The Science And Engineering of Durable Ultralow PGM Catalysts

2010 Annual Fuel Cell Technologies Merit Review

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Project ID #FC010

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Collaborations

National Labs

- LANL
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  - *Mahlon Wilson*
  - *Mark Nelson*
  - *Neil Henson*
  - *Ivana Matanovic*

Universities

- UNM
  - *Prof. Abhaya Datye*
  - *Elena Berliba-Vera*
- UCR
  - *Prof. Yushan Yan*

Industry

- Ballard
  - *Siyu Ye*
  - *David Harvey*

Technical Targets/Barriers

Technical Targets:
Decrease PGM content while increasing mass activity and lifetime

Table 3.4.12 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2005 Status [a]		Stack Targets	
		Cell	Stack	2010	2015
Platinum group metal total content (both electrodes)	g / kW (rated)	0.6	1.1	0.3	0.2
Platinum group metal (pgm) total loading [b]	mg PGM / cm^2 electrode area	0.45	0.8	0.3	0.2
Cost	$ / kW	9	55 [c]	5 [d]	3 [d]
Durability with cycling					
Operating temp ≤80°C	hours	>2,000	~2,000 [e]	5,000 [f]	5,000 [f]
Operating temp >80°C	hours	N/A [g]	N/A [g]	2,000	5,000 [f]
Electrochemical area loss [h]	%	90	90	<40	<40
Electrocatalyst support loss [h]	mV after 100 hours @ 1.2V	>30 [i]	N/A	<30	<30
Mass activity [i]	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.28	0.11	0.44	0.44
Specific activity [i]	μA / cm^2 @ 900 $mV_{iR\text{-}free}$	550	180	720	720
Non-Pt catalyst activity per volume of supported catalyst	A / cm^3 @ 800 $mV_{iR\text{-}free}$	8	N/A	>130	300

Barriers:

- PGM catalysts are difficult to synthesize in configurations other than quasi-spherical particles
- PGM area specific activity may decrease with decreasing particle size
- Durability may decrease with greater PGM surface area to volume ratios

Project Objectives & Relevance

- *Development of durable, high mass activity Platinum Group Metal cathode catalysts -enabling lower cost fuel cells*

- *Elucidation of the fundamental relationships between PGM catalyst shape, particle size and activity-will help design better catalysts*

- *Optimization of the cathode electrode layer to maximize the performance of PGM catalysts-improving fuel cell performance and lowering cost*

- *Understanding the performance degradation mechanisms of high mass activity cathode catalysts –provide insights to better catalyst design*

- *Development and testing of fuel cells using ultra-low loading high activity PGM catalysts-validation of advanced concepts*

Collaborative Task Assignments

- Theoretical Understanding Of Roles Of PGM Catalyst Shape, Size, Support Interactions And Catalyst Layer Architecture On Cathode Mass Activity And Durability
  - Optimization Of PGM Catalyst Morphology With Guidance From Computational Studies (LANL)
  - Optimization Of Catalyst Layer Architecture With Guidance From Microstructural Simulations (Ballard)
- Experimental Synthesis And Characterization Of New Geometry PGM Catalysts
  - Synthesis of Novel Pt Nanoparticles (UCR, UNM, LANL)
  - Synthesis of Pt Nanotubes (UCR)
  - Synthesis of Pt Nanowires (UCR UNM,LANL)
- PGM Structural Characterization by TEM, XRD, Neutron Scattering
  - HRTEM Morphology Studies (ORNL) (UNM)
  - Advanced X-ray Diffraction Studies (LANL)
  - Neutron Scattering Studies (LANL)
  - Thermodynamic Characterization of PGM catalysts (UNM LANL)
  - Electrochemical Characterization of PGM catalysts (LANL)
- Understanding Catalyst Nucleation And Support Interactions
  - Inverse Chromatography Studies Of Precursor-Support Interactions (LANL UNM)
  - PGM-Support Interaction Studies (UNM)
- Fuel Cell Testing Of Novel PGM Catalysts (LANL Ballard)
  - Testing of novel catalysts in fuel cells (LANL Ballard)
  - Fuel cell post testing materials characterization (LANL ORNL)

Approach

- *Use contemporary theoretical modeling and advanced computational methods to understand and engineer the new catalysts*

- *Model and design appropriate catalyst architectures to maximize the performance of our novel catalysts*

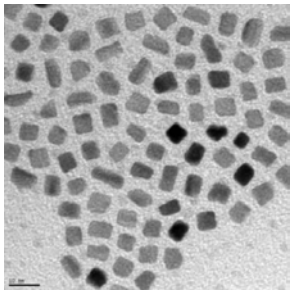
- *Investigate catalyst-support interactions and their effects on durability and mass activity will also be investigated*

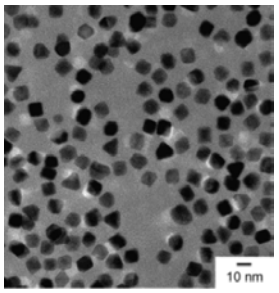
- *Study and test the performance of the catalysts in electrochemical cells, single cell-fuel cells and fuel cell stacks*

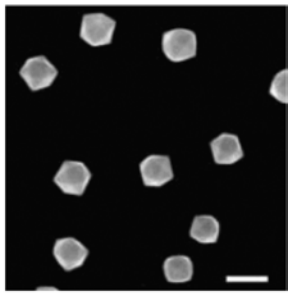
- *Extensively characterize new materials before and after fuel cell operation*

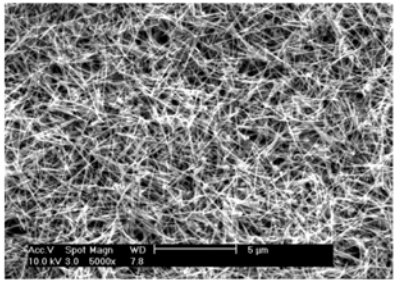
Approach

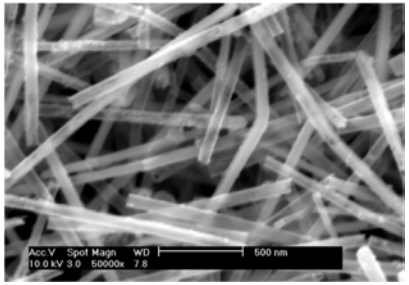
- Synthesis of new PGM materials/novel supports using differing shapes and sizes: cubes, octahedron, tetrahexahedral, wires and tubes etc.
- TEM SEM and X-ray, neutron characterization of structures
- Electrochemical ORR kinetics measurements
- Electrochemical and calorimetric studies of stability
- Optimization of electrode structure
- Fuel cell testing
- DFT modeling of catalyst activity and particle stability

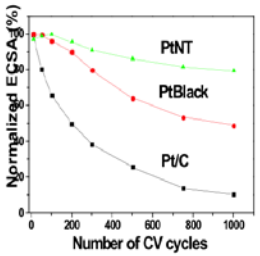


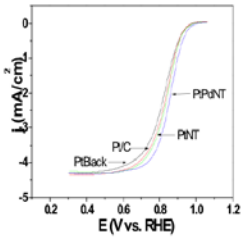


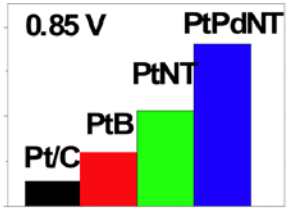












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Milestones

Month/Year	Milestone or Go/No-Go Decision
Feb-10	Synthesis of novel catalyst support architectures. We have successfully synthesized Pt on novel carbon and conducting polymer nanowires.
March-10	Milestone: initial fuel cell testing of novel catalysts (ahead of schedule). We have commenced fuel cell testing of the novel catalysts
April-10	Milestone: Initial characterization of Pt nanowire catalysts. We have begun SEM, XRD and TEM investigations of our catalysts.

Budget

DOE Cost Share	Recipient Cost Share	Total
6,000,000	528,685	6,528,685
92%	8%	100

Yr 1	Yr 2
1,500,000	1,550,000

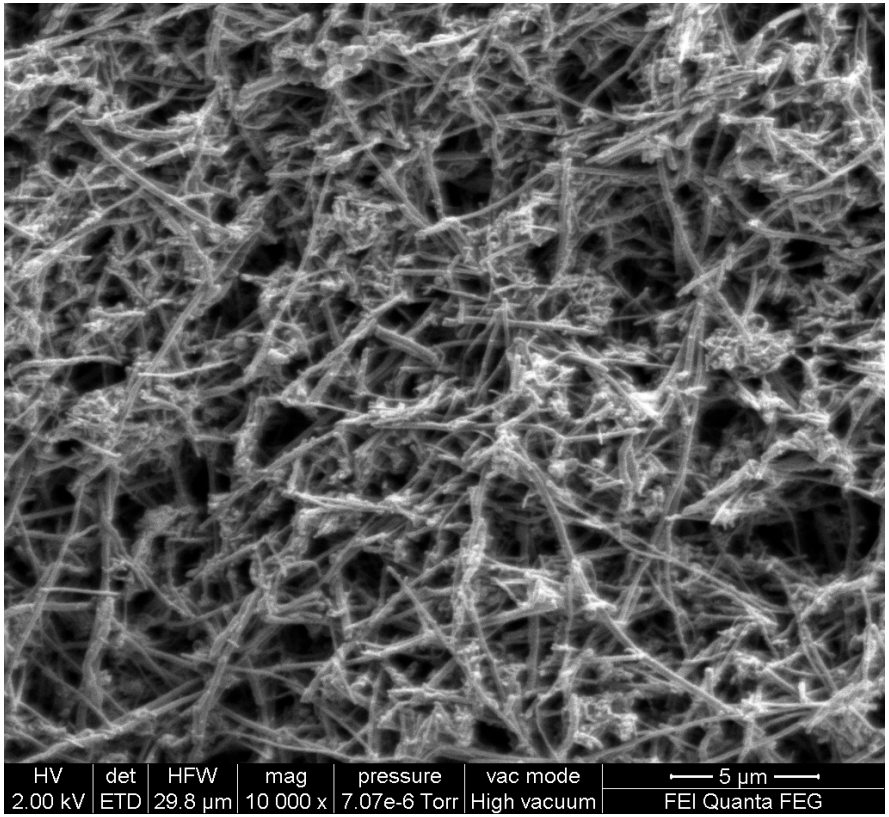
Participant	FY09-10 (Year 1)
LANL	$1,400,000
ORNL	$100,000
Universities	$275,000
Industry (Ballard)	$158,000
TOTAL Year 1	$1,933,000

