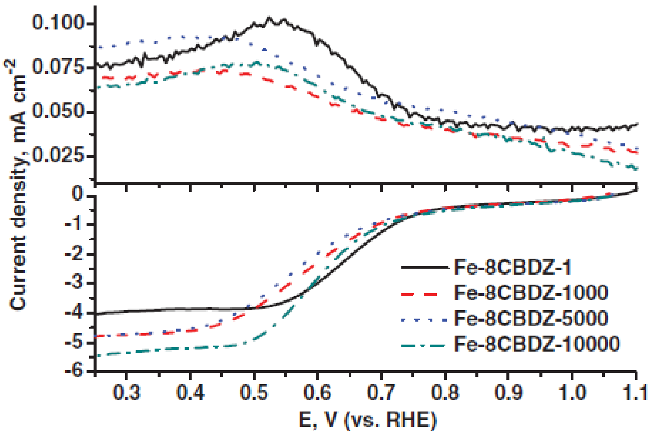
Enhanced fuel cell performance through introduction of micro/macropores

University of New Mexico Templated Catalysts

RDE

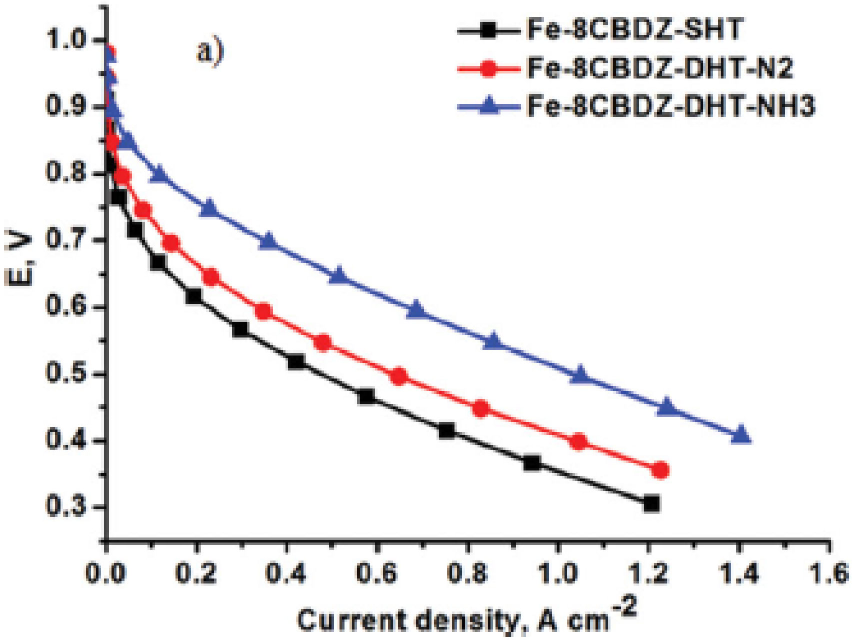


0.6 – 1.0 V cycling in O_2 saturated electrolyte



Fuel Cell

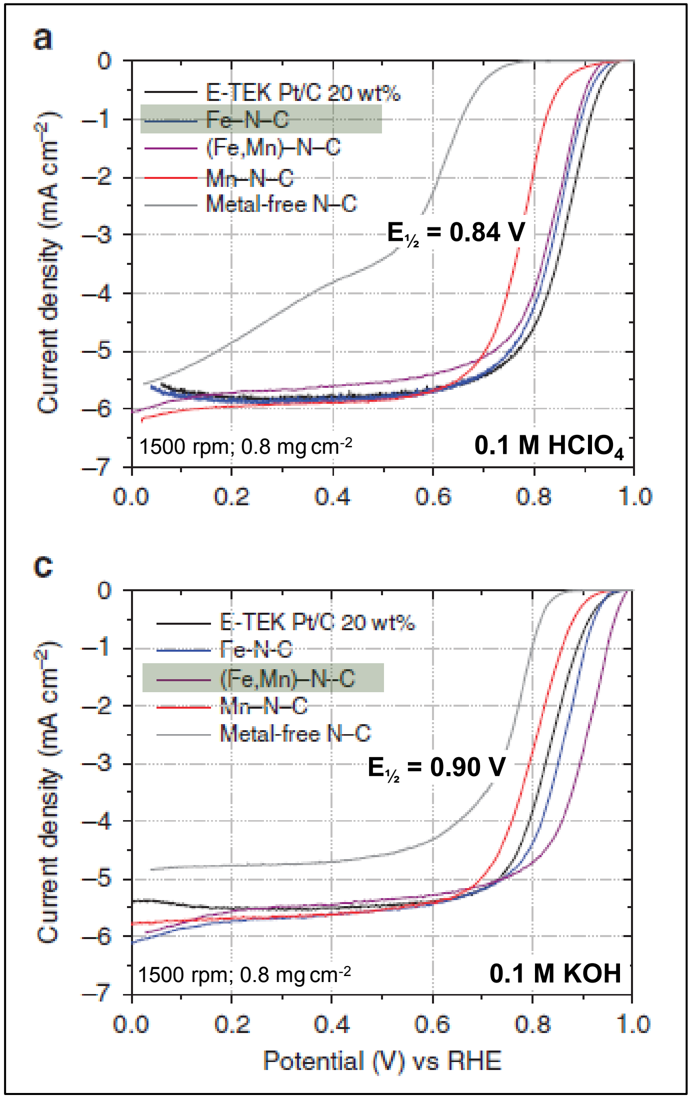
H_2-O_2 1.7 bar (gauge)



Serov *et al.*, *Adv. Energy Mater.* **4**, 1301735, 2014

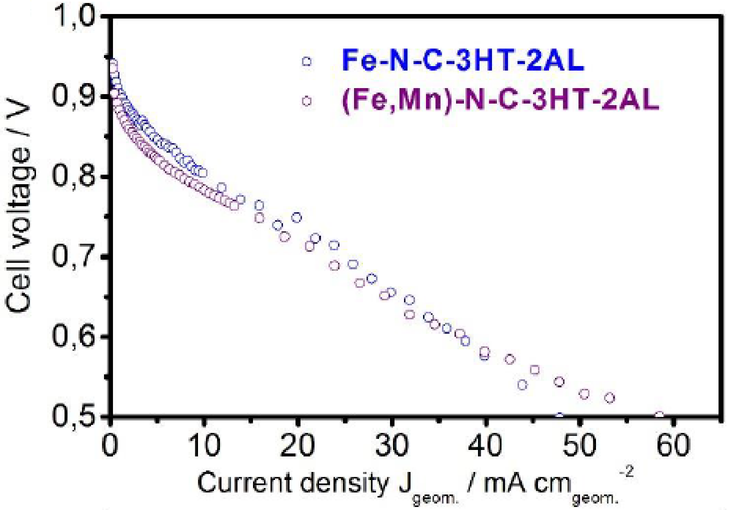
Enhanced fuel cell performance achieved through templating synthesis method

Technical University Berlin Modified PANI-Fe-C: Activity



Sahraie *et al.*, *Nat. Commun*. **6:8618**, 1-9, 2015

H_2-O_2 1.0 bar; catalyst loading 2 mg cm^{-2}

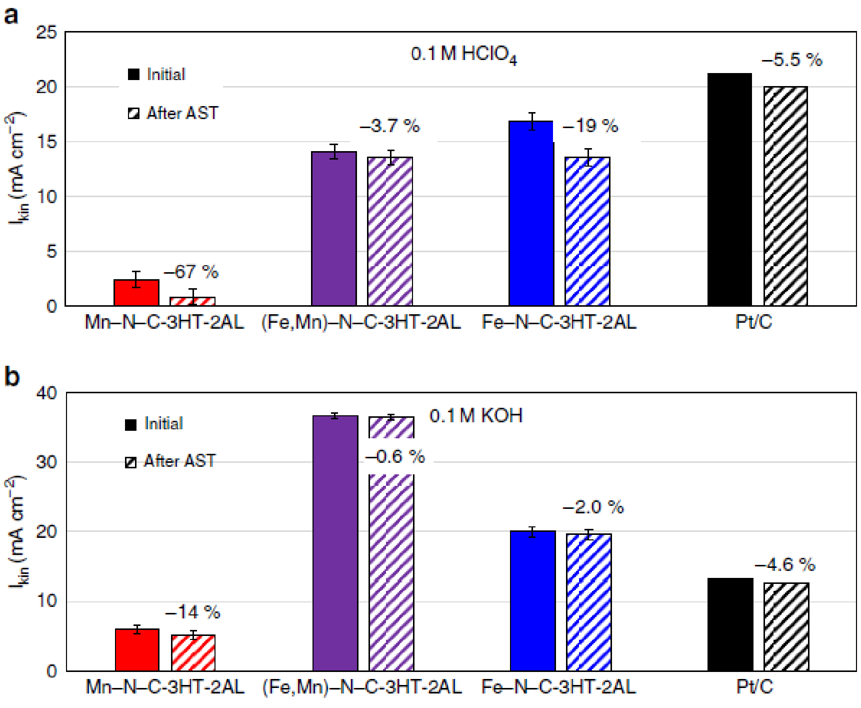


- High ORR activity demonstrated in both acid and alkaline electrolytes in RDE testing
- Much lower performance recorded in the fuel cell, pointing to observed at times discrepancies between RDE and fuel cell data in the field

