

Performance Improvement of Fuel Cell using Platinum Functionalized Aligned Carbon Nanotubes

Jingbo Liu*, Yuan Yuan*, Gabriel Goenaga**, Di-Jia Liu**

* Texas A&M University-Kingsville, Kingsville, TX, USA, kfjll00@tamuk.edu,
yuan.1023366@gmail.com

** The Argonne National Laboratory, Argonne, IL 60439 USA, goenaga@anl.gov, djliu@anl.gov

ABSTRACT

The short-term goal of this research was to improve the 'performance' of proton exchange membrane fuel cell (PEMFC), via development of aligned carbon nanotubes (ACNT) which provide certain catalytic advantages. PEMFCs are devices which can generate electricity using alternative green resources. The benchmark for improved performance includes better device endurance and decreased platinum (Pt) loading. The long-term goals are to: 1) provide guidelines for design of new materials; 2) promote nanocatalyst applications towards alternative energy; and 3) integrate several advanced instrumentation into nanocharacterization and fuel cell (FC) performance.

Keywords: carbon nanotubes, chemical vapor deposition, electrochemistry, nanocharacterization,

1 INTRODUCTION

Fuel cells (FCs) are green energy resources, which spontaneously convert chemical energy into electricity via reduction and oxidation reactions (Redox), releasing heat and water in the process. One design of FC is known as PEMFCs, which consist of a solid nafion membrane as the electrolyte, utilizing H₂ or bio-fuel as a fuel supply; and noble metal as the catalyst^[1,2]. PEMFCs provide direct electricity for stationary and portable applications with high energy conversion efficiency, low pollutant emissions, simple design and operation, and flexible fuel supply. However, current PEMFC designs encounter problems in materials compatibility, manufacturing cost, and performance degradation^[3]. Numerous attempts have been made to improve the performance and durability of PEMFCs. One problem area is carbon supported Pt and its alloy based catalyst, which are plagued by high expense and low resistance to carbonaceous species or use of Pt alloy (which has low resistance to corrosion)^[4]. Thus, use of non-Pt metal catalysts is desired; but their durability and carbonaceous species tolerance is and requires further investigation^[5]. The originality of this approach is use of ACNTs as catalyst. Other advantages which contribute towards improved performance are rapid gas diffusion and chemisorption of the gas reactants. ACNT hydrophobicity also provides a new tool to prevent cathode flooding, resulting in long-term device stability^[6].

2 EXPERIMENTAL

The experimental approach consists of three major steps, (i) synthesis of aligned carbon nanotubes, (ii) nanostructural characterization of the catalyst and (iii) electrochemical catalyst testing. For synthesis of the nanotubes and construction of membrane electrode assembly (MEA), reagents, chemicals and solvents were obtained from VWR International (West Chester, PA) and Sigma-Aldrich (St Louis, MO) unless otherwise specified. The reagents were reagent grade and were used without further purification. Doubly-distilled and 0.2 micron filtered (Milli-Q) water was used in the dissolution of reactants.

The steps were accomplished through chemical vapor deposition to control the diameter and length of nanotubes, utilization of scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), and Raman spectroscopy to determine the morphology; elemental composition and molecular interactions between nanotubes and platinum (Pt); and electrochemical performance was conducted using an Electrochemical Incorporation test stand to determine the redox reaction kinetics.

2.1 Aligned Carbon Nanotubes Synthesis

ACNTs were synthesized using chemical vapor deposition (CVD) with a xylene-ferrocene solution as the precursor. Xylene was the carbon source, while ferrocene provided the iron metal nanoparticles, which function as seeds for the nanotubes growth. Three 5 cm² quartz substrates are placed inside quartz reaction tube with 1 inch diameter. The tube was placed in a two stage furnace and tightly sealed to air. The first stage of the furnace was set at 225 °C, which was enough to vaporize the solution. The second stage was held at 725 °C and was used to carbonize the vaporized solution, depositing the iron nanoparticles on the quartz substrates, and allowing the carbon nanotubes to grow around the iron seeds. The solution with the chemicals was then injected into the reaction tube, on the low temperature stage, using argon and hydrogen as the carrier gases, at flow rates of 100 and 50 mL/min respectively. The chemicals injection rate was 0.225 and 0.250 mL/min.