LANL Low PGM Synthesis

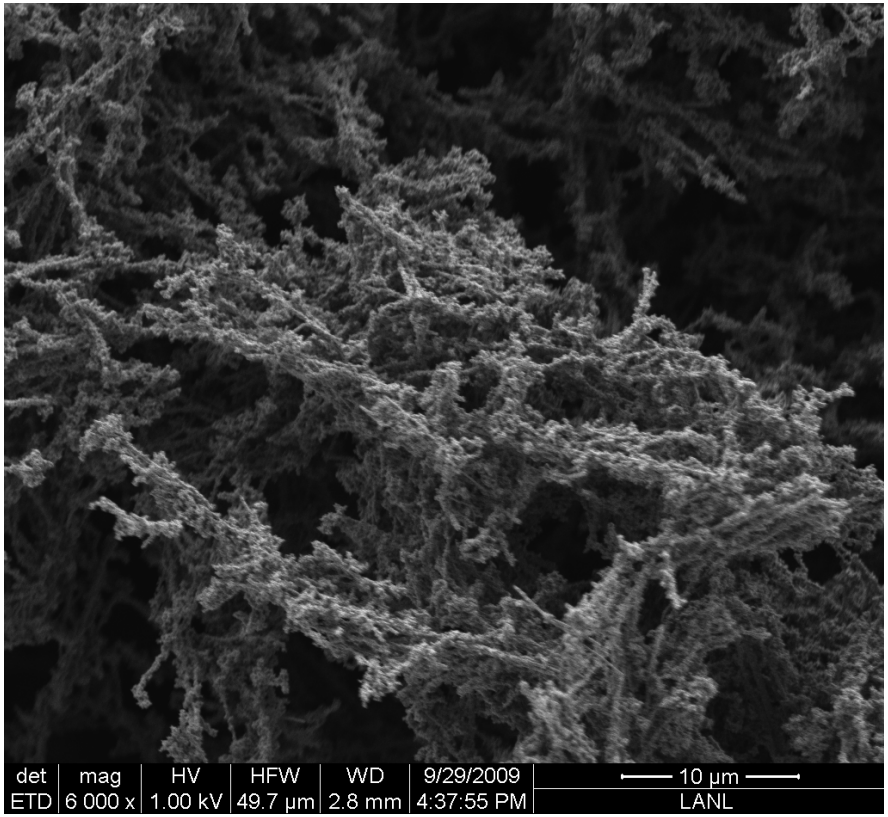
- Develop novel geometry supported catalysts:
  - Carbons-
    - Pyrograf nanowires
    - Multiwall Carbon Nanotubes (MWCNT)
  - Conducting Polymers:
    - Fibron Polypyrrole
    - Chemically deposited Polypyrrole
    - Electrochemically deposited and aligned Polypyrrole
- Investigate anchoring chemistries:
  - Interfacial monolayers
- Low PGM loading deposition
  - Chemical
  - Electrochemical
  - Physical Vapor Deposition
  - RF Sputtering

Activated Pyrograf w/ PPy Coatings

Light deposit

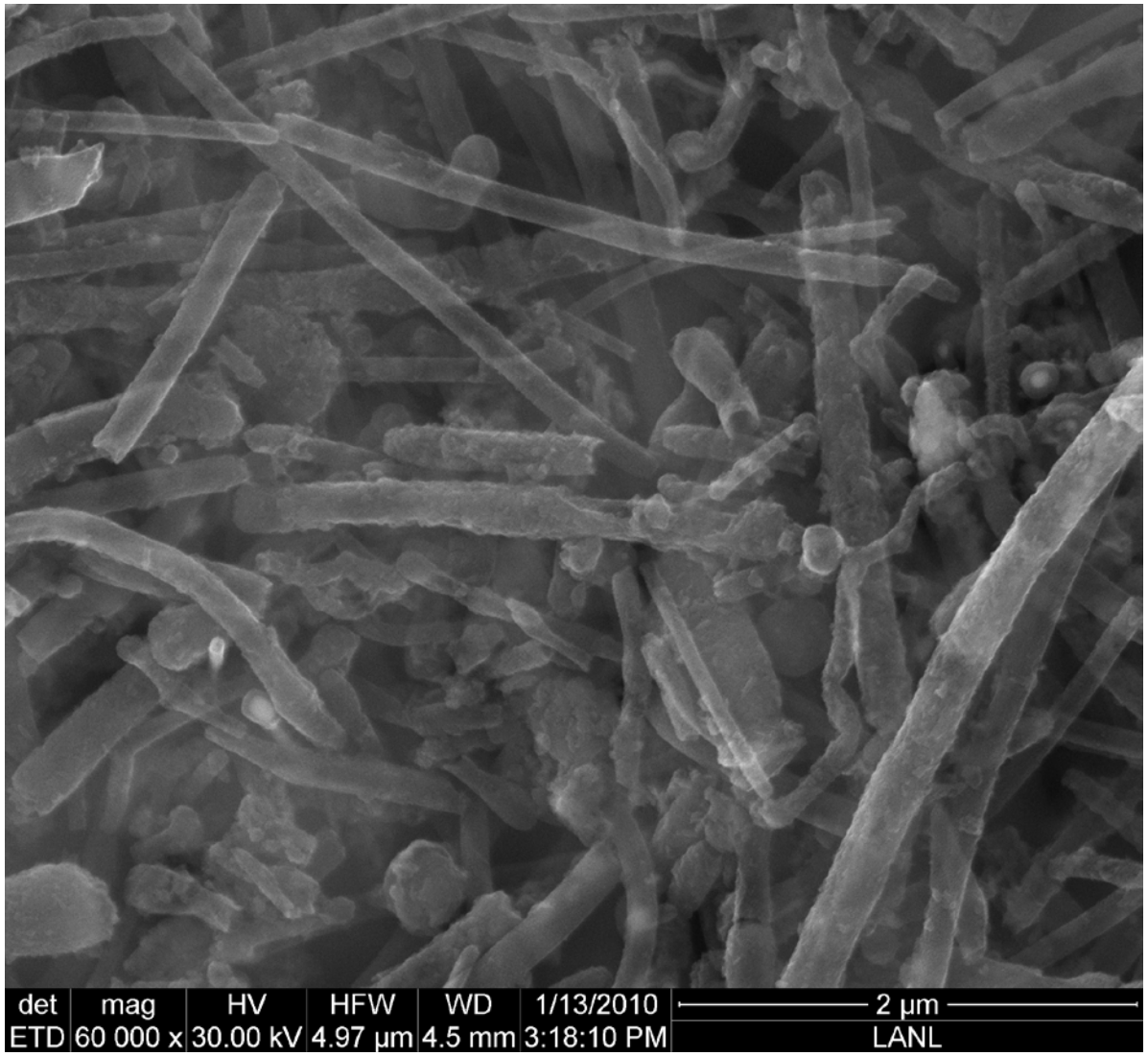


Heavy deposit



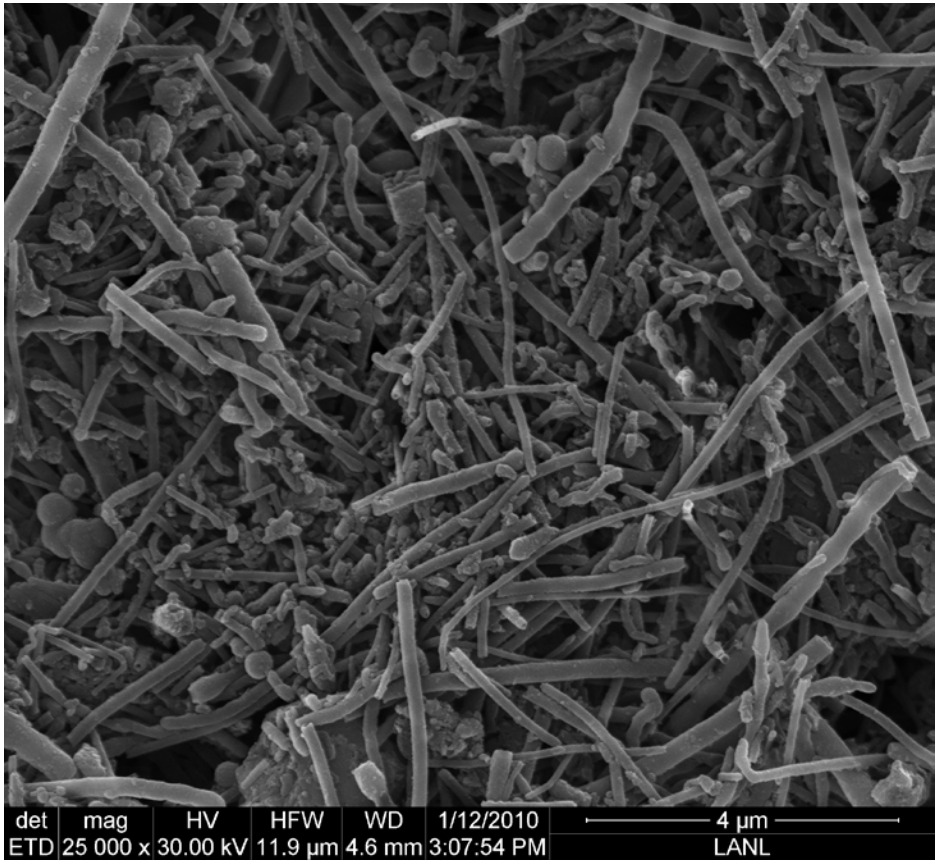
bulk chemical pyrrole deposition

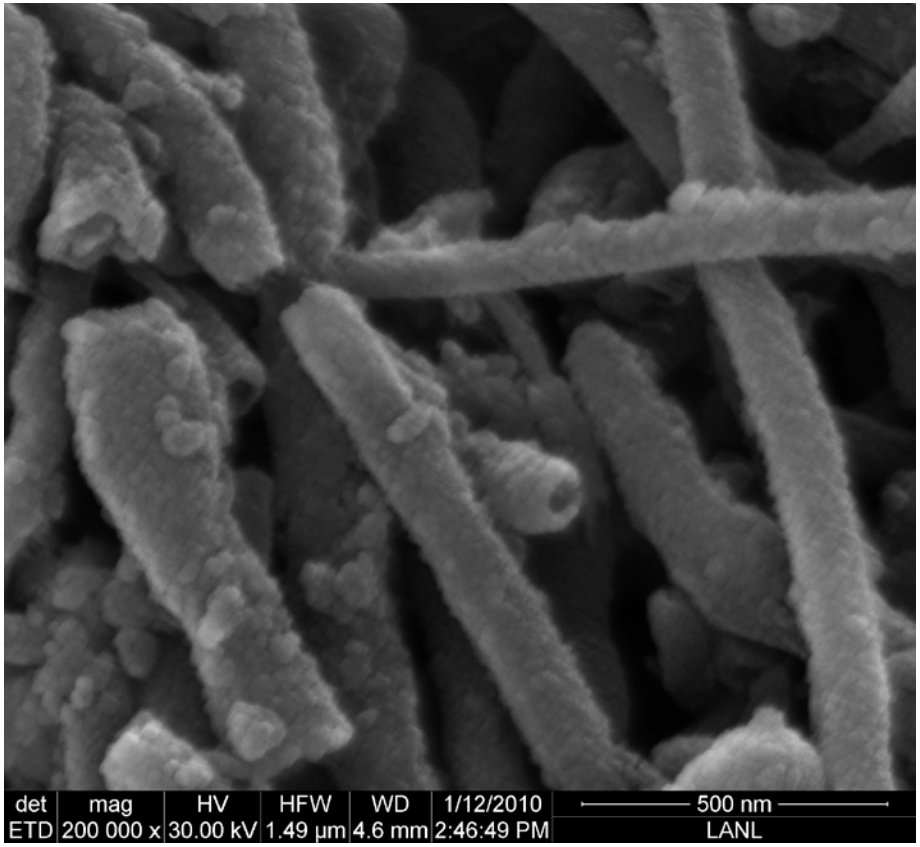
Improving Adhesion Using Titanium Interlayers:



Activated Pyrograf w/ Ti sputter (0.018 mgTi/cm^2)

Activated Pyrograf w/ Ti & 0.05 mg Pt/cm^2 Sputter Deposition





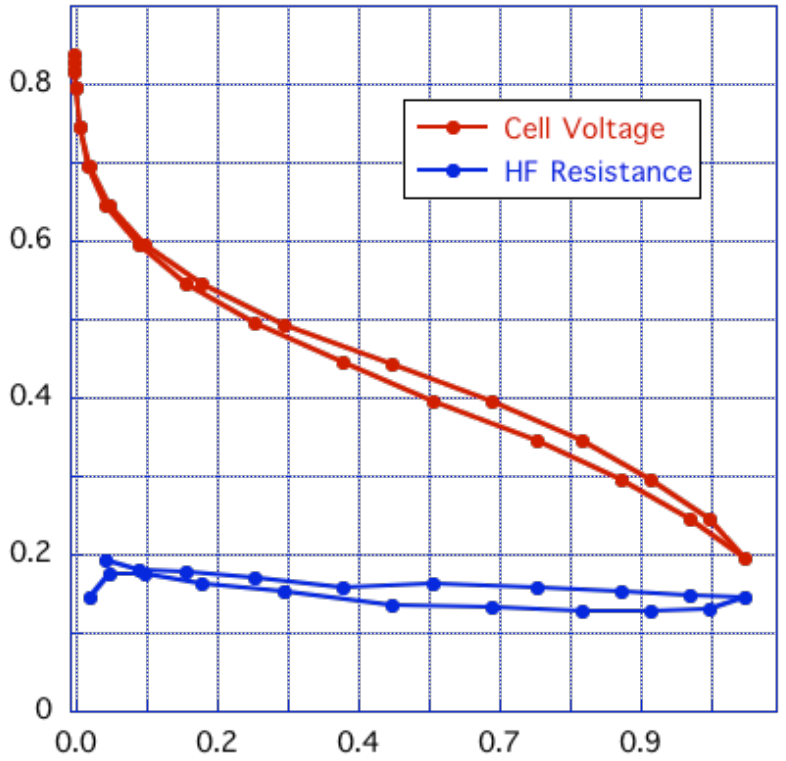
•Uniform Pt coating 20 nm particles

Fuel Cell Preconditioning w/ Activated Pyrograf / Ti / 0.042 mg Pt/cm^2

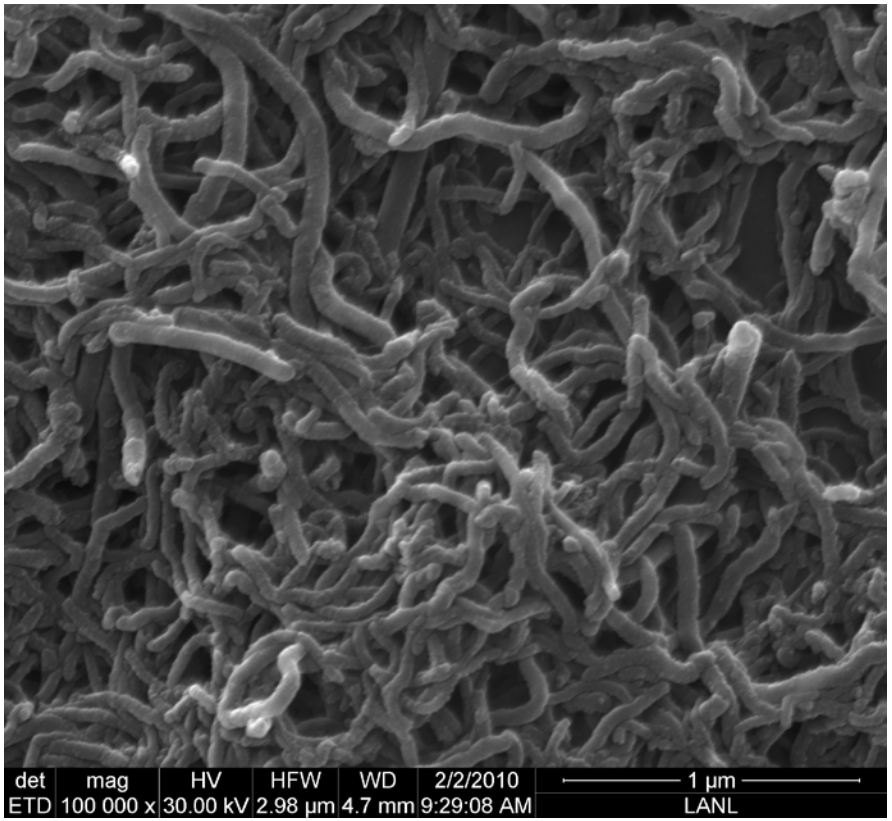
Activated Pyrograf w/ Ti & Pt Sputter Deposition

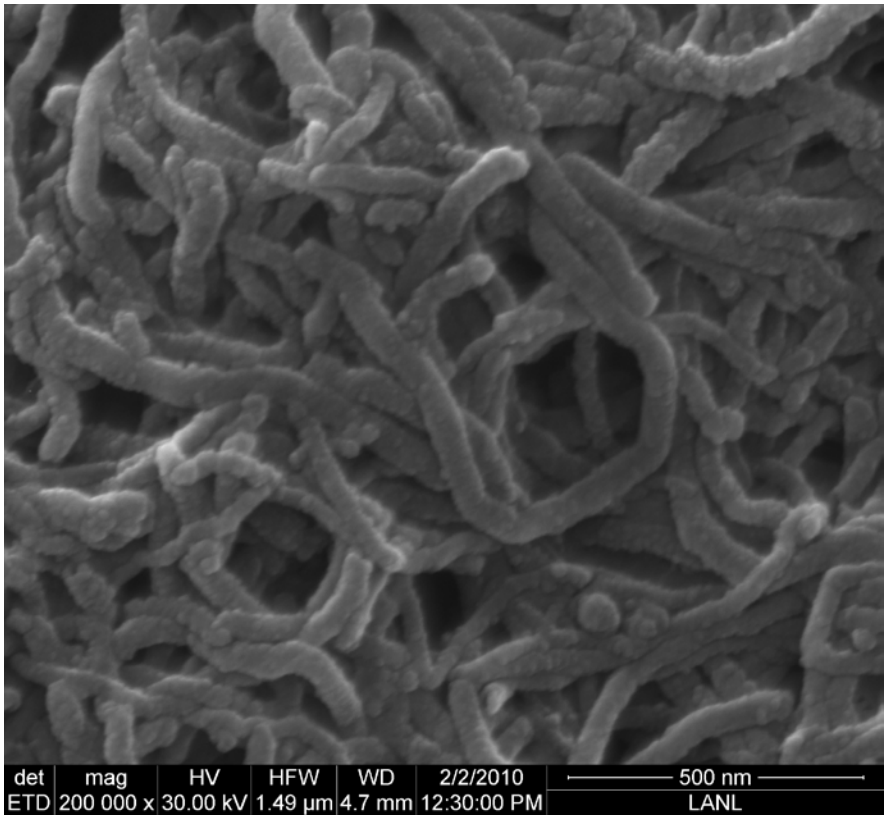
Kinetic region losses at low cathode loadings

Need to improve ionomer catalyst interface



Activated MWCNTs 0.05 mg Pt/cm^2





~ 8 nm crystallites (XRD) & uniform coating

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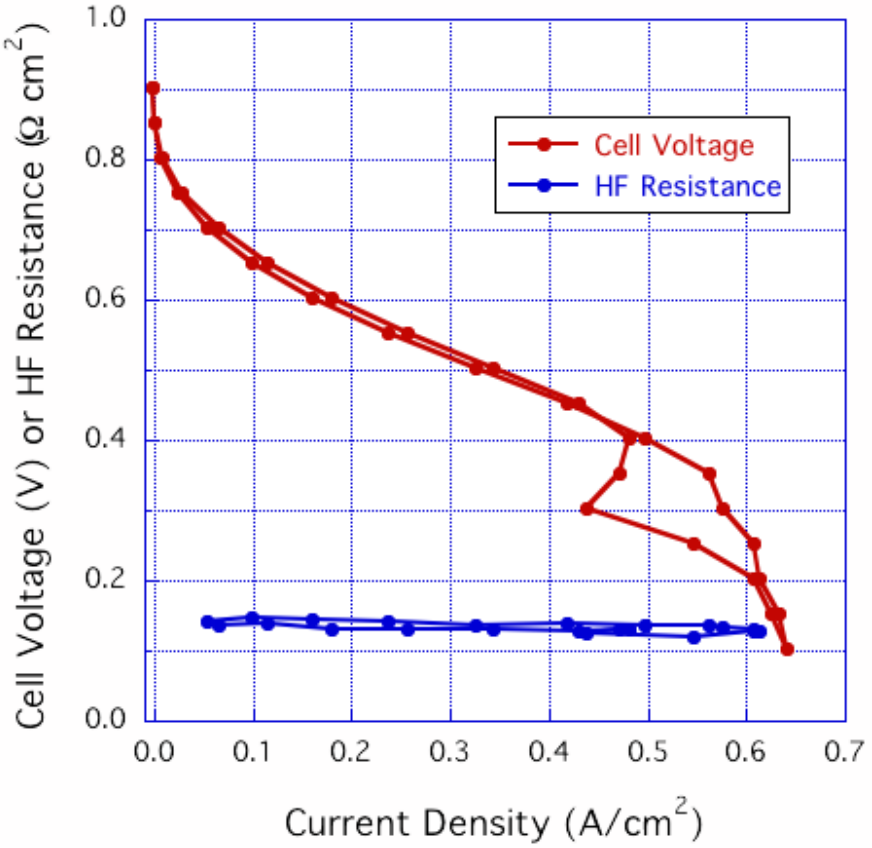
Fuel Cell testing Pt Sputter Deposited MWCNT's