Technical University Berlin Modified PANI-Fe-C: Durability

RDE

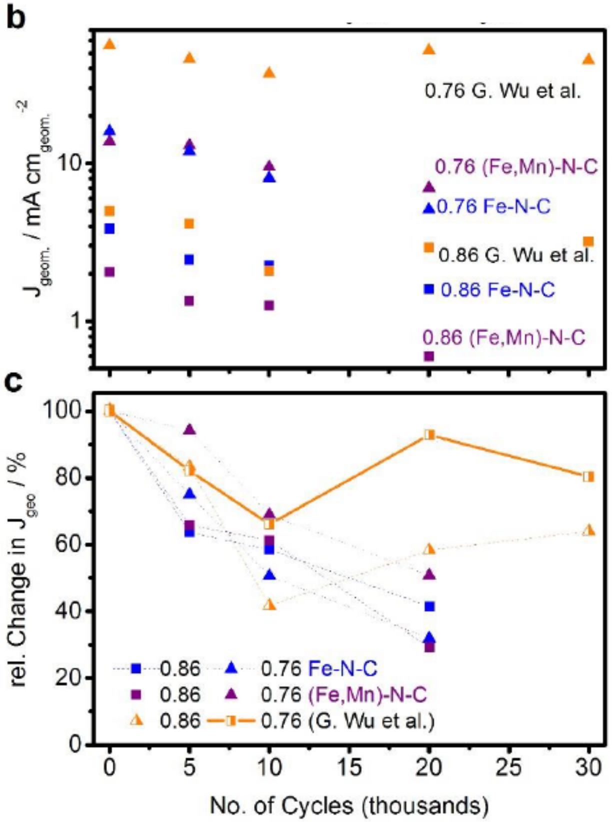
AST: 9,000 potential cycles; 0.5 – 1.3 V; 50 mV s^{-1}; N_2-saturated electrolyte



Sahraie *et al.*, *Nat. Commun*. **6:8618**, 1-9, 2015

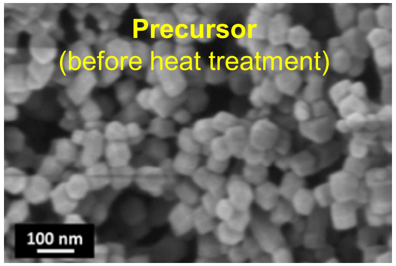
Fuel Cell

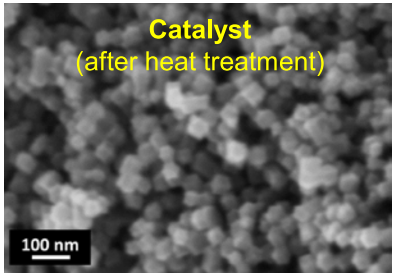
AST: 0.6 – 1.0 V; under N_2 flow



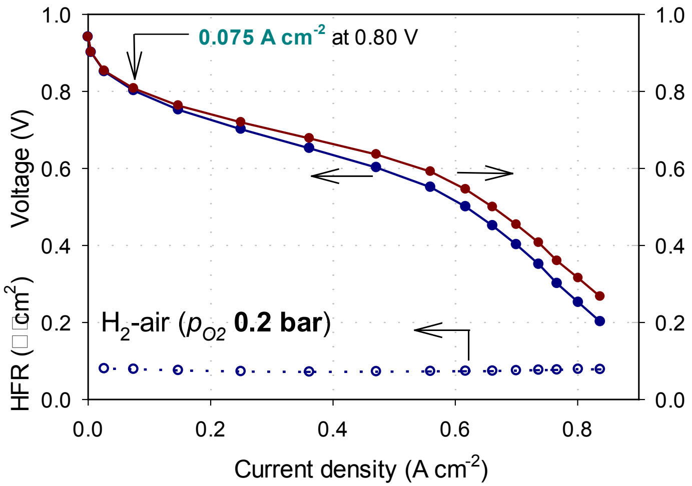
Good durability measured with RDE not demonstrated in fuel cell measurements

University at Buffalo: Atomically Dispersed Fe-based Catalyst

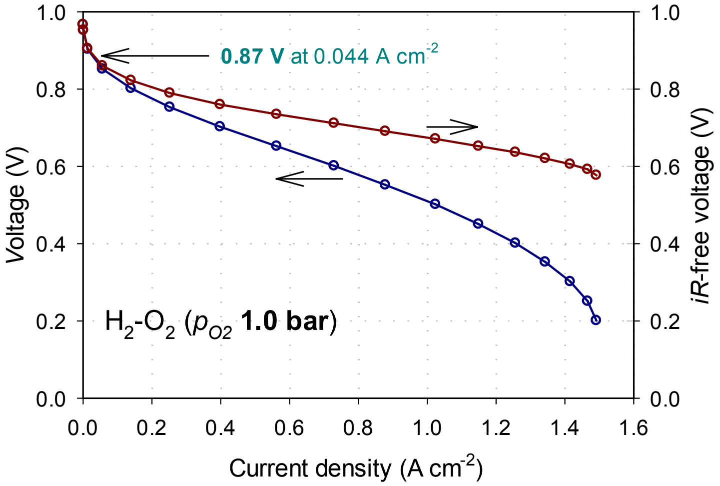


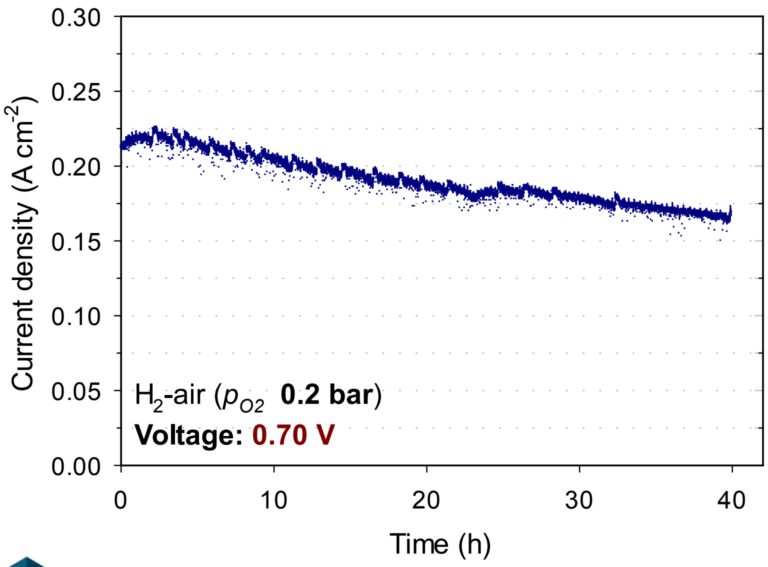


Anode: 0.3 mg$_{Pt}$ cm^{-2} Pt/C, H_2, 200 sccm, p_{H2} 1.0 bar; **Cathode:** 4.0 mg cm^{-2}, air, 200 sccm; **Membrane:** Nafion®, 211; **Cell:** 80°C, 100%RH



Anode: 0.3 mg$_{Pt}$ cm^{-2} Pt/C, H_2, 50 sccm, p_{H2} 1.0 bar; **Cathode:** 4.0 mg cm^{-2}, O_2, 100 sccm; **Membrane:** Nafion®, 115; **Cell:** 80°C, 100%RH

