The Challenge of Mass Transport Resistance in Catalyst Layers and Its Impact to Performance at High Current Density

Di-Jia Liu

Argonne National Laboratory

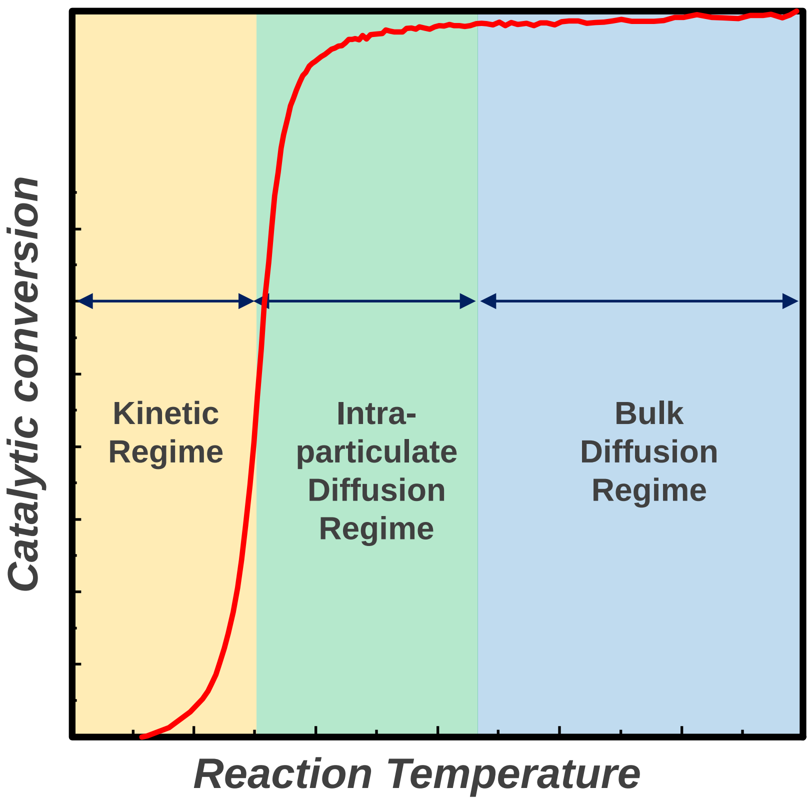
Presented at DOE CATALYSIS WORKING GROUP MEETING

Wednesday, July 27, 2016

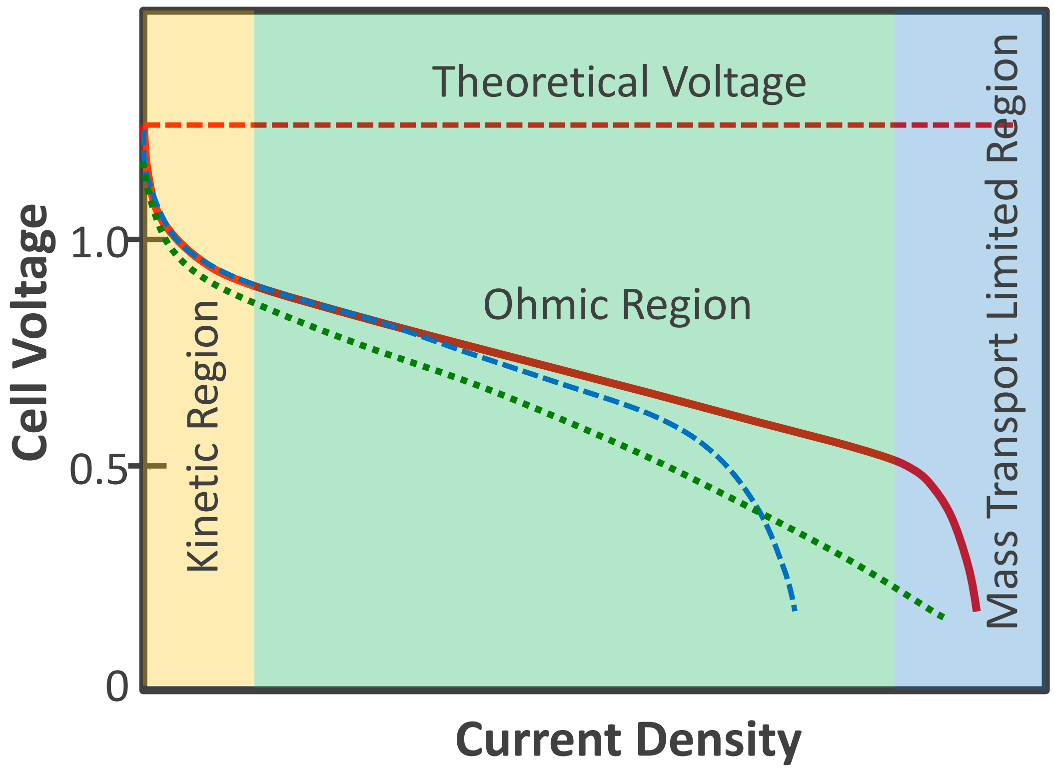
Argonne National Laboratory

Mass Transport Limited Region in Fuel Cells

Heterogeneous Catalytic Conversion



Fuel Cell Polarization Curves

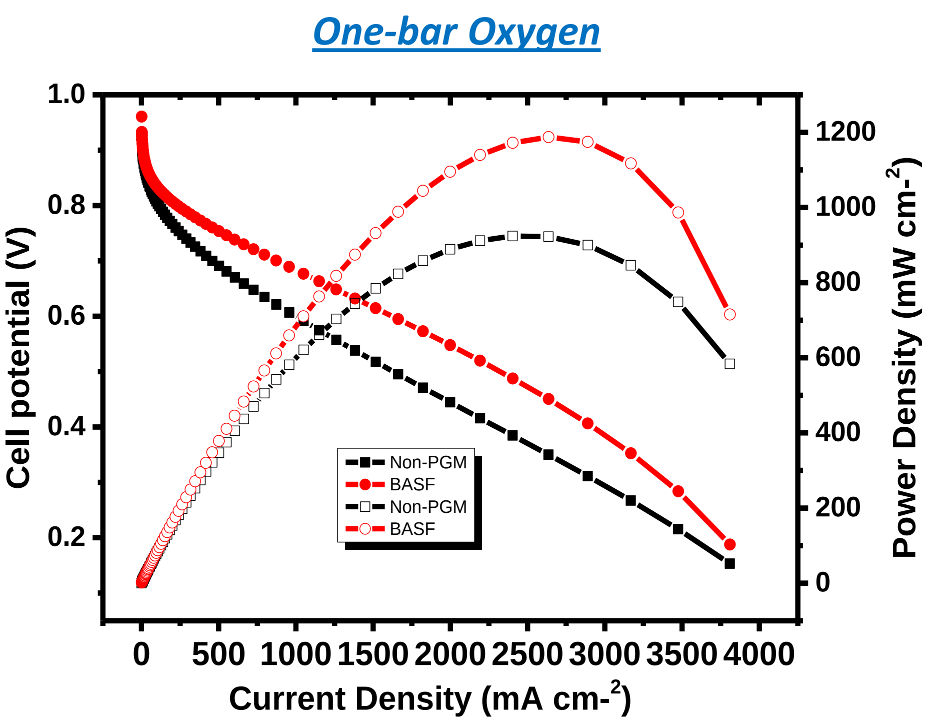


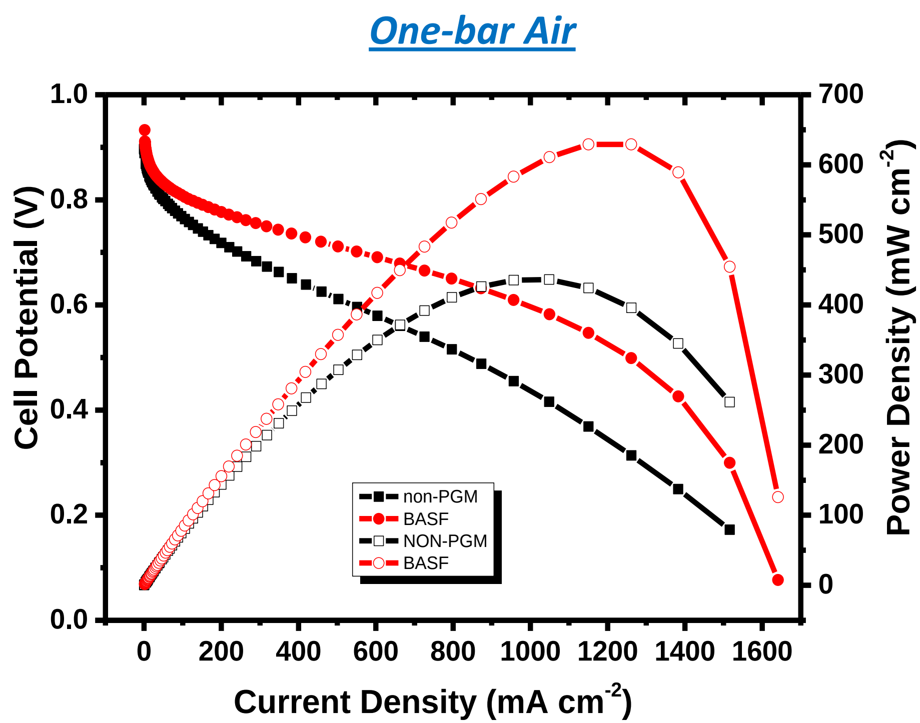
Availability → Accessibility → Activity

Key Factors Hampering Fuel Cell Performance at High (or low) Current Domain

- Lack of Activity – low turn-over-frequency (TOF)
- Lack of Accessibility – active site not near triple-phase boundary
- Lack of Accessibility – mass transport resistance
- Lack of Availability – insufficient active site density
- Lack of Reactant – mass transfer rate < conversion rate

Examples of Performance Differences at High Current Region between PGM and PGM-free Catalyst Electrodes

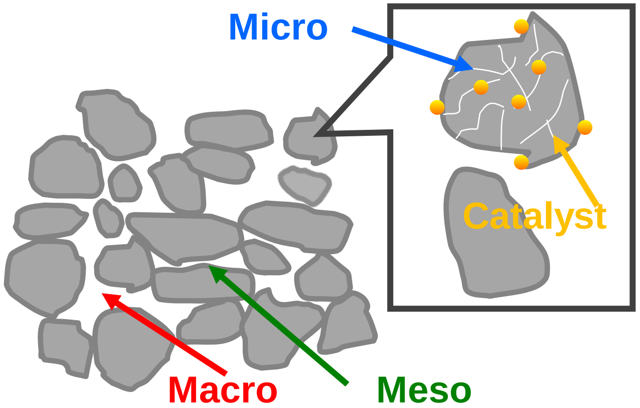




Condition: P_{air} or P_{O2}= P_{H2} = 1 bar (back pressure = 7.3 psig) fully humidified; T = 80 °C; N-211 membrane; 5 cm² MEA; PGM-free cathode catalyst = 3.5 mg/cm², anode catalyst = 0.3 mg_{Pt}/cm². Commercial BASF MEA, cathode catalyst = 0.35 mg_{Pt}/cm² , Anode catalyst = 0.2 mg_{Pt}/cm²

Challenges in Catalytic Structure using Conventional Carbon Support

- **Micro→meso→macro tiered structure held by vdW force**
- **Mass transfer through propagation of different porosities (Knudsen vs. molecular diffusions)**
- **Charge/heat transfer through particle contact percolation**

