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DOE Hydrogen Program

Novel PEMFC Using Aligned Carbon Nanotubes as Electrodes in MEA

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U.S. Department of Energy

UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

DOE Hydrogen Program

Timeline

- Start – January 2007
- End – December 2008
- % Completion – 65%

Budget

- Total Project Funding
  - DOE $ 1,000 K
- Funding Received in FY07
  - $ 420 K
- Funding for FY08
  - $ 580 K

Barriers

- Barriers
  A. Durability
  B. Cost
  C. Performance
- Target
  - MEA Cost: $10/kW
  - Durability: 5000 h @ 80ºC

Partners

- Interaction/Collaboration
  - LANL: Training class on MEA preparation
  - Plug Power: Consulting

Objective

DOE Hydrogen Program

- To develop a novel aligned carbon nanotube (ACNT)-based membrane electrode assembly and fuel cell with:
  - improved efficiency
  - reduced Pt usage
  - simplified stack design

Characteristic	Units	DOE Technical Target 2010	DOE Technical Target 2015
Platinum group metal total loading	Mg PGM/cm^2 electrode area	0.3	0.2
Durability with cycling Op. Temp ≤ 80 C Op. Temp ≥ 80 C	 Hours Hours	 5,000 2,000	 5,000 5,000
Electrocatalyst area loss	%	<40	<40

Milestones

DOE Hydrogen Program

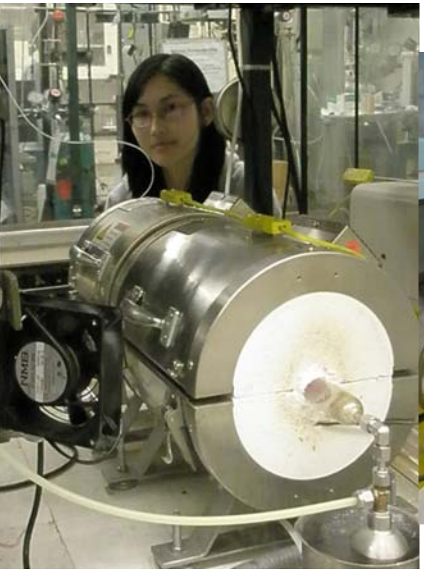
- **Prepare and characterize the structure and activity of two transition metal functionalized and one Pt decorated ACNT samples as electrode catalysts. 07/07 √**
- **Develop a transferring method to apply the ACNT layer to the membrane electrolyte with nanotube orientation intact. 07/07 √**
- **Fabricate one or more catalyzed ACNT-based MEA with carbon nanotube alignment intact. 03/08 √**
- **Assemble and evaluate the performance of one or more PEM fuel cells with the MEA composed of ACNT-based electrode catalysts (July 2008). 07/08 →**

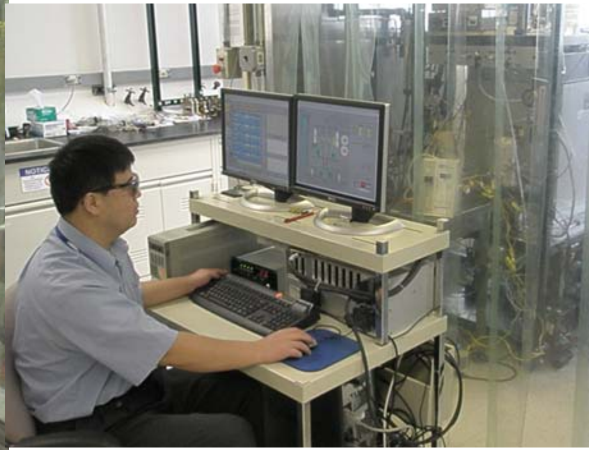
We are on track to complete an aggressive plan covering the entire process development of a new ACNT based MEA/PEMFC concept

Approach

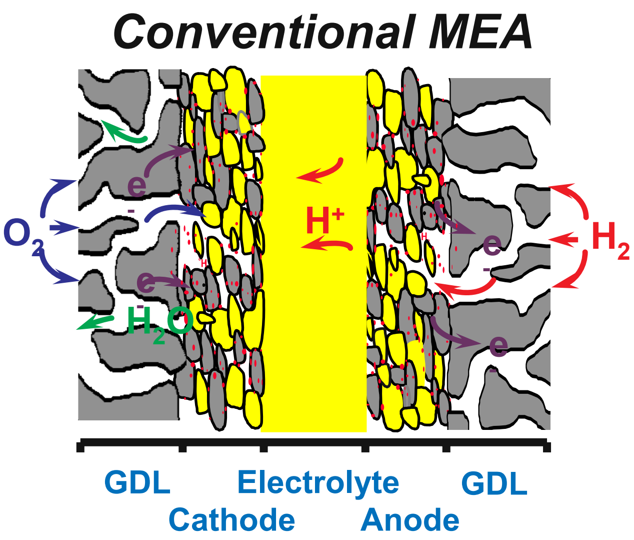
DOE Hydrogen Program

Task1. ACNT Growth & Catalyzing	Task 2. ACNT MEA Development	Task 3. Packaging & Testing
■ ACNT layer synthesis ■ Catalyzing through CVD & wet chemistry ■ Structure & activity characterization	■ ACNT coating & transfer method development ■ ACNT based MEA process development	■ Packaging method optimization ■ Cell performance evaluation

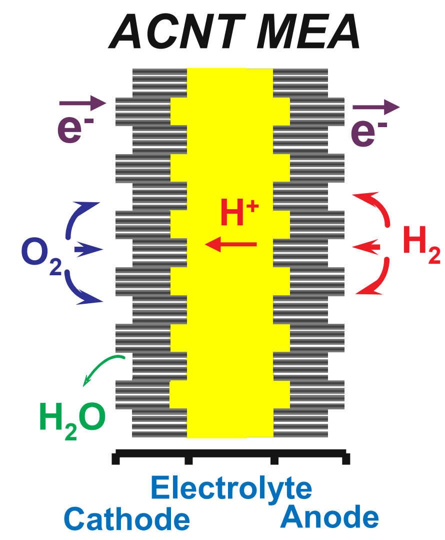


Expected Benefits of ACNT as Nanostructured MEA Support



- Catalyst utilization
- Support stability
- electrical & thermal conductivity
- Mass transport
- Built-in catalytic activity