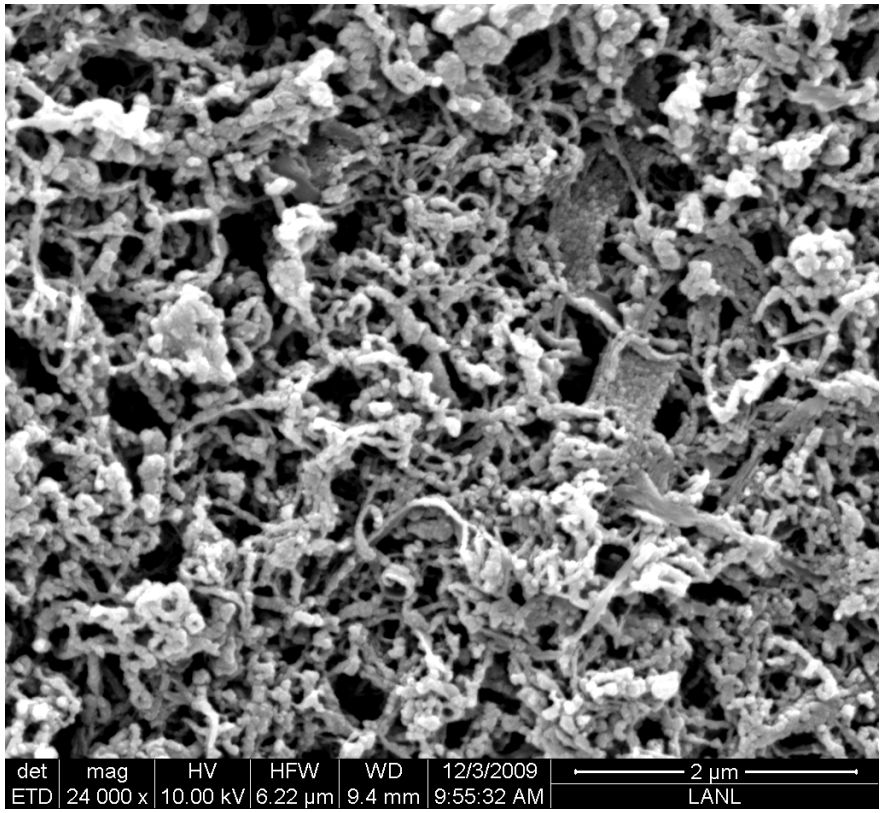
Multiwall Nanotubes Pt Sputter Deposition 0.05mg Pt/cm^2

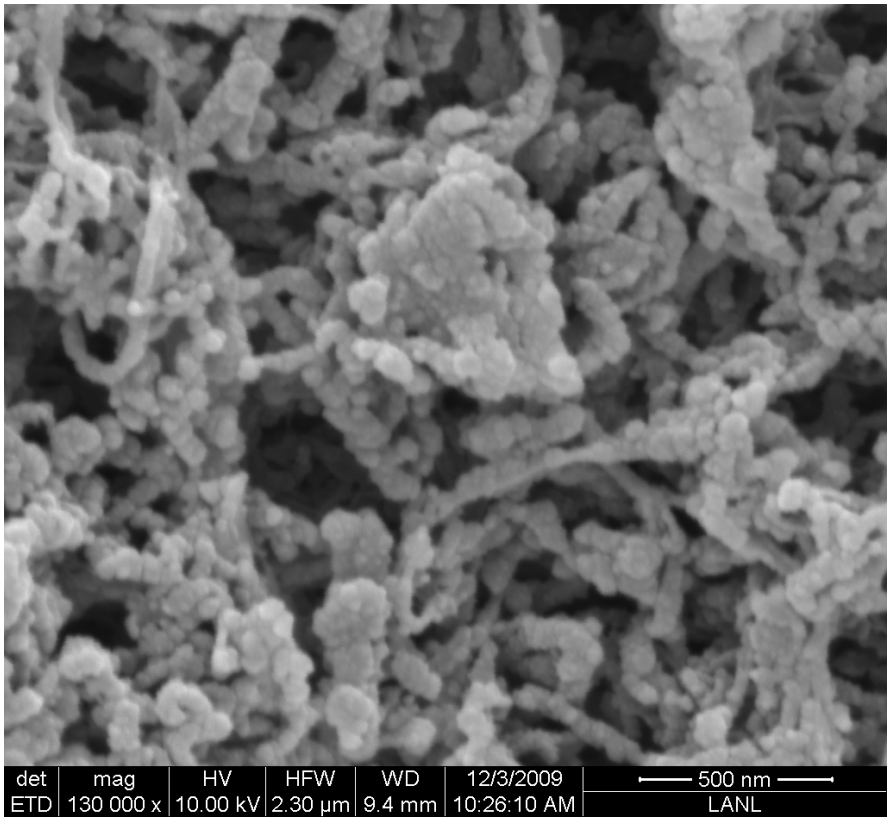
Kinetic region losses at low cathode loadings

Again need to improve ionomer catalyst interface



Pt on Polypyrrole- Fibron Materials





Fibron PPy w/ 0.05 mg Pt/cm^2 sputter deposition

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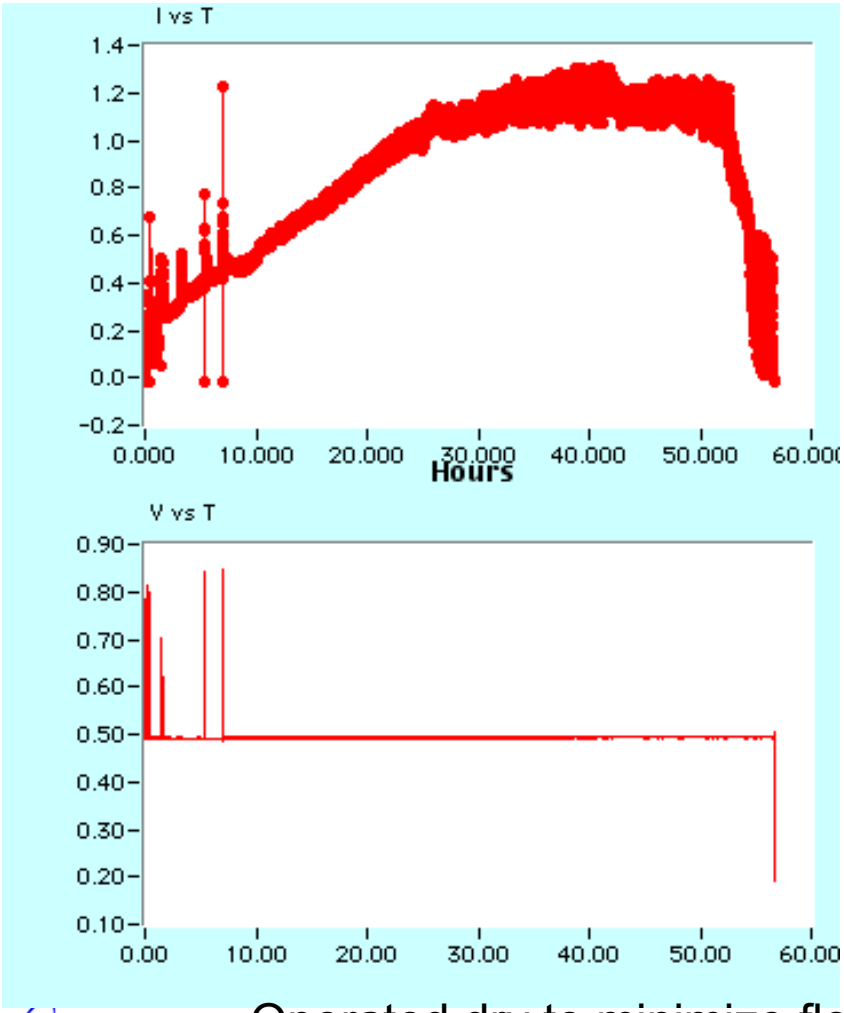
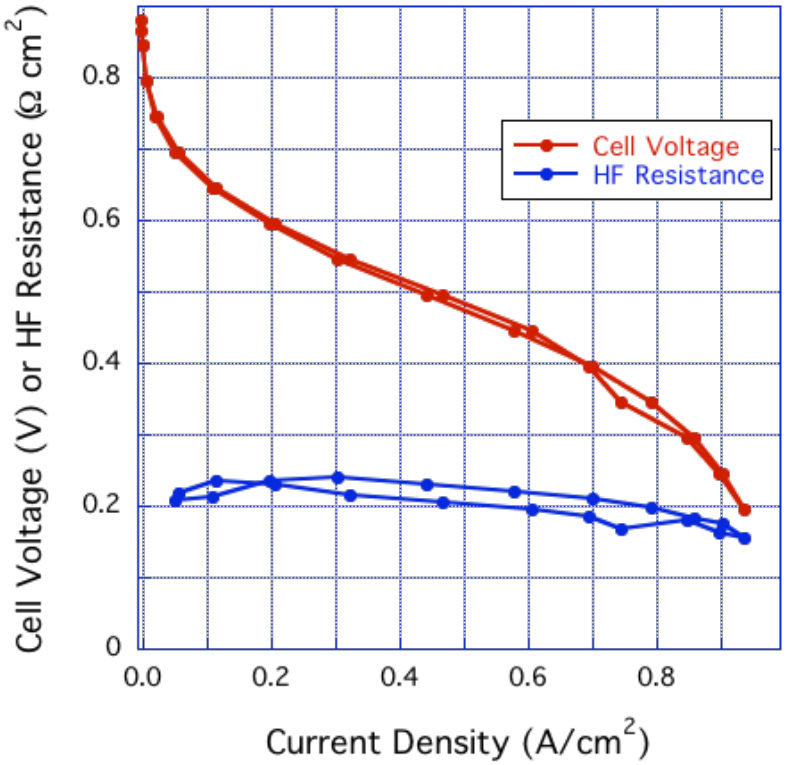
Fuel Cell Testing of Fibron Supported Pt 0.035mg Pt/cm^2

