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DOE Hydrogen Program

Novel PEMFC Using Aligned Carbon Nanotubes as Electrodes in MEA

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of Energy

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**Project ID
FC 48**

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

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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 @ 80°C

Partners

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

Objective

- 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	Hours	5,000	5,000
Op. Temp ≥ 80 C	Hours	2,000	5,000
Electrocatalyst area loss	%	<40	<40

- 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

Task 1. ACNT Growth & Catalyzing

- ACNT layer synthesis
- Catalyzing through CVD & wet chemistry
- Structure & activity characterization

Task 2. ACNT MEA Development

- ACNT coating & transfer method development
- ACNT based MEA process development

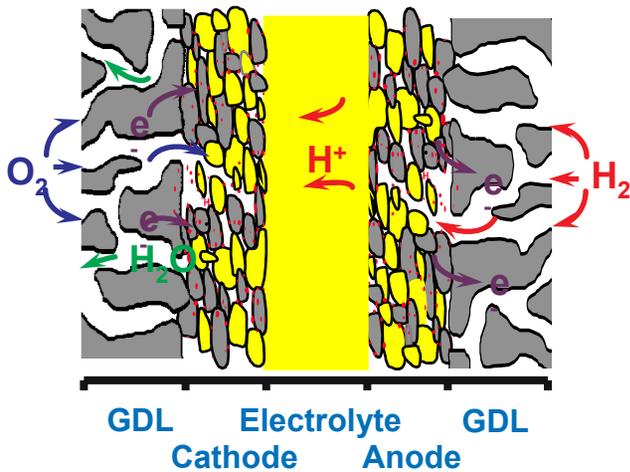
Task 3. Packaging & Testing

- Packaging method optimization
- Cell performance evaluation



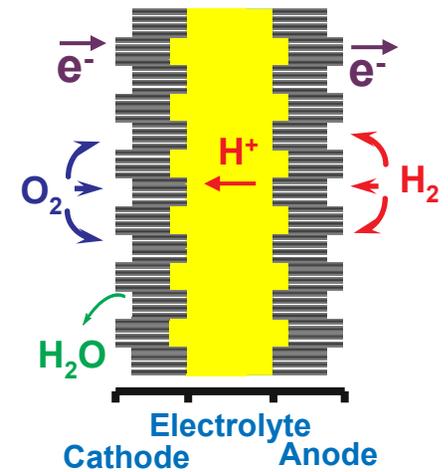
Expected Benefits of ACNT as Nanostructured MEA Support

Conventional MEA



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

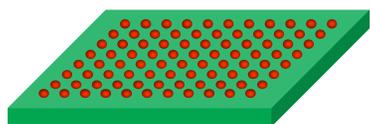
ACNT MEA



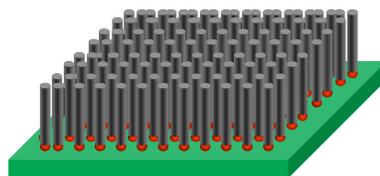
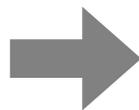
- Methods of preparing uniform, high density aligned carbon nanotube (ACNT) layers with adjustable thickness were successfully developed through chemical vapor deposition (CVD) technique.
- A variety of wet chemistry methods were developed to catalyze both unactivated (hydrophobic) and activated (hydrophilic) 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

- 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



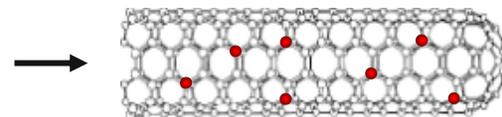
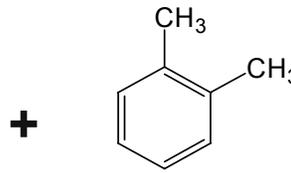
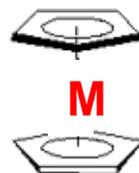
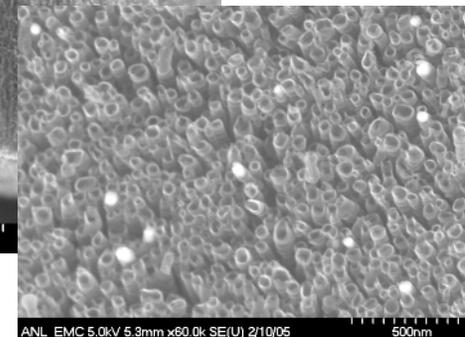
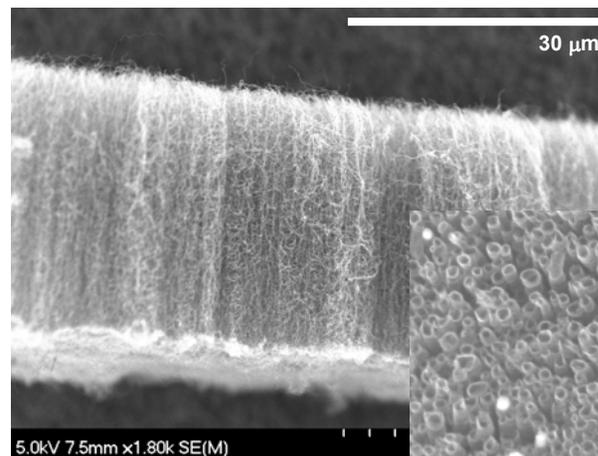
Seeding Catalyst



