The Science And Engineering of Durable Ultralow PGM Catalysts

2010 Annual Fuel Cell Technologies Merit Review

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Project ID #FC010

Collaborations

National Labs

- LANL
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  - *JoseMari Saniñena*
  - *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 [j]	A / mg Pt @ 900 $mV_{IR\text{-}free}$	0.28	0.11	0.44	0.44
Specific activity [j]	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*

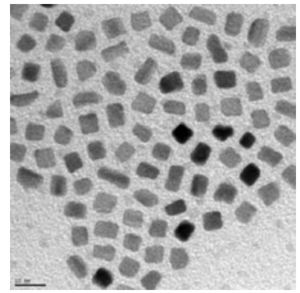
- *Investigate catalyst-support interactions and their effects on durability and mass activity will also be investigated*

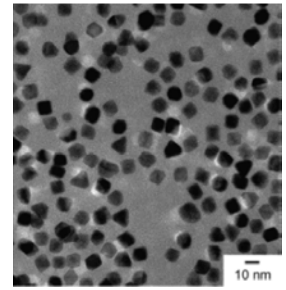
- *Study and test the performance of the catalysts in electrochemical cells, single cell-fuel cells and fuel cell stacks*

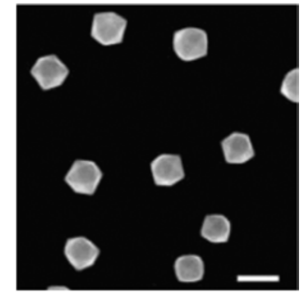
- *Extensively characterize new materials before and after fuel cell operation*

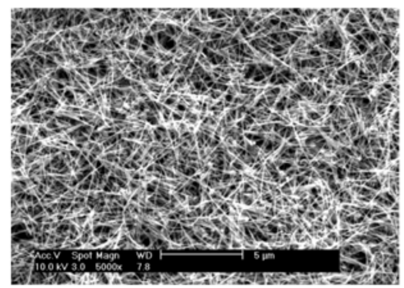
Approach

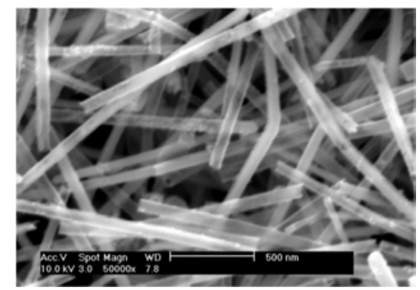
- Synthesis of new PGM materials/novel supports using differing shapes and sizes: cubes, octahedron, tetrahexahedral, wires and tubes etc.
- TEM SEM and X-ray, neutron characterization of structures
- Electrochemical ORR kinetics measurements
- Electrochemical and calorimetric studies of stability
-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

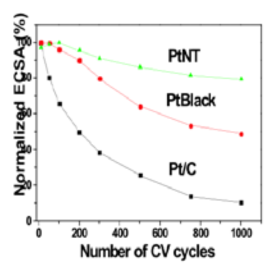


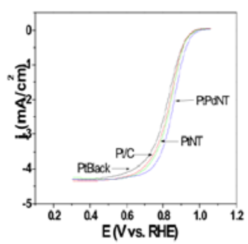


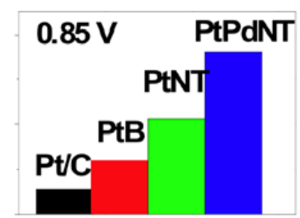












Milestones

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

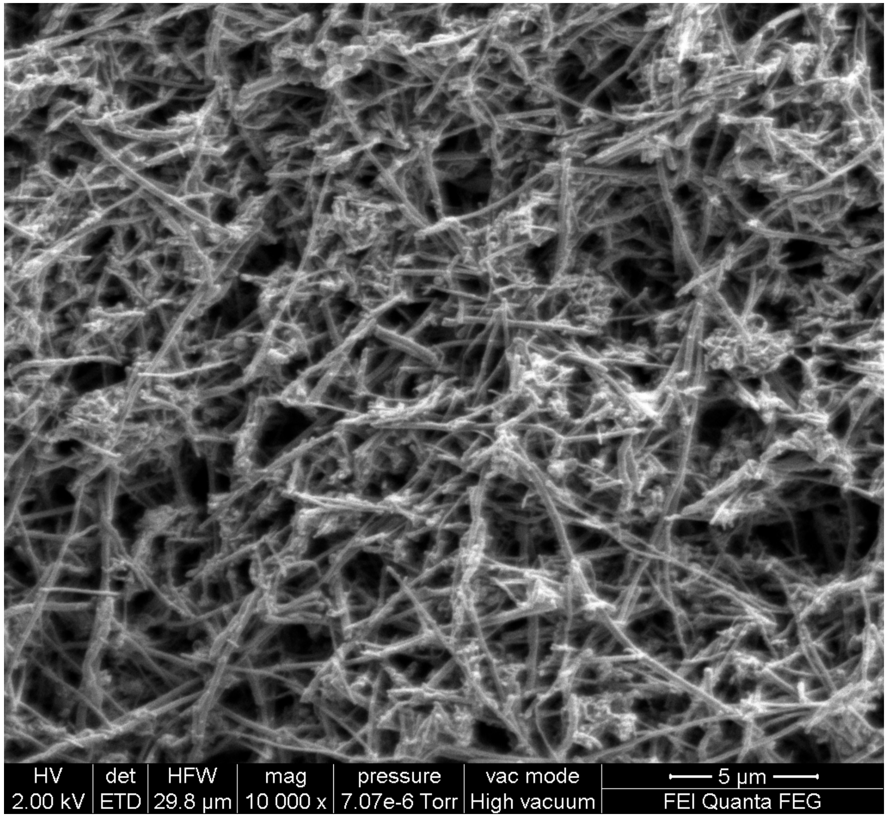
Participant	FY09-10 (Year 1)
LANL	$1,400,000
ORNL	$100,000
Universities	$275,000
Industry (Ballard)	$158,000
TOTAL Year 1	$1,933,000

LANL Low PGM Synthesis

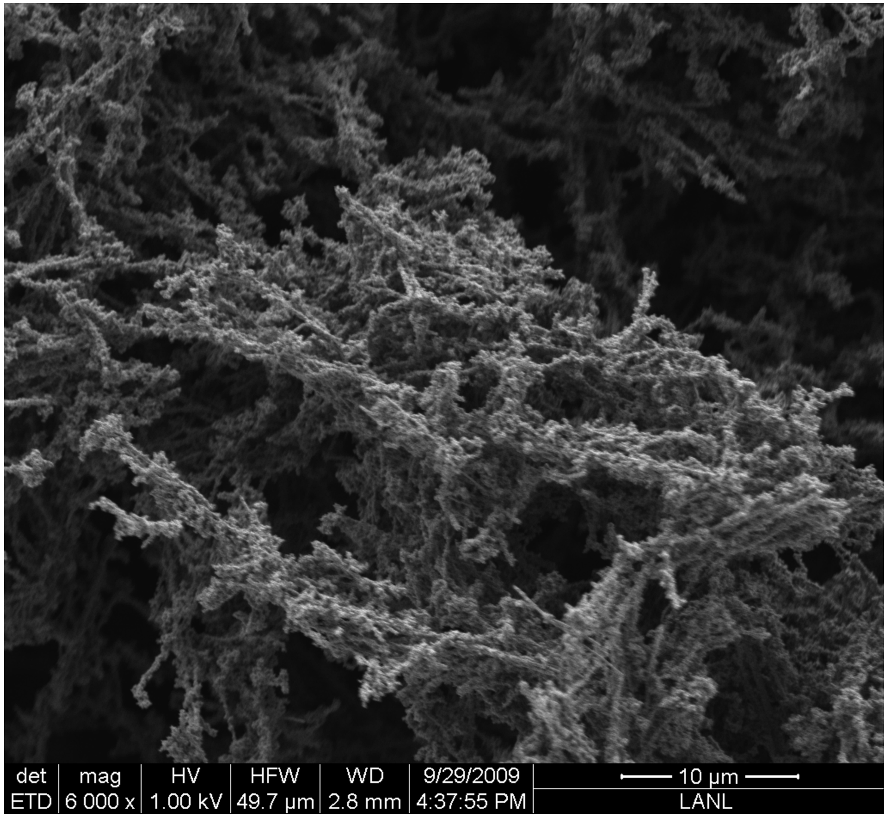
- Develop novel geometry supported catalysts:
  - Carbons-
    - Pyrograf nanowires
    - Multiwall Carbon Nanotubes (MWCNT)
  - Conducting Polymers:
    - Fibron Polypyrrole
    - Chemically deposited Polypyrrole
    - Electrochemically deposited and aligned Polypyrrole
- Investigate anchoring chemistries: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