N212 membrane 80 C catalyzed ELAT 0.25mg Pt/cm^2 anode





Operated dry to minimize flooding

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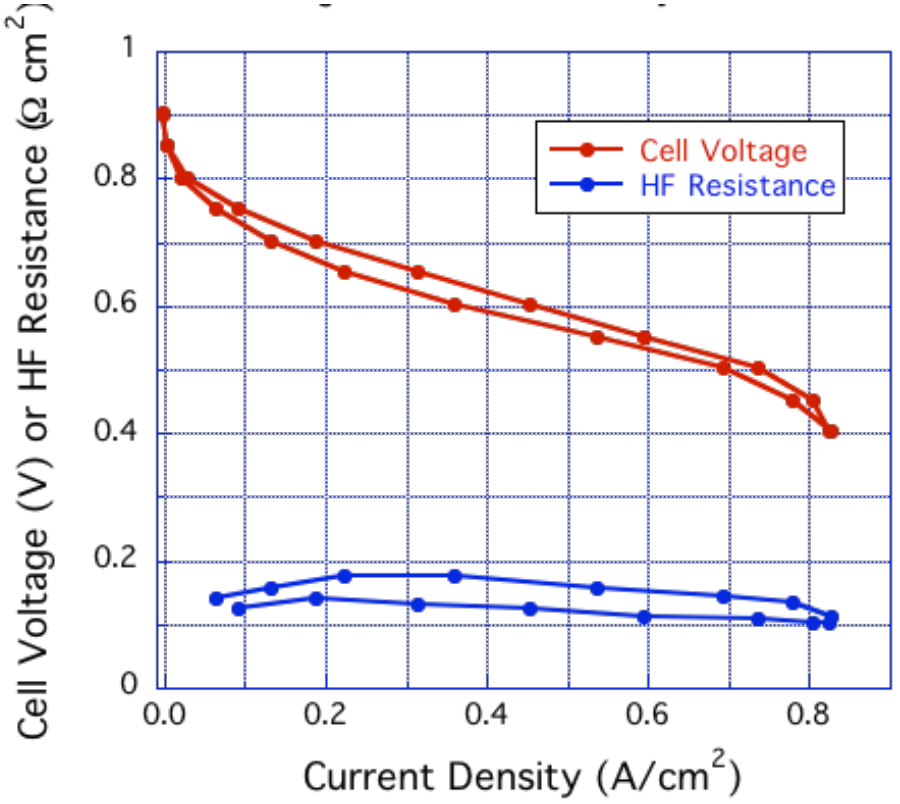
Fuel Cell Testing of Fibron Supported Pt 0.05mg Pt/cm^2

- The addition of recast Nafion® (Ion Power) to the Electrode/GDL structure improves the kinetic region of the fuel cell polarization curve
- Increases catalyst utilization
- Optimal amounts of recast Nafion® at electrode membrane interface needs to be determined



Significant performance improvement with recast Ionomer added to the interface

Preparation Of Pt Catalyst On LANL Polypyrrole Nanowires

PROS:
- High surface area
- Low Pt load
- Electronic and ionic conductivity
- Reversible redox activity
- Can be reduced or heat treated to further stable support

CONS:
- Hydrophilic
- Degradation behavior unknown

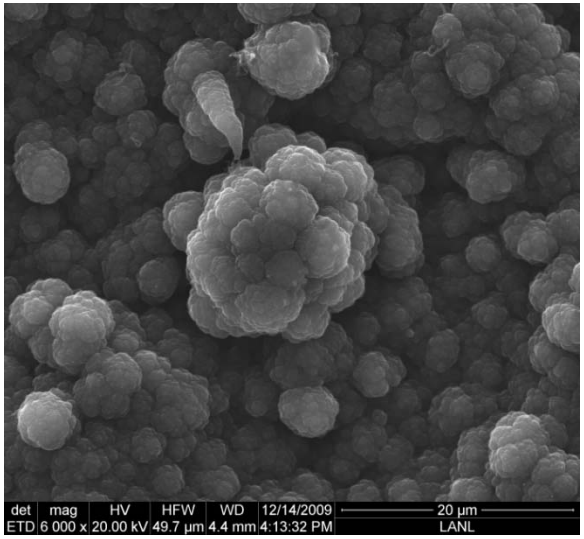
Approach 1:

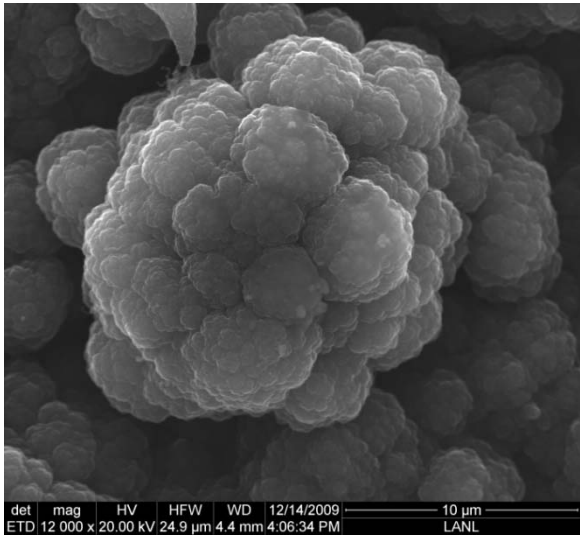
1. Electropolymerization of PPY nanowires (with heparin, starch, etc) on GDL's with different %Teflon® and porous structure
2. Vapor deposition of Pt onto PPY nanowires
3. Assembly of fuel cell using a half MEA as anode and the prepared GDL with PPY/Pt nanowires as cathode

Approach 2:

1. Electropolymerization of PPY nanowires (with heparin, starch, etc) on solid electrodes (glassy carbon, stainless steel, etc)
2. Vapor deposition of Pt onto PPY nanowires
3. Transfer of PPY/Pt nanowires by hot press to prepare an MEA having the prepared GDL with PPY/Pt nanowires as cathode

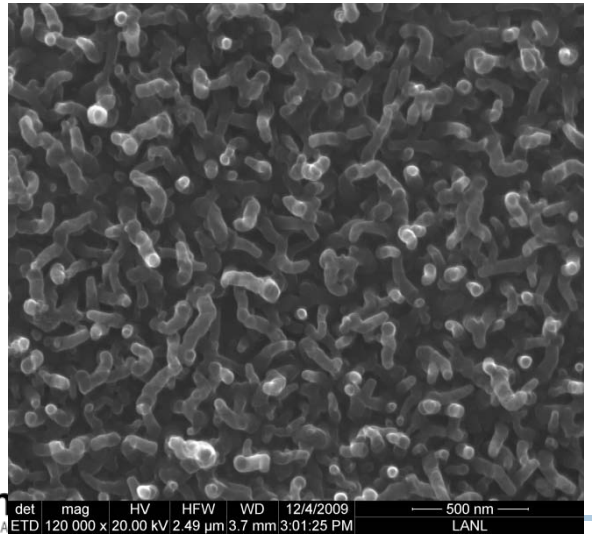
Electropolymerization of PPY dendrites

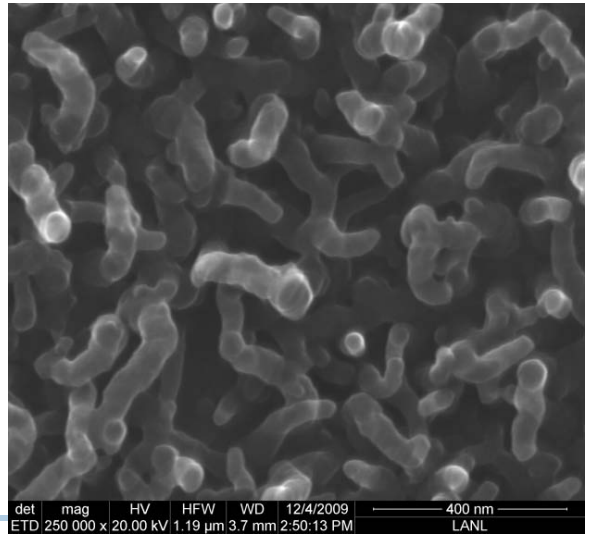




Electropolymerization of PPY nanowires on Glassy-Carbon

PPY/Heparin on Glassy-Carbon

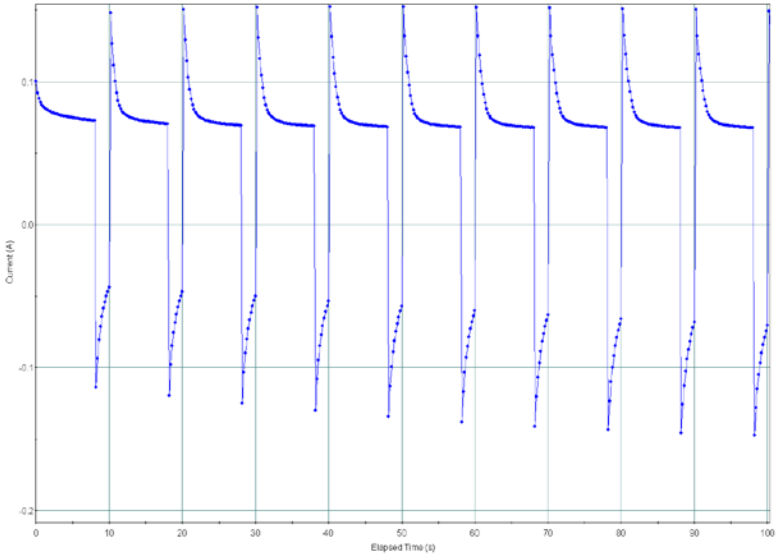




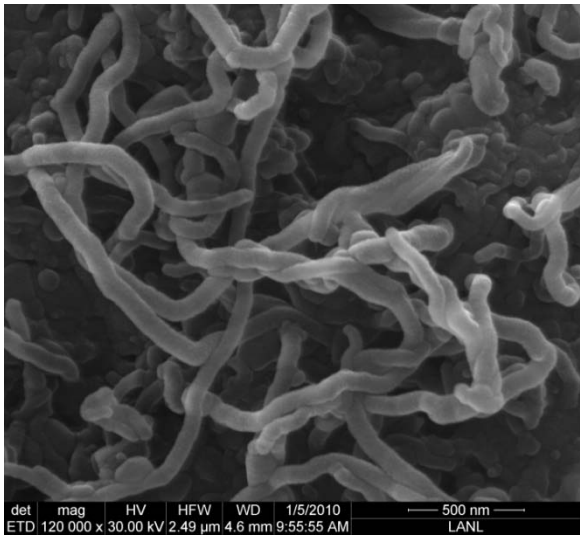
Electropolymerization of PPY nanowires on GDL

Electrochemical Cell

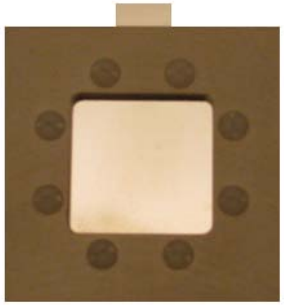
Electropolymerization of PPY nanowires using multipotential steps +0.85V (8s) / -0.3V (2s) vs Ag/AgCl



