

V.C.4 PEMFC using Aligned Carbon Nanotubes as Electrodes in MEAs

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Project End Date: December 31, 2008

- Power density: 650 W/L
- Cost: \$45/kW_e

Accomplishments

- Methods of preparing dense, uniform ACNT layers with adjustable thickness were successfully developed using the chemical vapor deposition (CVD) technique.
- A variety of solution impregnation methods were developed to catalyze ACNTs with good metal dispersion. A co-CVD process was developed to functionalize ACNT by directly depositing Pt through a gas phase reaction.
- An MEA fabrication method was successfully developed to transfer ACNT to Nafion[®] membranes. ACNT MEAs showed improved performance over commercial products in single-cell tests.



Objectives

- To develop a method of preparing aligned carbon nanotubes (ACNTs) as the electrode catalyst support for proton exchange membrane fuel cells (PEMFCs).
- To develop a method of fabricating membrane electrode assemblies (MEAs) and PEMFCs using ACNT-based electrodes.
- To demonstrate the performance of ACNT-based PEMFCs.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells Section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project aims to develop an MEA with an innovative architecture using ACNTs as the electrode catalyst support. It targets a simplified cell design with reduced platinum loading, enhanced power density, and improved support stability. The successful outcome of the project would support the development of PEMFCs that meet DOE 2010 stack targets:

Introduction

Carbon nanotubes (CNTs) have been considered as a promising material for the electrocatalyst supports of the PEMFC [1-3]. The desirable attributes of CNTs include their unique geometric shape, high surface area, graphitic structure with better thermal/electric conductivities, and stability in the oxidative PEMFC cathode environment. Our project aims at developing a novel MEA using catalyst-decorated, vertically-aligned CNT layers as the electrode support. The potential advantages of ACNT-based MEAs include improved thermal and charge transfer through the direct contact between the electrolyte and current collectors and maximum exposure of the catalyst site to gas reactant through a uniform support geometry. Furthermore, a 3-dimensional MEA with improved water management and fuel utilization can be fabricated by using a patterned substrate with micron precision for ACNT growth.

Approach

Our approach consists of three main tasks: a) ACNT growth and catalyzing technique development, b) ACNT-based MEA fabrication, and c) ACNT-based fuel cell packaging/testing. A template-free, CVD method is used to prepare the ACNT layer as the electrode catalyst support. The ACNT materials thus prepared are catalyzed through gas phase or wet chemistry methods with uniformly dispersed metal crystallites and maximum exposure of the catalyst sites. To fabricate

ACNT-based MEAs, a transfer technique is developed to implant the catalyzed nanotubes over the membrane electrolyte surface with the alignment intact. The final step of the development is to identify the proper design and conditions to package the ACNT-MEA into the single-cell test fixture and to evaluate the performance of the ACNT-PEMFC.

Results

During the last fiscal year, we have successfully accomplished all the major milestones. Key progress can be summarized as the following:

Growing and Catalyzing the ACNT Layer: The goal of nanotube growth is to produce a uniform layer with equal tube lengths, diameters, and density with controllable total thickness. We employed the CVD process using two alternative precursor mixtures and preparation conditions, one in which the input mixture contained ferrocene dissolved in xylene and the other one using iron phthalocyanine. Each of these methods produces ACNT layers with different graphitic structures and morphologies. Shown in Figure 1 is a scanning electron microscope (SEM) image of a typical ACNT layer prepared using the ferrocene/xylene mixture at 750°C. The ACNTs thus prepared typically have diameters ranging from 20 to 50 nm and adjustable length from 5 μm to 50 μm . The density of the tubes ranges from 10^8 to 10^9 tubes/ cm^2 which corresponds to the enhancement of geometric surface area by a factor of ~1,000 to 4,000.

Following ACNT growth, we have developed two parallel catalyzing methods to functionalize the carbon nanotubes with Pt metal crystallites. ACNTs generated from the CVD process generally are highly hydrophobic. A solution-based technique was developed to overcome the hydrophobicity issue and generated uniformly

dispersed Pt particles. An example is given by the SEM image in Figure 2(a). Another catalyzing method is decoration of the carbon nanotube surface with Pt during the CVD process. In this case, Pt was added using an organo-metallic precursor through chemical deposition following ACNT growth. Highly dispersed metal crystallites can also be produced with proper control of the reaction condition, as is shown in Figure 2(b).