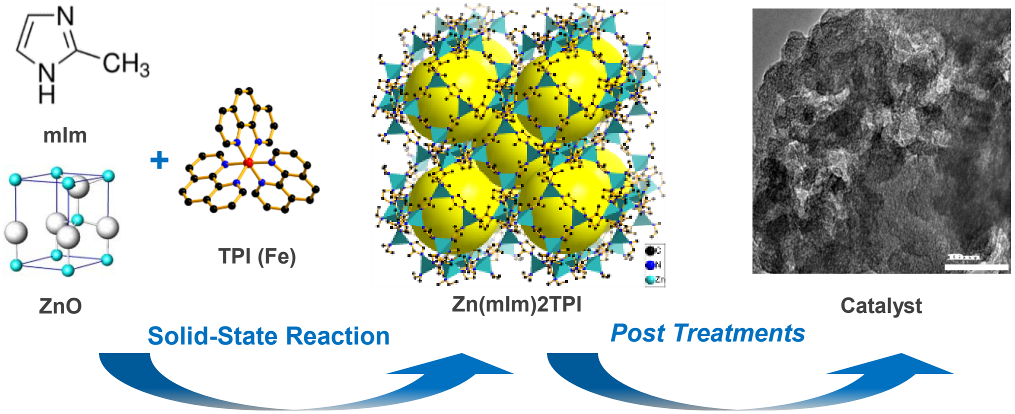




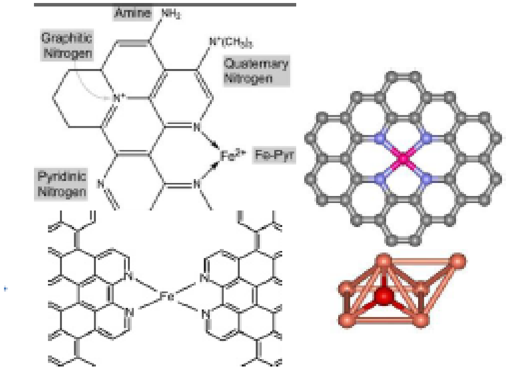
- UB unsupported catalyst derived from a homemade "Fe-MOF" precursor; unique cubic morphology preserved after heat treatment; all Fe atomically dispersed
- High ORR activity in H_2-air (**0.075 A/cm^2** at **0.80 V**) and H_2-O_2 fuel cell (**0.87 V** at **0.044 A/cm^2**, *iR*-free)
- Initial testing (April 2016) revealing for the first time very promising performance durability of a non-PGM catalyst under viable fuel cell operating conditions: **ambient air feed** and **high voltage** (0.70 V)

PGM-free catalysts to reduce cost

Zeolitic Imidazolate Framework Catalyst (D.J. Liu *et al.*, ANL)

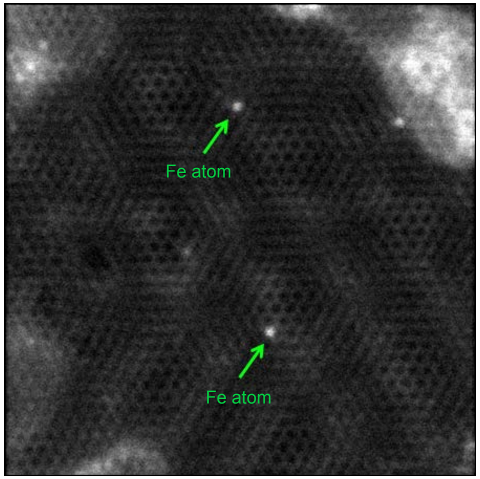


Fe-Metal Organic Framework Catalyst (S. Mukerjee *et al.*, NEU/UNM)



M-N-C catalyst

Cyanamide-Polyaniline-Fe-C Catalyst (P. Zelenay *et al.*, LANL)



Progress toward achieving PGM-free catalyst and MEA targets:

- 0.9 $V_{IR\text{-}free}$, 100% RH O_2, 1.5 bar: **14-24 mA/cm^2**
  - 2014 status: 9-15 mA/cm^2
  - Target: 44 mA/cm^2 @ 0.9 VIR-free
- 0.8 V, 100% RH air, 1.5 bar: **90-110 mA/cm^2**
  - 2014 status: 25-75 mA/cm^2
  - Target: 300 mA/cm^2 @ 0.8 V

Still need knowledge of active site and degradation modes

Nancy Garland, EFCF2015 Presentation, Lucerne, Switzerland, July 2015; https://www.hydrogen.energy.gov/pdfs/review15/fc000_papageorgopoulos_2015_o.pdf.

Durability – Main Trends

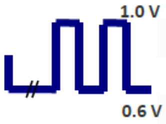
Northeastern University Fe-MOF Catalyst: Cycling Durability

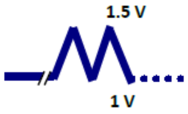
- Nissan evaluates catalyst durability using two protocols: load cycling and start-stop cycling to simulate FC stack conditions.

Protocols for Nissan and DOE Durability Working Group

Condition	Nissan Load cycling	Nissan Start-stop cycling
Temperature (°C)	80	80
Gas condition Cathode	N2	N_2
Gas – Anode	H2	H2
Voltage scan (V)	[0.6,1.0]	[1.0, 1.5]
Scan rate (mV/s)	6s/cycle	500
Catalyst loading (mg/cm²)	0.6	
No of cycles	10,000	1000