Activated Pyrograf w/ PPy Coatings

Light deposit

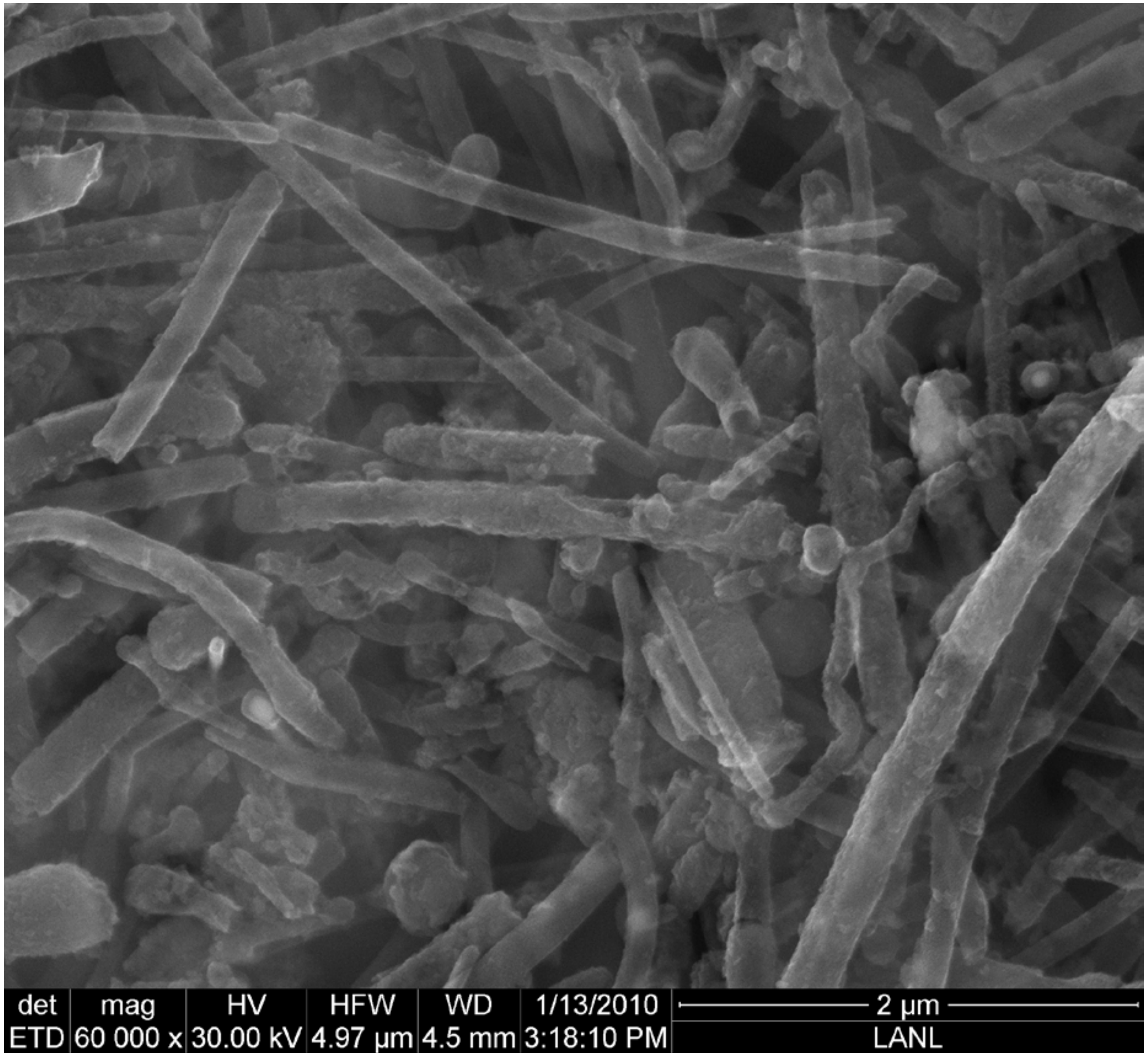


Heavy deposit



bulk chemical pyrrole deposition

Improving Adhesion Using Titanium Interlayers:



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

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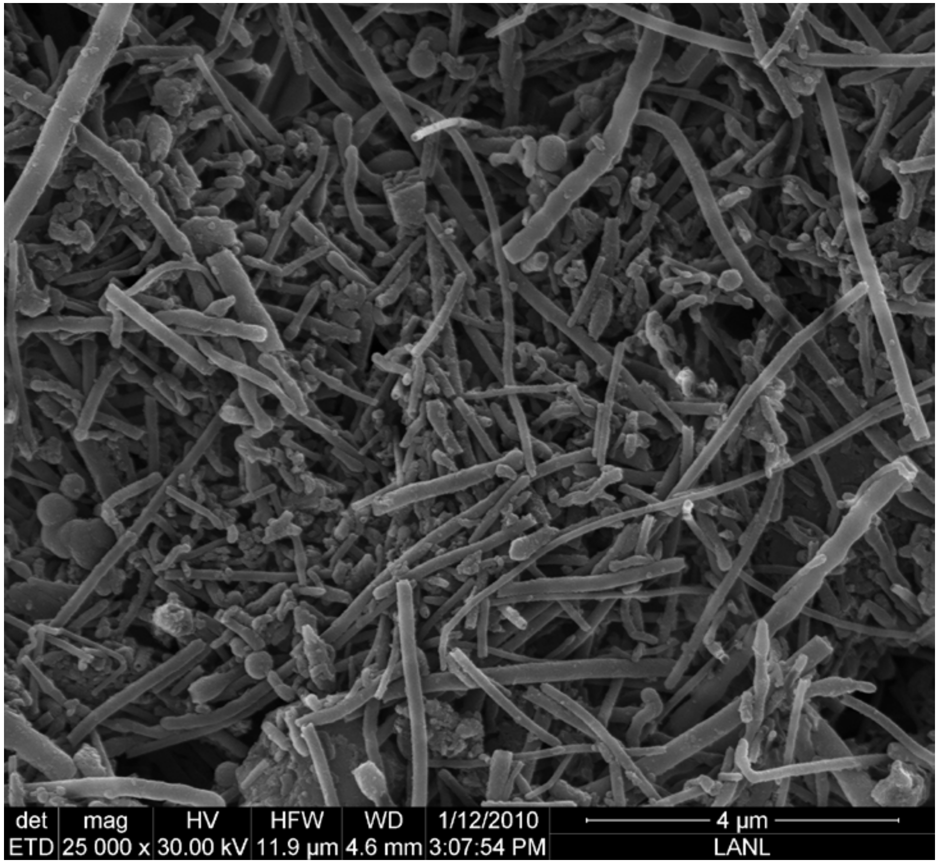
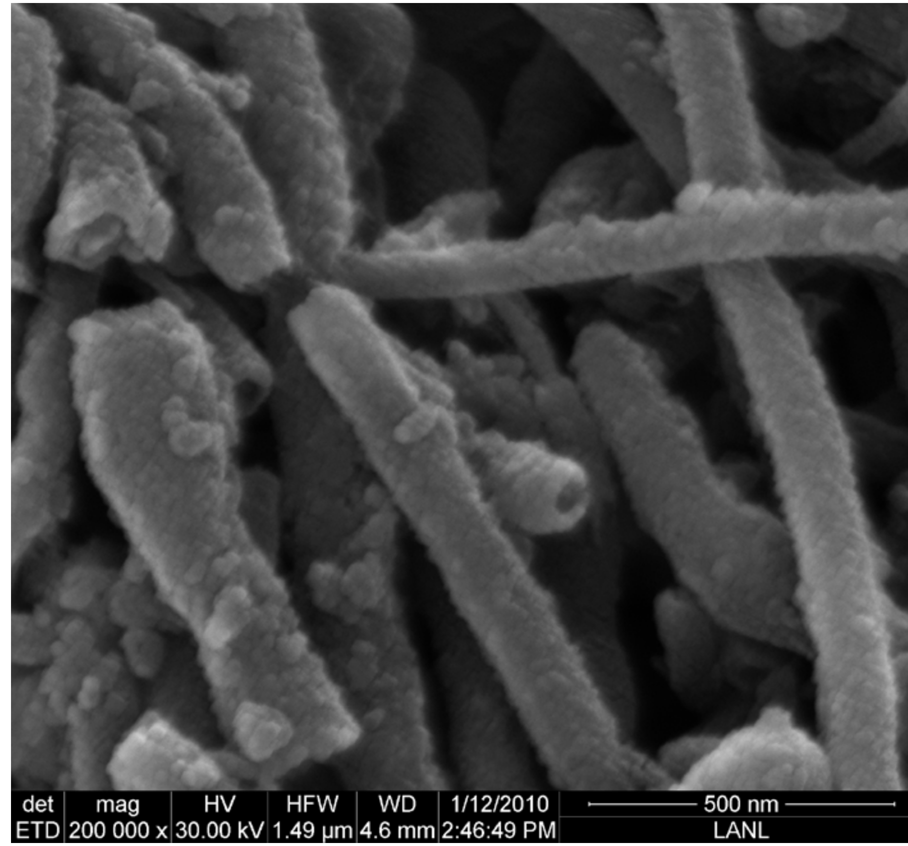
Activated Pyrograf w/ Ti & 0.05 mg Pt/cm^2 Sputter Deposition