2.2 Membrane Electrode Assembly

The anodic and cathodic materials were then placed on two sides of the Na-form nafion membrane. Hot pressing technique was used to fabricate the membrane electrode assembly (MEA) under temperature of 210 °C and pressure of 600 pound-forces per square inch gauge (psig) for 5 to 10 mins. Teflon and glass substrate were carefully removed from the MEA, which was treated using boiling sulfuric acid (0.5 M H₂SO₄) and distilled water for 1-2 hrs. Acid treatment was used to exchange ions from Na⁺ to H⁺ to increase the ionic conductivity. The MEA was treated with distilled water to remove the Na⁺, Fe²⁺ or other impurities for 1 hr. An MEA schematic is shown in *Figure 1A*.

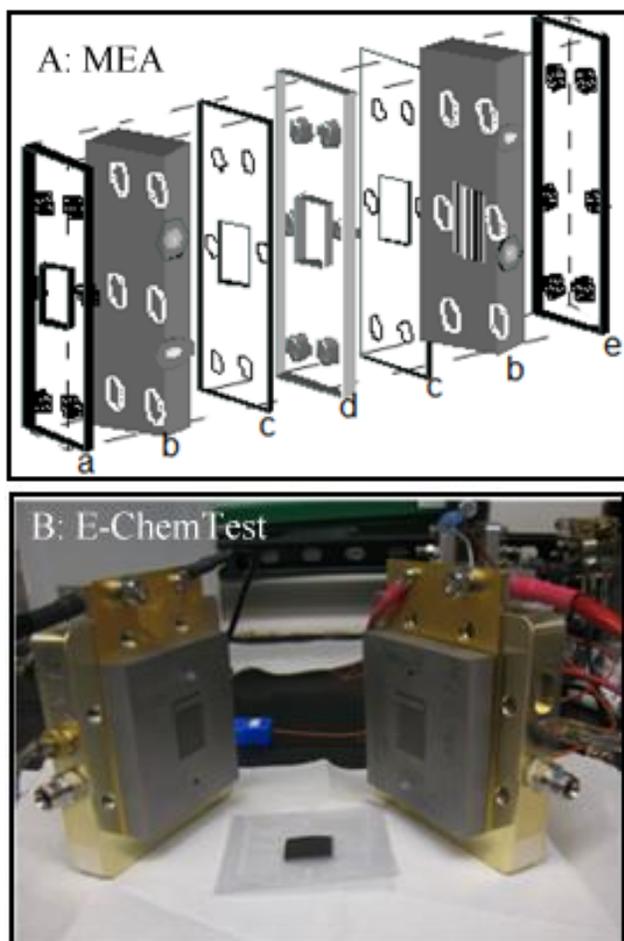


Figure 1: Schematic of MEA (A) and electro-chemical test of PEMFC device (B), a-silicon heater; b-separator plates; c-gaskets; d-MEA; e-current collector

2.3 Nanocharacterization of PEMFCs Device

The surface morphology, cross-sectional images and the thickness of the aligned carbon nanotubes were determined using a field emission scanning electron microscope (JSM-7600F) equipped with X-ray energy dispersive

spectroscopy (Chemistry Department, Texas A&M University-Kingsville, TAMUK). An accelerating voltage of 20 kV and high vacuum of *ca.* 1.0×10^{-5} mbar were employed. The substrate for cathode and membrane electrode assembly (MEA) was mechanically fractured using a razor blade, enabling easier estimation of the PEMFC thickness. Raman spectroscopic analysis was conducted to evaluate the vibration mode, electron structure of Pt and multiwall nanotubes. Raman / Fourier transform infrared spectroscopy (FTIR, Hariba Jobin-Yvon LabRam IR system), confocal microscope (Materials Characterization Facility, TAMU) was also used to obtain highly specific fingerprints for identification of chemical, molecular properties. For Raman spectroscopy a fiber optic coupler was used with laser excitation of 632 nm with the scan range of 100-6000 cm^{-1} with a fixed resolution of 0.3 $\text{cm}^{-1}/\text{pixel}$ at various scan lines.

2.4 Electrochemical Test of PEMFCs Device

The ACNT-MEA testing activity area was 5 cm^2 and was mounted in a single cell, with graphite bipolar plates and a single-serpentine flow field. Commercially available carbon cloth treated with Teflon was used as the gas diffusion layer (GDL) for anode and cathode, and inserted between the MEA and the bipolar plates. The assembled single cell was attached to an Electrochem Inc. test stand to record the current-voltage (I-V) polarization curves, which recorded MEA stack performance (*Figure 1B*). The PEMFCs device was initially conditioned for about 8-10 hours until it reached the desired temperature and humidity conditions, using argon gas in the anode and oxygen gas in the cathode respectively, (according to the U.S. Fuel Cell Council test protocol). After constant I was reached, the polarization (I-V) curves were measured by potentiostatically cycling V between 0.2 and 1 V. All tests were conducted at a cell temperature of 75 °C with H₂ gas in the anode and air or O₂ gas in the cathode. The gas flow rates were 100 mL/min at 1.2 bar and 300 mL/min at 1.5 bar for the anode and cathode, at relative humidity of 100 % respectively.