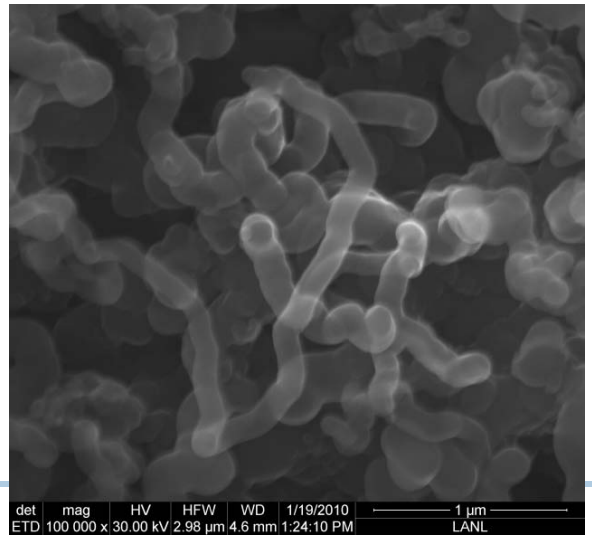
PPY/Heparin on GDL



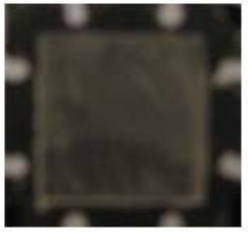
Electrode Holder



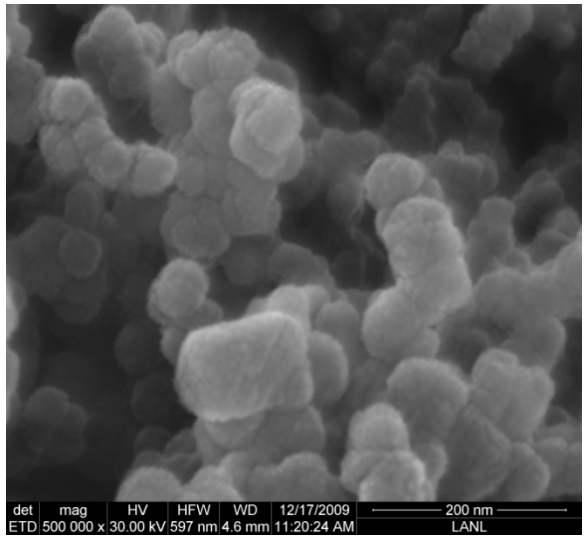
PPY/Starch on GDL



PPY/Pt nanowires on GDL

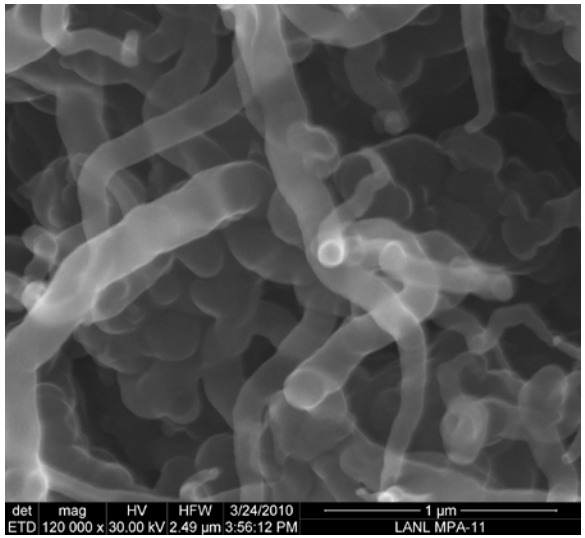


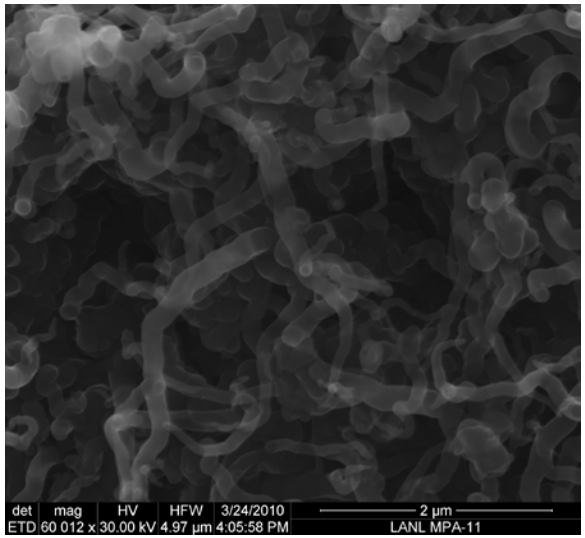
PPY/Pt nanowires on GDL

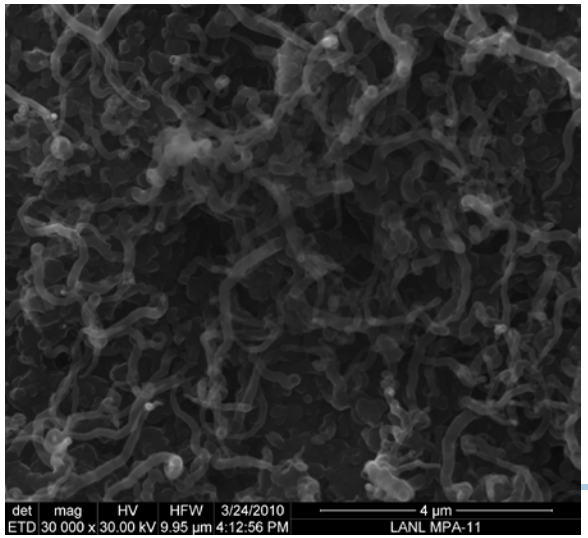


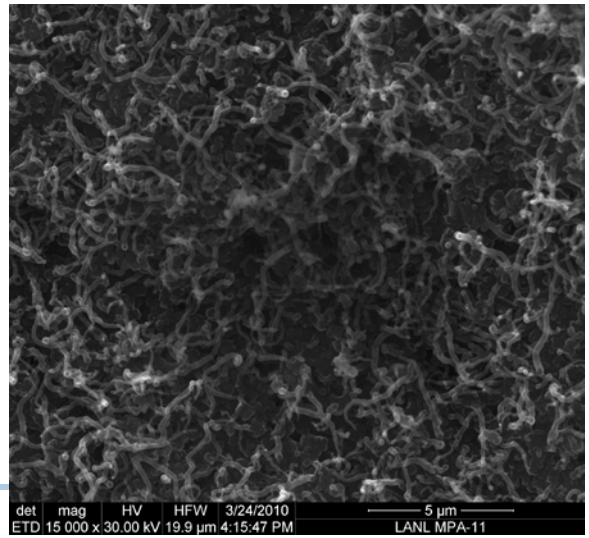
Electropolymerization of PPY Nanowires on GDL (SGK-GDL-24BC: 5% Teflon® Substrate ; 23% Teflon® MPL)

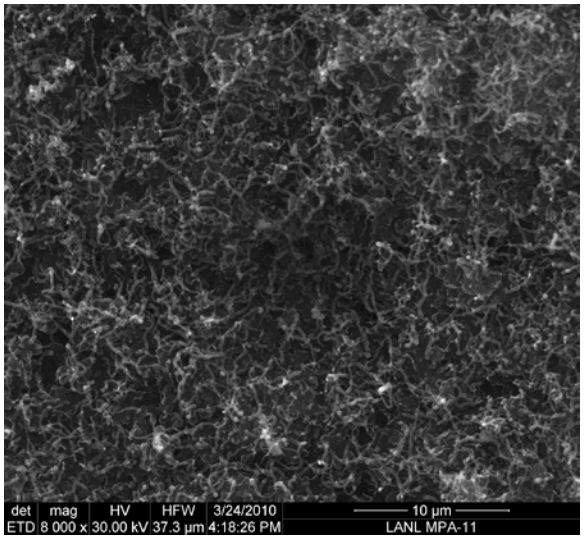
[Py]=0.1M ; [starch]=0.02wt%
Multipotential steps: +0.85V (8s) / -0.3V (2s) vs Ag/AgCl
t=20min







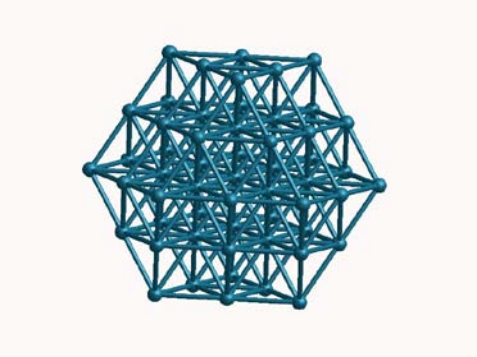




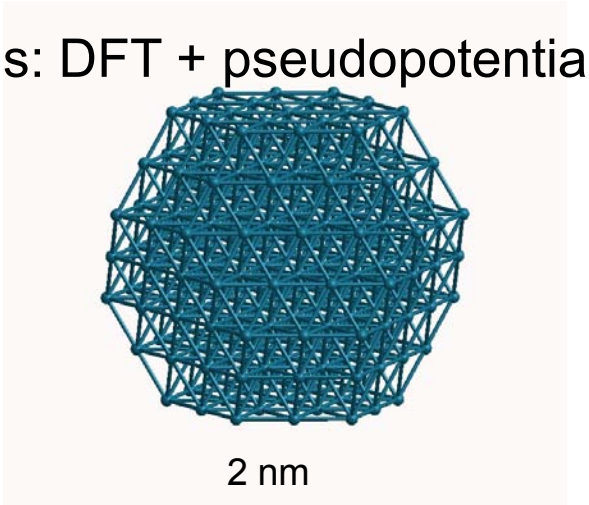
Design of Active and Durable Nanocatalysts for FC Guided by Computational Methods

Stability of nanoparticles versus geometry- relative to bulk Pt

Effect of nanoparticle size and structure on adsorption of O and OH on platinum nanostructures –
electronic structure calculations: DFT + pseudopotentials + PW



1 nm



2 nm

Uncoordinated atoms at edges and vertices can be seen to have a high chemical reactivity (B. C. Han *et al.* Phys. Rev. B 77, 075410 (2008))