Accomplishment Summary

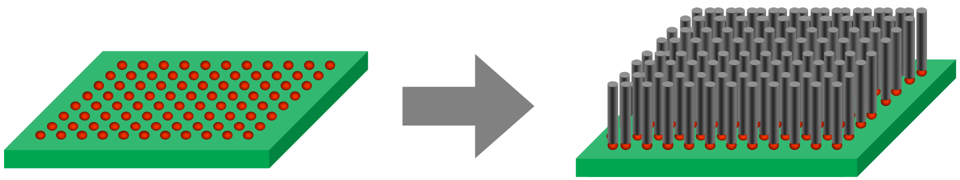
DOE Hydrogen Program

- Methods of preparing uniform, high density aligned carbon nanotube (ACNT) layers with adjustable thickness were successfully developed through chemical vapor deposition (CVD) technique.
- A variety of wet chemistry methods were developed to catalyze both unactivated (hydrophobic) and activated (hydrophilic) ACNT surface with good metal dispersion and catalytic activity
- CVD processes were developed to catalyze ACNT by directly depositing highly dispersed Pt through gaseous phase or incorporating transition metal active site into graphene surface.
- MEA fabrication method was successfully developed to transfer ACNT to Nafion membrane with the alignment intact.
- ACNT-MEA's evaluation was initiated; promising performance was observed in single cell tests.

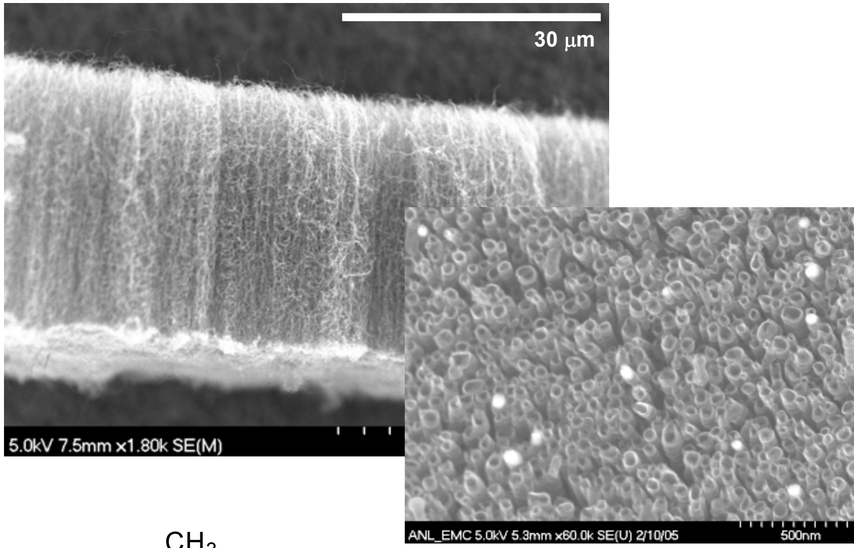
Accomplishments – Task 1: Growing ACNT Layer as Catalyst Support

DOE Hydrogen Program

- Developed a chemical vapor deposition (CVD) method to produce uniform, highly graphitic aligned nanotube layer using low cost, industrial materials
- Optimized process through the design-of-experiment to synthesize ACNT with high surface area and adequate thickness as catalyst support for PEMFC



Seeding Catalyst ***Growing ACNT***

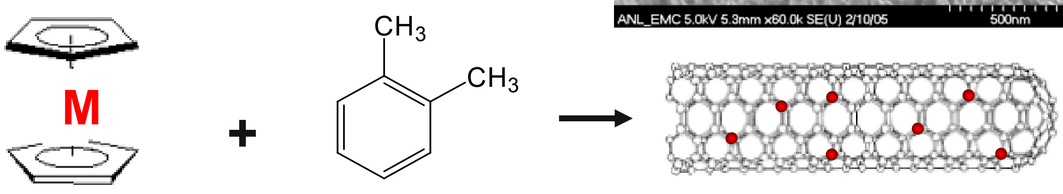


Fabricating ACNT as catalyst support in MEA

- **Multi-walled CNTs**
- **10 nm < Diameter < 100 nm**
- **5 µm < Length < 100 µm**
- **Surface area ~ 100 m^2/g**
- **Density ~ 10^8-10^9 tubes/cm^2**
- **Surface enhancement factor**

  ACNT-MEA: 800 to 4000

  XC72-MEA: ~5000



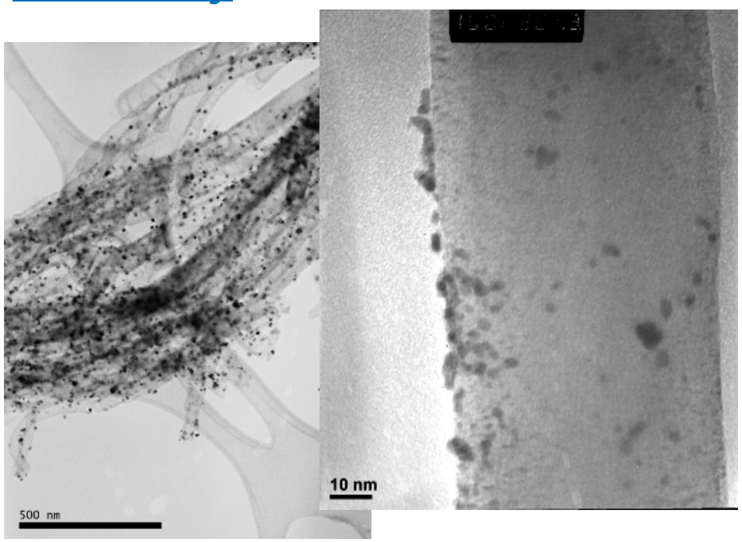
Chemistry and materials adapted in Argonne's process