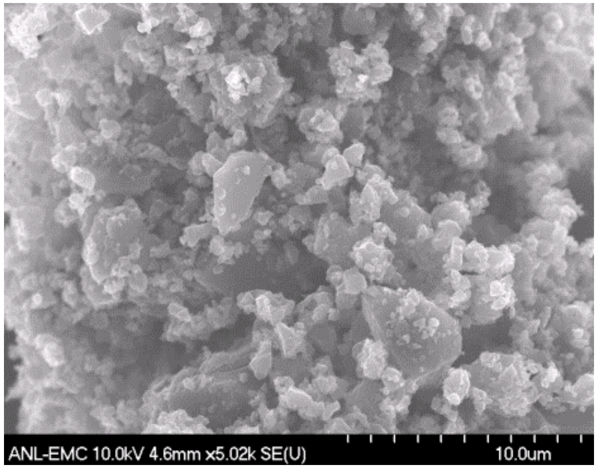


Gas diffusion inside electrode

$D_{eff} = \varepsilon D/\tau;\ \varepsilon = \text{porosity}$

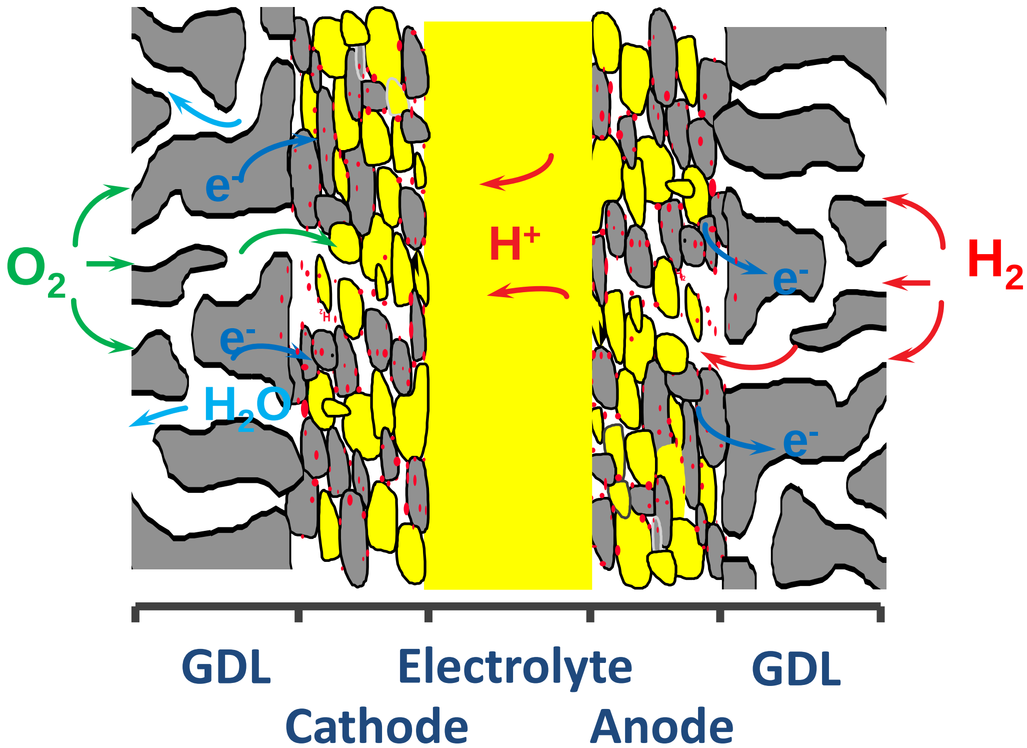
$\tau = (path\ l/straight\ l)^2$

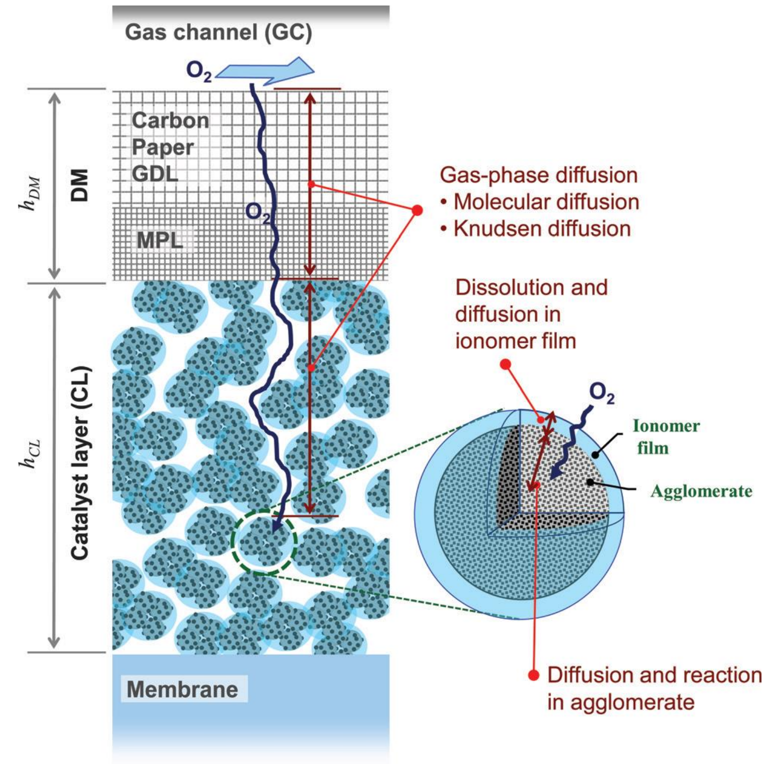
$$1/D_{eff} = 1/D_{micro} + 1/D_{meso} + 1/D_{macro}$$



Challenges in Electrode Architecture using Conventional Carbon Support

Conventional Membrane Electrode Assembly

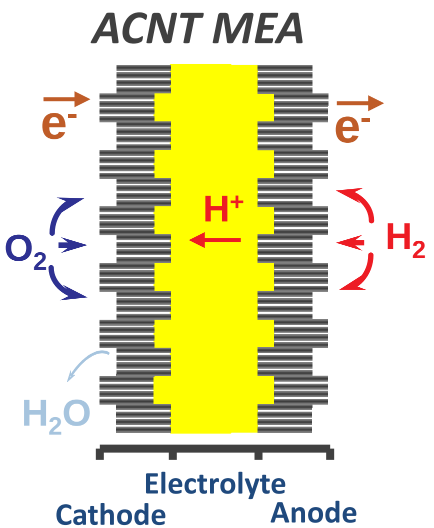




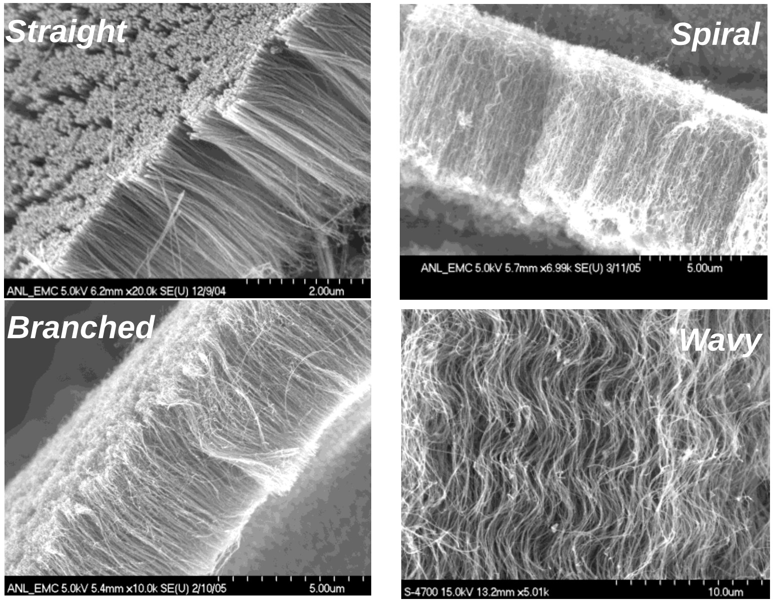
Nonoyama, *et. al*. *JES* 158 (4) B416, (2011)

Aligned Carbon Nanotube (ACNT) as Catalytic Support for PEMFC

Advantages of ACNT based MEA

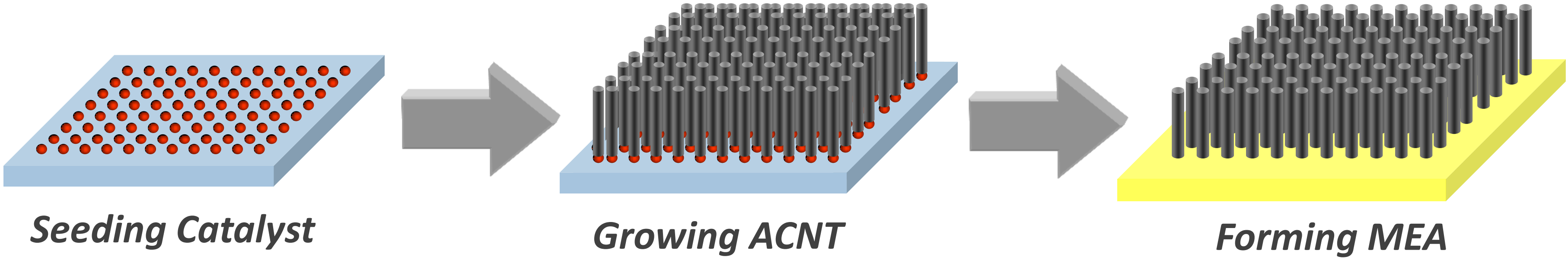


- Better catalyst utilization
- Better support stability
- Better electrical & thermal conductivity
- Better water management
- Better mass transport
- Functionalized ACNT as PGM-free catalyst

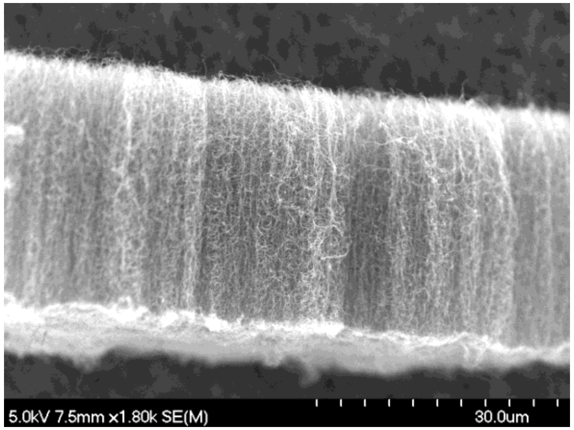


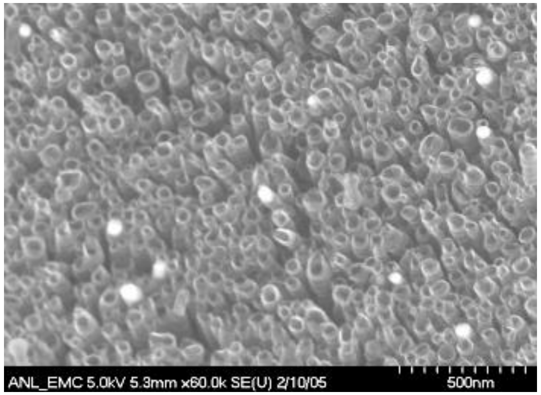
J. Yang, G. Goenaga, A. Call and D.-J. Liu*, *Electrochem. Solid-State Lett*, (**2010**) 13 (6) B55-B57,
J. Yang, D.-J. Liu*, N. Kariuki and L, X. Chen, *Chem. Comm*. 3 (**2008**) 329 – 331
D.-J. Liu*, J. Yang, N. Kariuki, G. Goenaga, A. Call, and D. Myers, (**2008**), *ECS Trans*, 16 (2) 1123-1129
J. Yang and D.-J. Liu*, *Carbon* 45 (**2007**) 2843–2854.
D.-J. Liu, J. Yang and D. Gosztola, *ECS Transc*. (**2007**) 5(1) 147-154