Fabricating ACNT-Based MEAs: The technology we developed to transfer the ACNT layer to the membrane electrolyte surface is similar to the conventional hot-press approach with some modifications. The key variation is in the approach of applying Nafion[®] ionomer to the ACNT layer as an adhesion/ion-conducting medium. Three different methods were developed to apply a thin layer interface between the ACNT layer and the polymer electrolyte for different engineering requirements. Shown in Figure 3 is an SEM image of an ACNT layer sitting on top of a thin

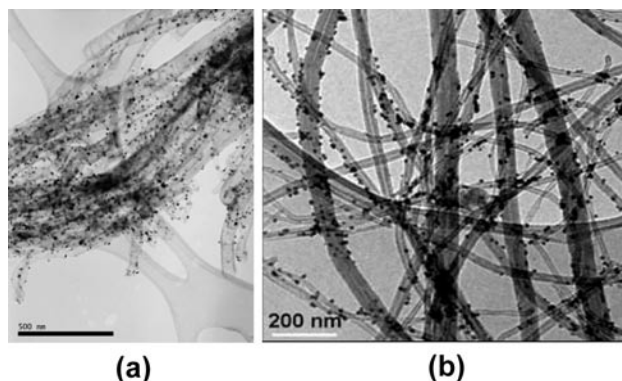


FIGURE 2. SEM images of platinum metal crystallites dispersed over carbon nanotube using (a) wet chemistry approach and (b) co-CVD method.

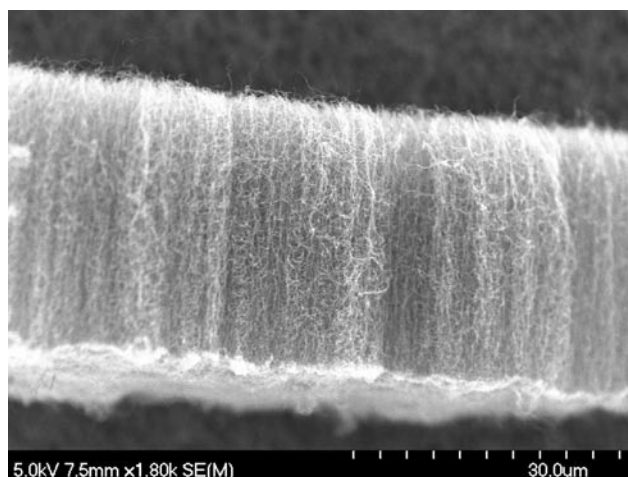


FIGURE 1. SEM Image of a Typical ACNT Layer Prepared by CVD Method

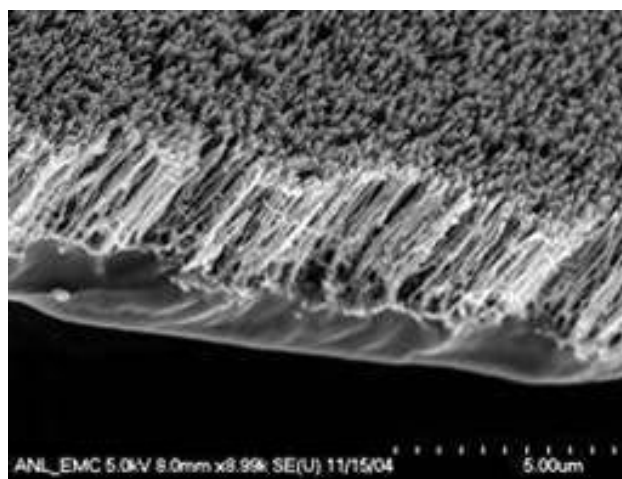


FIGURE 3. SEM image of ACNT bundles over a layer of dried Nafion[®] ionomer film.

film of dried ionomer. Our single-cell evaluation showed that all three methods produced functional MEAs.

Single-Cell Packaging and Testing: The ACNT-MEAs thus prepared were assembled into a single-cell test module. Modifications from conventional packaging parameters were made to ensure the optimal electrical contact between the ACNT electrode and the gas diffusion layer while keeping the integrity of the nanotube layer unchanged. ACNT-based single cells were tested using hydrogen on the anode and air or oxygen on the cathode. For comparison, an ink-based commercial MEA was also tested under similar conditions. The polarization curves and power densities for both tests are plotted in Figure 4. Improved performance, particularly in the high current density region, was observed for the ACNT-MEA, supporting the hypothesis of mass transport improvement for the ACNT-based electrode.