Accomplishments – Task 1: Catalyzing ACNT with Pt through Wet Chemistry

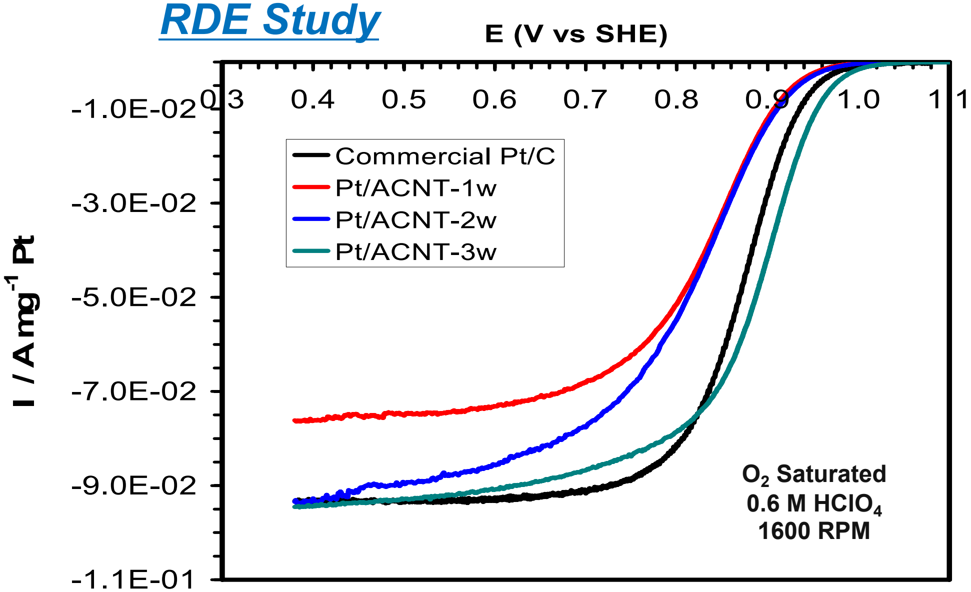
DOE Hydrogen Program

- Developed two surface modification methods to overcome the ACNT hydrophobicity without altering the nanotube alignment
- Modified three wet chemistry methods (micelle, redox, impregnation) to catalyze ACNT surface with or without surface modification; achieved good metal dispersion and excellent activity using industrial catalytic precursors

TEM Study



RDE Study

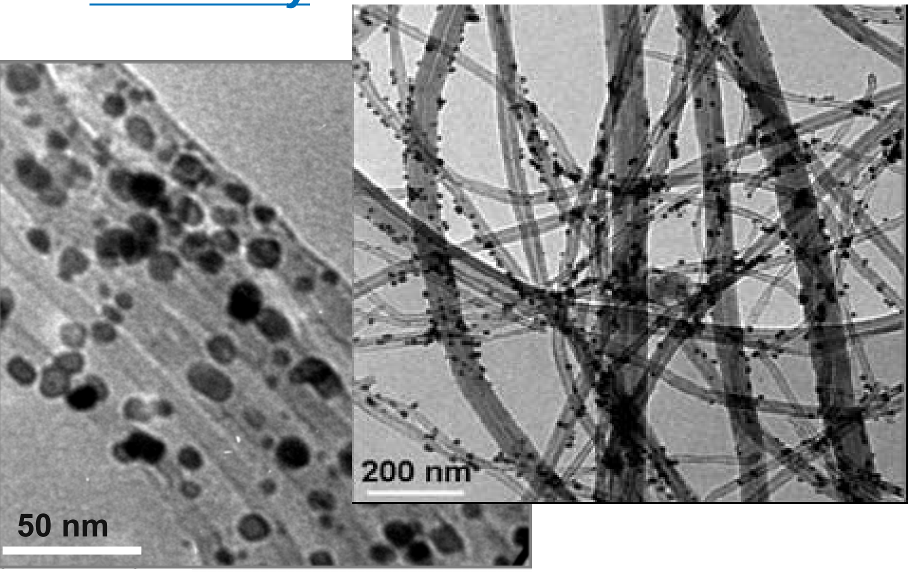


Imagining and electrochemical activity studies showed Pt in ACNT is well-dispersed with comparable kinetics to benchmark commercial catalyst

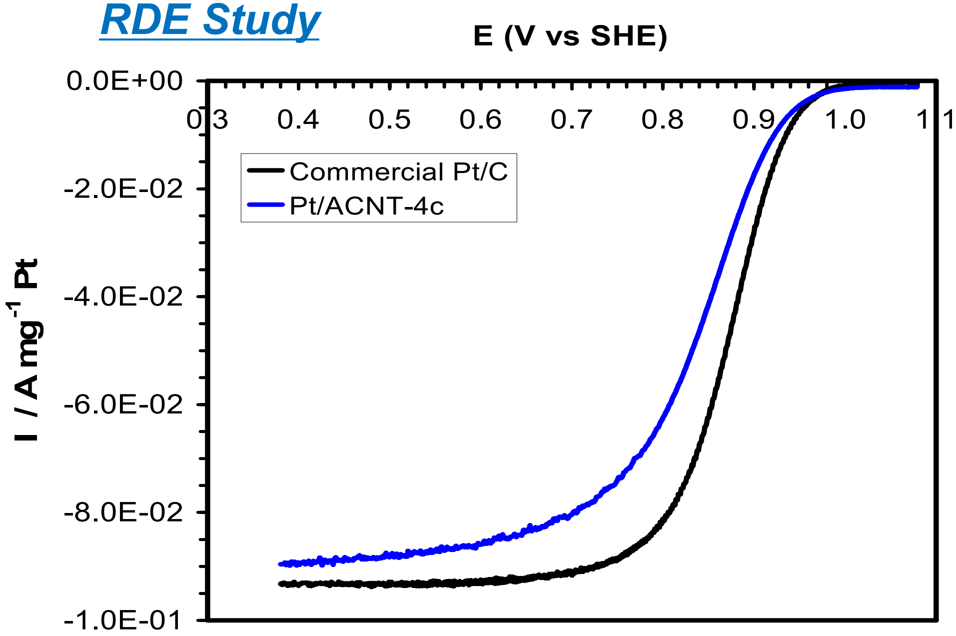
Accomplishments – Task 1: Catalyzing ACNT with Pt through CVD