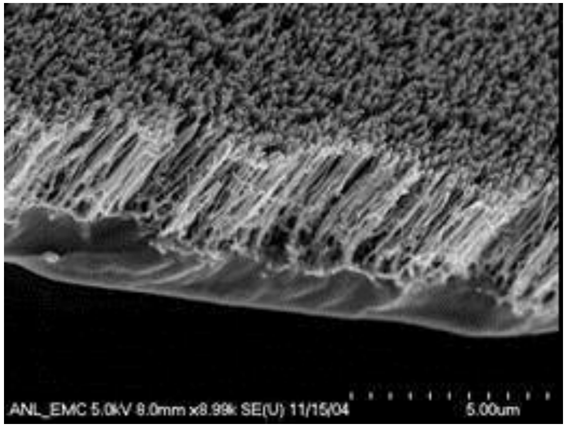
Process of Fabricating ACNT as Catalyst Support of MEA



Fabricating ACNT as catalyst support in MEA







"Method of fabricating electrode catalyst layers with directionally oriented carbon support for proton exchange membrane fuel cell", Liu & Yang, **US Patent 8,137,858**

"Catalytic Membranes for Fuel Cells", Liu & Yang, **US Patent 7,927,748**

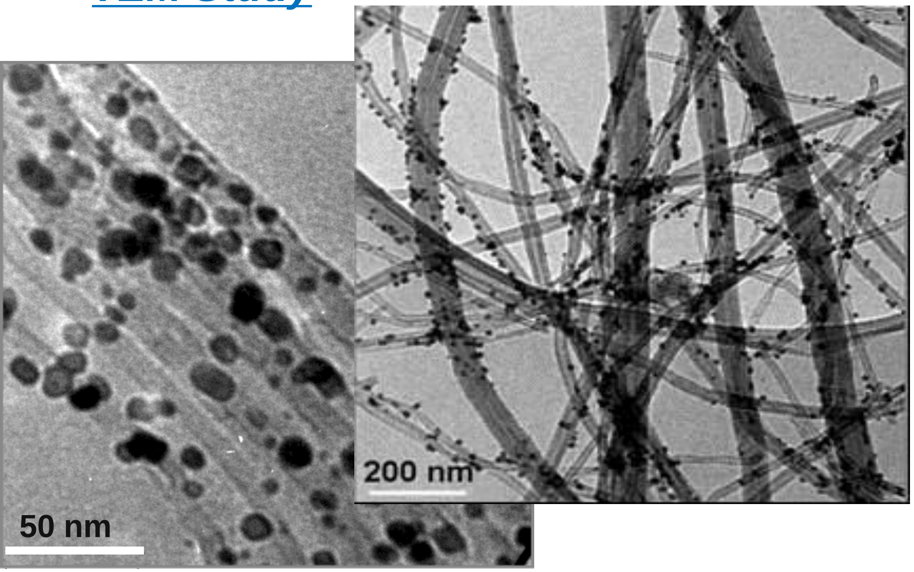
"Aligned carbon nanotube with electro-catalytic activity for oxygen reduction reaction". Liu, Yang & Wang, **US Patent 7767616**

"Method of fabricating electrode catalyst layers with directionally oriented carbon support for proton exchange membrane fuel cells", Liu, Yang & Wang, **US Patent 7,758,921**

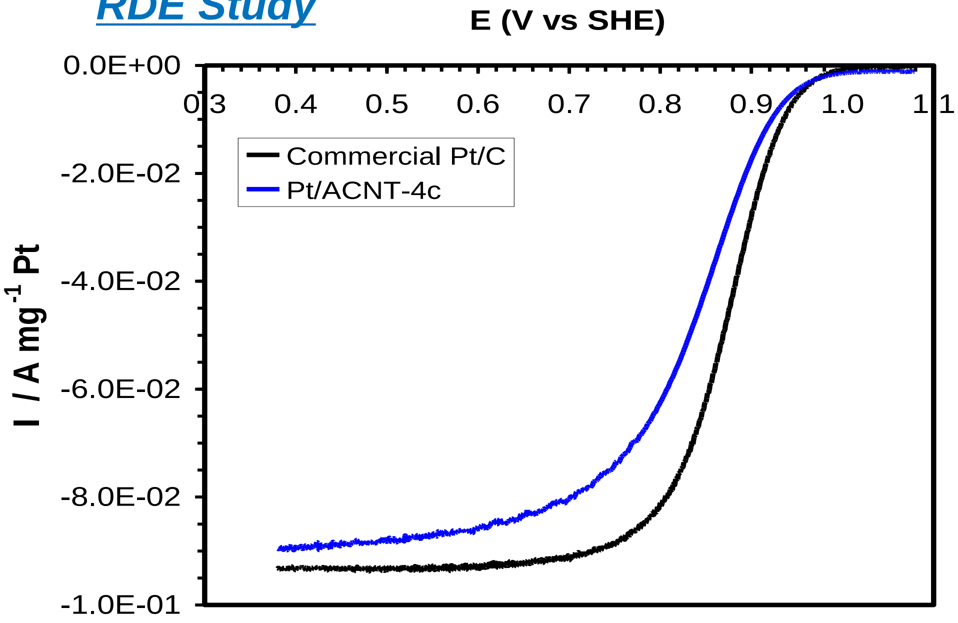
Catalyzing ACNT with Pt via Dry and Wet Chemistries

- Bifunctional solvents needed to avoid nanotube bundling
- CVD processes enable >20 wt% Pt incorporated in ACNT
- Highly dispersed Pt with particle sizes from 2 nm ~6 nm was observed
- Relatively uniform distribution through depth of ACNT layer was observed

TEM Study



RDE Study



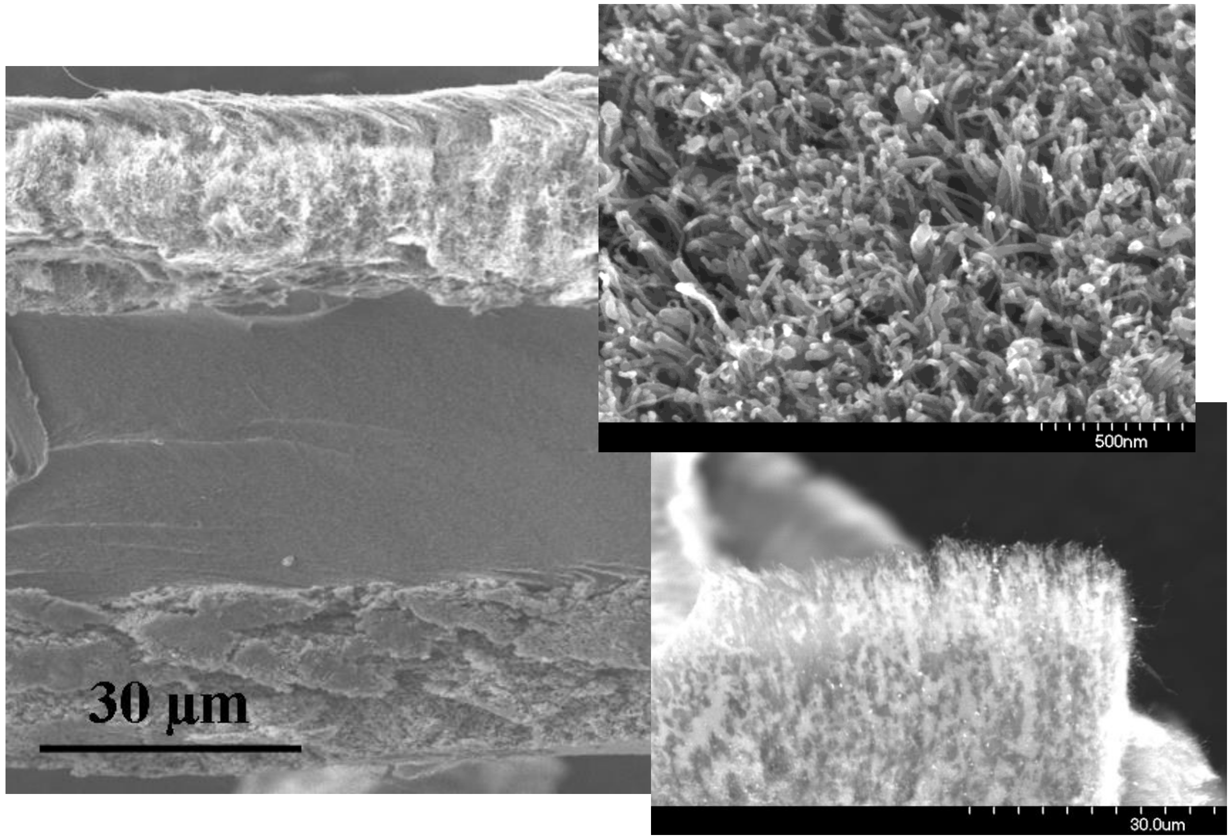
Pt/ACNT prepared through CVD process demonstrated very good electrochemical activity even with highly hydrophobic surface