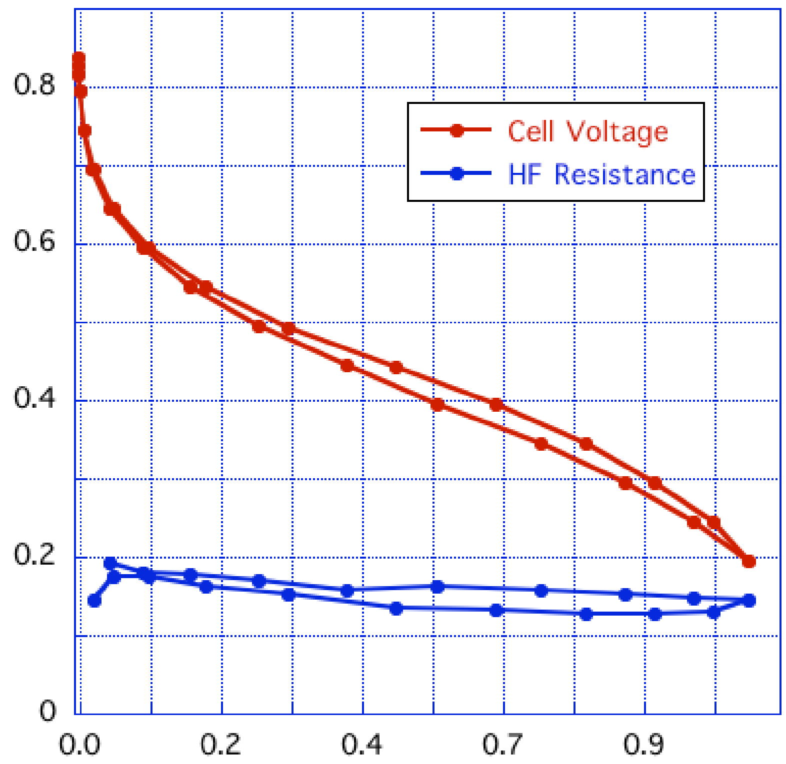
- Uniform Pt coating 20 nm particles

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

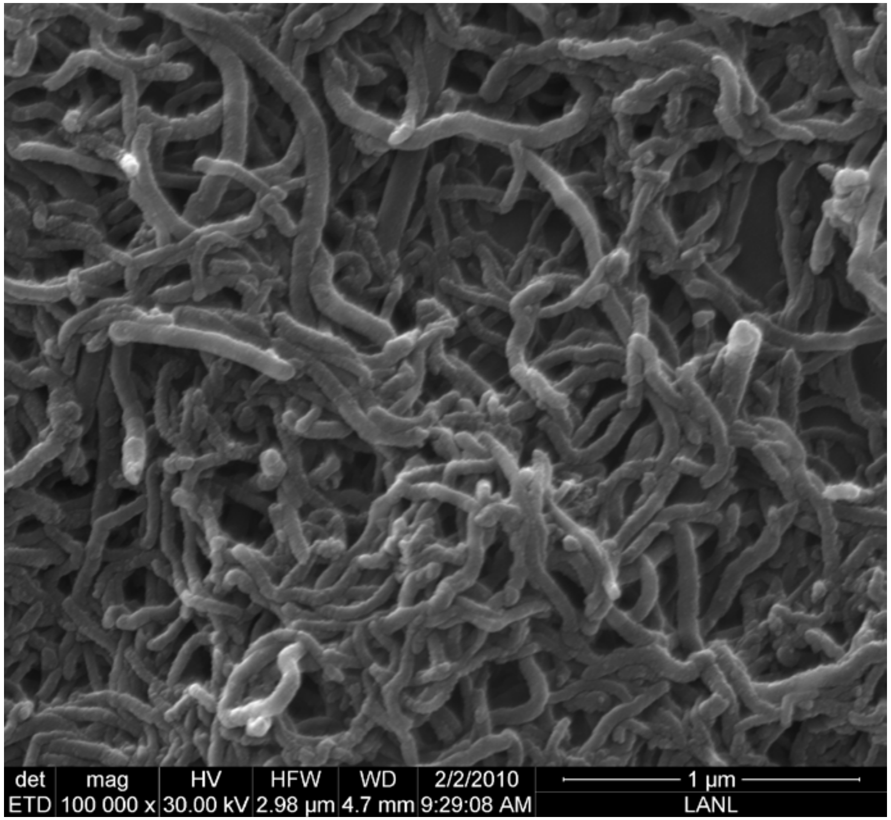
Activated Pyrograf w/ Ti & Pt Sputter Deposition

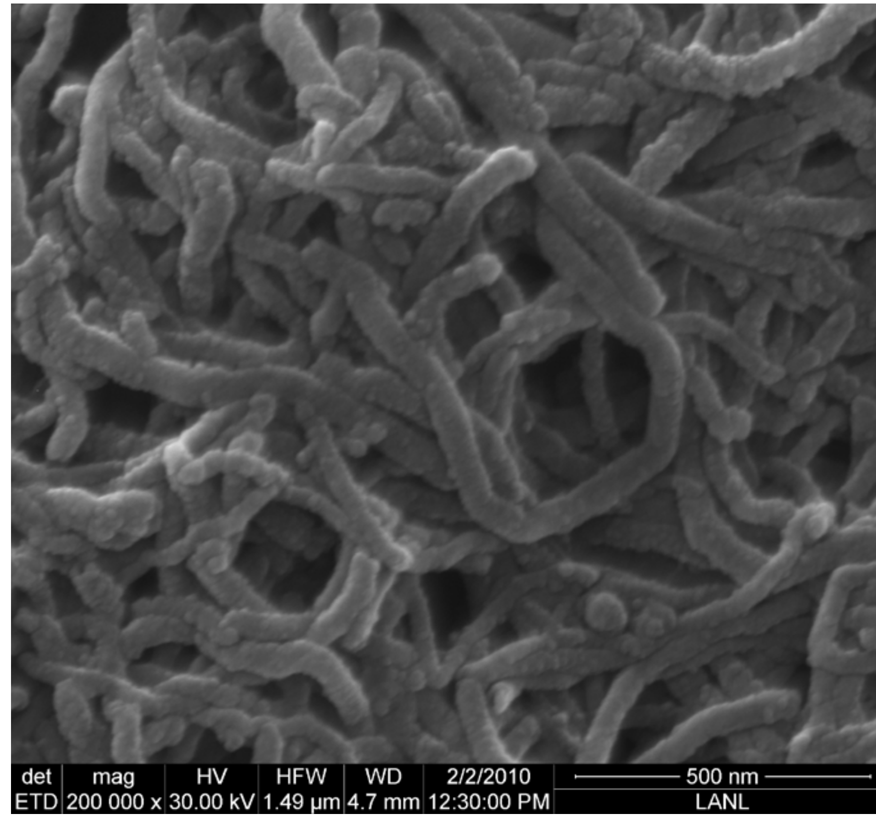
Kinetic region losses at low cathode loadings

Need to improve ionomer catalyst interface



Activated MWCNTs 0.05 mg Pt/cm^2





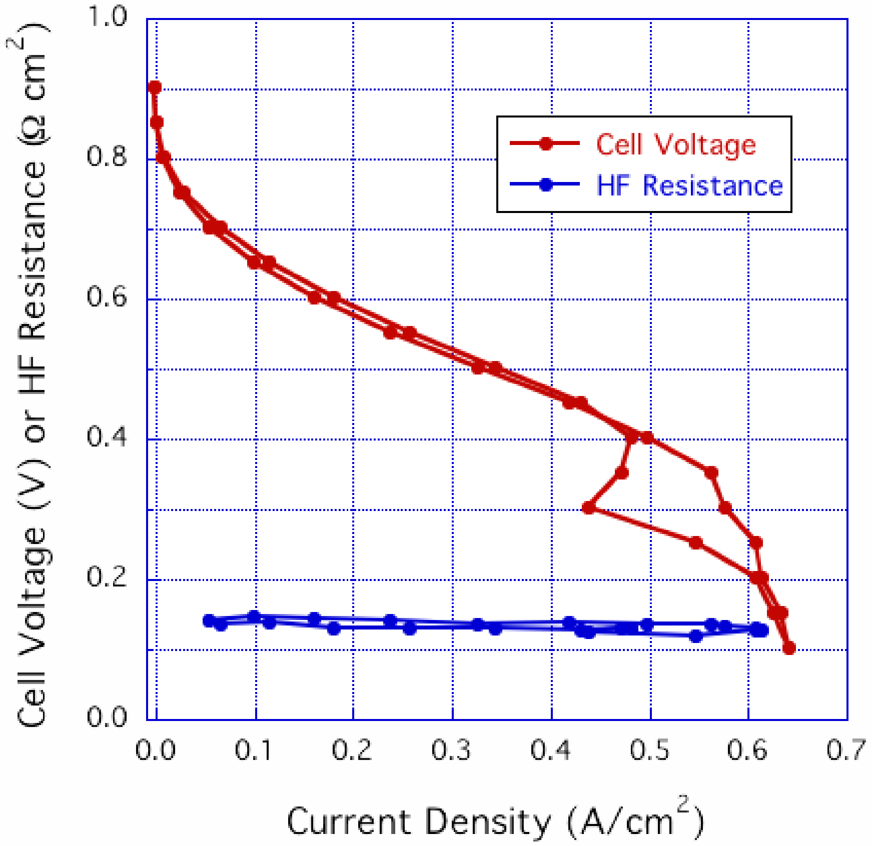
~ 8 nm crystallites (XRD) & uniform coating