- Develop a co-CVD process which enables to >20 wt% Pt incorporated in ACNT with high dispersion (particle size = 2 to 8 nm) in one step
- Good electrocatalytic activity was observed in RDE studies

TEM Study



RDE Study



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

Accomplishments – Task 1: Functionalizing ACNT through Transition Metal – Nitrogen Doping

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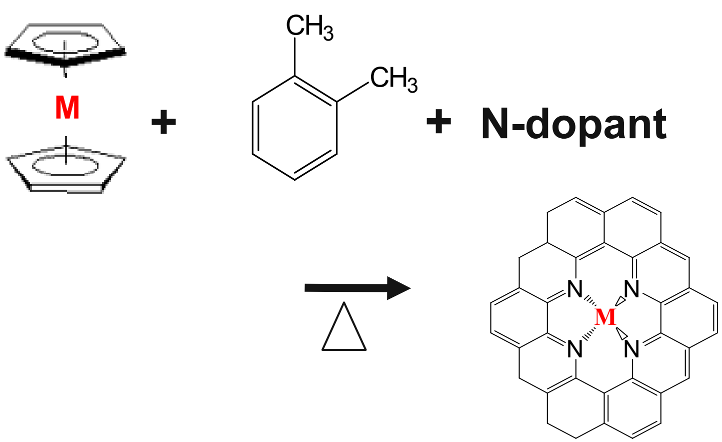
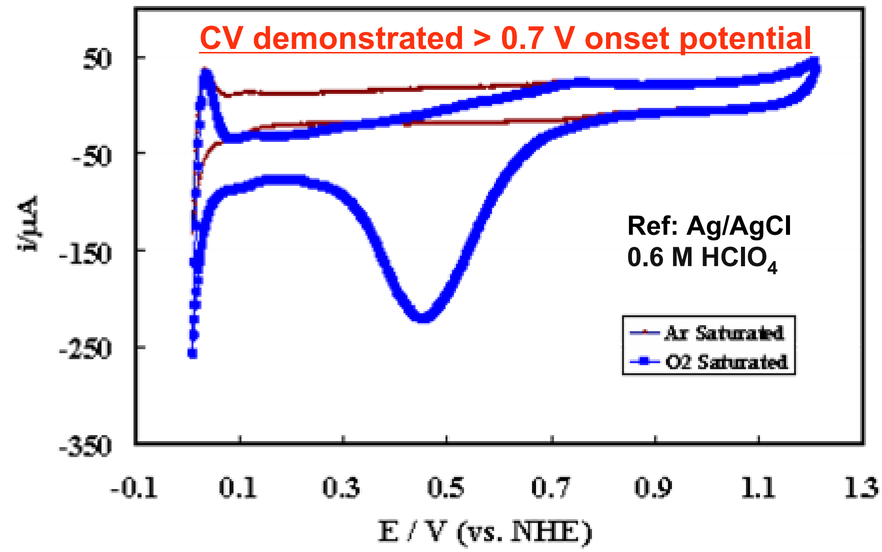
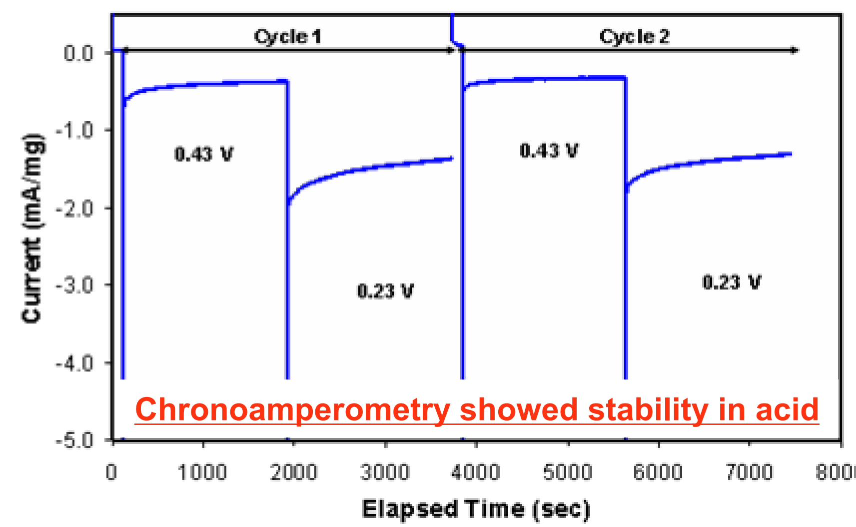
- Develop a CVD method to functionalize ACNT surface with atomically embedded nitrogen and transition metals as catalytic site.
- The sites are active toward oxygen reduction reaction and stable in acidic/ oxidative environments



N-dopant = NH_3, pyridine, etc.
M = Fe, Co, etc.