Growing ACNT

Fabricating ACNT as catalyst support in MEA

- Multi-walled CNTs
- $10 \text{ nm} < \text{Diameter} < 100 \text{ nm}$
- $5 \text{ }\mu\text{m} < \text{Length} < 100 \text{ }\mu\text{m}$
- Surface area $\sim 100 \text{ m}^2/\text{g}$
- Density $\sim 10^8\text{-}10^9 \text{ tubes}/\text{cm}^2$
- Surface enhancement factor
ACNT-MEA: 800 to 4000
XC72-MEA: ~ 5000

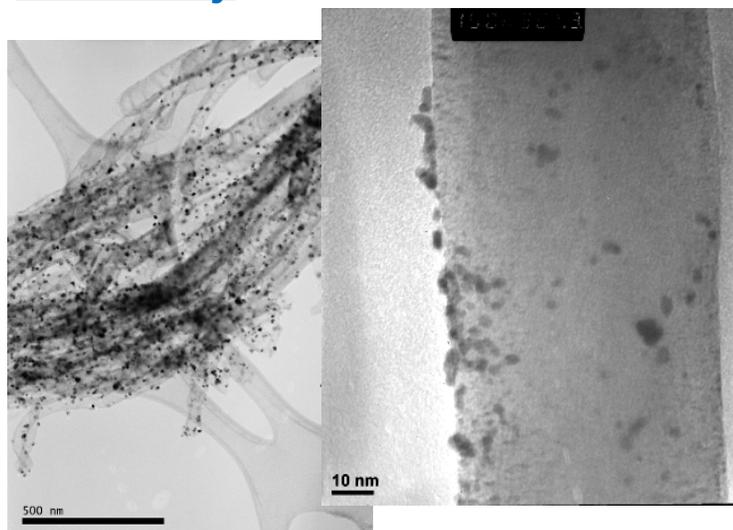


Chemistry and materials adapted in Argonne's process

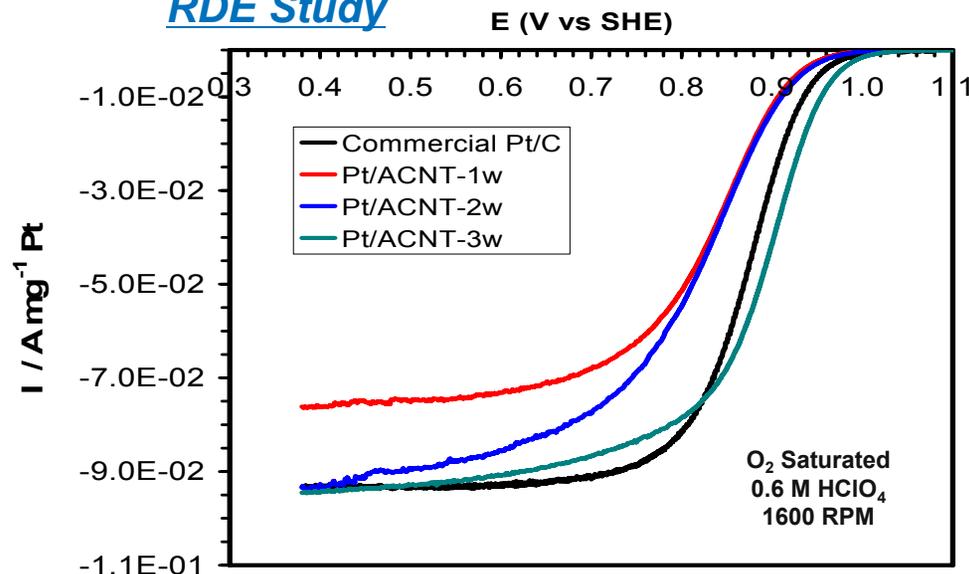
Accomplishments – Task 1: Catalyzing ACNT with Pt through Wet Chemistry