Load cycling

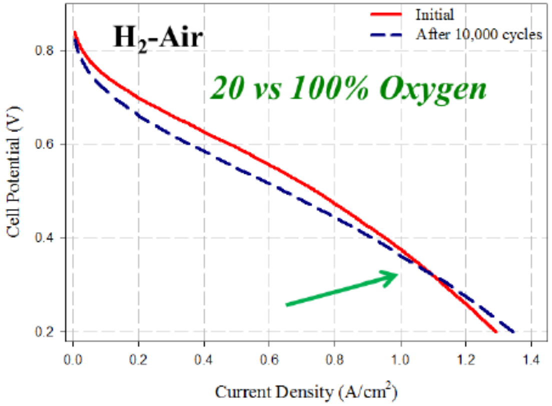


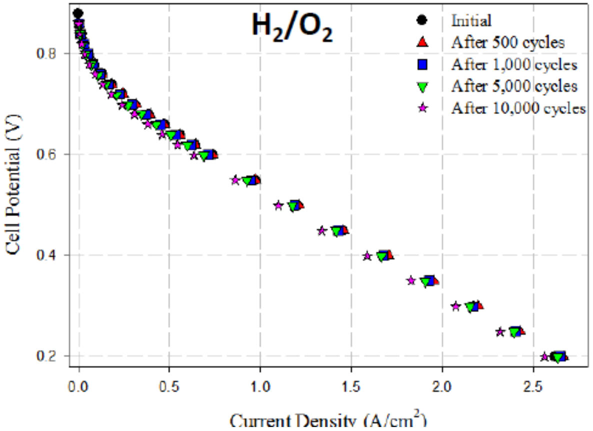


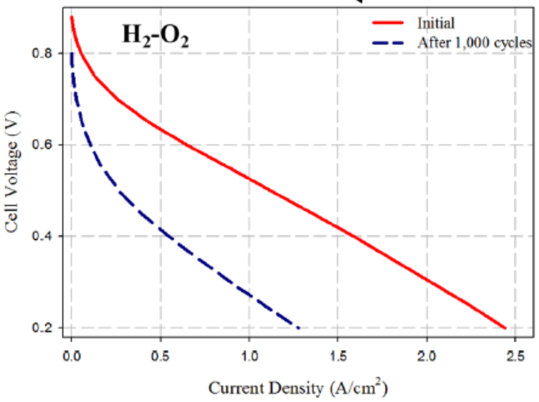
Start-stop cycling

Load Cycling

Start-stop Cycling



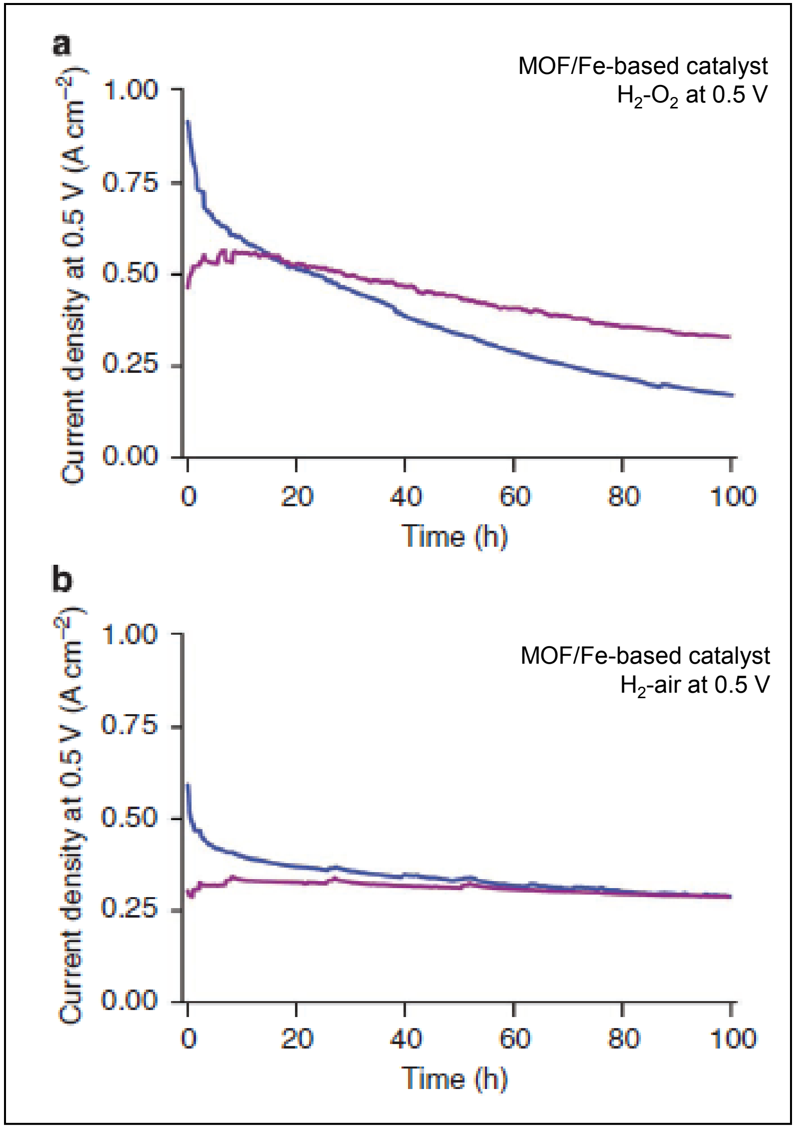




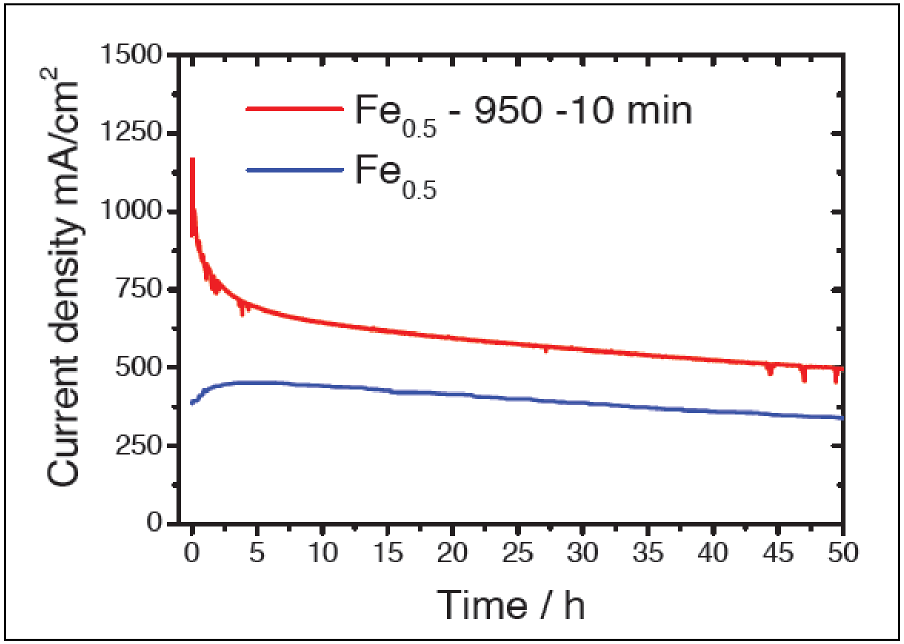
S. Mukerjee, 2015, 2015 DOE Annual Merit Review, Arlington, Va.

- Little performance loss observed following 10,000 cycles between 0.6 and 1.0 V in N_2
- Severe loss after cycling between 1.0 and 1.5 V (to mimic startup/shutdown conditions)

INRS and University of Montpellier MOF Catalysts: Fuel Cell Durability



Proietti *et al.*, *Nat. Commun*. **2:416**, 1-9, 2011

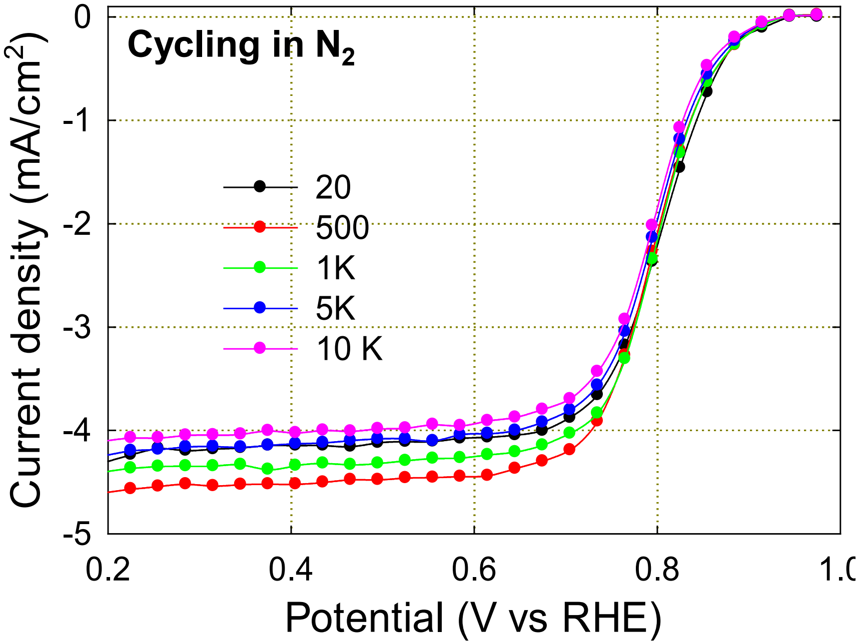


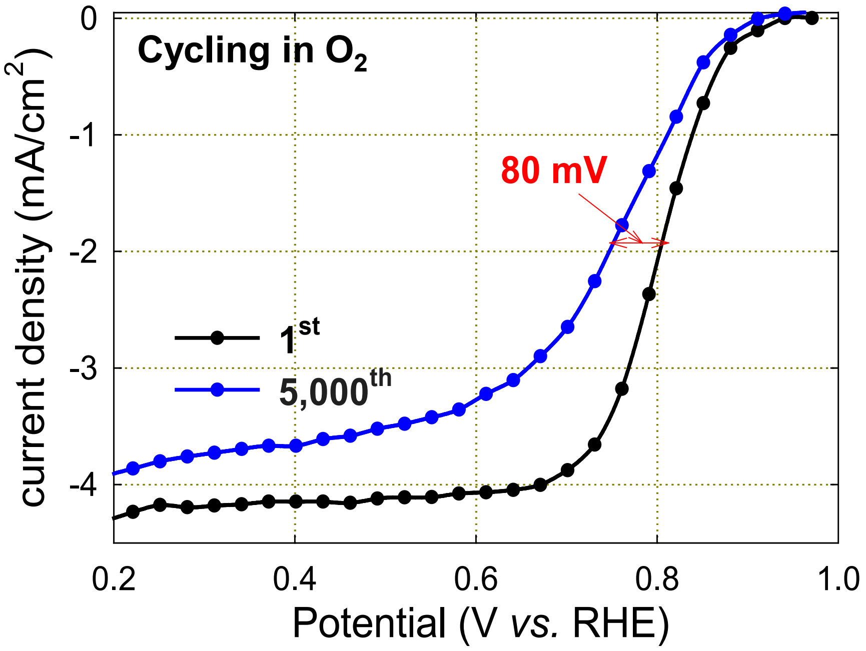
Zitolo *et al.*, *Nat. Mater*. **14**, 937–942, 2015

- Performance loss of most active PGM-free catalysts in the acidic fuel cell cathode exceeding 50% in 100 hours
- Prevalent activity-stability trade-off

Los Alamos PANI-Fe-C Catalyst: Cycling Durability

RDE: 0.6 mg cm^{-2} PANI-Fe-C ORR catalyst, 900 rpm; 25ºC; reference electrode: Ag/AgCl, (3 M NaCl); counter electrode: graphite rod; steady-state potential program: OCP, 300 s, 30 mV steps, 30 s/step; Cycling: N_2, 0.6-1.0 V, 50 mV/s.





G. Wu *et al*, *Chem. Commun.*, 2010, **46**, 7489-7491

Typical behavior: While showing good potential-cycling stability in N_2 atmosphere, PGM-free catalysts tend to lose performance much faster in air or O_2 (*ca.* 80 mV at $E_{½}$ in the case shown).