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



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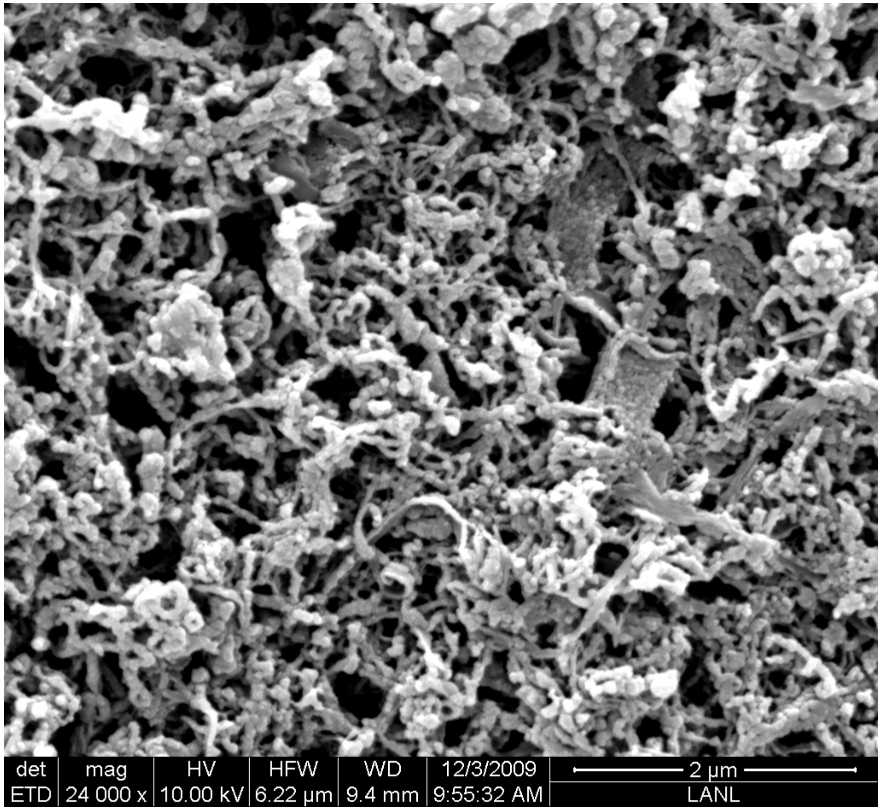
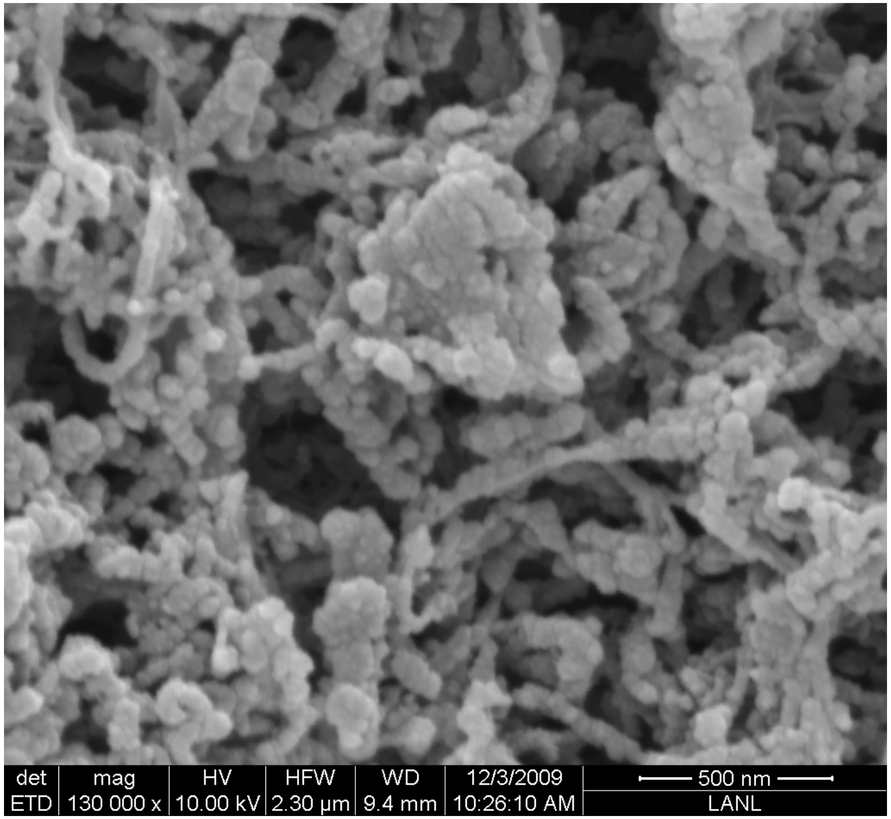
Pt on Polypyrrole- Fibron Materials

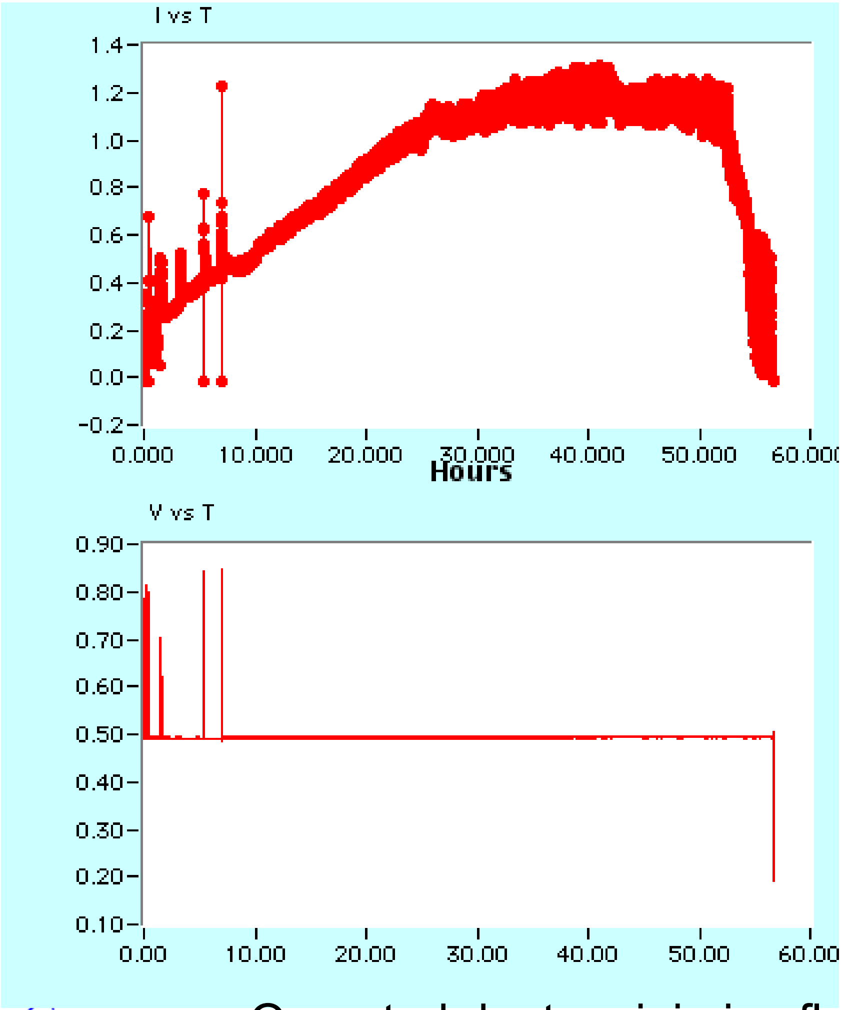


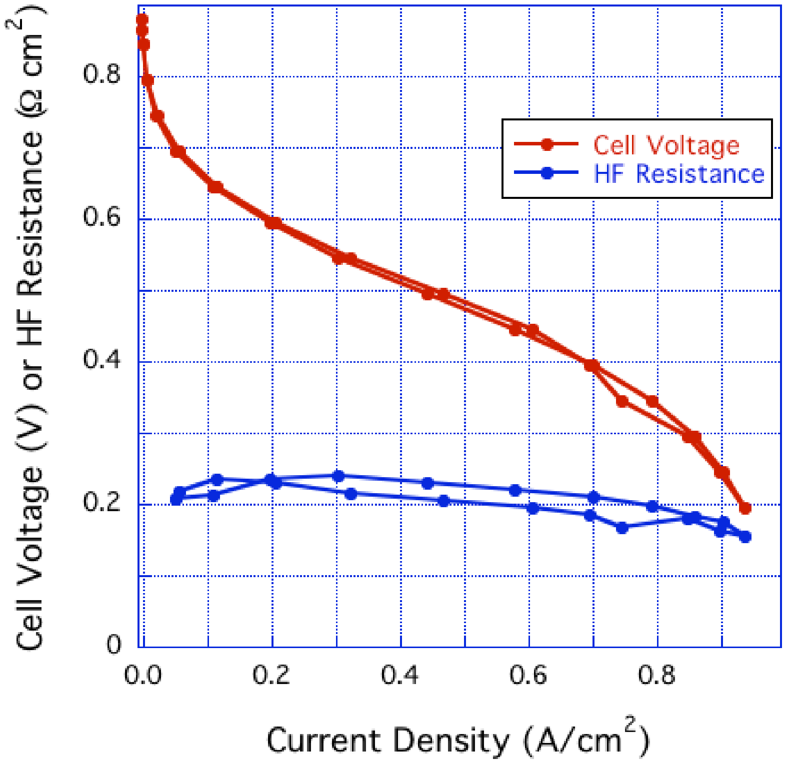


Fibron PPy w/ 0.05 mg Pt/cm^2 sputter deposition

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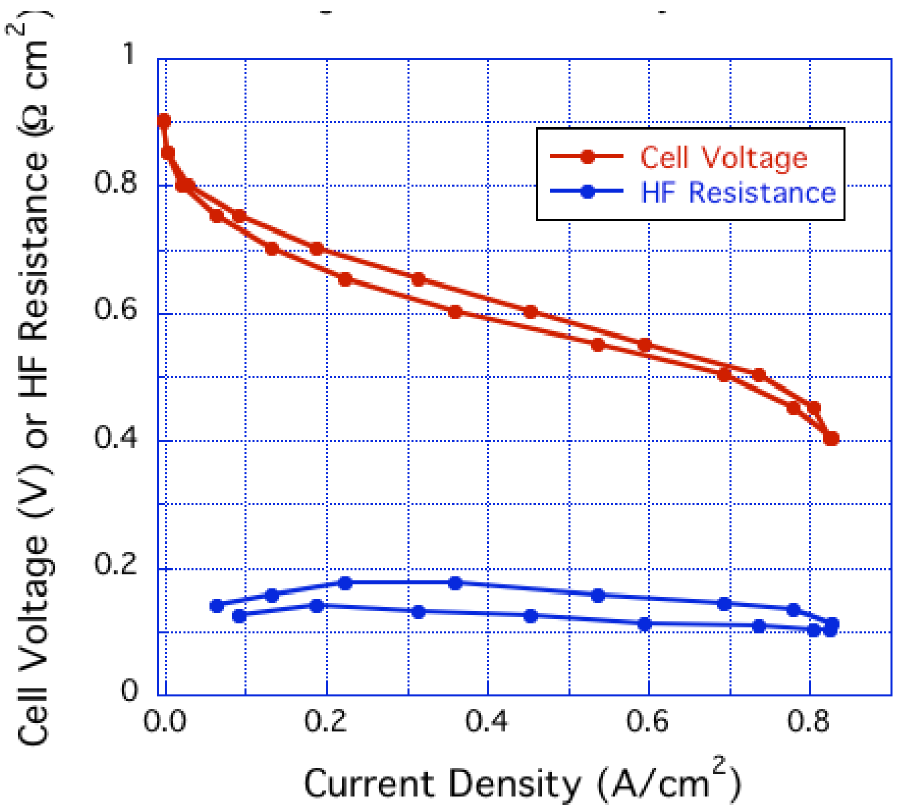
Fuel Cell Testing of Fibron Supported Pt 0.05mg Pt/cm^2