Cross-section Characterization of ACNT-MEA

ACNT Cathode Layer

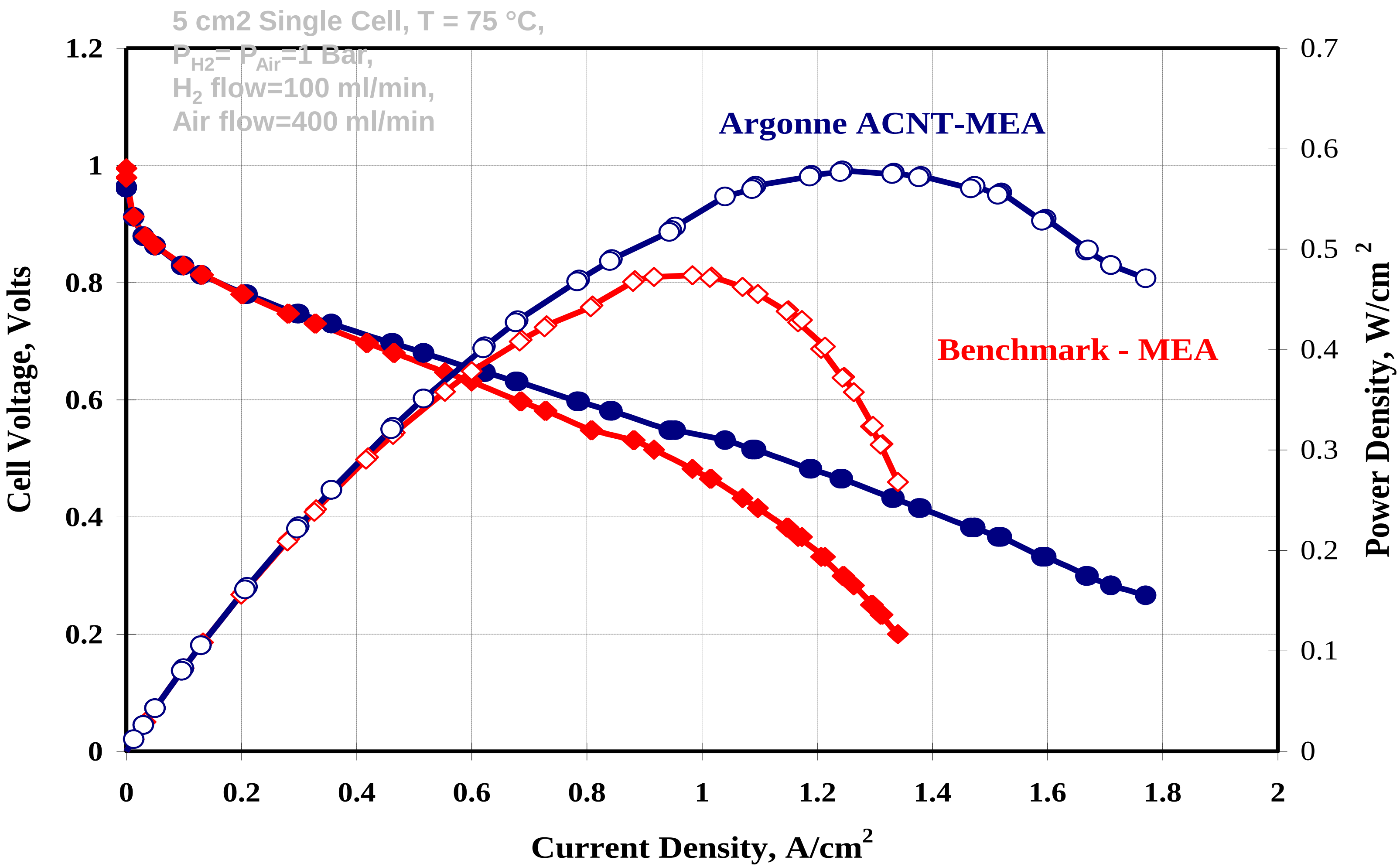
Nafion® Membrane Layer

Ink-based Anode Layer



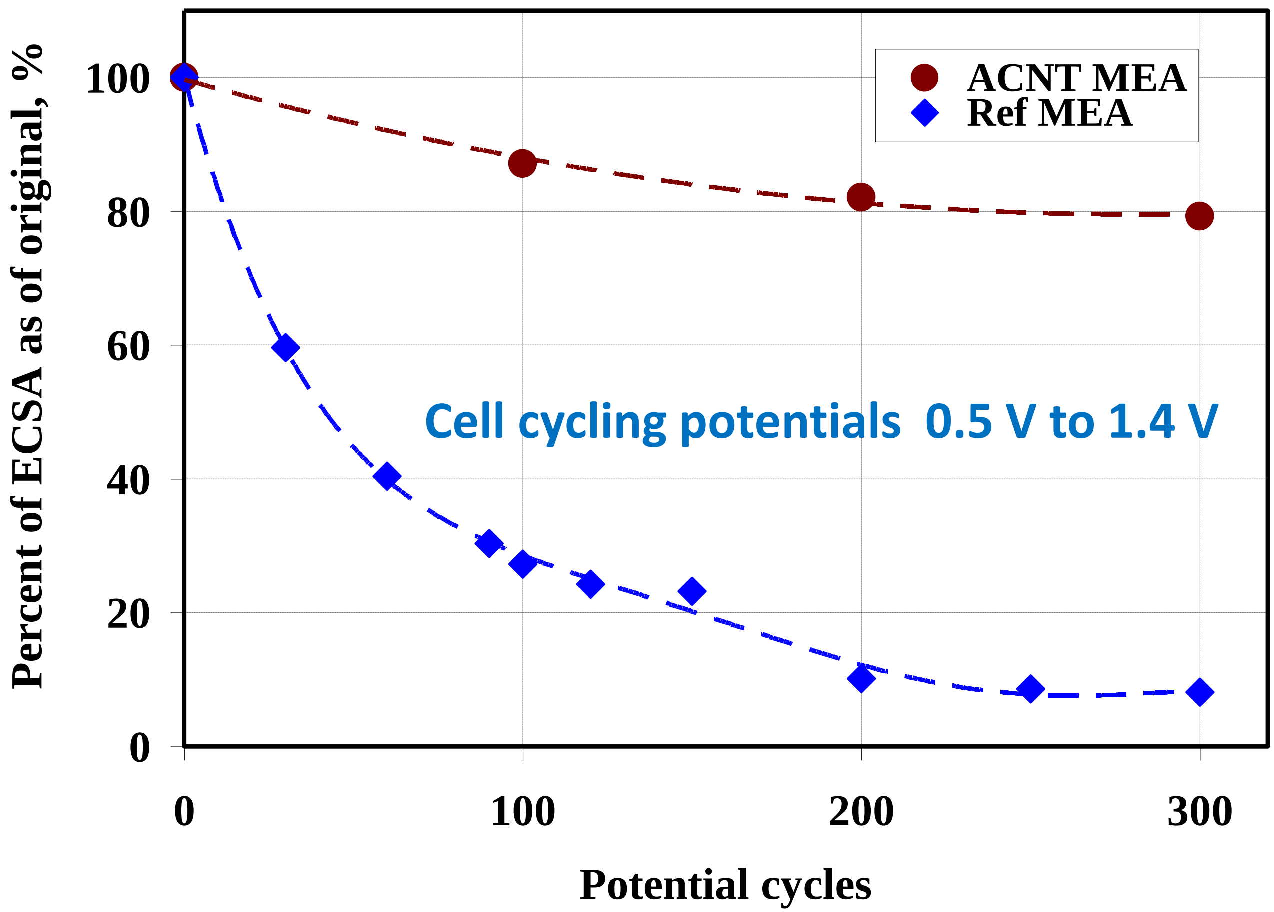
SEM Images of ACNT-MEA

Single Cell Test



Single cell test demonstrated improved polarization using ACNT based MEA

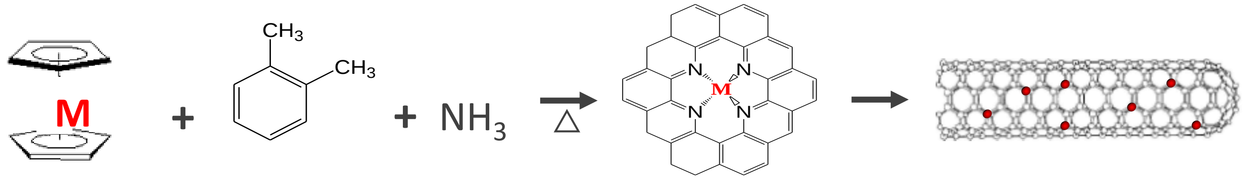
Support Stability Significantly Improved during Potential Cycling



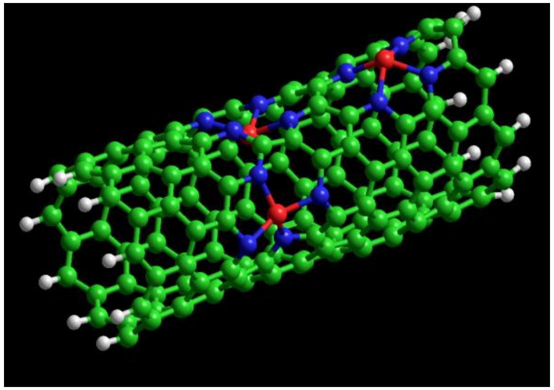
Improved electrocatalytic surface area retention is due to more stable graphitic ACNT

ACNT as PGM-free Catalysts

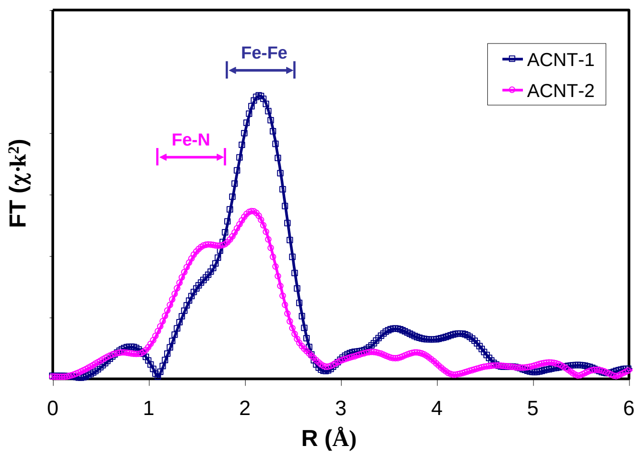
Synthesize TM/N/C active site over carbon nanotubes