Performance *vs.* Cost

DFMA Cost Analysis of Stack with PGM-free *vs.* PGM Cathodes

Category	PANI		Ternary NSTF
Catalyst	**PANI-C-Fe**		**PtMnCo/NSTF**
\$/kg catalyst	**\$74 - \$129/kg**		***ca.* \$41,000/kg**
Loading	**4.0 mg/cm^2**		**0.153 mg$_{Pt}$/cm^2**
Catalyst used	**383 g/system**		**22 g/system**
Catalyst cost at baseline conditions and 500,000 systems/year	**\$28/system**		*ca.* **\$900/system**
Stack Cost for 80kW$_{net}$ system and 500,000 systems/year	**Requires 2 stacks; 372 cells per stack at 377 cm^2/cell**		**Requires 1 stack; 372 cells per stack at 299 cm^2/cell**
Power Density	**330 mW/cm^2**	**475 mW/cm^2**	**834 mW/cm^2**
\$/kW$_{net}$ for 500,000 systems/year	**\$31.3/kW$_{net}$**	**\$24.2/kW$_{net}$**	**\$24.2/kW$_{net}$**

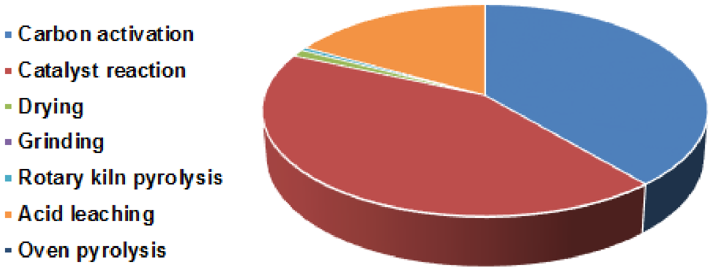
STRATEGIC ANALYSIS

Initial Design for Manufacture & Assembly (DFMA) cost analysis by Strategic Analysis highlighting the need for improved PGM-free catalyst activity.

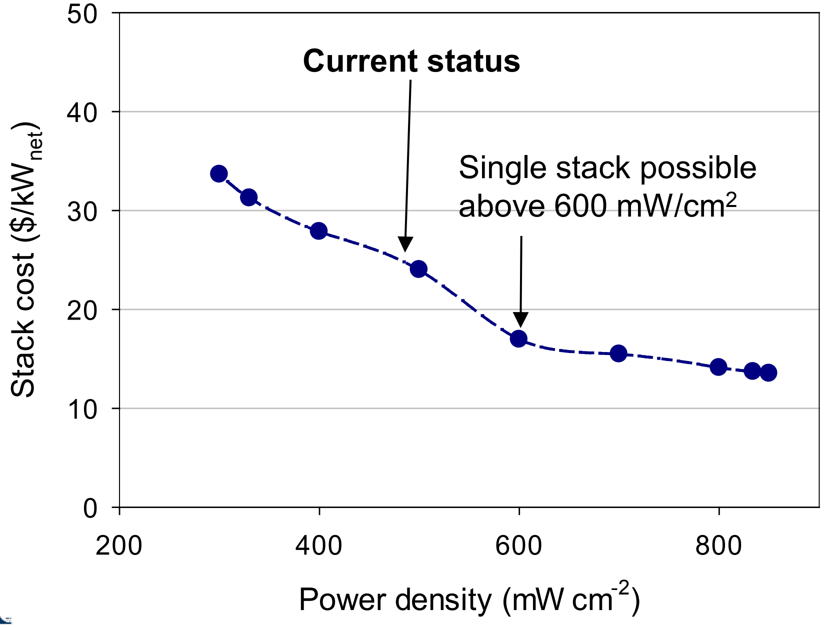
DFMA Cost Analysis: Summary

Catalyst Cost for 80 kW Stack ($/kW)				
Production (systems/year)	1,000	10,000	100,000	500,000
$/kW	0.62	0.43	0.37	0.35

PANI-Fe-C Catalyst Manufacturing Cost Breakdown



Effect of MEA Power Density on Stack Cost (H_2-air; 1.5 bar total H_2 and air pressure)



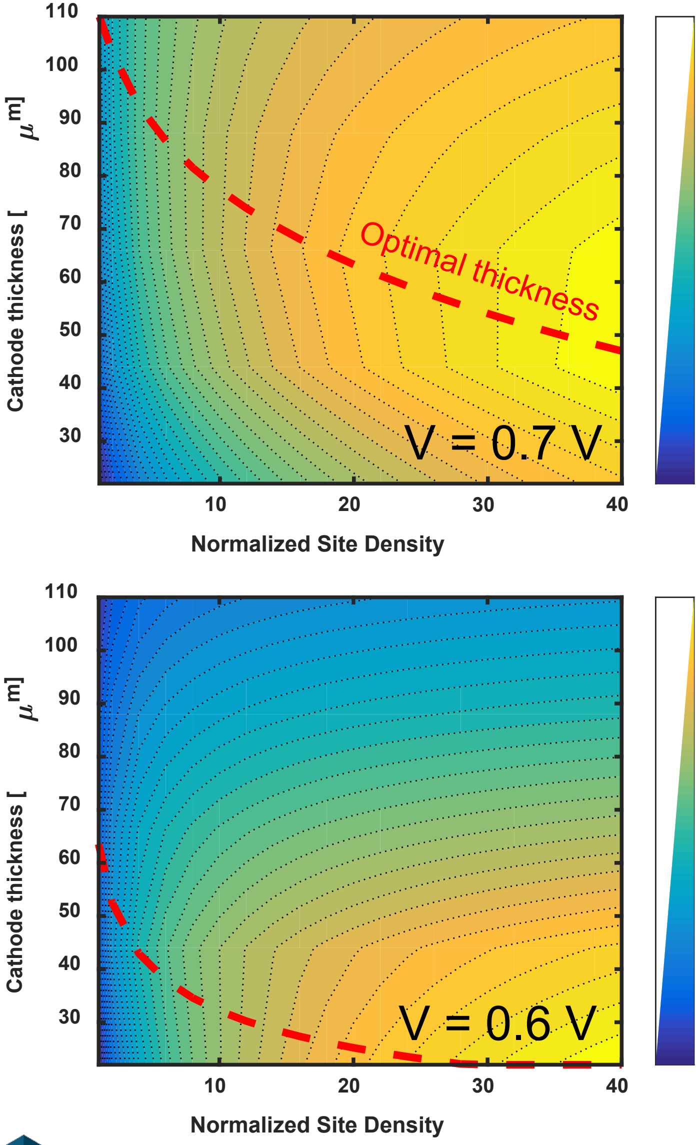
Current status

Single stack possible above 600 mW/cm^2

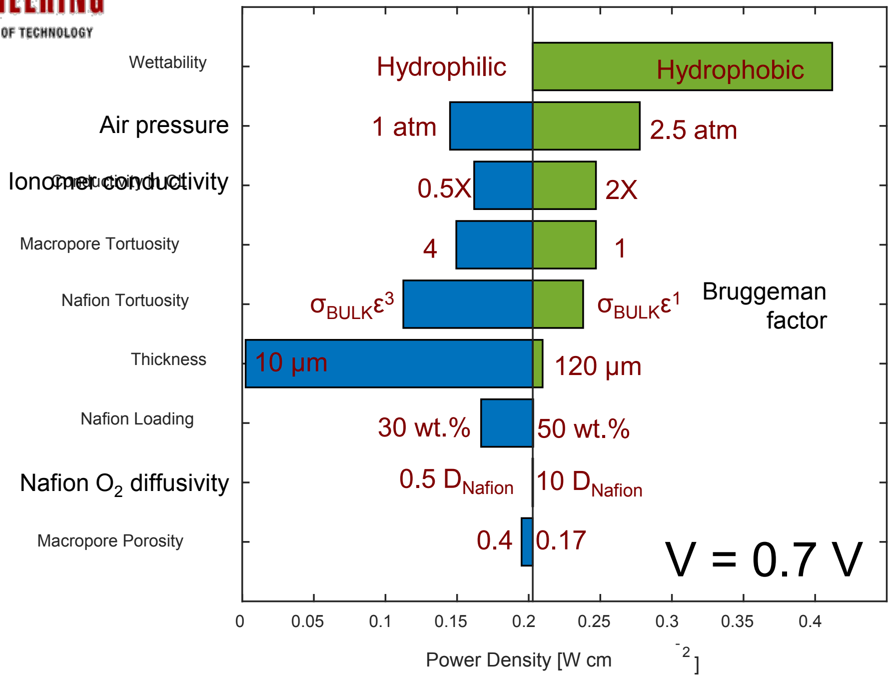
- Preliminary analysis of PANI-Fe-C cost confirming major per-stack cost advantage of non-PGM ORR catalysts over the state-of-the-art Pt-based catalysts (a factor of *ca.* **30**)
- Specific power density of non-PGM MEAs **in need of improvement from the current level** of < **500 mW cm^{-2}** in order for catalyst cost to make significant impact on the stack cost