- 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

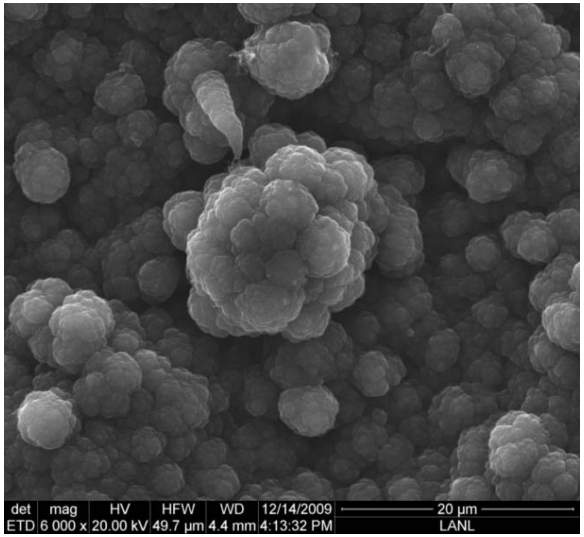
Approach 1:

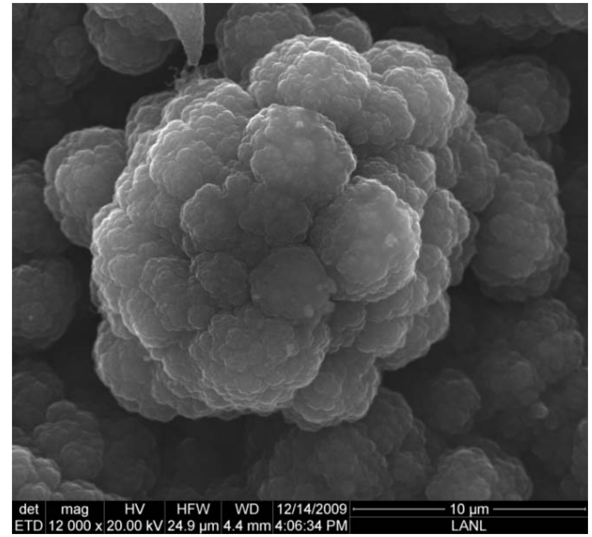
1. Electropolymerization of PPY nanowires (with heparin, starch, etc) on GDL's with different %Teflon® and porous structure
2. Vapor deposition of Pt onto PPY nanowires
3. Assembly of fuel cell using a half MEA as anode and the prepared GDL with PPY/Pt nanowires as cathode

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

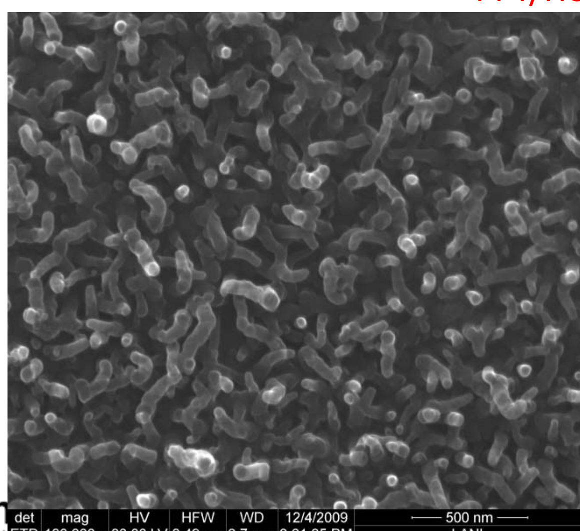
Electropolymerization of PPY dendrites

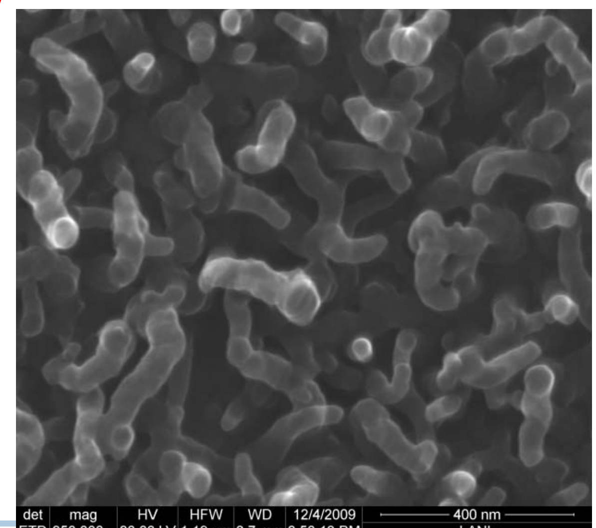




Electropolymerization of PPY nanowires on Glassy-Carbon

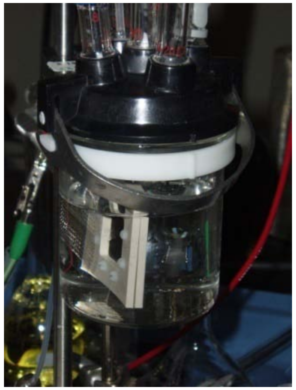
PPY/Heparin on Glassy-Carbon



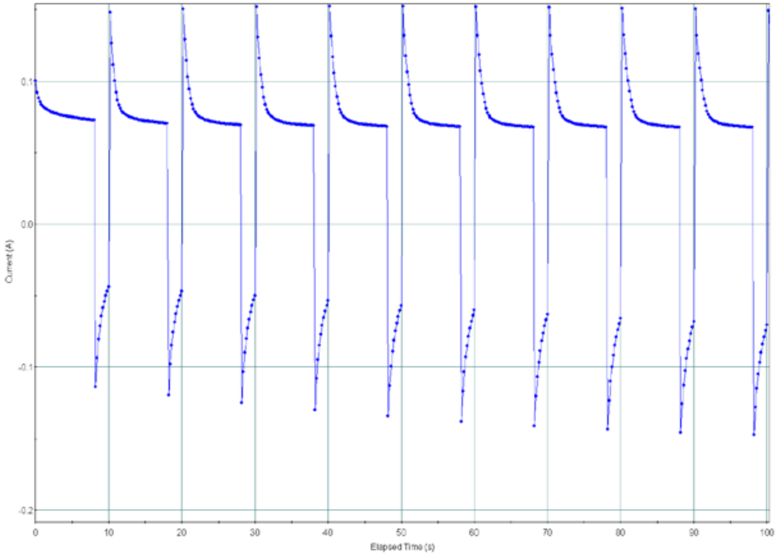


Electropolymerization of PPY nanowires on GDL

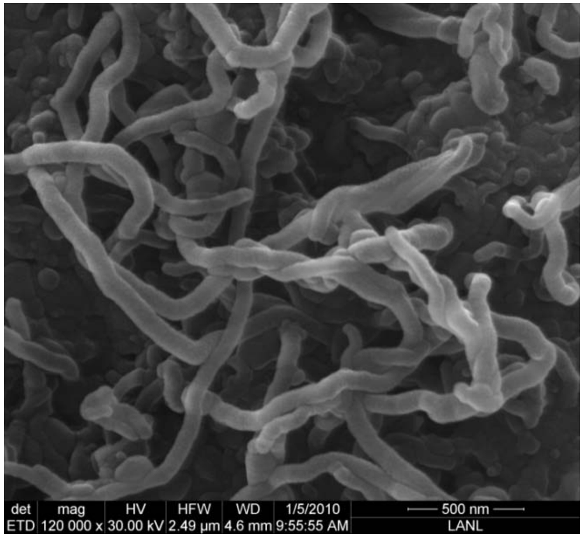
Electrochemical Cell



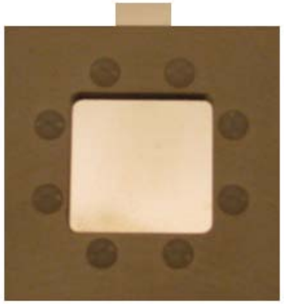
Electropolymerization of PPY nanowires using multipotential steps +0.85V (8s) / -0.3V (2s) vs Ag/AgCl