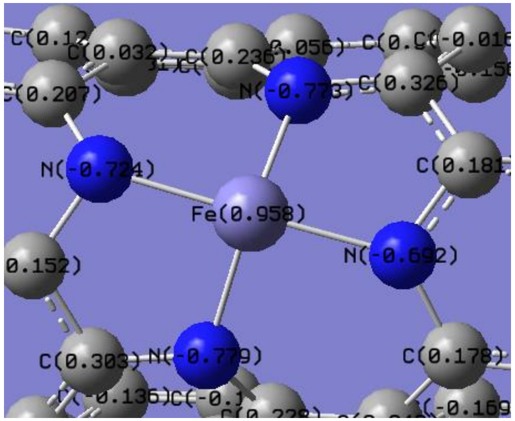


TM precursor *HC's* *N-dopant* *Active site* *CNT*



Study N-ligated TM active site structure by XAS and DFT calculation

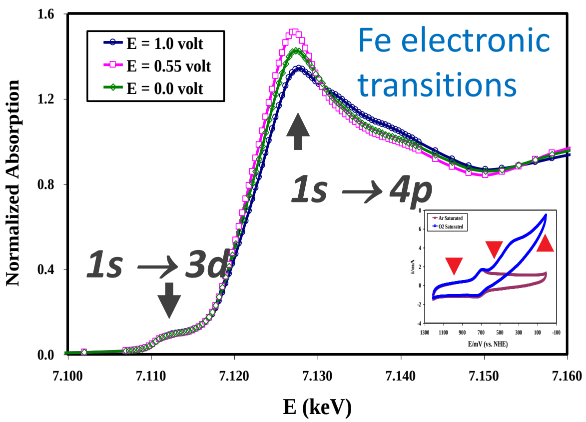


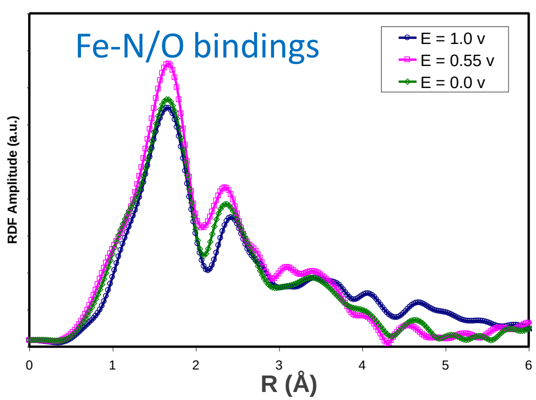


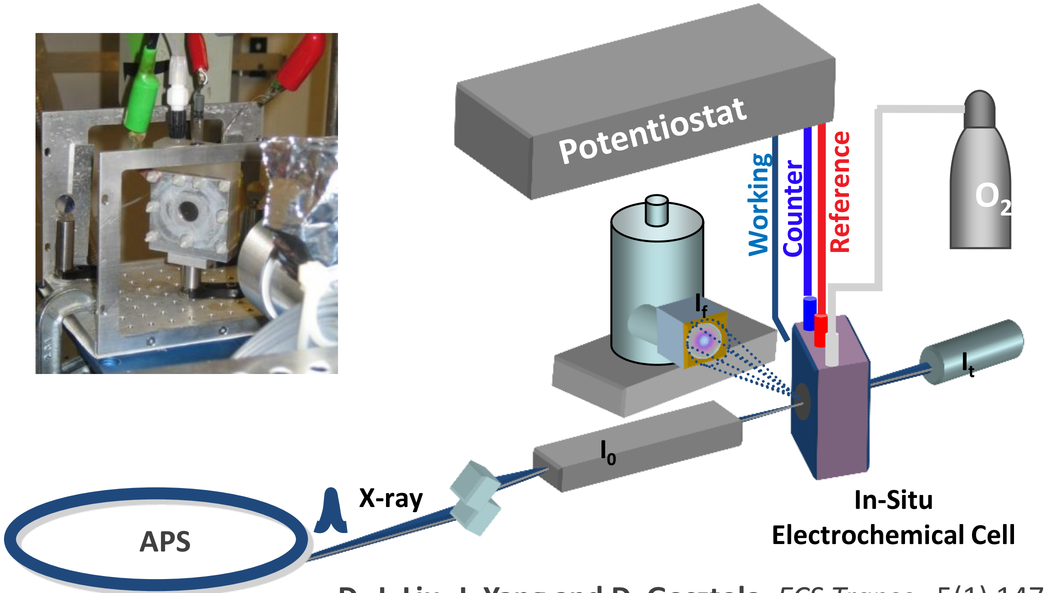
Shell	N	R (Å)
Fe-N	4.2	1.95

J. Yang, D.-J. Liu, N. Kariuki, L. Chen, *Chem. Comm*. **3,** 329 (2008)
A. Titov, P. Zapol, P. Kral, D.-J. Liu, & L. Curtiss, *J. Phys. Chem*. C. **113**, 21629 (2009)

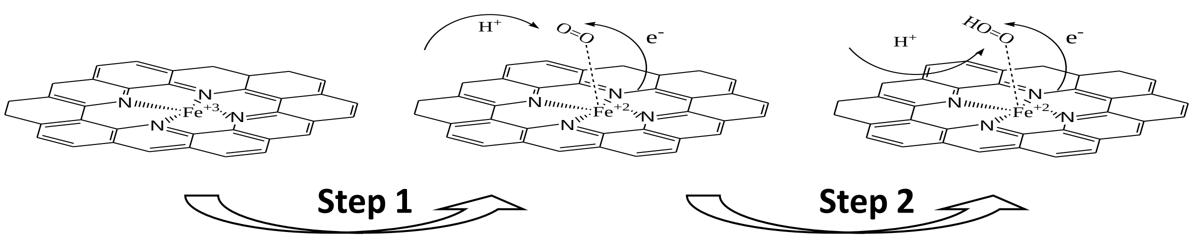
Probing Active Site Redox Mechanism by *In Situ* X-ray Absorption Spectroscopy







D.-J. Liu, J. Yang and D. Gosztola, *ECS Transc*. 5(1) 147 (2007).



TM oxidation state and coordination structure under different polarization potentials revealed O_2 binding and conversion kinetics during ORR

Design Non-PGM Catalyst using "Support-free" Precursors

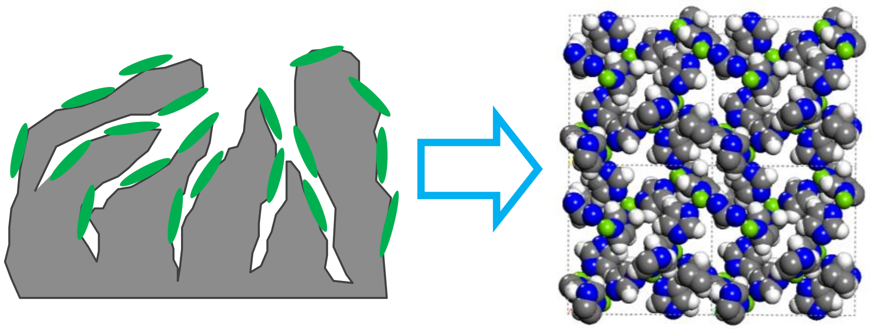
Catalytic Activity ∝

Turn-Over-Freq. x *Site Density*

- Different transition metals & organic ligands
- Different metal-ligand coordination

- Carbon "Support-free"
- High & uniformly distributed active site density

From carbon supported to "support-free" catalyst



"Reality-check" on Non-PGM Activity

$i\ (A/cm^2) = 1.6 \times 10^{-19} \times TOF\ (e^-/site \cdot s) \times SD\ (cm^{-3}) \times \tau\ (cm)$*

Achievable Current Density @ 0.8 V

(Cathode loading @ $4 mg \cdot cm^{-2}$ / 1 bar O_2)

- **170 mA/cm²** for 1% Fe, or
- **340 mA/cm²** for 2% Fe loading

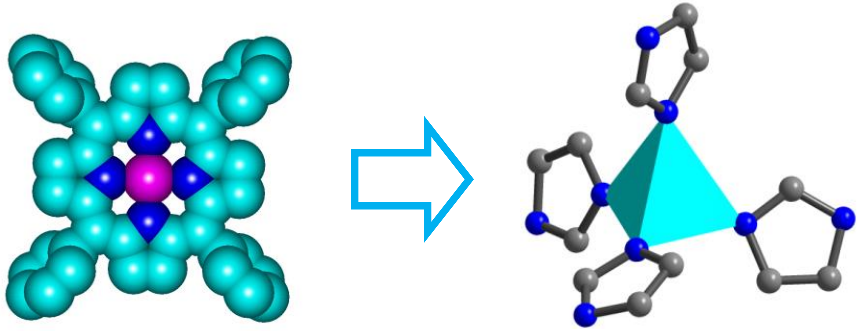
Critical assumption:

a) TM site atomically dispersed & fully utilized

b) TOF = 1/10 of Pt (**2.5** e^-/site.s)

* Gasteiger, *et al*. Applied Catalysis B: Environmental 56 (**2005**) 9

From 2D to 3D - Breaking away from 50-year tradition of supported square-planar precursor

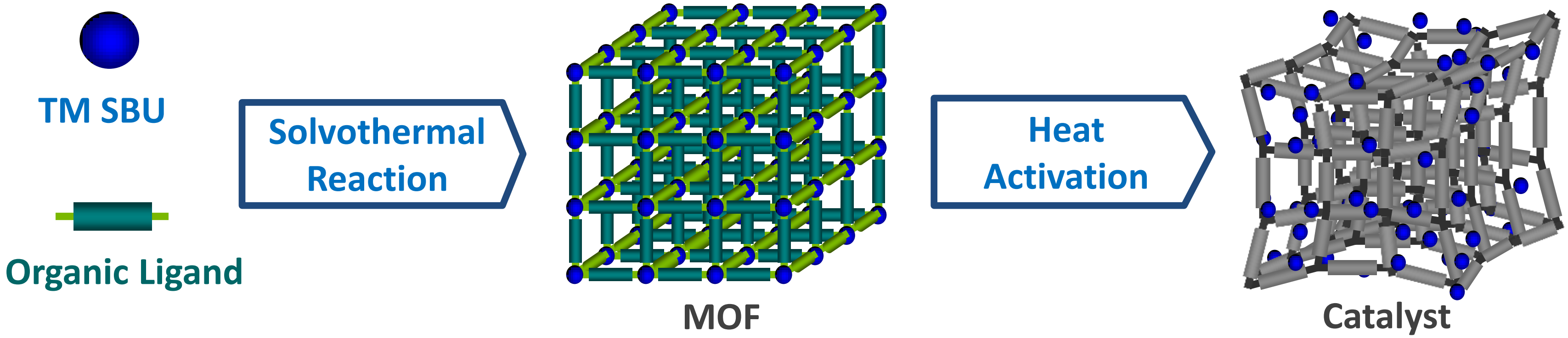


R. Jasinski, *Nature*, (**1964**)

Ma, Goenaga, Call and Liu, *Chemistry: A Euro. J* (**2011**)

MOFs as Precursors for non-PGM Catalysts

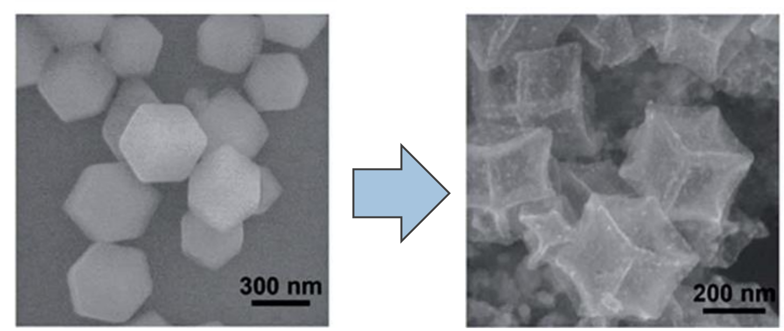
Synthesis of MOF-based non-PGM Catalyst (Why "burn a perfectly good crystal"?)



"Non-Platinum Group Metal Electrocatalysts Using Metal Organic Framework Materials and Method of Preparation",
D.-J. Liu, S. Ma, G. Goenage, US Patent 8,835,343

Advantages of MOF based non-PGM Catalyst

- Highest precursor density for active site conversion
- Well-defined coordination between metal (SBU) & ligand
- Porous 3-D structure with high SSA and uniform micropores
- Large selection of existing MOF compositions



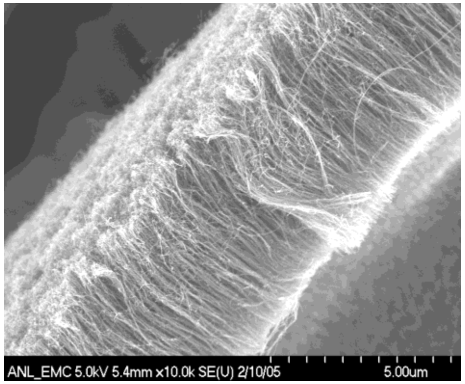
ANL Non-PGM Catalyst IP Portfolio

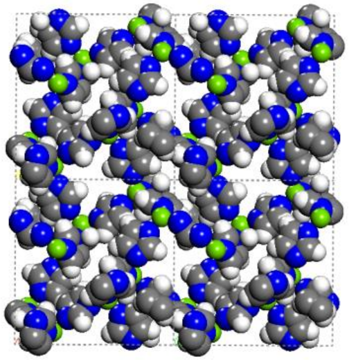
- Developed Fe/N/C decorated CNT catalyst for ORR and demonstrated FeN4 active site structure
  - ***Chem. Comm*. 3,** 329 (2008)
  - ***US Patent*** *7,927,748*
  - ***US Patent*** 7767616
  - ***US Patent*** 8,137,858
  - ***US Patent*** 7,758,921

- Developed metal-organic framework (MOF) based non-PGM catalyst and started “support-free” approach
  - ***Chemistry: A European Journal***, 17 2063 (2011)
  - ***US Patent*** 8,835,343
  - ***US Patent Application*** 20150180045

- Developed binary MOF non-PGM catalyst, achieved measured volumetric current density and power density
  - ***Chemical Science*, 3 (11),** 3200 (2012)