Parametric Study of Cathode Performance

Power Density *vs.* Thickness and Site Density/Activity



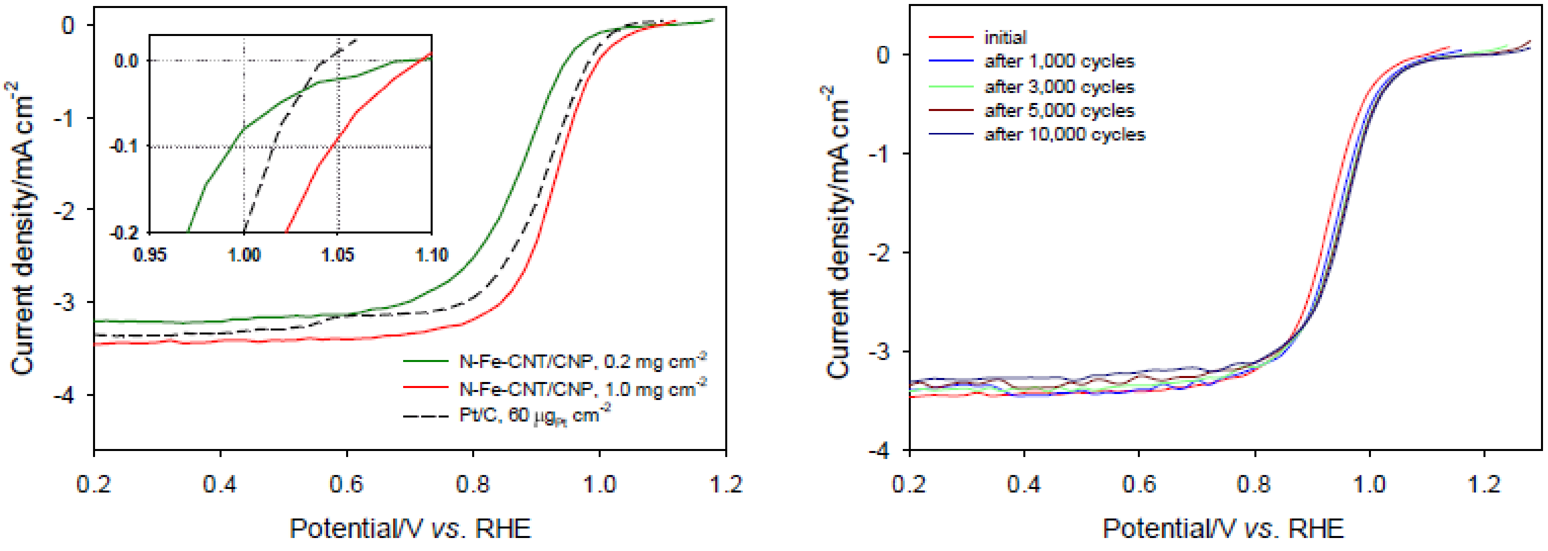
Cathode Parameter Sensitivity



- Increase in active site density/activity needed for power density targets at optimal thickness:
  - **15×** for 0.4 W/cm^2 at 0.70 V
  - **5×** for 0.5 W/cm^2 at 0.60 V
- Key properties for electrode development:
  - More electrode hydrophobicity to reduce flooding
  - Higher conductivity or lower tortuosity of the ionomer

Alkaline Environment

Los Alamos N-Fe-CNT/CNP Catalyst in Alkaline Electrolyte

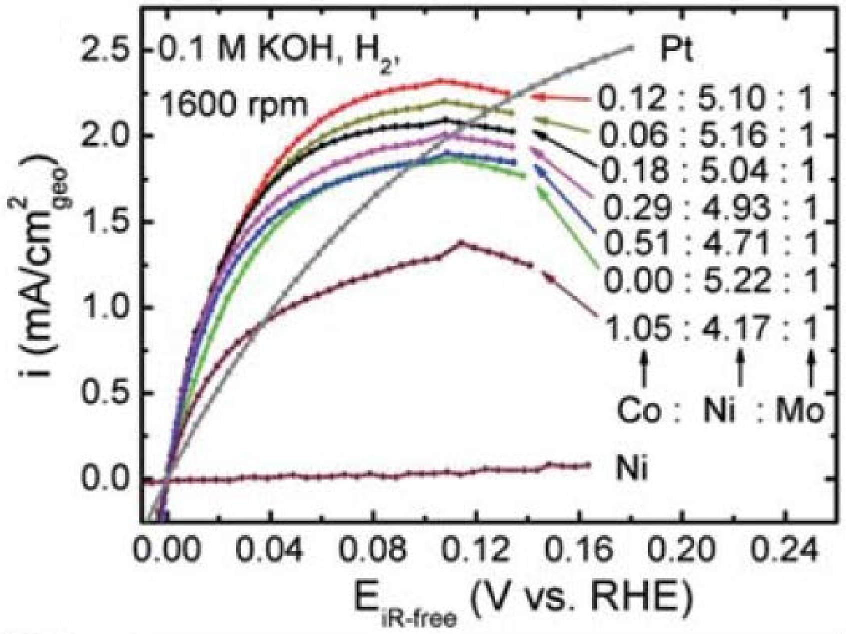


Chung *et al.*, *Nat. Commun.* **4:1922**, 2013

High ORR activity and durability demonstrated in alkaline electrolyte in RDE tests

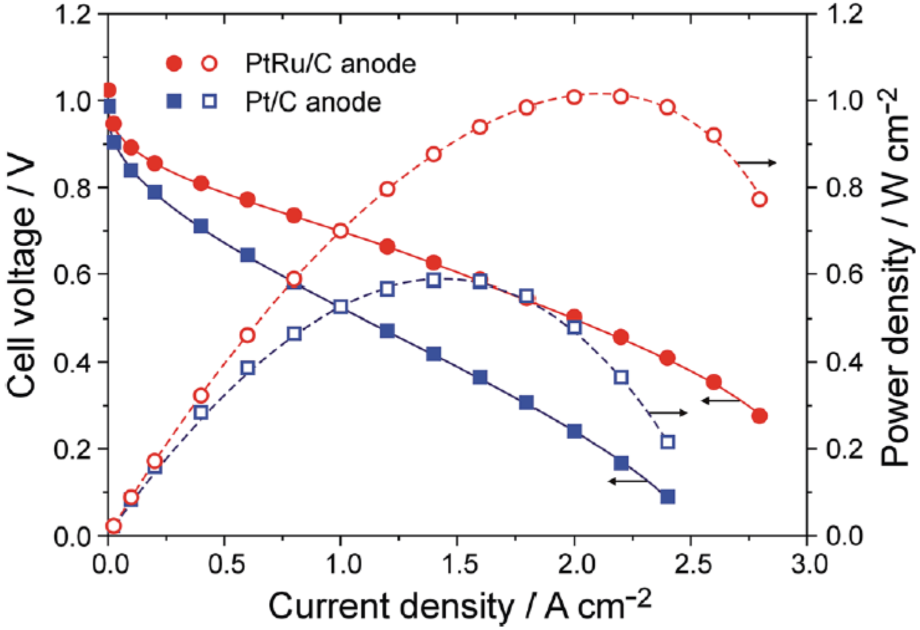
PGM-free HOR Catalysts for AMFCs: Status *vs.* PGM Catalysts

Sheng *et al.*, *Energy Environ. Sci.*, 2014, **7**, 1719-1724



Steady state polarization curves of the HOR on electroplated **Ni**, **NiMo**, **CoNiMo** and **Pt** disk. Ratios specified correspond to atomic ratios of metals in the plating solution.