- 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

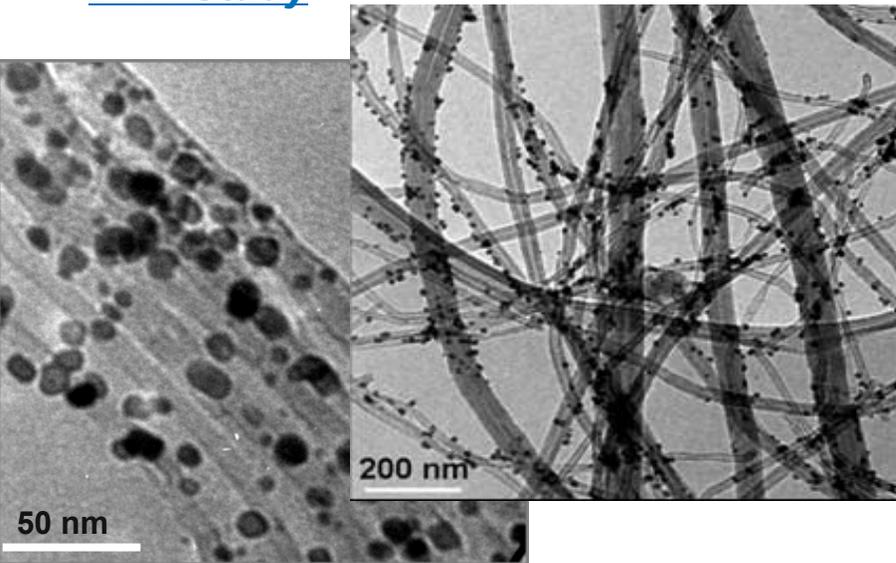


Imaging and electrochemical activity studies showed Pt in ACNT is well-dispersed with comparable kinetics to benchmark commercial catalyst

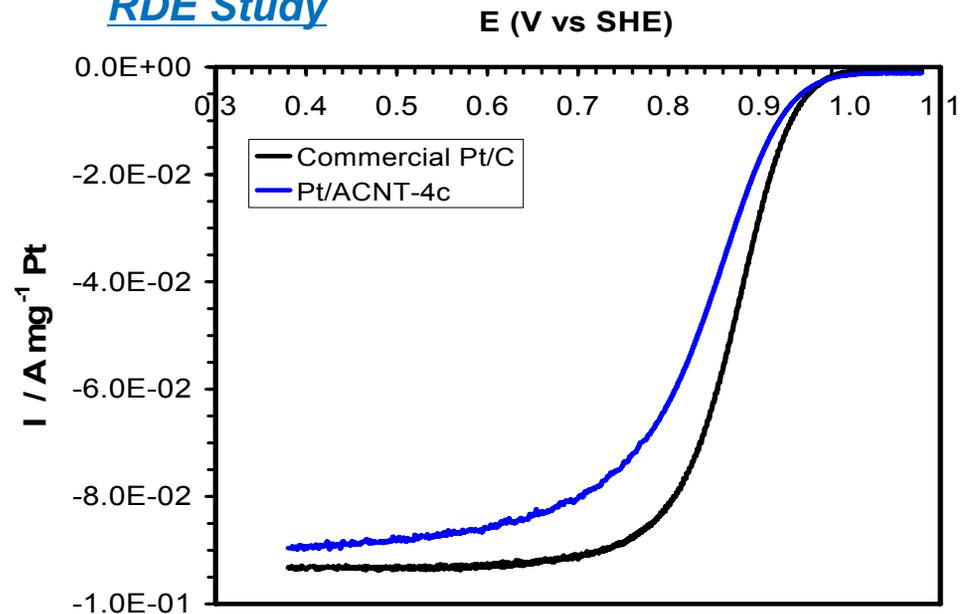
Accomplishments – Task 1: Catalyzing ACNT with Pt through CVD