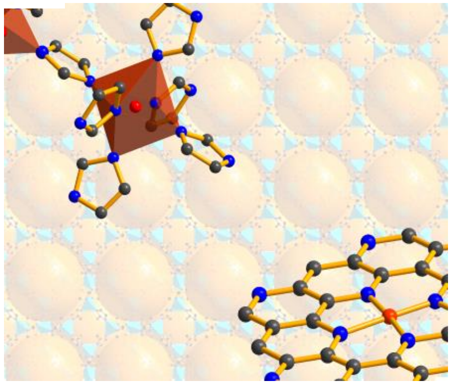
Aligned Carbon Nanotube





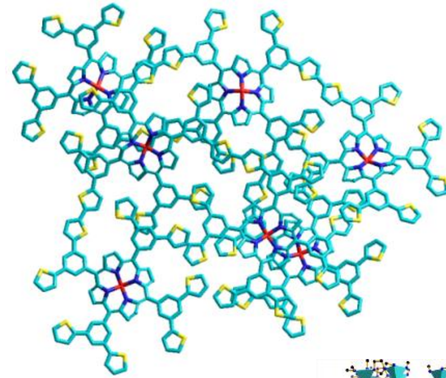
Co-Zeolitic Imidazolate Framework (ZIF)

Fe-ZIF/ZIF-8 binary MOF System



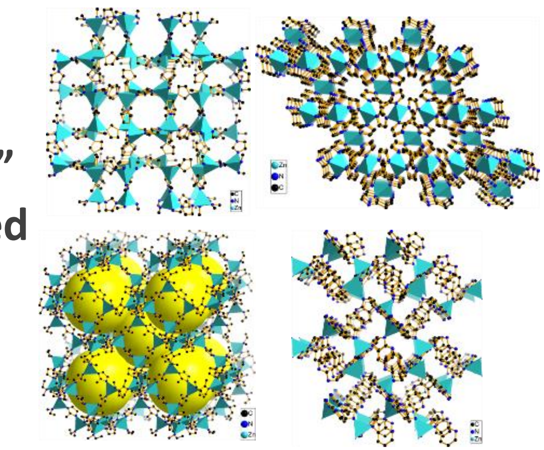
ANL Non-PGM Catalyst IPs (continued)

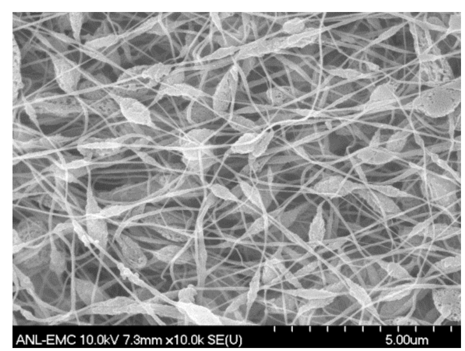
- Developed non-PGM catalyst using porous organic polymer (POP), achieved peak power density of 730 mW/cm^2
  - ***Angew. Chem. Int. Ed.* 52 (32)**, 8349 (2013)
  - ***US Patent*** 9012344
  - ***US Patent Application*** 20150194681
- Developed “one-pot” synthesis approach for low-cost production of a broader range of MOF-base non-PGM catalyst
  - ***Advanced Materials***, *26*, 1093, (2014)
  - ***US Patent Application*** 20130273461
  - ***US Patent Application*** 20150056536
- Developed the first nano-network non-PGM catalyst, achieved peak power density of **870 mW/cm^2**
  - ***Proceedings of National Academy of Sciences,*** 112(34), 10629 (2015)
  - ***US Patent*** 9,350,026



Fe/Co–POP

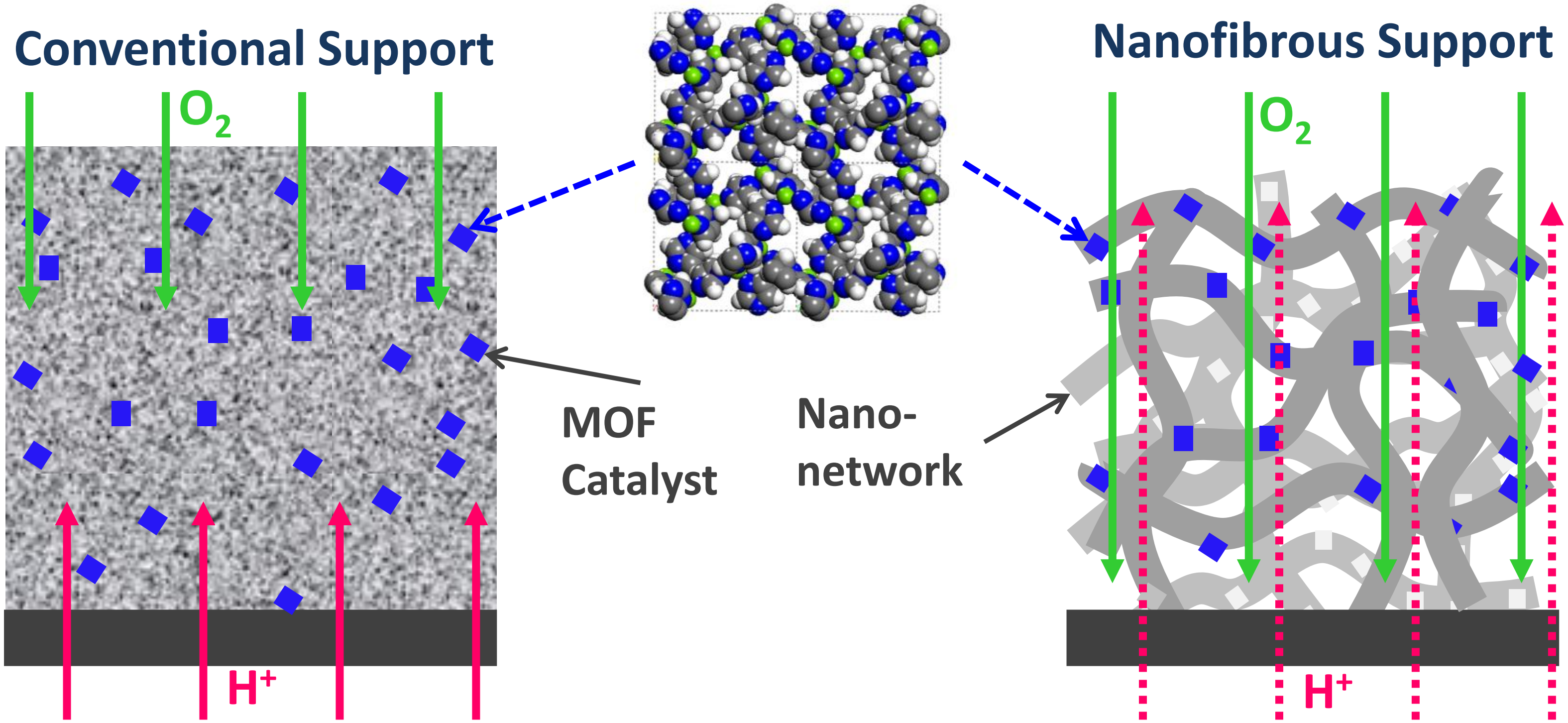
“One-pot” Synthesized ZIFs



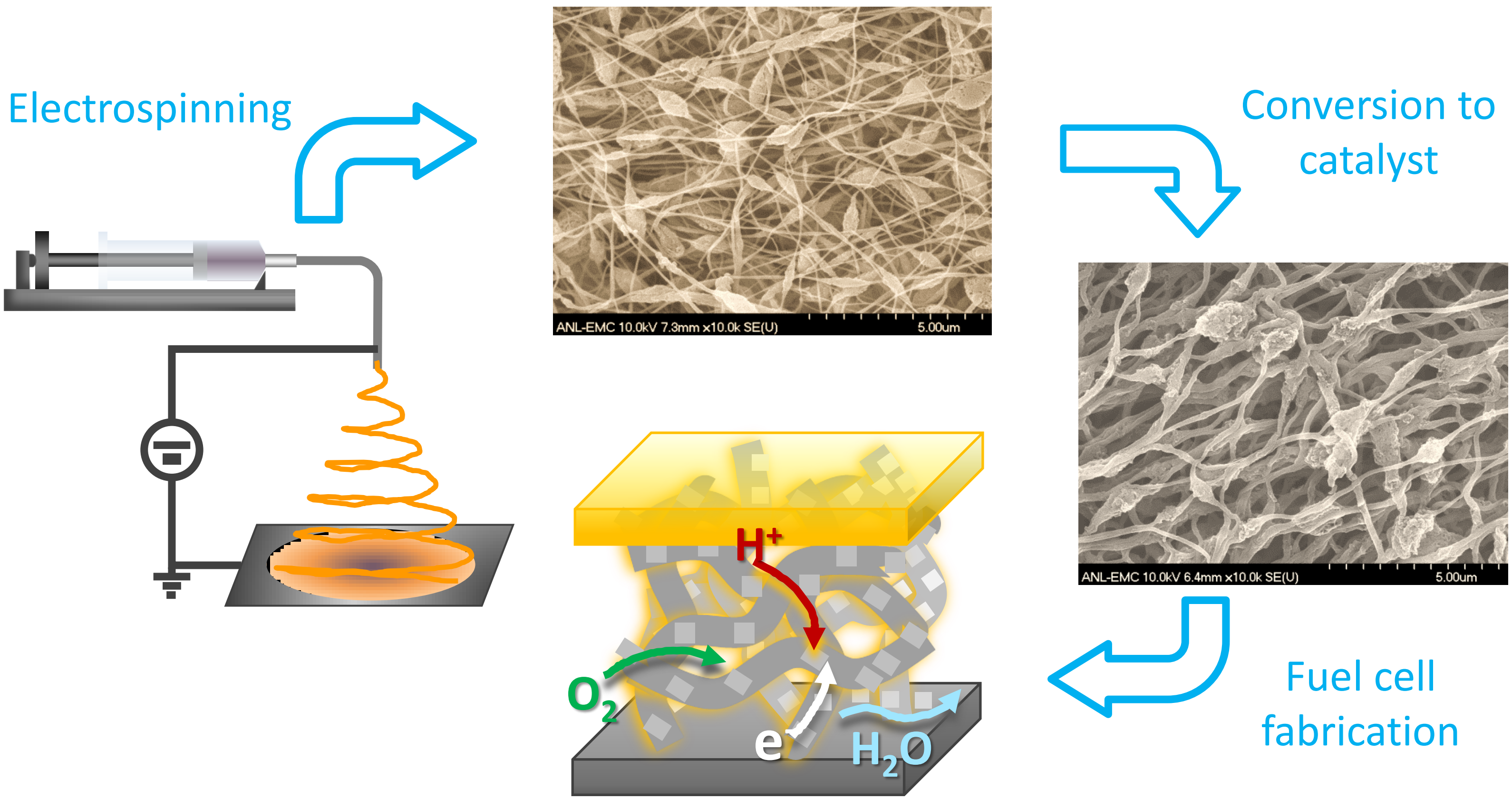


Nanofibrous Network

Catalytic Mass/Charge Transport Improvement in Graphtic Nanonetwork Architecture



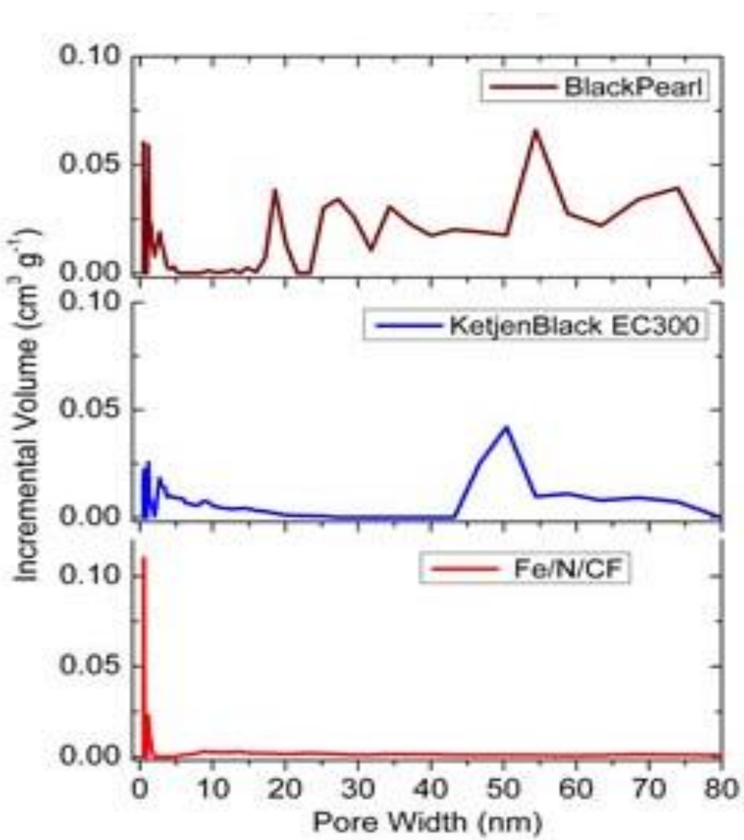
Process of Preparing PGM-free Catalyst with Porous Nano-network Architecture