Accomplishments – Task 1: Understanding of Non-Pt Active Site through Advanced Characterization Techniques

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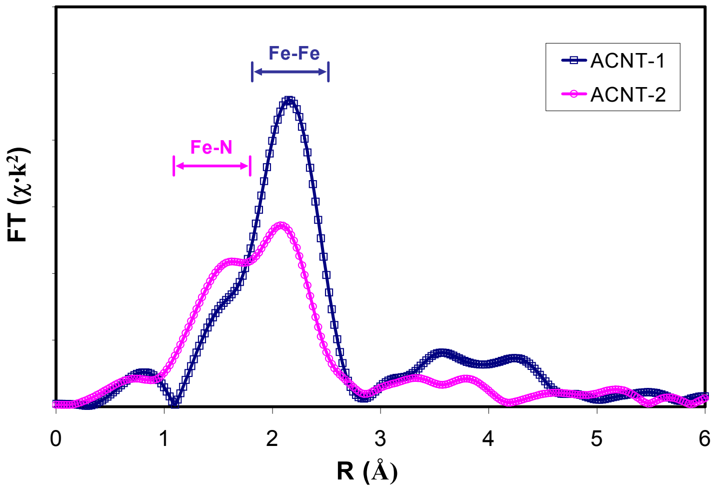
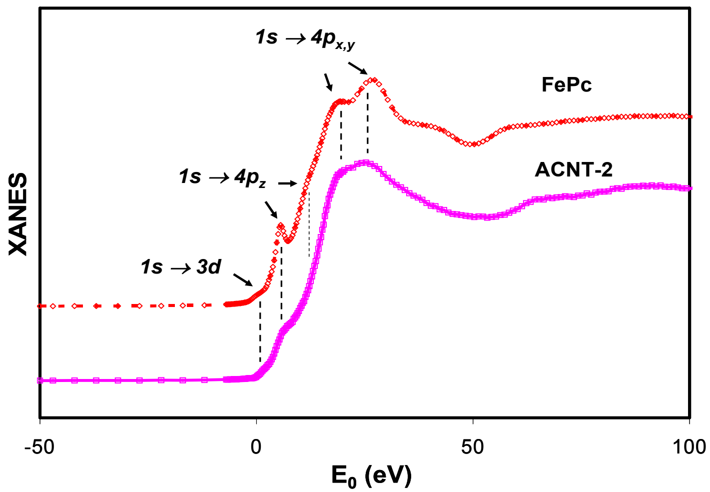
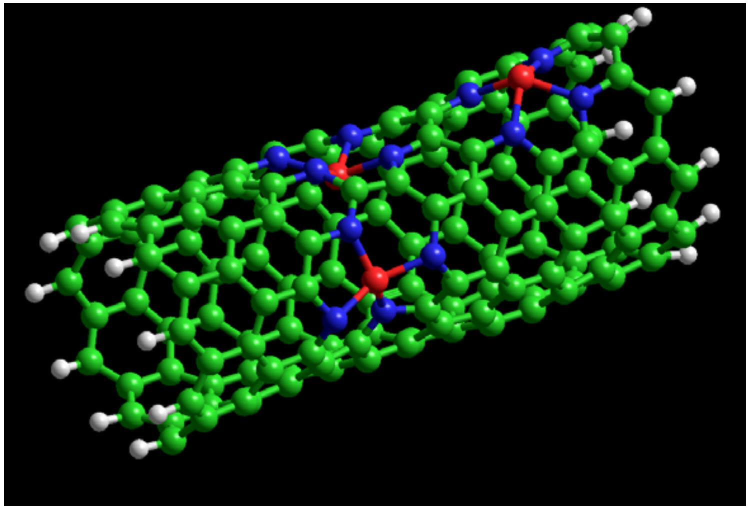
EXAFS & XANES Studies





- *ex situ / in situ* X-ray absorption spectroscopy and HR-TEM identified structure of the ORR active sites

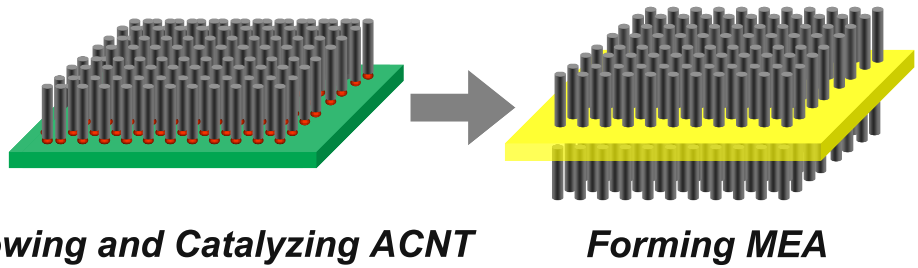


Active site structure - FeN_4

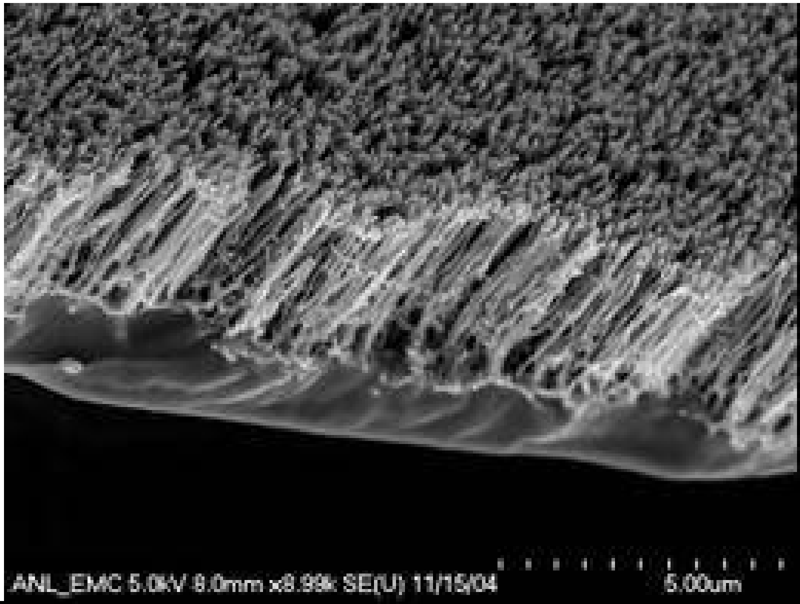
"Aligned carbon nanotubes with built-in FeN4 active site for electrocatalytic reduction of oxygen", J. Yang, D-J Liu, N. Kariuki, L. Chen, *Chem. Comm.* **3** (2008) 329 – 331