- 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



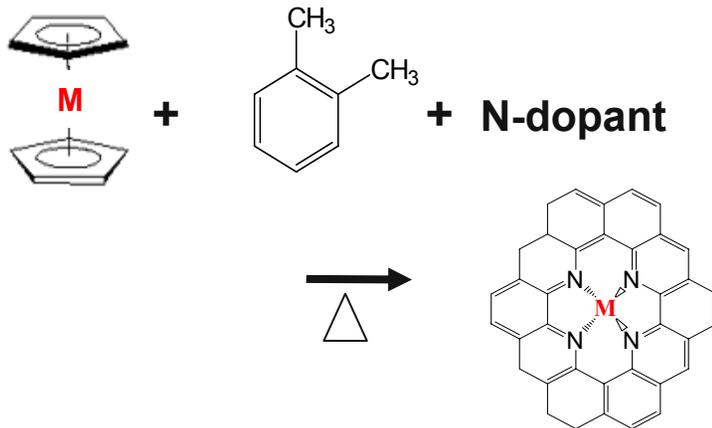
RDE Study



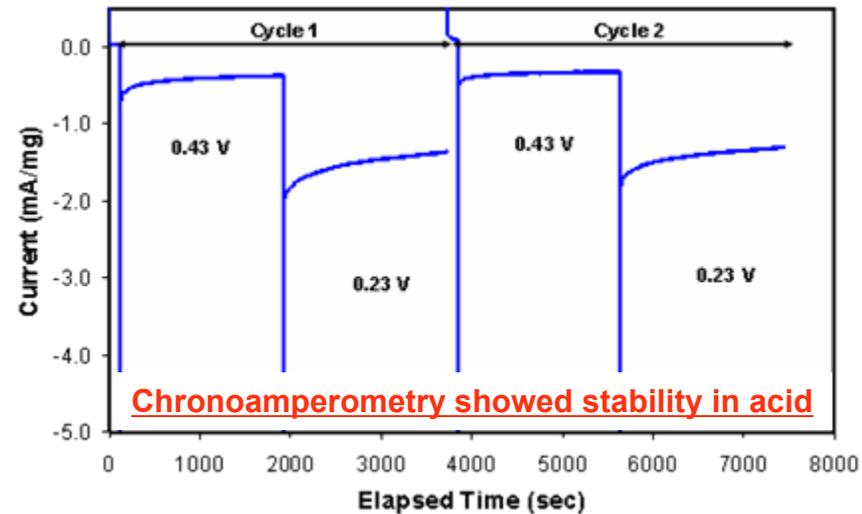
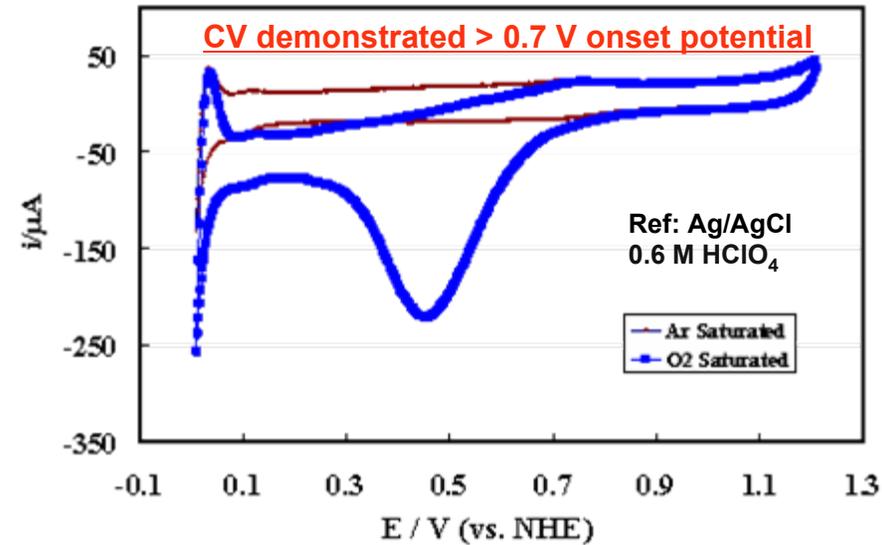
Pt/ACNT prepared through CVD process demonstrated good electrochemical activity even with highly hydrophobic surface

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

- 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

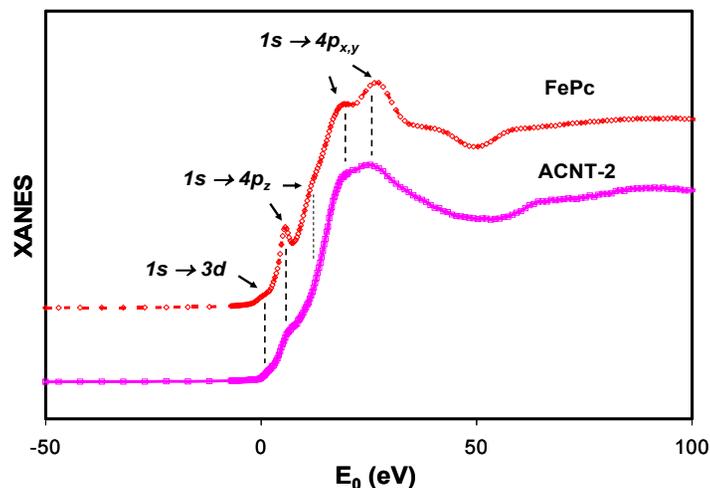
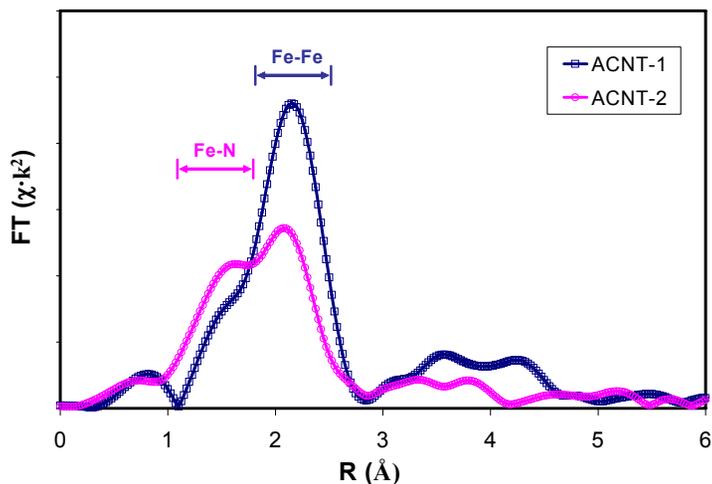


N-dopant = NH_3 , pyridine, etc.
M = Fe, Co, etc.