Wang *et al.*, *Energy Environ. Sci.*, 2015, **8**, 177-181



Performance of an H_2-O_2 AMFC using PtRu or Pt anode at 60°C; *a*QAPS-S_8 membrane; Pt/C cathode; metal loadings of both electrodes 0.4 mg/cm^2; 1.0 bar backpressure

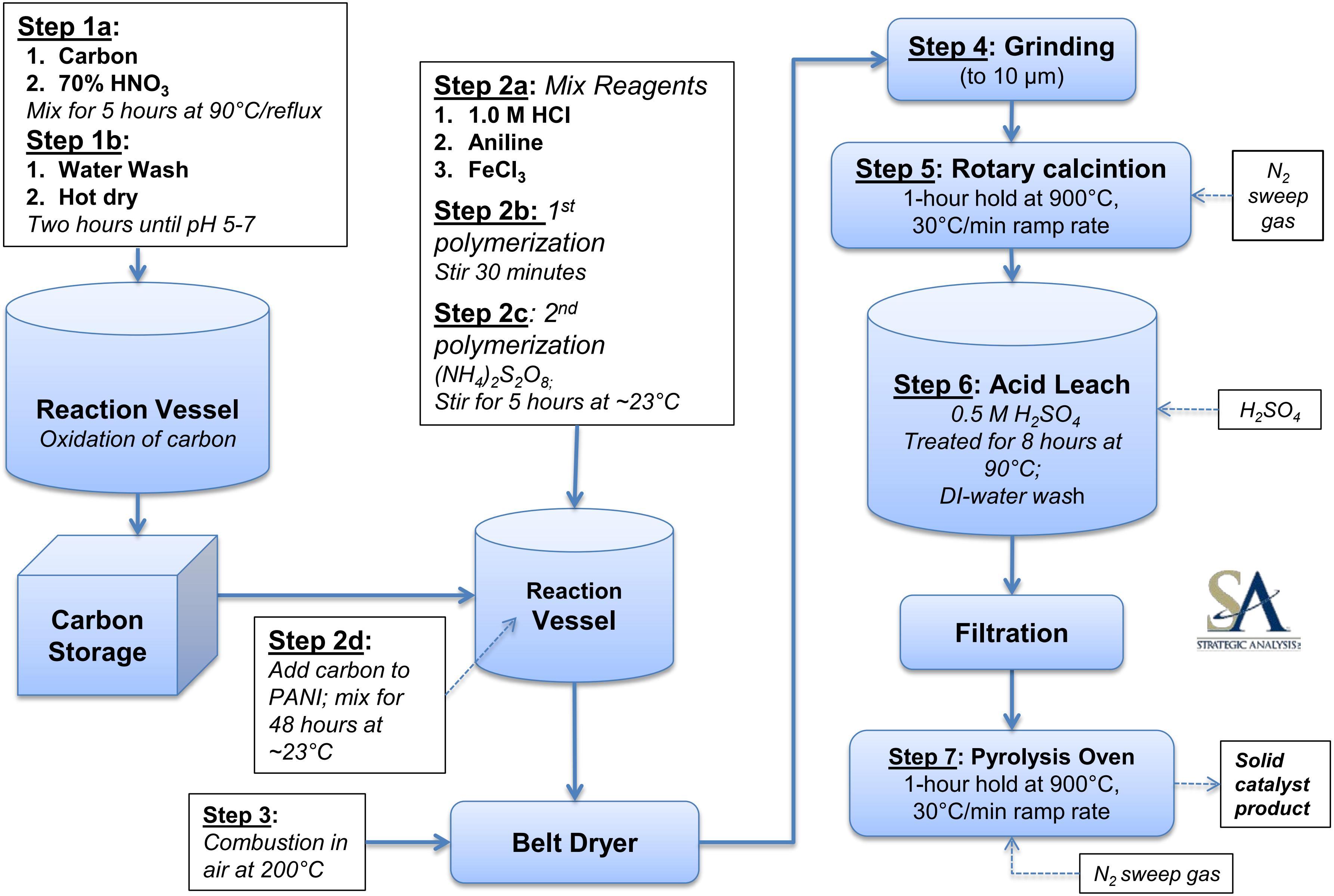
- While offering promising RDE performance state-of-the-art PGM-free anode catalysts still suffer from high HOR overpotential and degradation of PGM-free HOR catalysts
- HOR performance of the best PGM catalysts indicating high losses at the AMFC anode relative to the PEFC anode

State of the Art in PGM-free ORR Electrocatalysis: Summary

- According to automotive OEMs, PGM-free ORR catalysts will bring value to fuel cell systems for cars if they meet performance targets established for PGM catalysts
- In spite of impressive progress achieved in the past decade, PGM-free catalysts need further advancement to meet the above goal. The main challenges of the technology are:
  - (a) low ORR activity in the MEA
  - (b) limited durability
  - (c) heavy reliance on Fe-derived materials
- The acceleration of progress in PGM-free ORR electrocatalysis critically depends on focused catalyst design, guided by multi-scale modeling methods and facilitated by high-throughput methodologies for synthesis and screening, both of which are based on fundamental knowledge of reaction mechanisms and of catalyst design and synthesis.
- PGM-free ORR catalysts are highly attractive for other fuel systems, including AMFCs (high activity and stability), DMFCs (tolerance to methanol), PAFCs and HT-PEFCs (tolerance to phosphates)

Backup

Design for Manufacture & Assembly Cost Analysis: Catalyst Process



Step 1a:
1. **Carbon**
2. **70% HNO_3**

Mix for 5 hours at 90°C/reflux

Step 1b:
1. **Water Wash**
2. **Hot dry**

Two hours until pH 5-7

Reaction Vessel
Oxidation of carbon

Carbon Storage

Step 2a: *Mix Reagents*
1. **1.0 M HCl**
2. **Aniline**
3. **$FeCl_3$**

Step 2b: *1st polymerization*
Stir 30 minutes

Step 2c: *2nd polymerization*
$(NH_4)_2S_2O_8$;
Stir for 5 hours at ~23°C

Step 2d:
Add carbon to PANI; mix for 48 hours at ~23°C

Reaction Vessel

Step 3:
Combustion in air at 200°C

Belt Dryer

Step 4: Grinding
(to 10 μm)

Step 5: Rotary calcintion
1-hour hold at 900°C,
30°C/min ramp rate

N_2 sweep gas

Step 6: Acid Leach
0.5 M H_2SO_4
Treated for 8 hours at 90°C;
DI-water wash

H_2SO_4

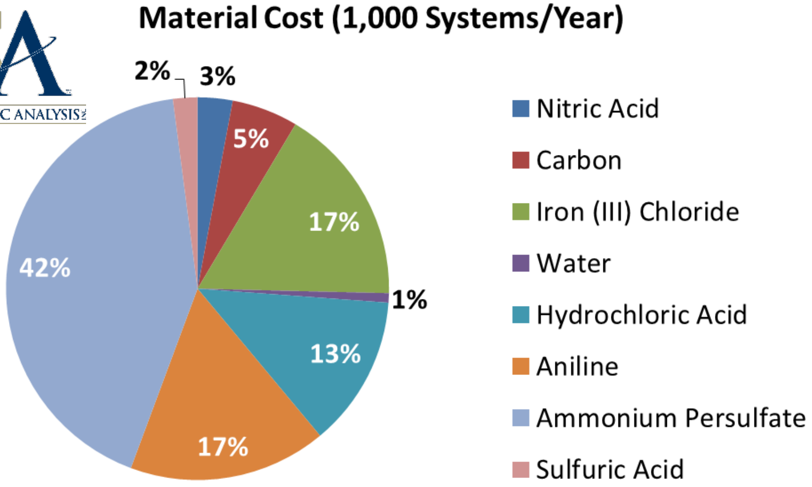
Filtration

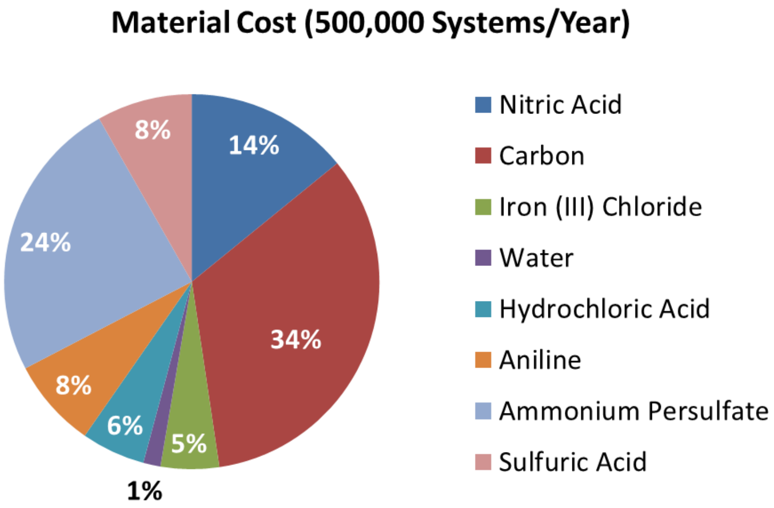
Step 7: Pyrolysis Oven
1-hour hold at 900°C,
30°C/min ramp rate