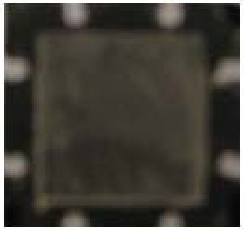
PPY/Heparin on GDL



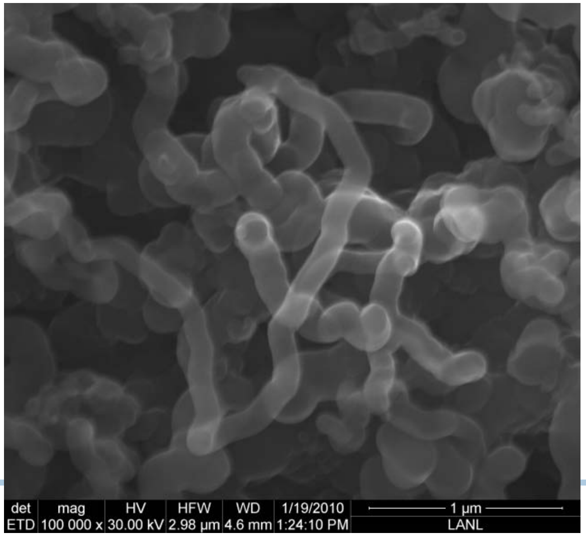
Electrode Holder



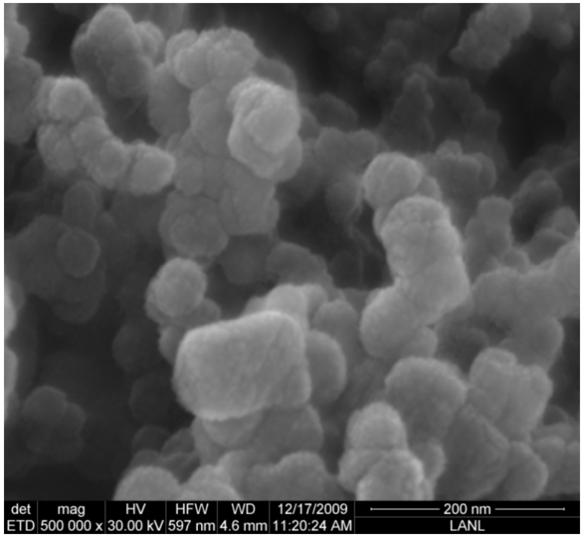
PPY/Pt nanowires on GDL



PPY/Starch on GDL

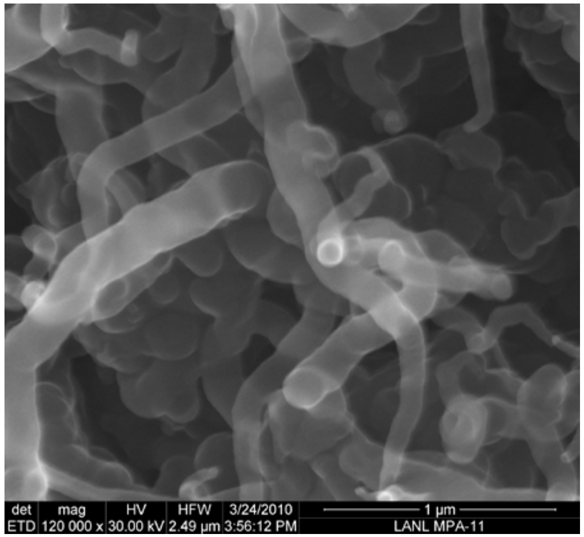


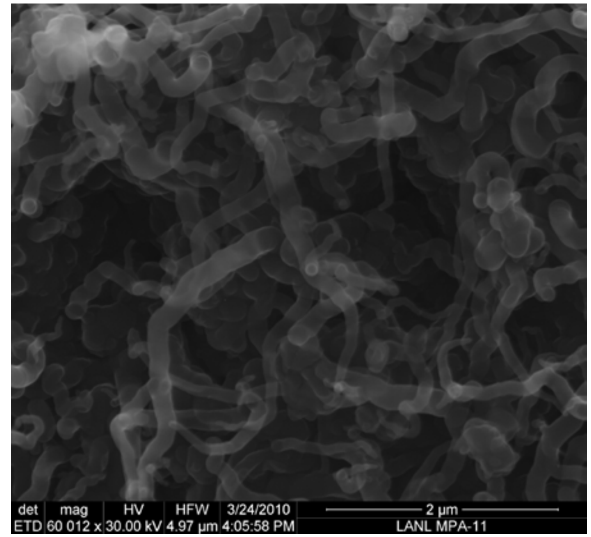
PPY/Pt nanowires on GDL

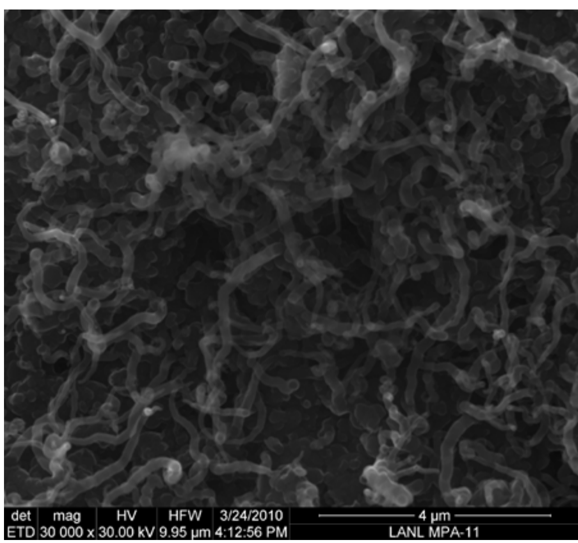


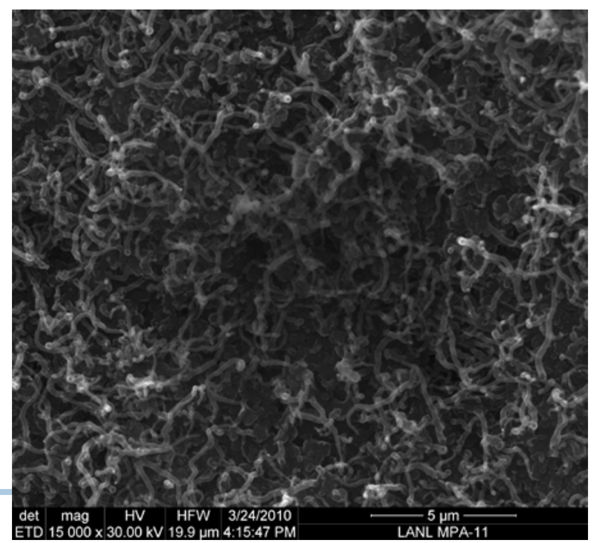
Electropolymerization of PPY Nanowires on GDL (SGK-GDL-24BC: 5% Teflon® Substrate ; 23% Teflon® MPL)

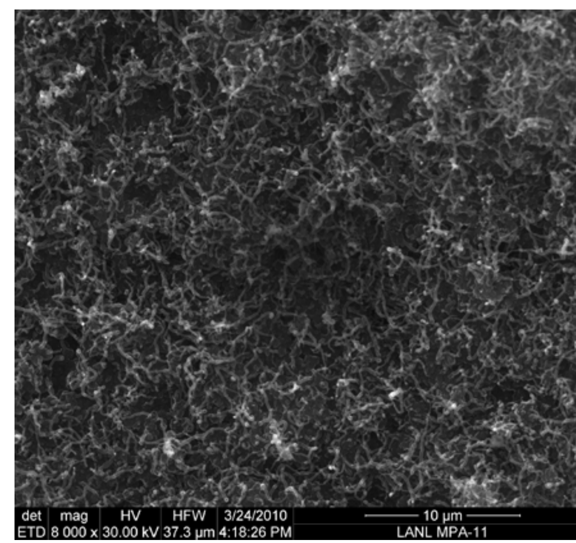
[Py]=0.1M ; [starch]=0.02wt%
Multipotential steps: +0.85V (8s) / -0.3V (2s) vs Ag/AgCl
t=20min







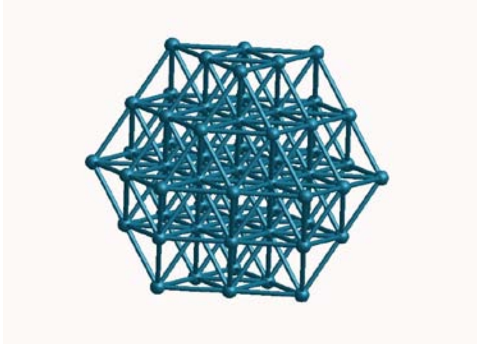




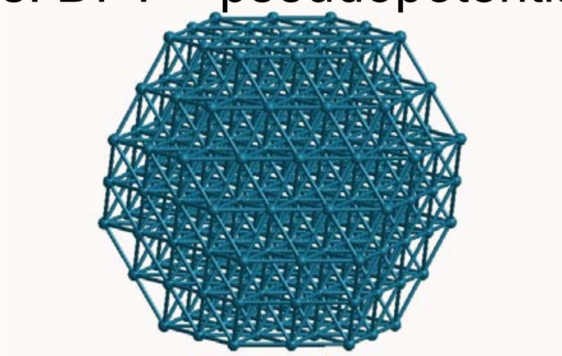
Design of Active and Durable Nanocatalysts for FC Guided by Computational Methods

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))