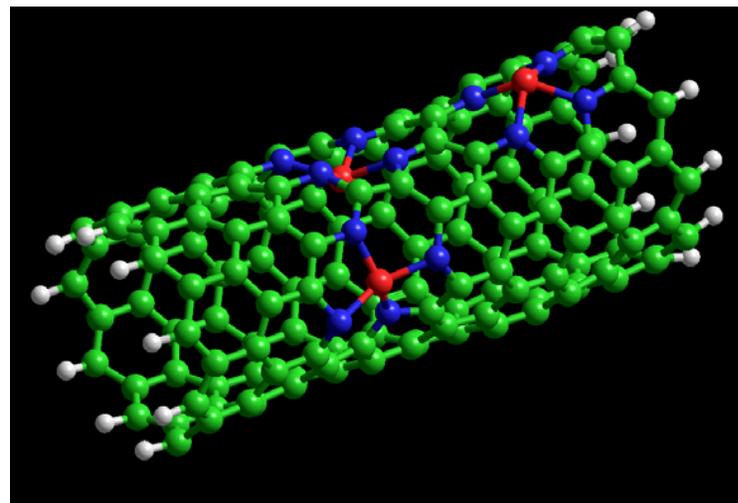


Accomplishments – Task 1: Understanding of Non-Pt Active Site through Advanced Characterization Techniques

EXAFS & XANES Studies



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



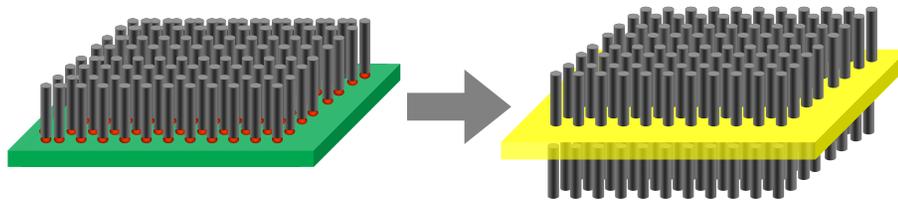
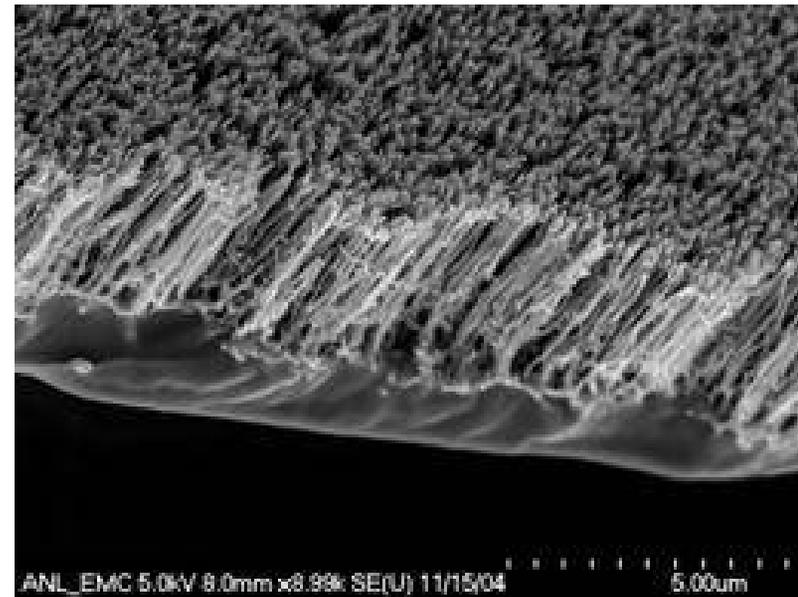
Active site structure - FeN₄