J. Shui, C. Chen, L. R. Grabstanowicz, D. Zhao and D.-J. Liu, ***Proceedings of National Academy of Sciences***, U. S. A. **2015,** vol. 112, no. 34, 10629

D.-J. Liu, J. Shui, C. Chen, "Nanofibrous electrocatalysts", **US Patent 9,350,026**

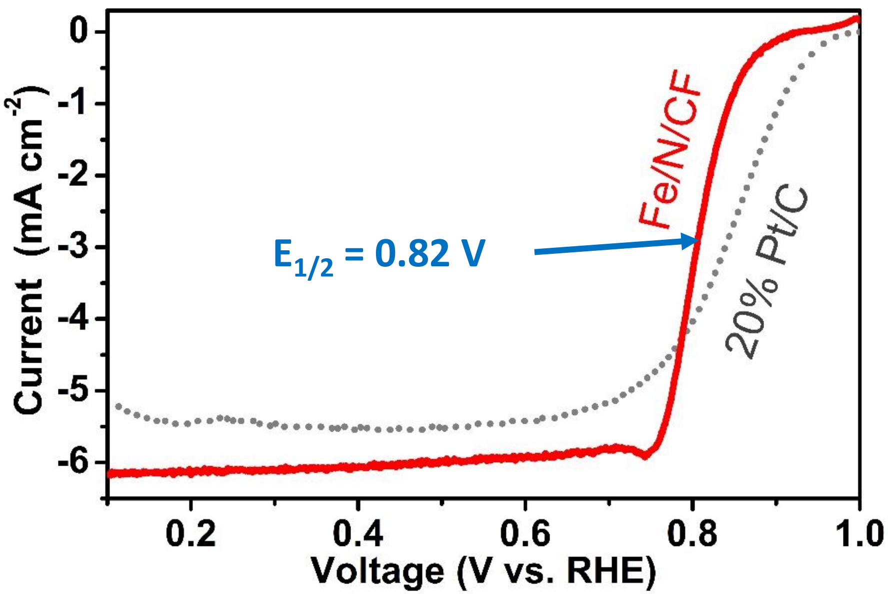
Unique Nanofiber Morphology - High Surface Area Nearly Exclusively Distributed in Micropore Region

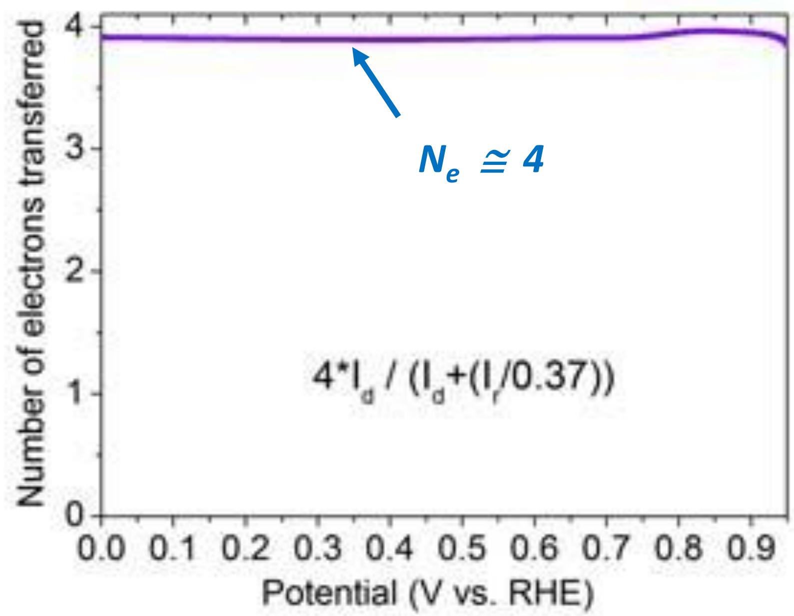


	Black Pearl	Ketjen Black	Fe/N/CF
BET ($m^2\ g^{-1}$)	**1432**	**798**	**809**
Surface Area of Pores ≤ 2nm ($m^2\ g^{-1}$)	**867**	**398**	**780**
Surface Area of Pores ≤ 50nm ($m^2\ g^{-1}$)	**960**	**507**	**788**
$S_{\leq 2nm}/S_{\leq 50nm}$	**90%**	**78%**	**99%**
Total Volume in Pores ≤ 80 nm ($cm^3\ g^{-1}$)	**0.955**	**0.508**	**0.330**
Volume of Pores ≤ 2nm ($cm^3\ g^{-1}$)	**0.371**	**0.167**	**0.271**
Volume of Pores ≤ 50nm ($cm^3\ g^{-1}$)	**0.766**	**0.463**	**0.323**
$V_{\leq 2nm}/V_{\leq 50nm}$	**48%**	**36%**	**84%**

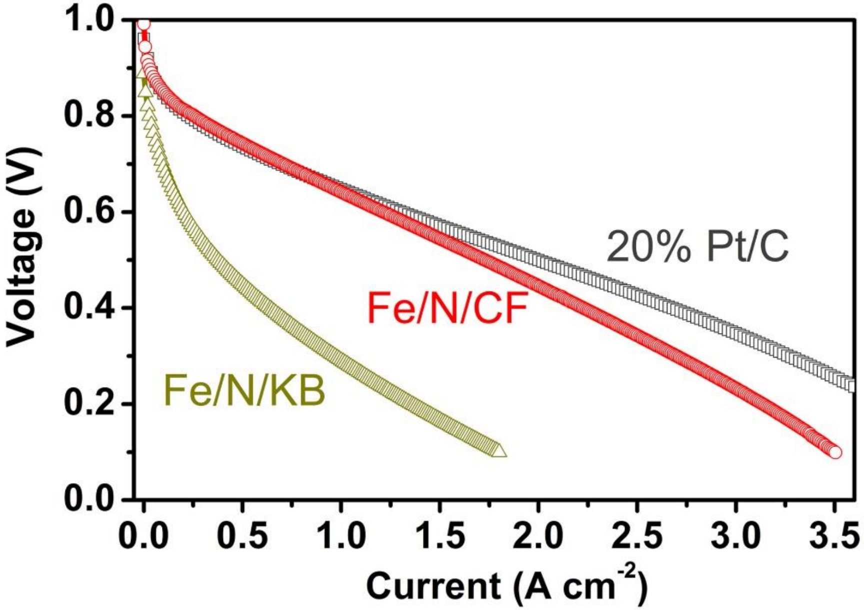
- High specific surface area (BET = 700 ~ 1251 m^2/g)
- High micro-porosity (Micro-pore vol./Total pore vol. > 80%)

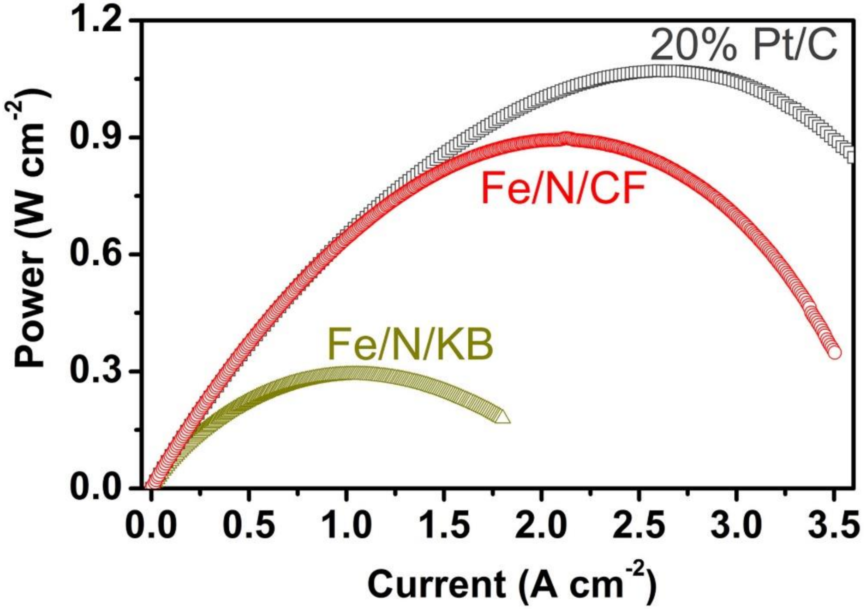
Excellent PGM-free Catalytic Activity Measured by RDE