3 RESULTS AND DISCUSSION

This study indicates that ACNT when used as PEMFC catalyst allows for novel structures to be created, which advanced gas diffusion through the Pt-functionalized array. This development enhanced chemisorption of the gas reactants and promotes greater energy conversion. ACNT hydrophobicity also provides a new approach to prevent cathode flooding, resulting in long-term PEMFC stability.

3.1 Nanocharacterization of PEMFCs Device

SEM analysis was employed to understand the morphology and dispersity of Pt-modified ACNTs to examine MEA microstructure in relation to its performance

and the stability of the electrocatalyst. From the SEM image, it can be seen that MEA displayed unique aligned structure of ACNTs with Pt deposition on their surfaces (**Figure 2**), which allows for fast gas diffusion through cathodic materials and chemisorbed on the surface of the catalyst. This will ensure that mass transfer is not the rate limiting step, but the electron transfer is. Consequently, MEA kinetics was enhanced. The diameter of the ACNTs was approximately 20-50 nm and length varied from 10-30 μm according to the different growth time period.

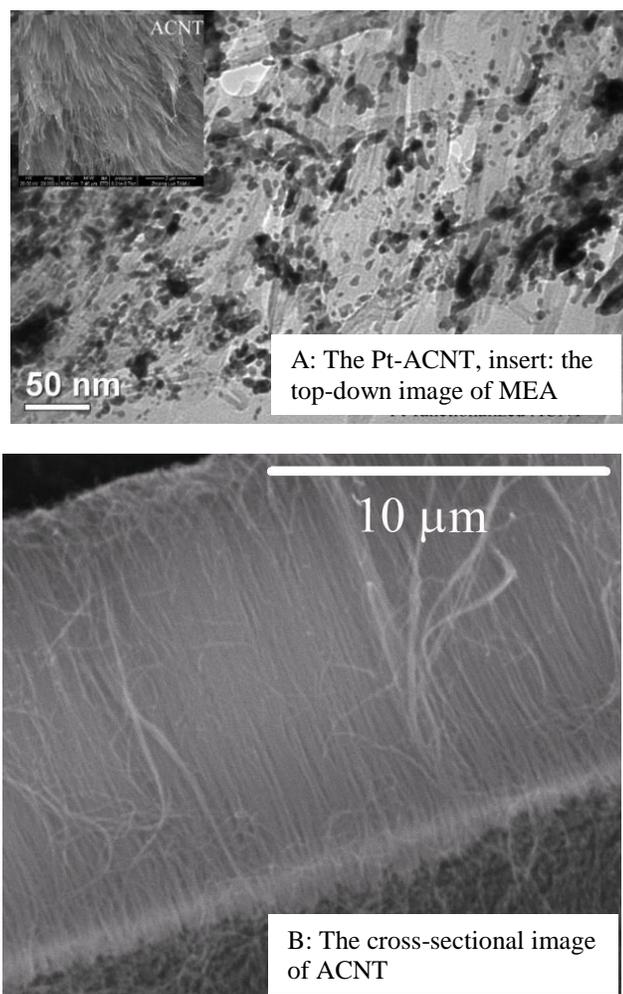


Figure 2: The SEM morphological image of Pt-functionalized ACNT and carbon nanotubes.

Raman spectroscopy also provided information to characterize one-dimensional (1D) ACNTs. From the spectra of the ACNT (**Figure 3**), it can be seen that the orderly arranged structure of the ACNT contributes significantly to its unique optical and spectroscopic properties, due to the 1D confinement. Various features of the ACNT are highly corresponding to the vibration modes. At the frequency of 1330.00 cm^{-1} , the vibration was resulting from the D mode; 1584.17 from G mode and 1759.28 cm^{-1} from M mode, respectively. At high

frequency of 2662.59 cm^{-1} , G' mode vibration was also detected. The Pt metal displayed two characteristic spectra at frequency of 483 cm^{-1} and 2085 cm^{-1} . Some satellites spectra were also seen due to the complexity of the MEA elemental composition and structure. More importantly, the mode frequency of ACNT and Pt depends on the laser excitation and the dimensional confinement.