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Summary

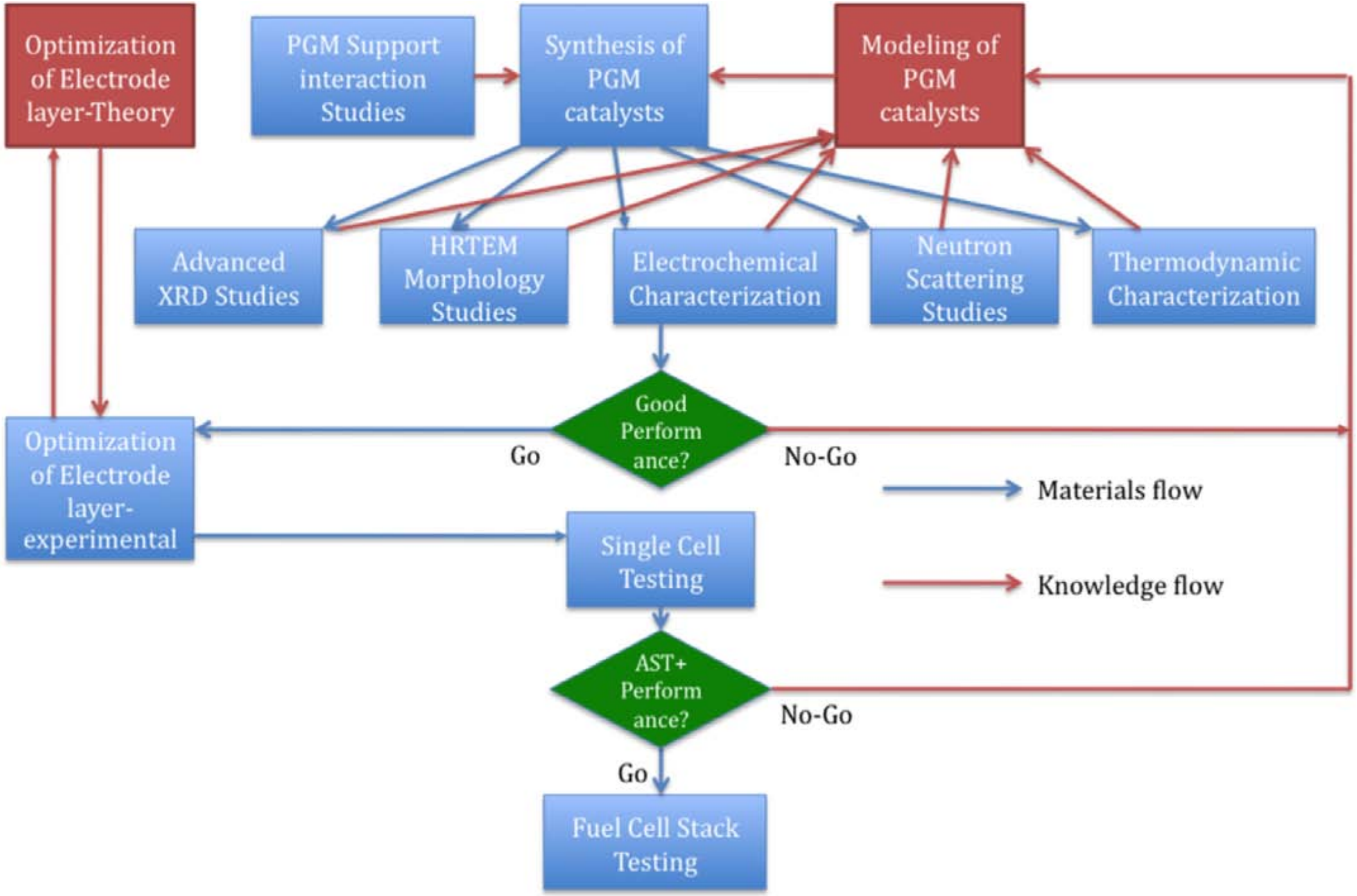
- We have synthesized novel Pt/ support structures using nanowire supports
  - Carbons
  - Conducting Polymers
  - Adhesion layers investigated
- Characterized new materials
- Fuel cell performance testing has commenced
- RDE measurements have begun
- DFT calculations commenced
- Calorimetry experiments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

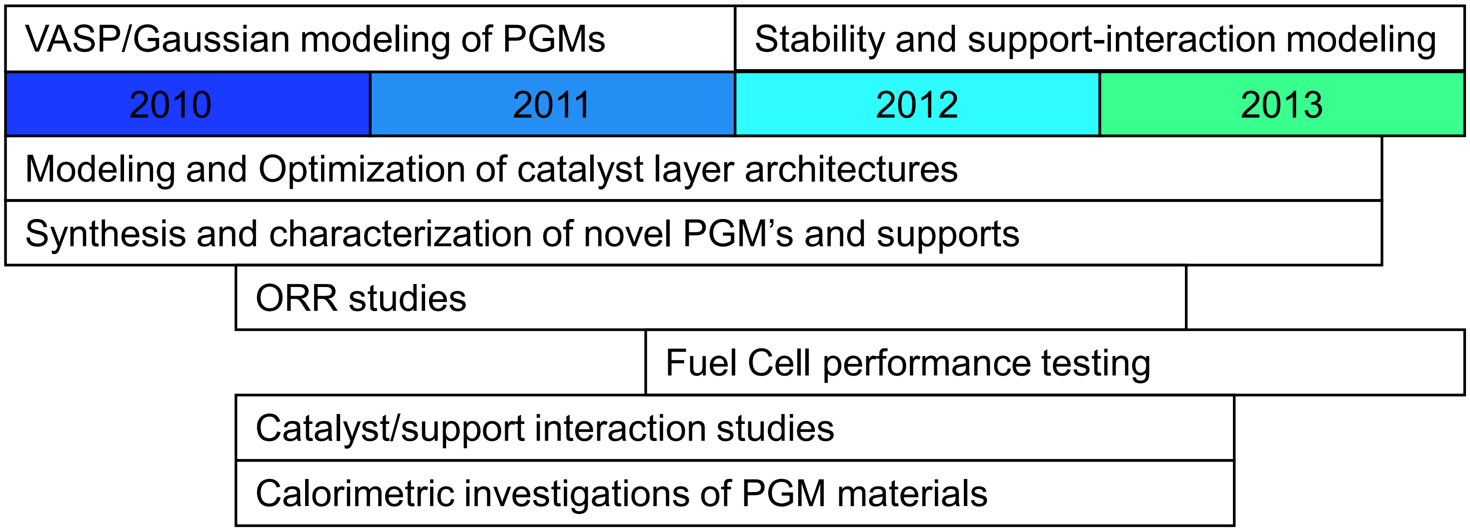
We gratefully acknowledge funding from the US DOE Office of Fuel Cell Technologies