Accomplishments – Task 2: ACNT-MEA Fabrication Process Development

- A process was successfully developed to transfer ACNT layer to Nafion® membrane surface with the nanotube alignment intact
- The process involves two binder-coating options and a hot-press method to produce a robust interface of ACNT and membrane
- ACNT transferring process is mainly applied to cathode at present; two sided ACNT-MEA is currently under development



SEM image of ACNT "glued" on thin layer of ionomer



Accomplishments – Task 2: 3D ACNT-MEA Development

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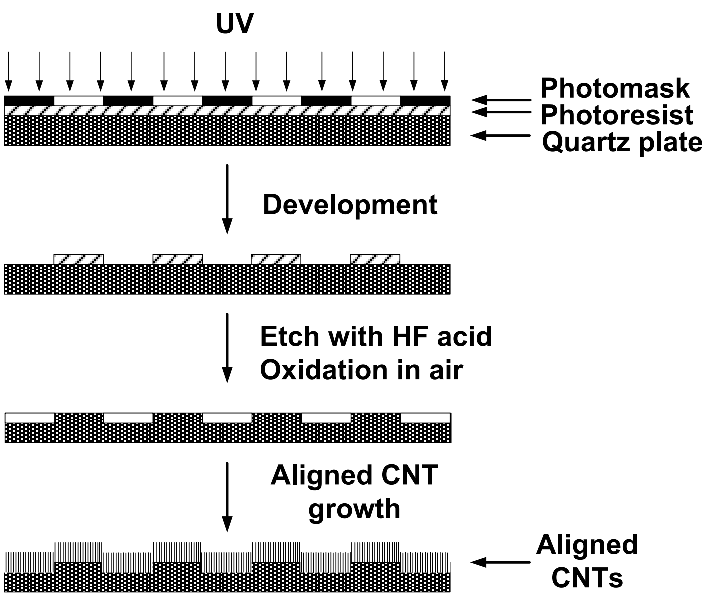
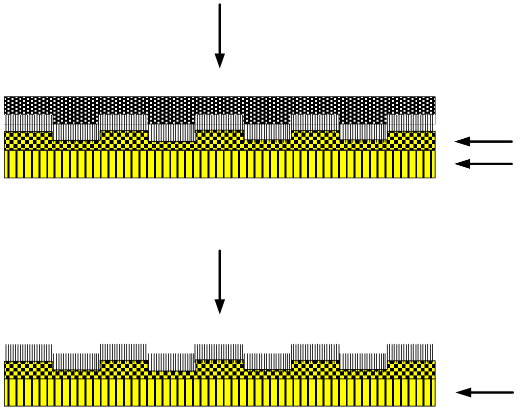
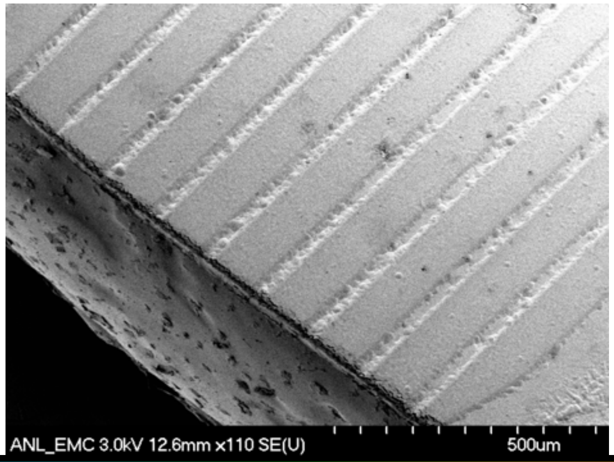
- A 3-D patterning process was developed to add gas distribution channel to ACNT layers on MEA