Summary

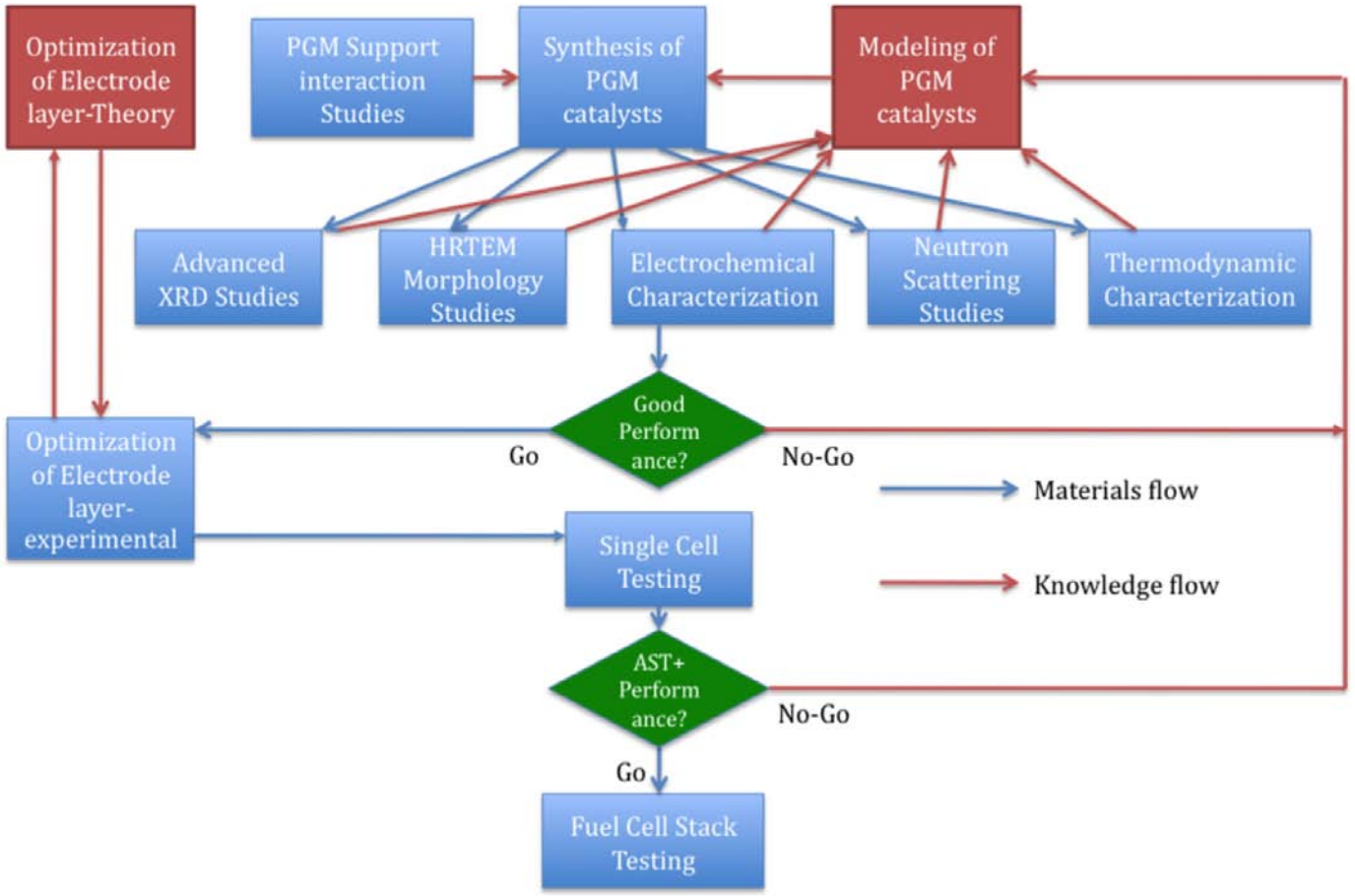
- We have synthesized novel Pt/ support structures using nanowire supports
  - Carbons
  - Conducting Polymers
  - Adhesion layers investigated
- Characterized new materials
- Fuel cell performance testing has commenced
- RDE measurements have begun
- DFT calculations commenced
- Calorimetry experiments started

Future Work

- Catalyst synthesis and optimization
- Oxygen reduction activity testing using rotating disk electrodes
- Fuel cell electrode performance and durability optimization
- Fuel cell testing and post-testing characterization
- DFT modeling
- Materials characterization- TEM SEM EDS
- Thermodynamic-calorimetric characterization

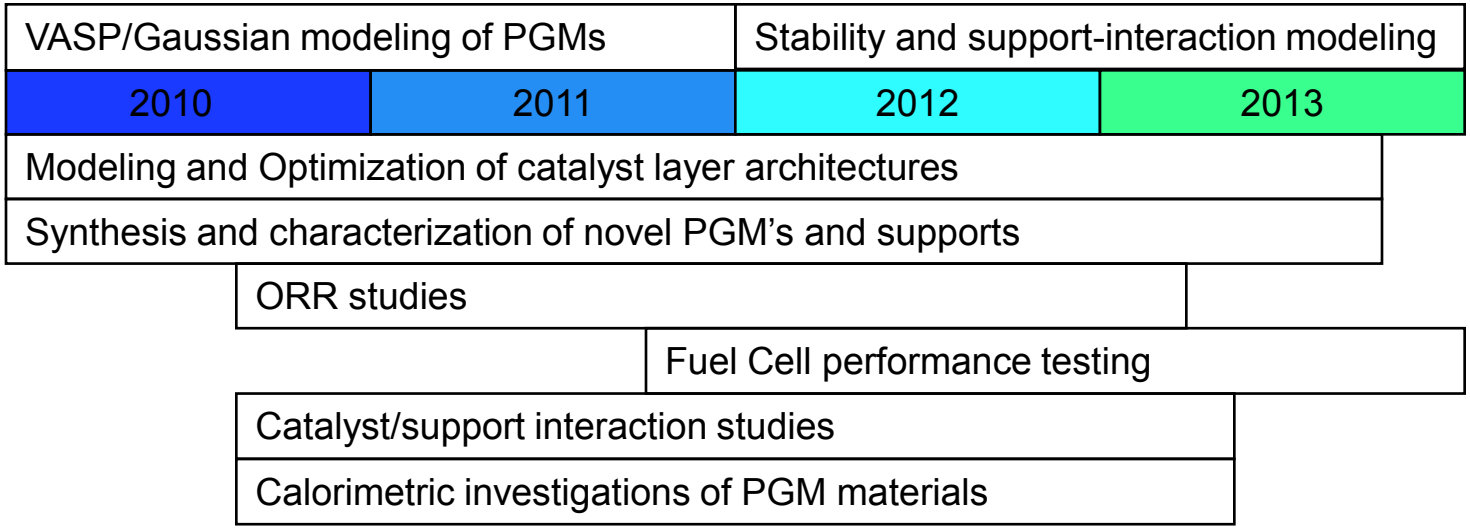
We gratefully acknowledge funding from the US DOE Office of Fuel Cell Technologies