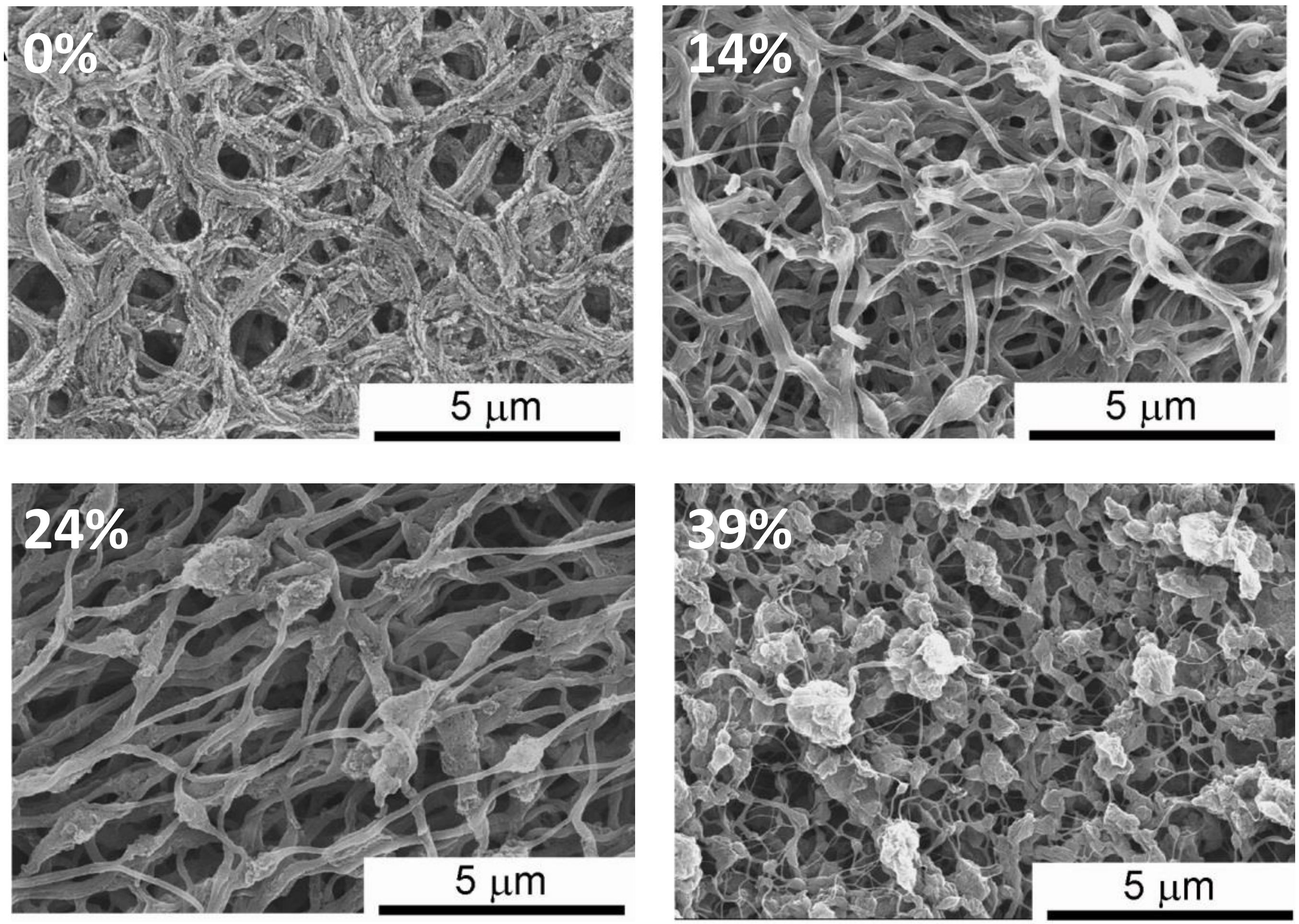


New Electrode Architecture Led to Very Good Performance at Single Cell Levels

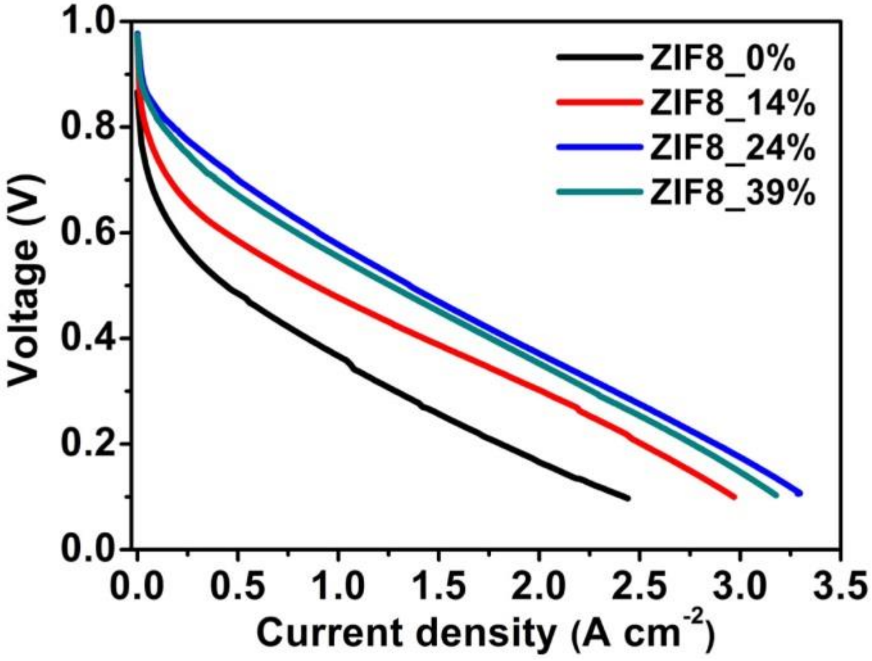


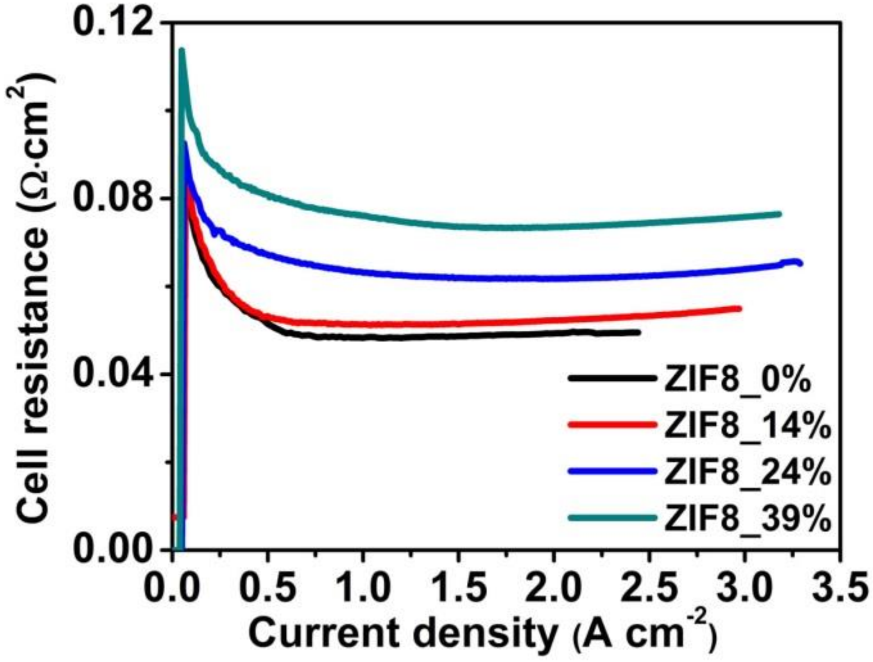


Nanofibrous Network Morphology is Sensitive to Composition of Electro-spin Mixture



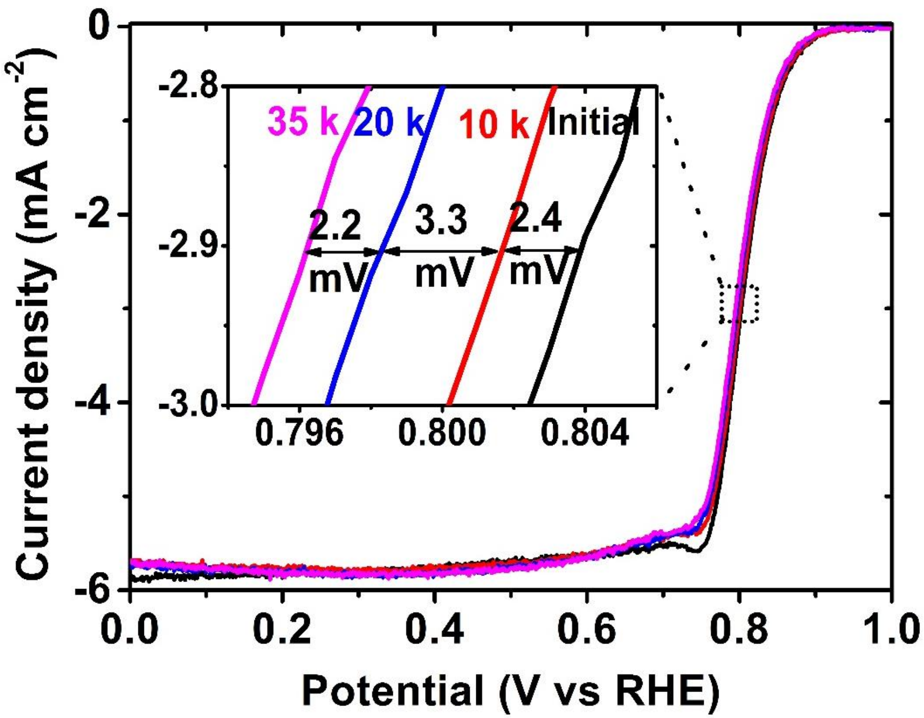
Morphology Impacts Electrode Architecture and Fuel Cell Performance



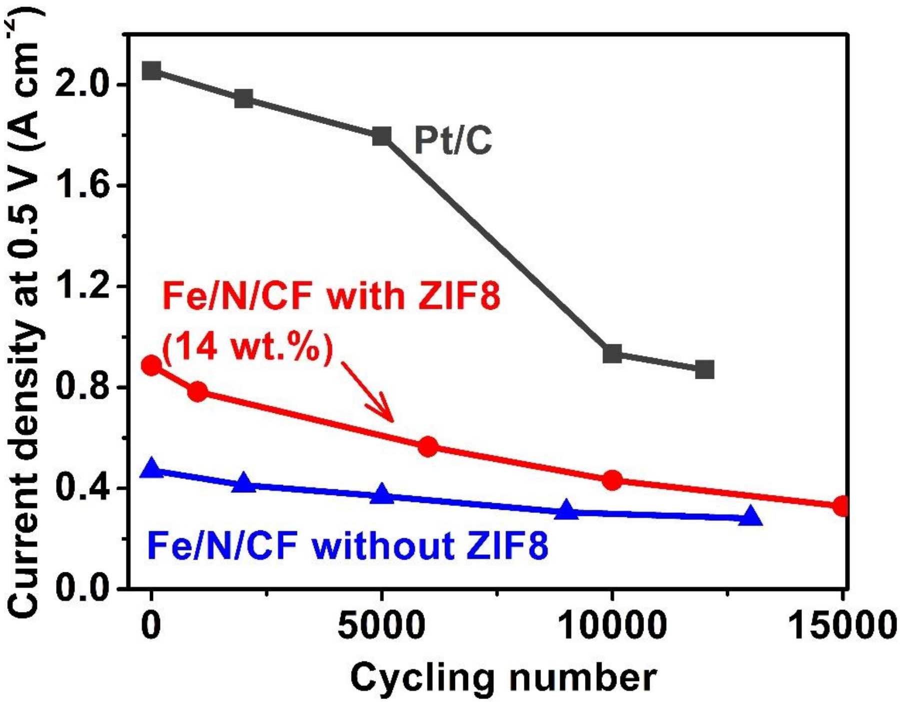


New Nanofibrous Network Showed Promise for Durability Improvement

RDE shows excellent activity retention under multi-potential (0.6 to 1.0 V) cycling in acidic media



Fuel cell accelerated stress test (AST) shows similar decay rate to that of commercial Pt/C MEA



Prospects of Porous Nanonetwork as New Support for PGM Catalyst

- Efficient mass transport
- Better thermal/electronic conductivity
- Stable graphitic network backbone
- High specific surface area
- Tailored surface compositions to promote catalyst-support interaction

Acknowledgement

- Fuel Cell Research - Shengqian Ma, Dan Zhao, Shengwen Yuan, Jianglan Shui, Gabriel Goenaga, Junbing Yang, Chen Chen, Heather Barkholtz, Lina Chong, Lauran Grabstanowicz, Alex Mason, Brianna Reprogle, Sean Comment, Zachary Kaiser, Debbie Myers

- US DOE, US DOE Office of Fuel Cell Technologies and Office of Science. The use of Advanced Photon Source and Electron Microscopy Center are supported by Office of Science, U. S. Department of Energy under Contract DE–AC02–06CH11357.