“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



Growing and Catalyzing ACNT

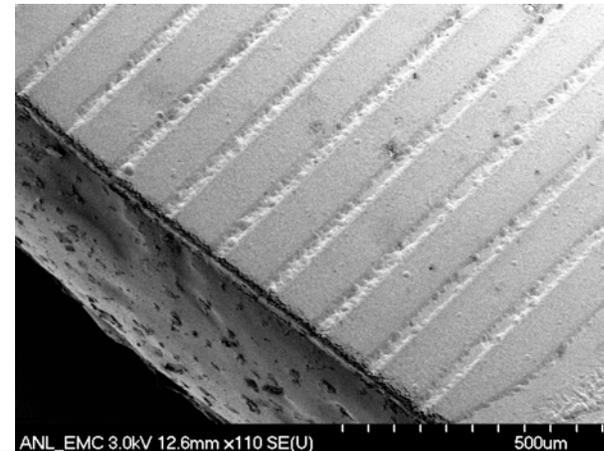
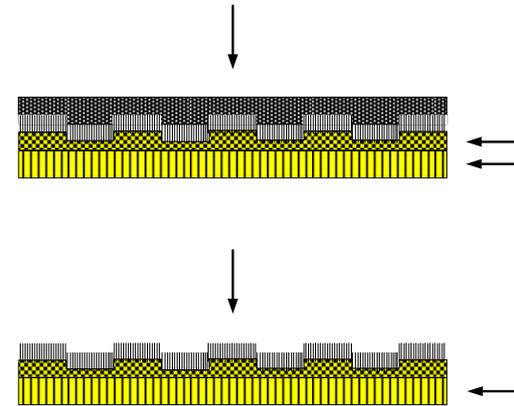
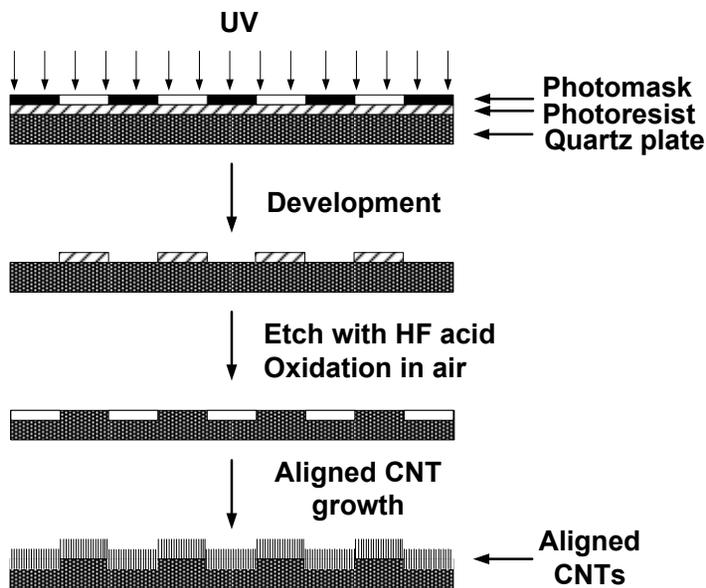
Forming MEA

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

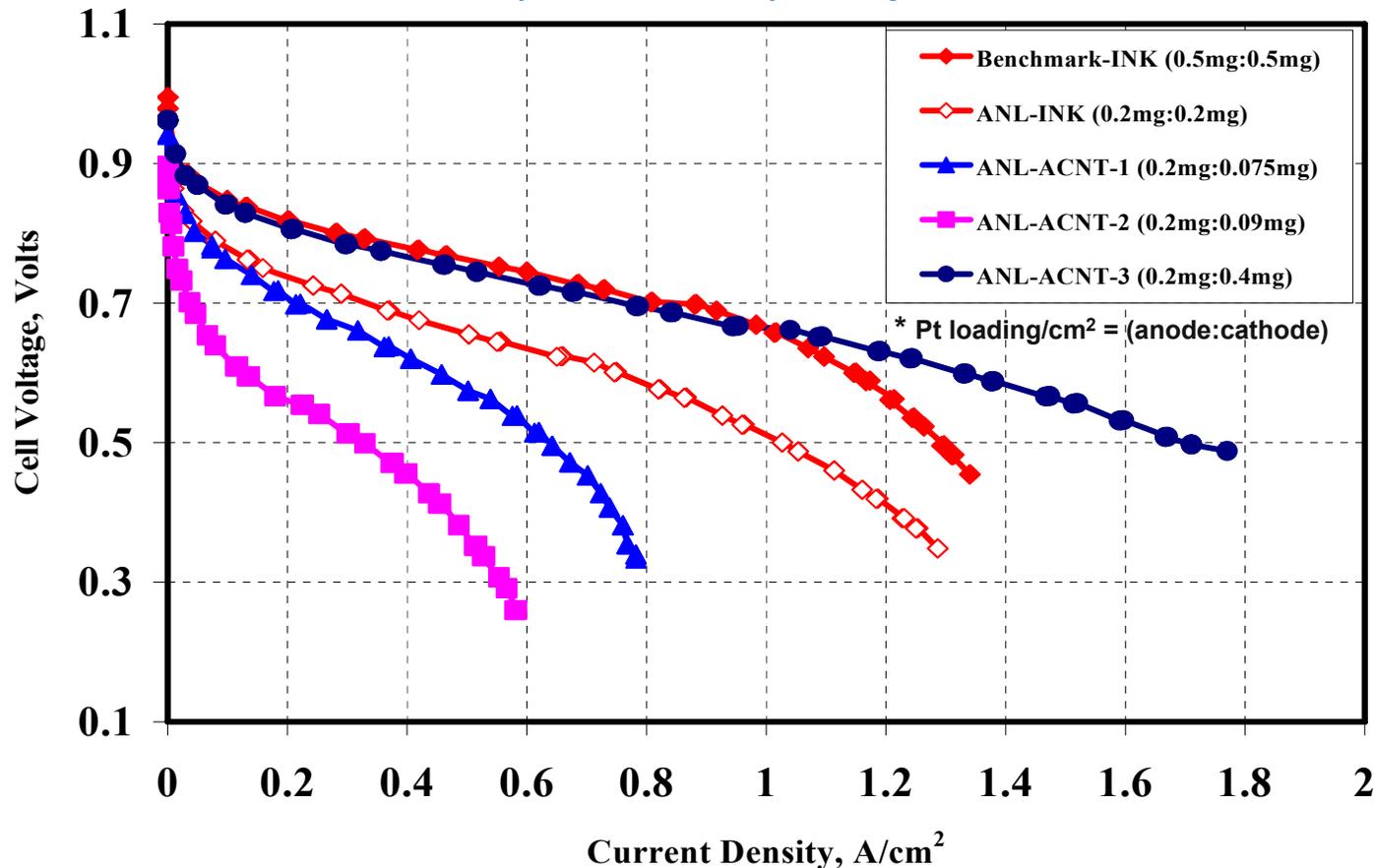
Accomplishments – Task 3: Cell Packaging & Testing