Technical Approach

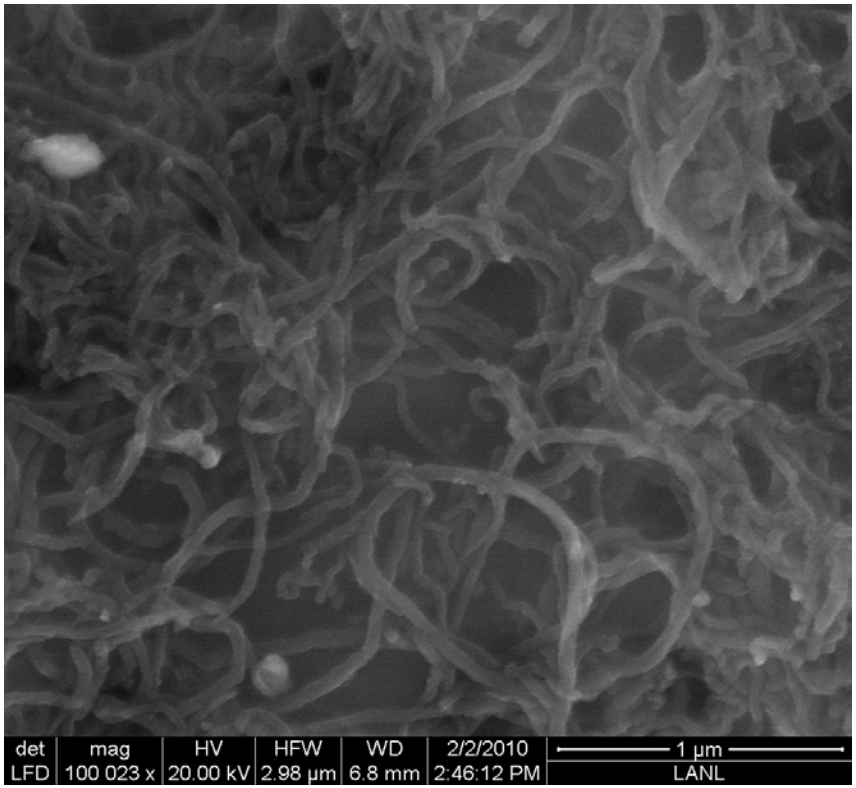


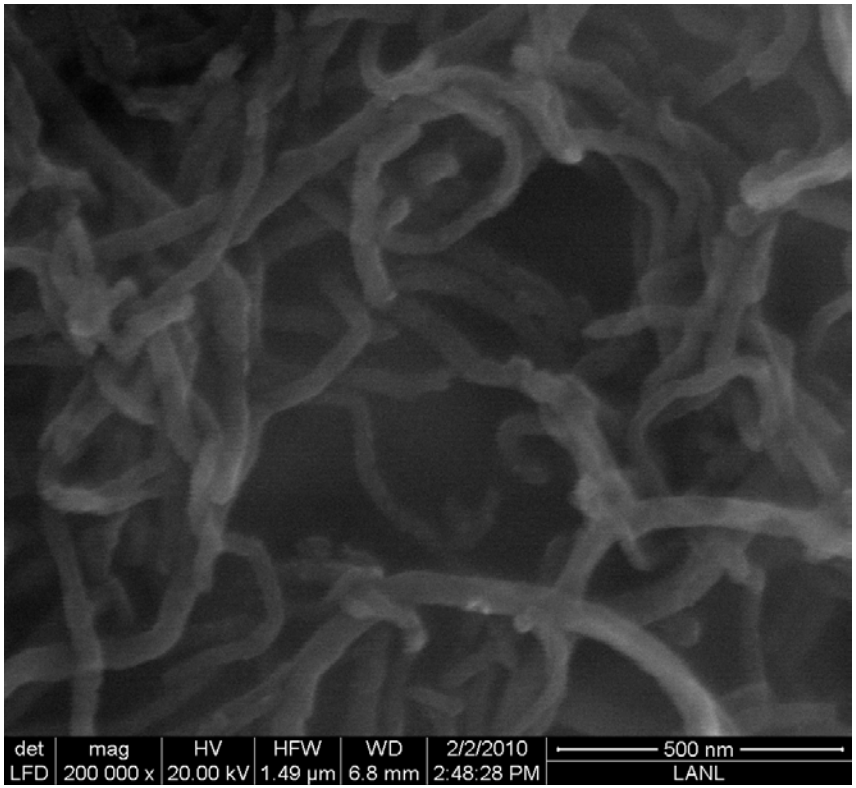
Timeline

Project initiated in Sept FY2009 for 4 years



Activated MWCNT's





•Surfaces pretreated with nitric acid etch

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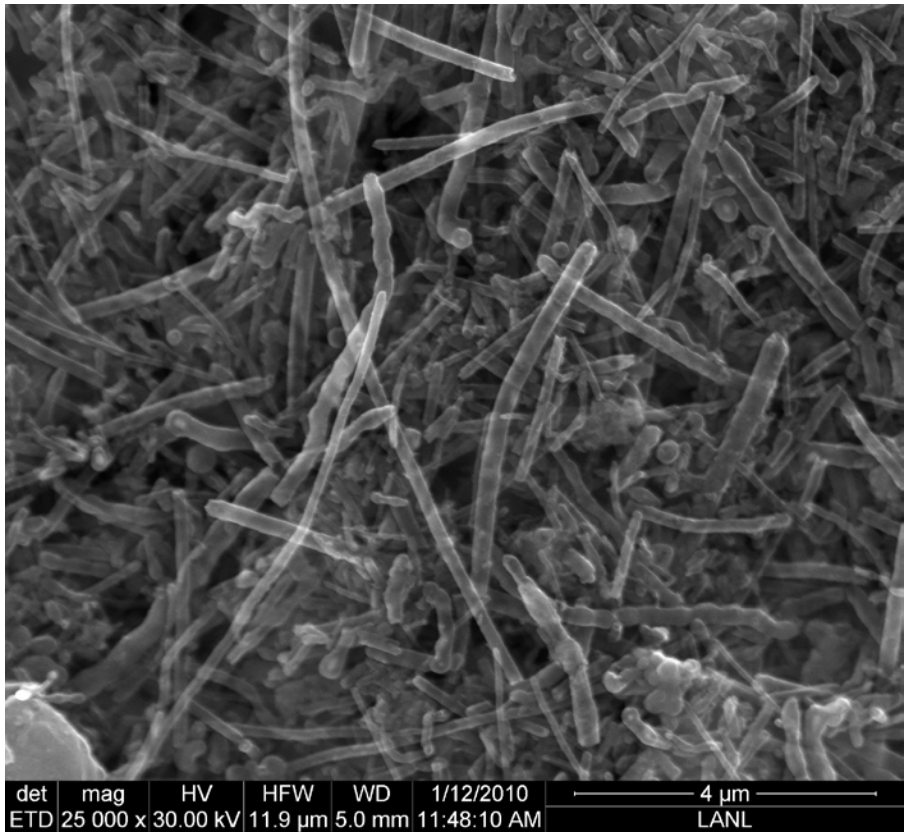
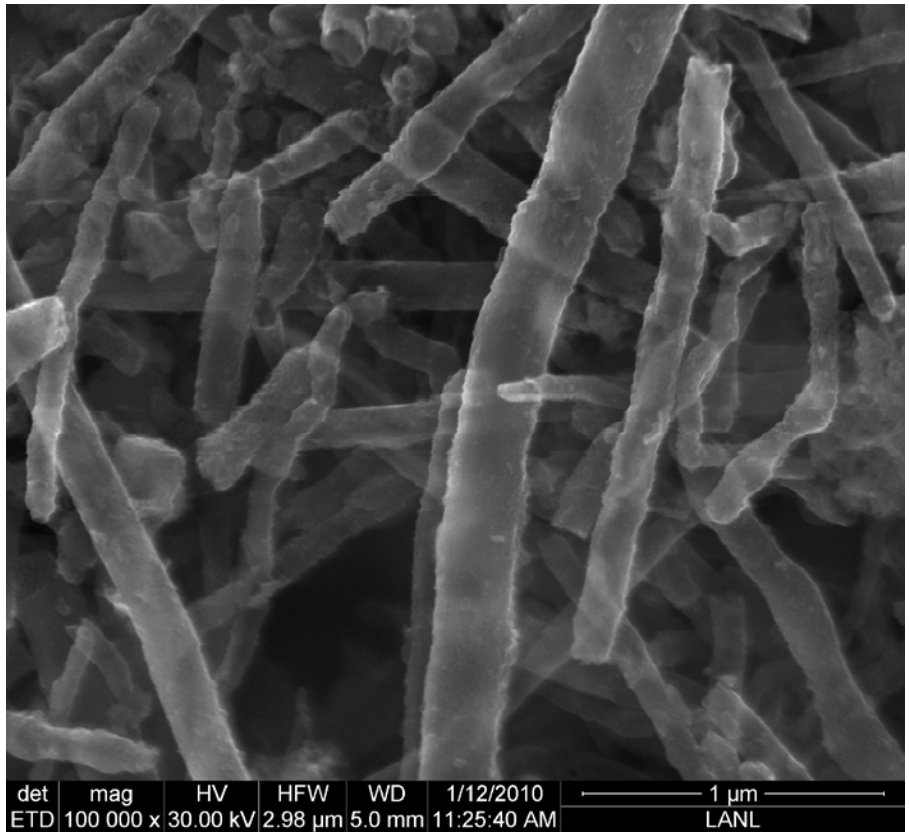
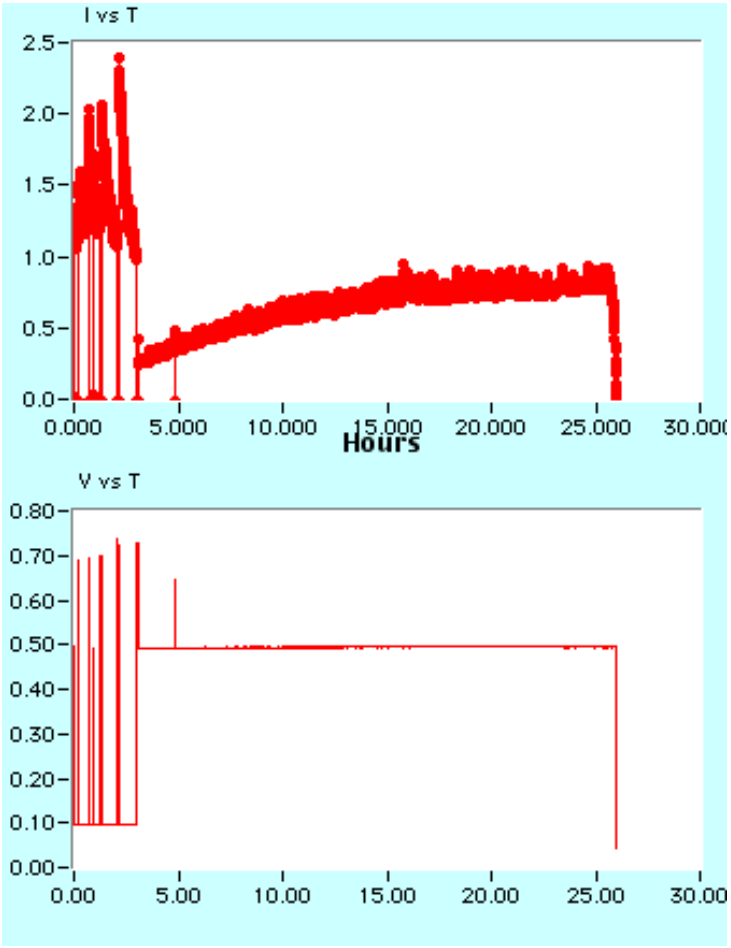
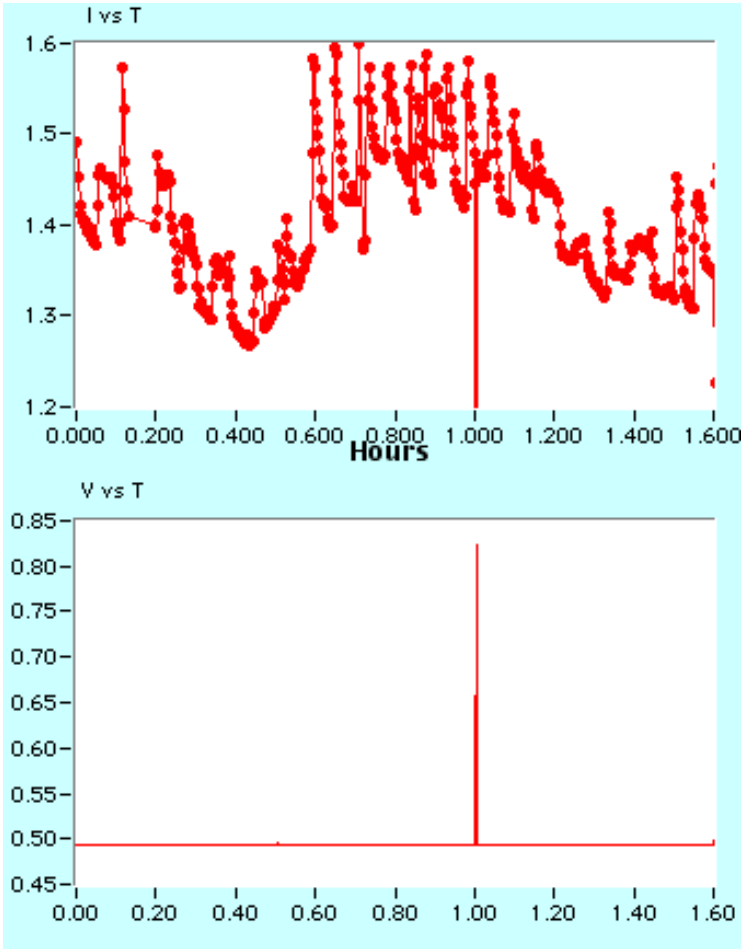
Activated Pyrograf Carbon Nanowire Supports





Fuel Cell Preconditioning w/ Activated Pyrograf / Ti / 0.042 mg Pt/cm^2





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Design of Active and Durable Nanocatalysts for FC Guided by Computational Methods

Situation when Pt is used as a cathode for oxygen reduction reaction (ORR) is more complex

Stability of nanomaterials in aqueous environment – Pourbaix diagrams the most stable state (geometry) of material as a function of pH and potential

Thermodynamics of ORR reaction

f*ree energy for oxygen reduction* (associative, dissociative mechanism) i.e energy diagrams – energy barriers connecting the intermediate states along the reaction path *for different topologies*

- model the water environment of the electrochemical cell
- thermodynamic parameters as a function of electrochemical potential