Technical Approach

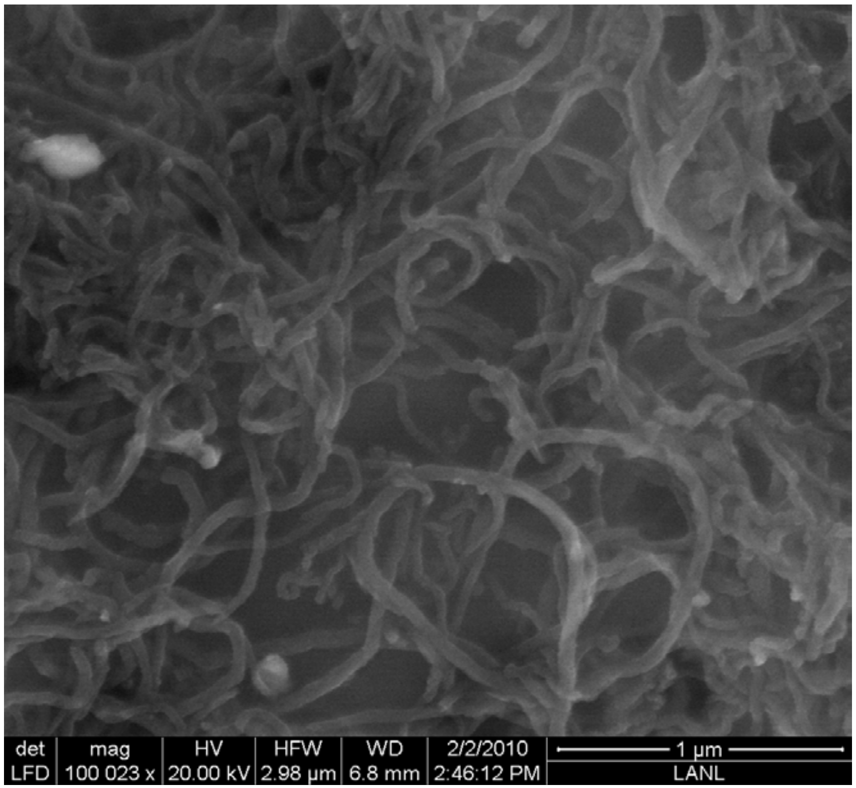


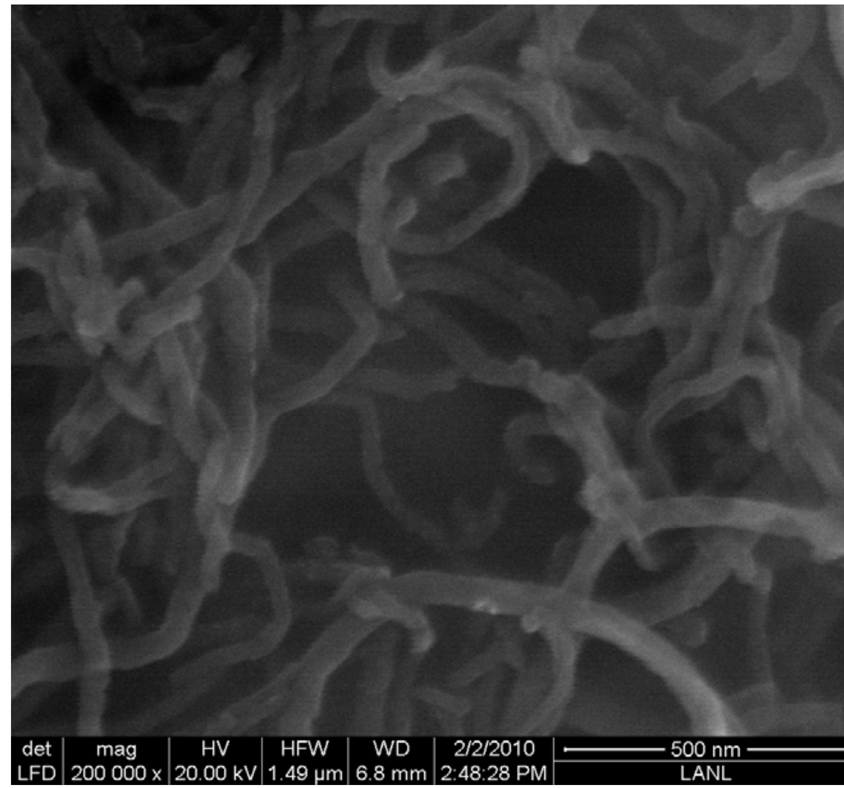
Timeline

Project initiated in Sept FY2009 for 4 years



Activated MWCNT's





- Surfaces pretreated with nitric acid etch

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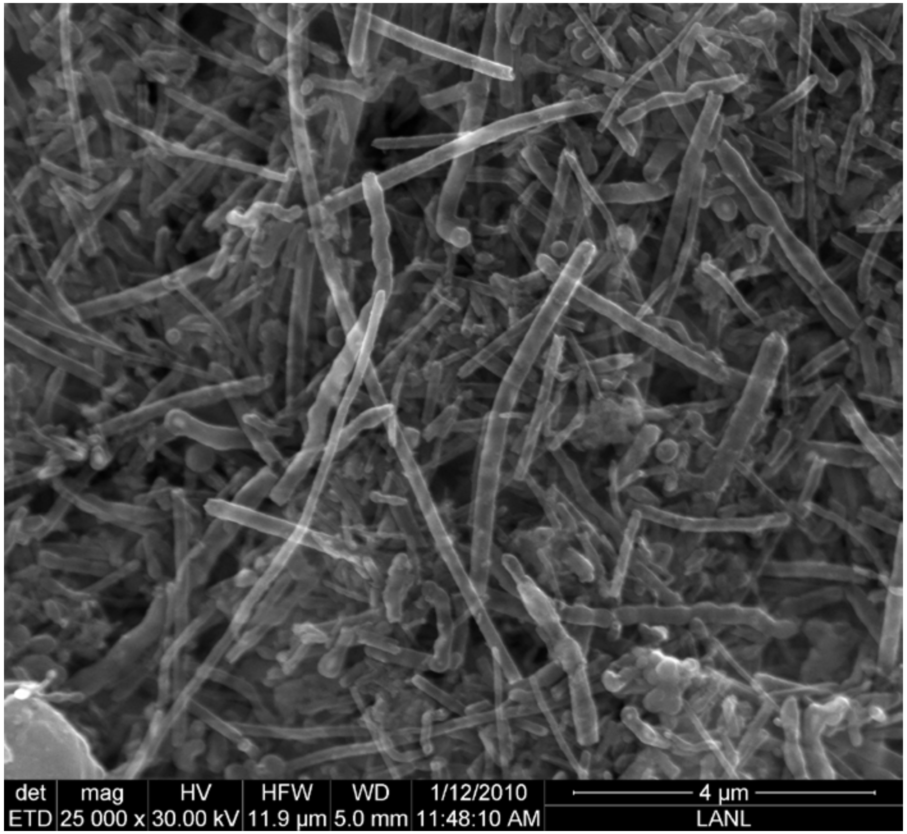
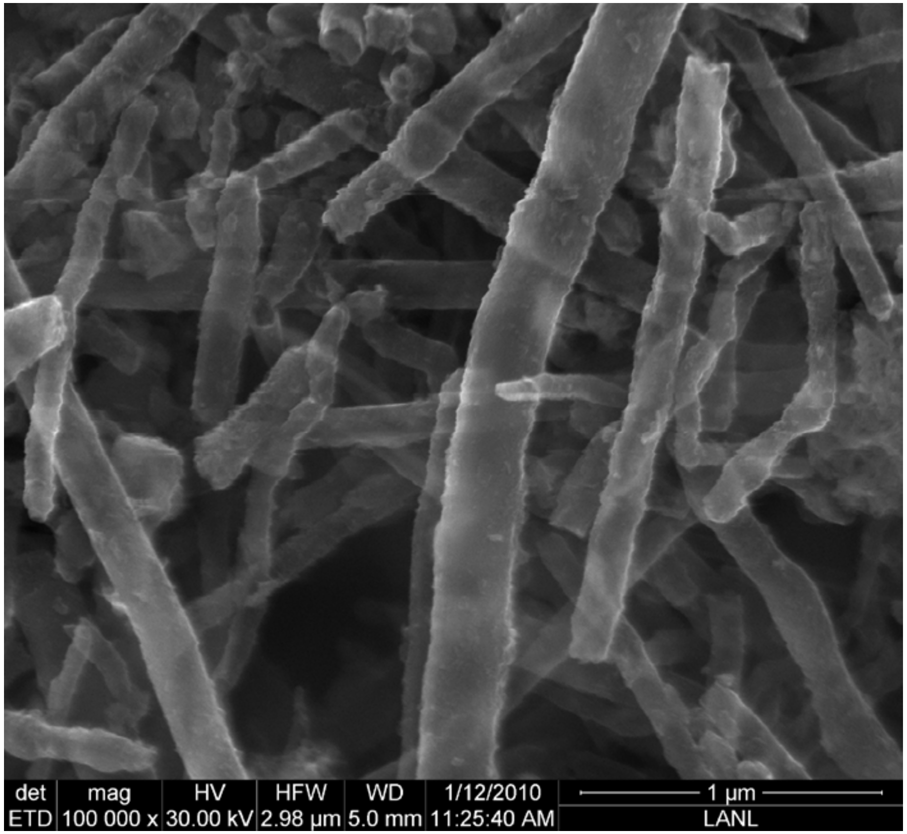
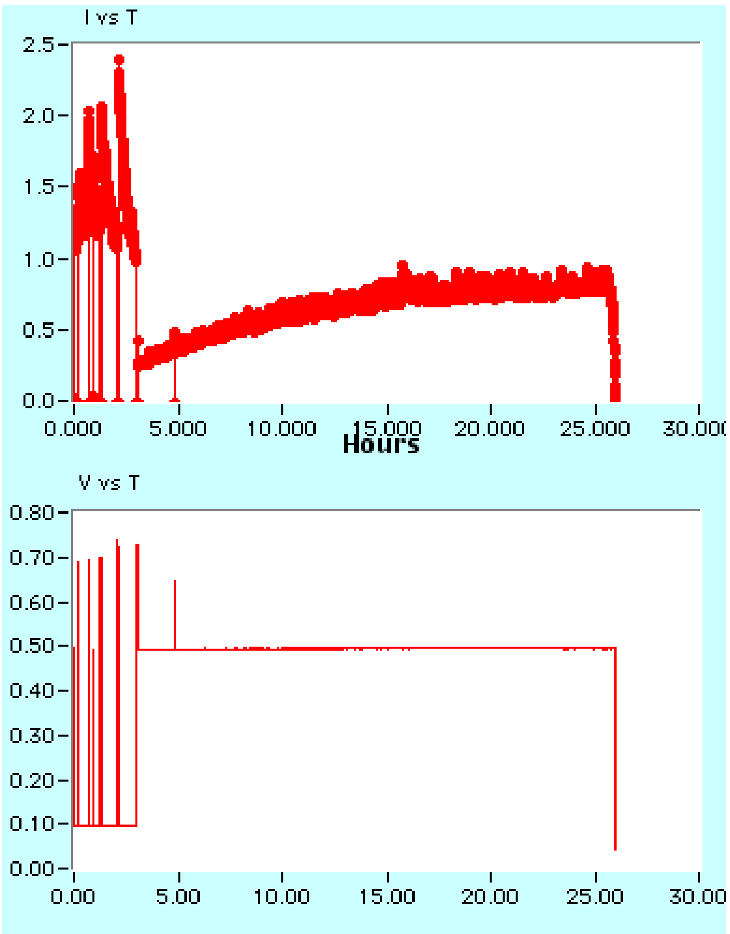
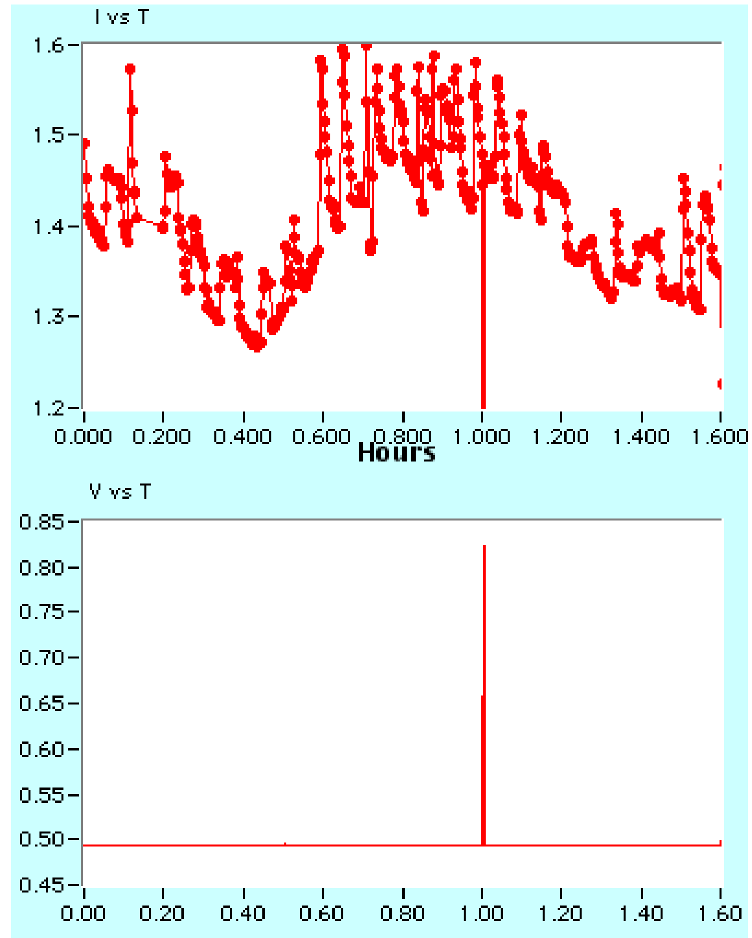
Activated Pyrograf Carbon Nanowire Supports





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





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