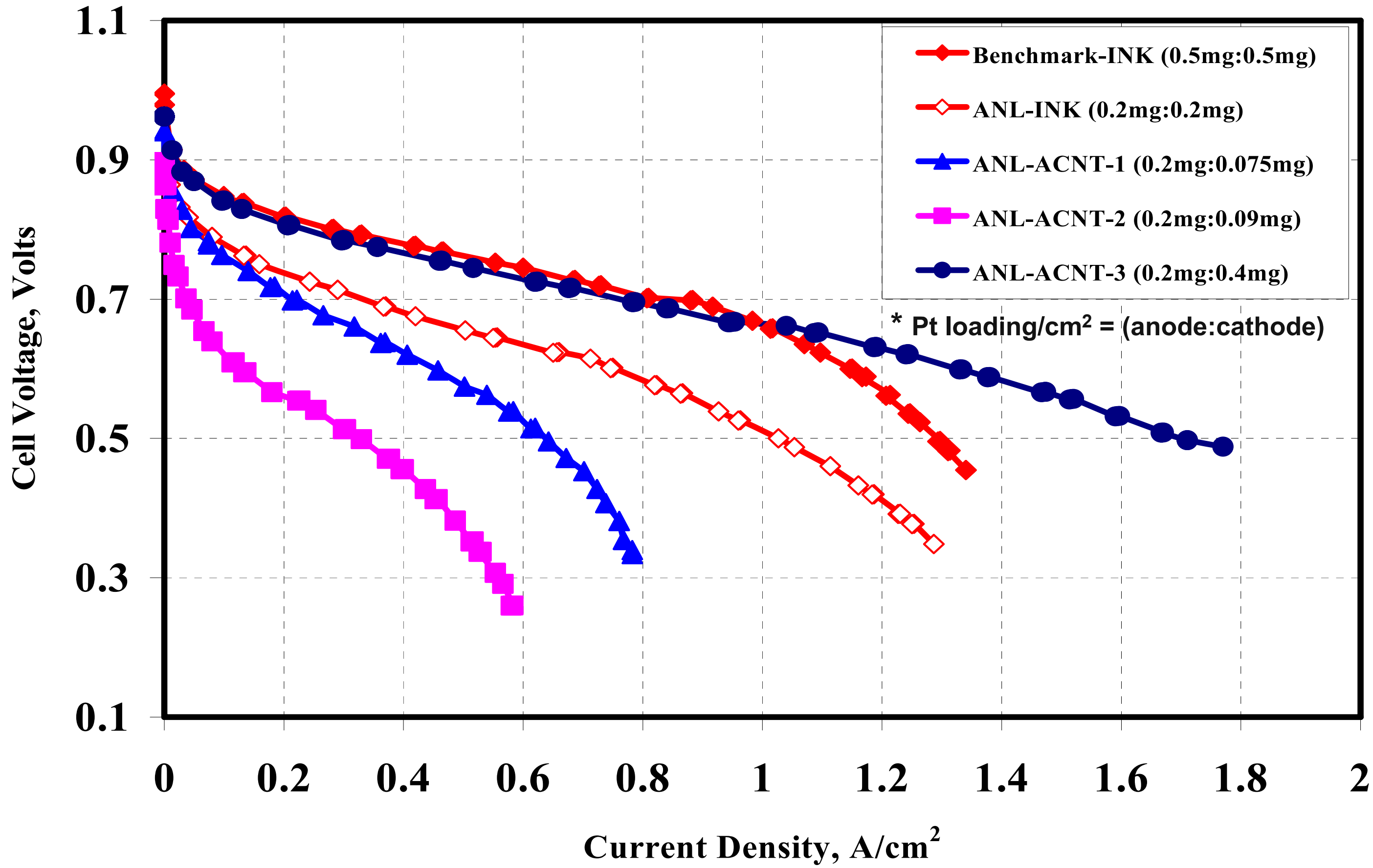




A 3-D ACNT layer pressed over Nafion® membrane with 25 μm channel width separated by 120 μm spacing

- The single cell test was initiated recently (March 2008) for five ACNT-MEAs prepared with different catalyzing methods; the improvement is continuing.

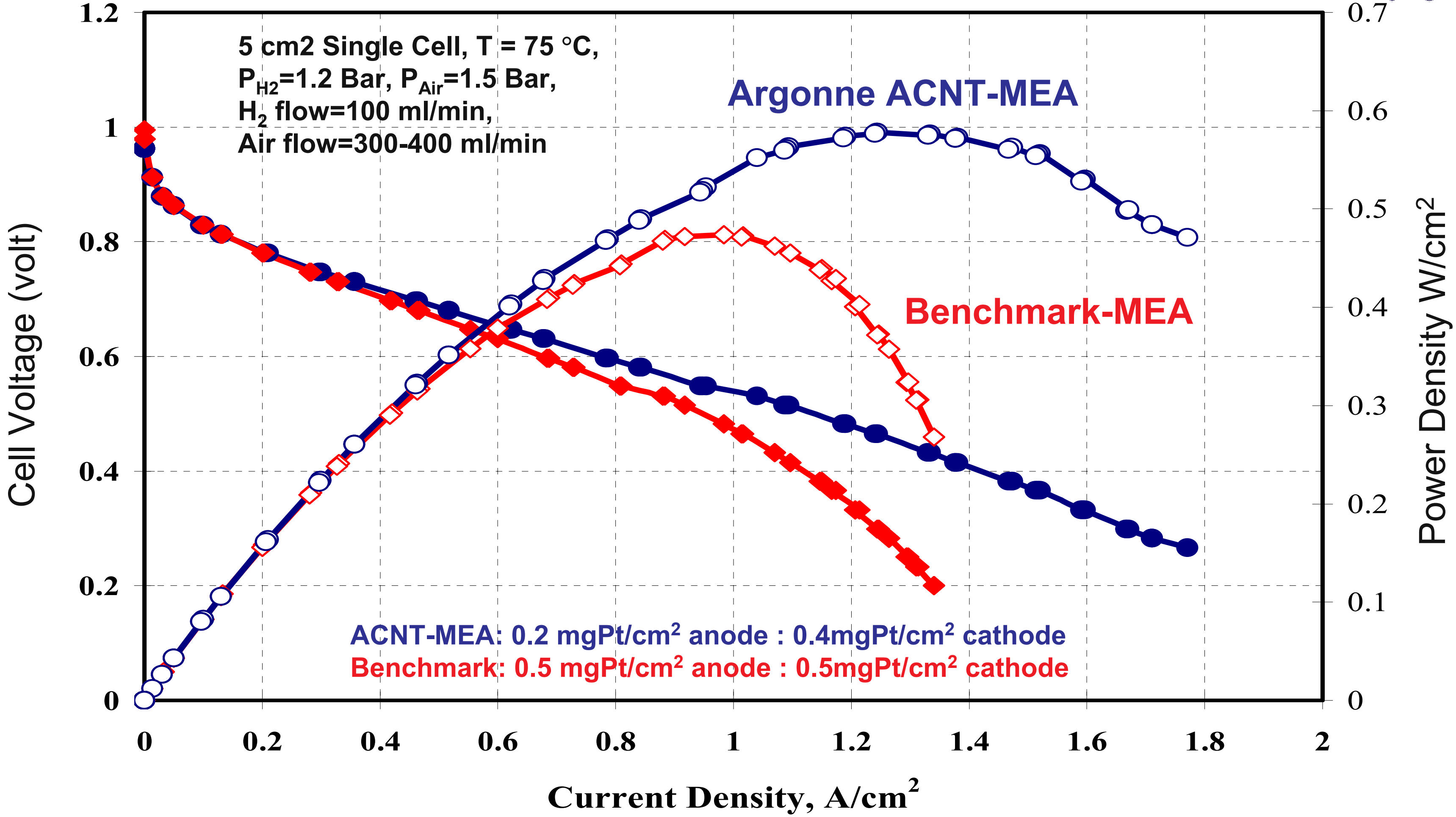
Polarization Curve (IR corrected) Comparison of Several MEAs