Conclusions and Future Directions

We successfully completed the project milestones in all three key technology areas during Fiscal Year 2008. Significant progress was made in ACNT growth, the catalyzing method, and MEA fabrication development. The preliminary single-cell tests demonstrated improved mass-transport and power density at equal or lower Pt loading. The project is on track for completion in the first quarter of FY 2009. Additional key tasks planned include:

- Complete the investigation of the relationship between ACNT layer geometry/morphology, catalyzing process, and cell performance aiming at further reduction of Pt loading.
- Initiate investigation of the feasibility of component (e. g. gas diffusion layer) reduction with ACNT-MEA.

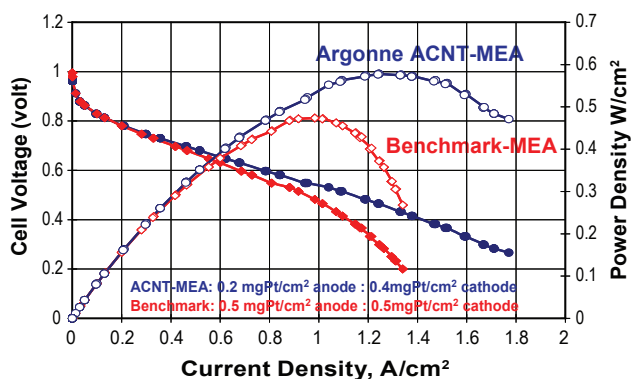


FIGURE 4. Polarization curves (solid symbols) and power densities (hollow symbols) obtained from the single-cell tests for ACNT-based MEA (circle) and commercial MEA (diamond). (5 cm² Single Cell, T = 75°C, P_{H₂} = 1.2 Bar, P_{Air} = 1.5 Bar, H₂ flow = 100 ml/min, Air flow = 300-400 ml/min)

Special Recognitions & Awards/Patents Issued

1. “Method of fabricating electrode catalyst layers with directionally oriented carbon support for proton exchange membrane fuel cell,” Di-Jia Liu and Junbing Yang, U.S. Patent Application 20060269827.
2. “Aligned carbon nanotube with electro-catalytic activity for oxygen reduction reaction,” Di-Jia Liu and Junbing Yang, U.S. Patent Application filed 2006.

FY 2008 Publications/Presentations

1. “Applications of nanomaterials & characterization methods in fuel cell technology”, Di-Jia Liu, Chicago Section of the Electrochemical Society Symposium, Argonne, IL, April 18, 2008.
2. “Functionalized aligned carbon nanotubes as Pt-free electrocatalyst with novel nanoarchitecture for PEMFC”, Junbing Yang & Di-Jia Liu, 20th Conference of North American Catalysis Society, Houston, Texas, June 17-22, 2007.
3. “Aligned Carbon Nanotubes Based Electrocatalyst for Polymer Electrolyte Membrane Fuel Cell”, Gabriel Goenaga, Nancy Kariuki, Junbing Yang, Ann Call and Di-Jia Liu, Chicago Catalysis Society Spring Symposium, Chicago, IL, May 13, 2008.
4. “Bimetallic palladium cathode electrocatalysts & new MEA concept development” Nancy Kariuki, Di-Jia Liu, Deborah J. Myers, Suhas Niyogi, Xiaoping Wang and Junbing Yang, LANL-NEDO-FC-Cubic Workshop, Tokyo, Japan, October 30, 2007.
5. “Aligned carbon nanotubes with built-in FeN₄ active site for electrocatalytic reduction of oxygen”, Junbing Yang, Di-Jia Liu, Nancy Kariuki and Lin X. Chen, *Chem. Comm.* **3** (2008) 329.
6. “3-D structured membrane electrode assembly with patterned aligned carbon nanotubes as electrode materials”, Junbing Yang and Di-Jia Liu, *Carbon* **45** (2007) 2843.

References

1. Y. H. Liu, B. Yi, Z. G. Shao, L. Wang, D. Xing, H. Zhang, *Journal of Power Sources*, **2007**; 163: 807-813.
2. W. Li, X. Wang, Z. Chen, M. Waje, Y. Yan, *Langmuir* **2005**; 21(21): 9386-9389.
3. J. M. Tang, K. Jensen, M. Waje, W. Li, P. Larsen, K. Pauley, Z. Chen, P. Ramesh, M. E. Itkis, Y. Yan, and R.C. Haddon, *J. Phys. Chem. C* **2007**, 111, 17901-17904.