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- 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 cm²

T = 75 °C

P_{H₂}=1.2 Bar, P_{Air}=1.5 Bar

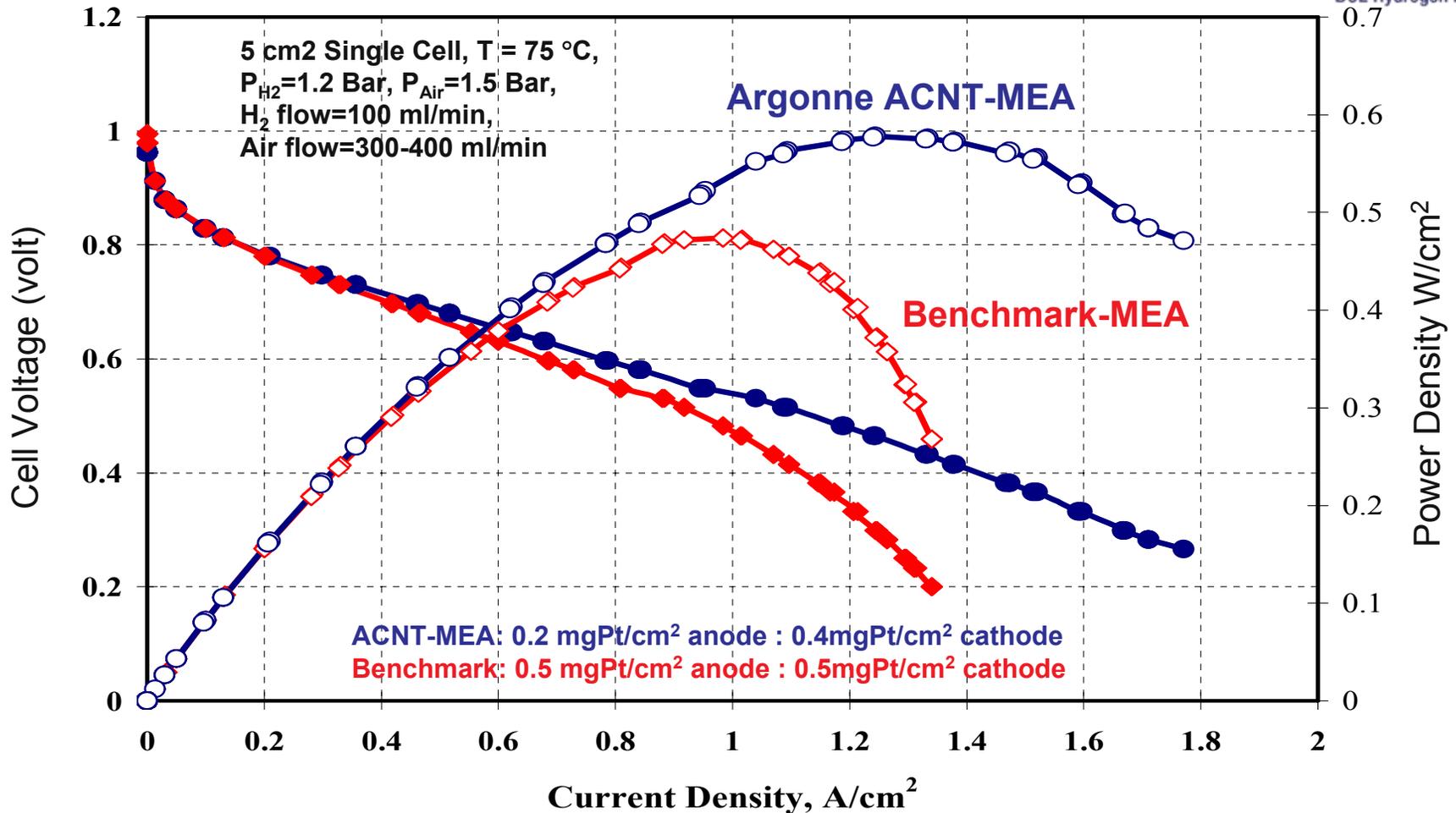
H₂ flow=100 ml/min

Air flow=300 – 400 ml/min

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



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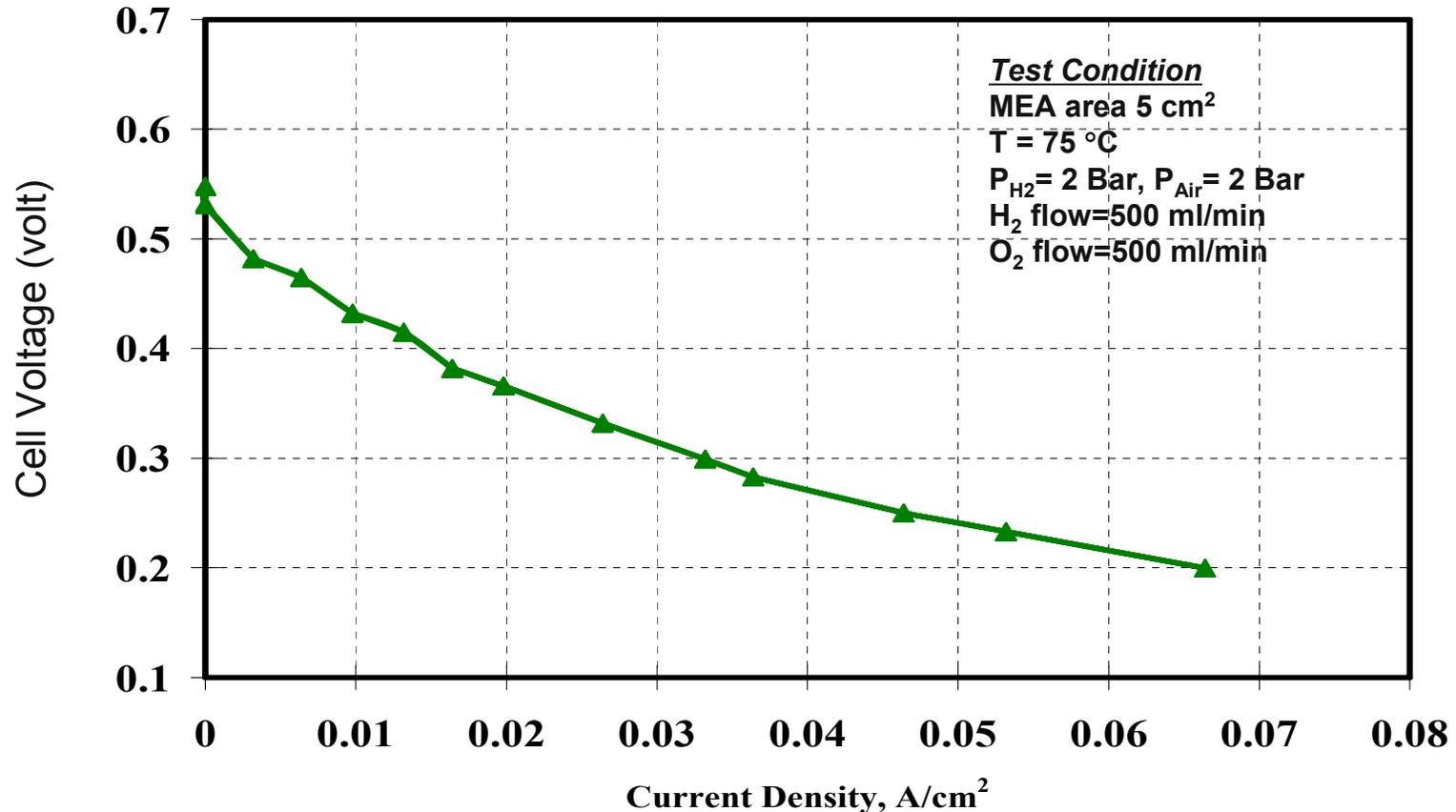


ACNT based MEA demonstrated promising power density and mass transport property improvement over the commercial benchmark in the single cell test

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



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- 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

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

- 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