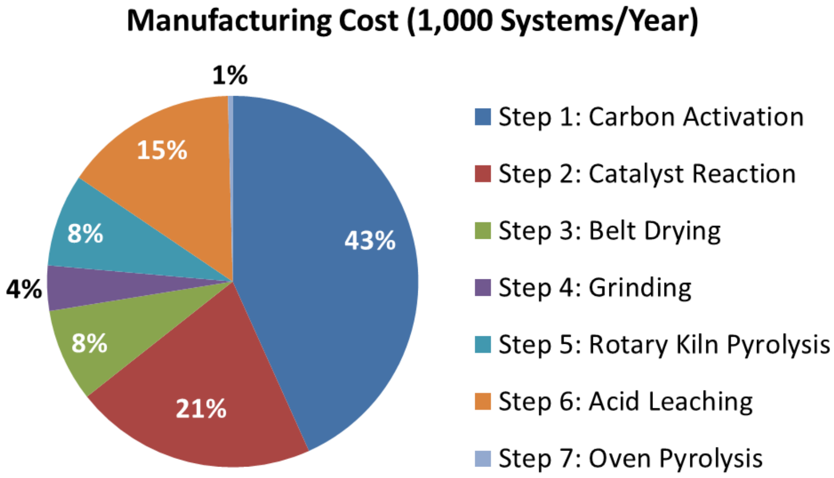
Solid catalyst product

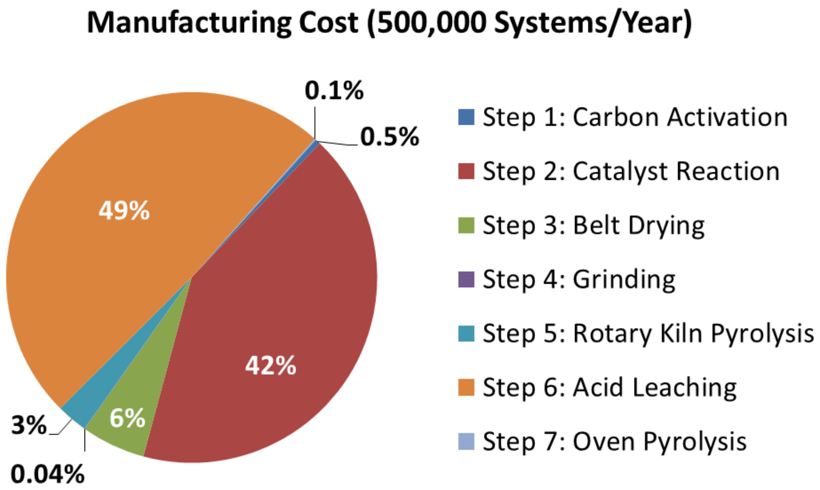
N_2 sweep gas

DFMA Cost Analysis: Breakdown by Step & Volume


Material Cost (1,000 Systems/Year)


Material Cost (500,000 Systems/Year)


Manufacturing Cost (1,000 Systems/Year)

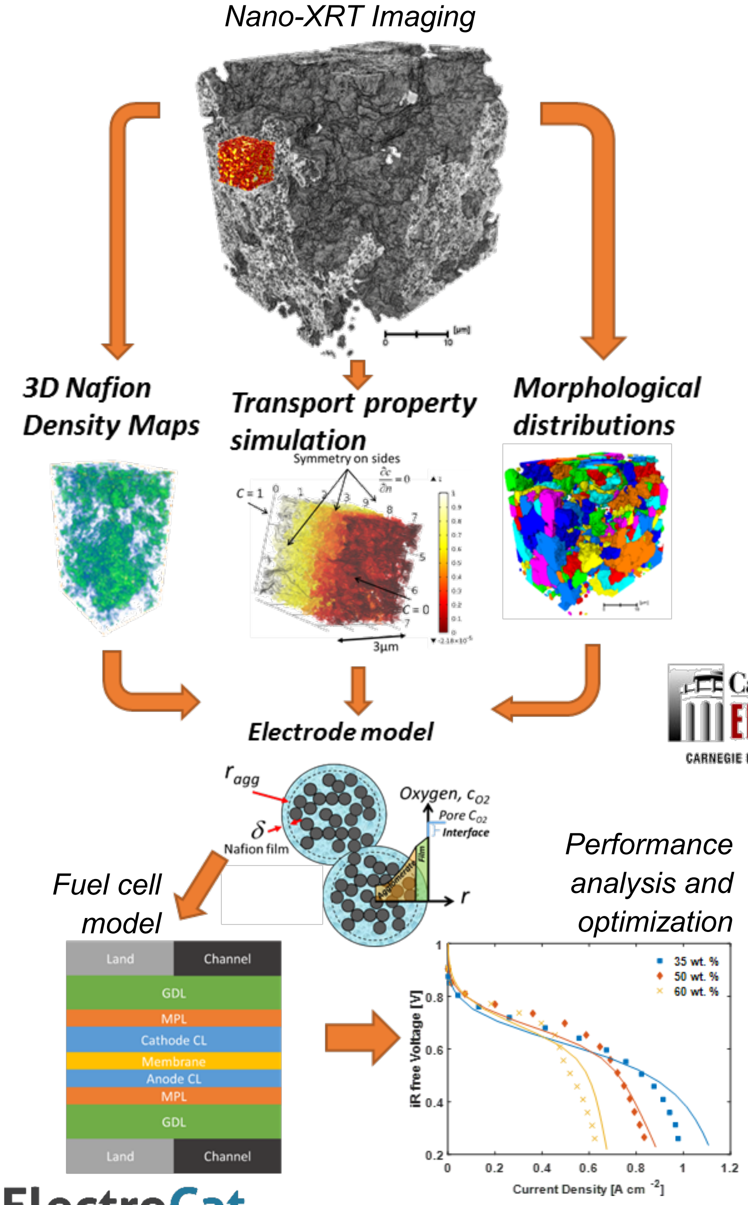

Manufacturing Cost (500,000 Systems/Year)

Total cost *ca.* $129/kg

Total cost *ca.* $74/kg

Cathode and Fuel Cell Modeling

Microstructurally Consistent Model Framework



Nano-XRT Imaging

3D Nafion Density Maps

Transport property simulation

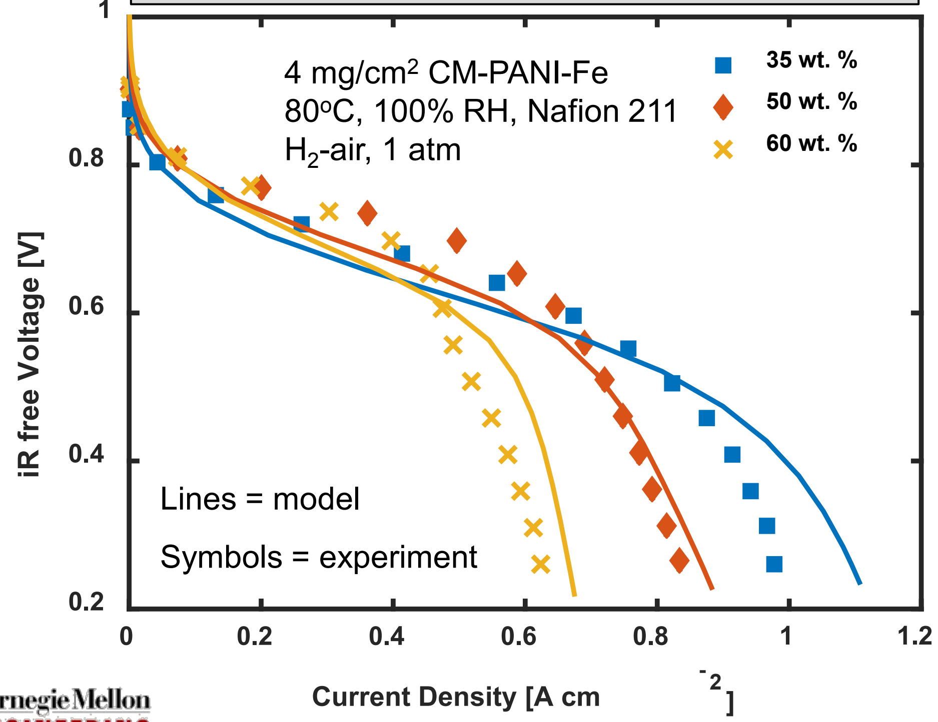
Morphological distributions

Electrode model

Fuel cell model

Performance analysis and optimization

Fuel Cell Polarization Curve Comparison



- Microstructurally consistent cathode model with morphology and transport property inputs from nano-XRT imaging and analysis
- Fitting of site activity site density at 0.8 V; conductivity from nano-XRT ionomer imaging and MES data
- Trends and values consistent with experiments