Single Cell Test Condition

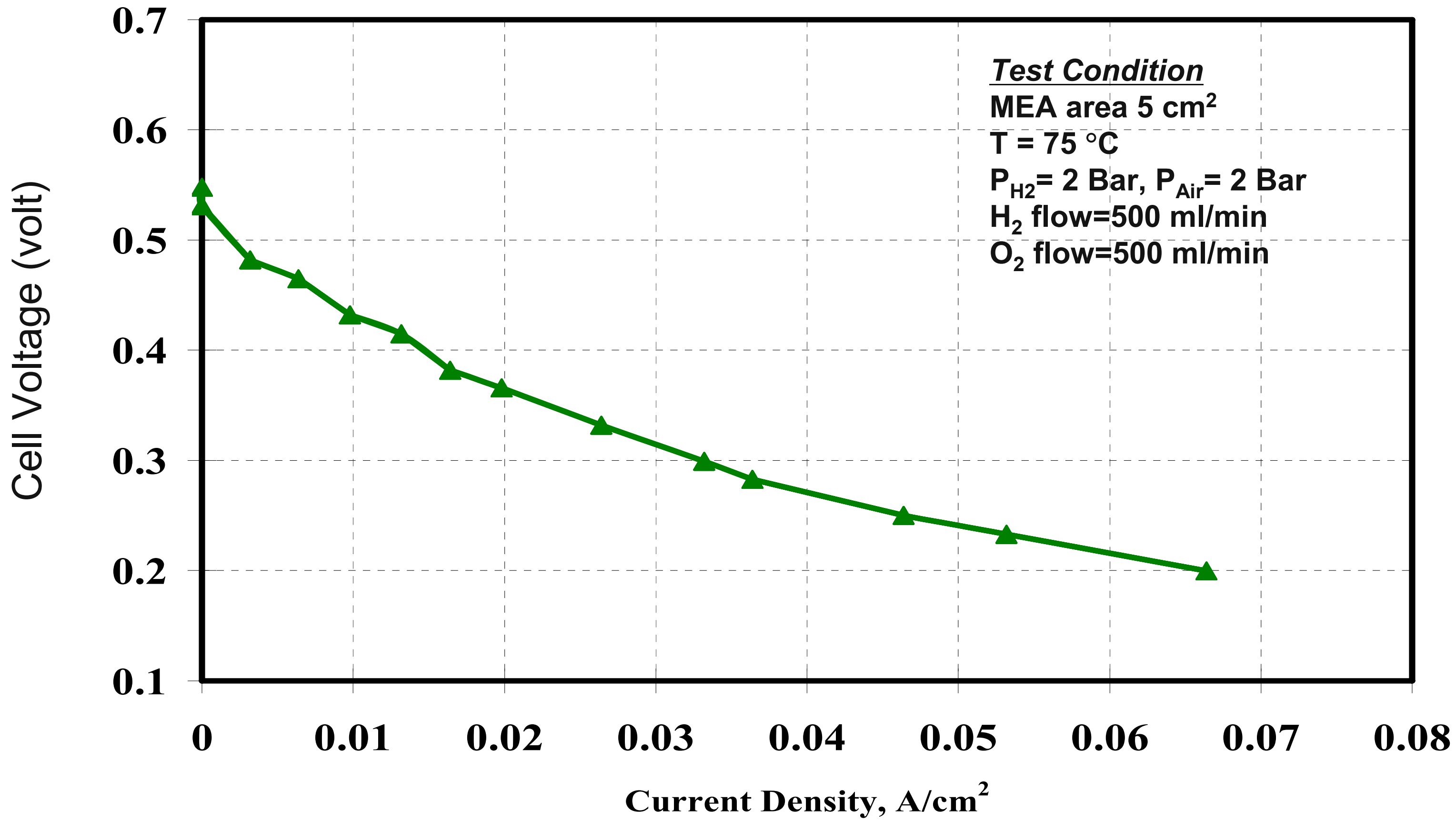
MEA area 5 cm^2
T = 75 °C
P_{H2}=1.2 Bar, P_{Air}=1.5 Bar
H_2 flow=100 ml/min
Air flow=300 – 400 ml/min

Accomplishments – Task 3: Comparing ACNT-MEA with Benchmark in Single Cell Test



ACNT based MEA demonstrated promising power density and mass transport property improvement over the commercial benchmark in the single cell test

Accomplishments – Task 3: Exploring TM/N doped ACNT-MEA in Single Cell Test



- Preliminary performance of ACNT- MEA was conducted where cathode consists of Fe/N doped nanotube, free of precious metal
- > 20 fold increase of activity is needed to compare with conventional fuel cell
- OCV also needs to be significantly increased for the fuel cell efficiency

Future Work

DOE Hydrogen Program

FY08

- Complete optimization of ACNT catalyzing process to further enhance Pt dispersion at reduced loading
- Complete optimization of ACNT based MEA fabrication/packaging process aimed at maximizing catalyst utilization and improving mass transfer and conductivity
- Initiate the investigation on the feasibility of fuel cell component (e. g. GDL) reduction through ACNT-MEA.

FY09

- Complete durability study on ACNT based PEMFC using the test protocol established by the DOE Office of HFCIT guideline

Summary

DOE Hydrogen Program

Relevance: Developing a carbon nanotube based MEA technology aimed at reducing cost, improving durability and performance of PEM fuel cell

Approach: Using ACNT as the platform, supported by the development in catalyzing method, MEA fabrication, fuel cell packaging and testing

Accomplishments:

- Several catalyzing methods and MEA transfer/fabrication processes tailored to ACNT as the electrode support material successfully developed
- Non-Pt catalytic active sites prepared and studied through transition metal and nitrogen doping and advanced characterization techniques
- Promising single cell performance at equal or reduced precious metal loading demonstrated in the preliminary tests

Collaboration: Argonne led team with support from LANL

Future Work:

- Continue optimizing catalyzing and MEA preparation techniques to improve cell performance at reduced metal loading
- Initiate stack component reduction and MEA durability studies