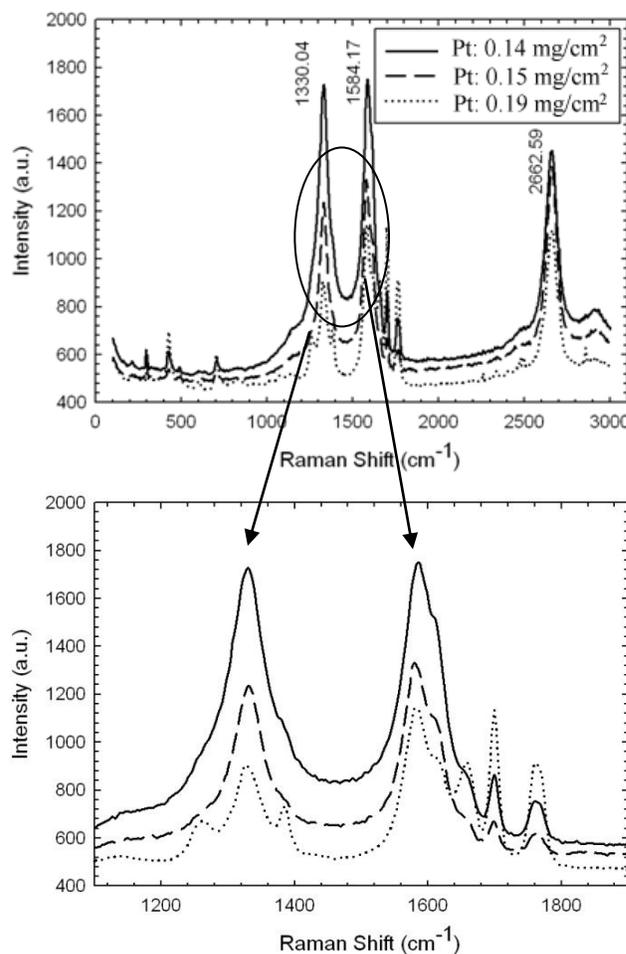


Figure 3: The Raman spectroscopic analysis of Pt-functionalized ACNT.

3.2 Electrochemical Test of PEMFCs Device

According to the protocol of United States Department of Energy (US DOE), the PEMFC was conditioned for 16 hours to obtain stabilized kinetics. The conditioning variables were controlled under flow rate of 100 mL/min for H_2 and 300 mL/min for O_2 . Cell temperature was maintained at $80\text{ }^\circ\text{C}$. In this study, the potential was kept at a constant value of 0.512, 0.597 and 0.699 V to ensure the polarization under low direct current (DC). The plot of cell potential as a function of exchange current density was shown in **Figure 4**. It can be seen that the cell performance was enhanced upon the conditioning and reached constant exchange current density after 8 to 10 hours according to the various PEMFC specimens. Thus, use of non-Pt metal

catalysts is desired. The novelty of this approach is the application of ACNTs which allowed for improved performance due to rapid gas diffusion and chemisorption of the gas reactants. ACNT hydrophobicity also prevented cathode flooding, resulting in long-term device stability. The kinetics PEMFC was evaluated using current density (i_0) averaged at 2500 mA/cm² when O₂ was used (**Figure 5**), which exhibited a maximum power density of 720 mW/cm². Whereas air was used as oxidant, the current density and power density were determined to be 1500 mA/cm² and 350 mW/cm², respectively. In both circumstances, the open circuit voltage was measured at 0.997 V. The PEMFC output was critical when used to power the apparatus. It's power density can be calculated using multiplication of potential by its associated exchange current density, noting that usually, the PEMFC device does not operate at maximum current density due to ohmic loss and concentration loss respectively. The former is resulting from the internal resistance loss and the latter is caused by the depletion of the reaction concentration. In our study, the fuel supplies (H₂) and oxidant (O₂ or air) were controlled at constant flow rate. Therefore, the concentration effect can be negligible.

4 CONCLUSION

The Pt-functionalized ACNT cathodic catalyst were obtained by chemical vapor deposition, wet chemistry impregnation, and followed by heat-treatment at 300 °C. The catalyst was characterized through SEM and Raman spectroscopy to determine the unique structure and molecular interaction between C and Pt atoms. The results show that the dense ACNT layers were directly grown on cathode materials with highly aligned structure, which favor the gas diffusion. The diameter of the ACNT was observed approximately 20-50 nm and length varied from 10-30 μm according to the different growth time period. The Pt nanoparticles were uniformly distributed on the surface of ACNT, whose size was ranged from 1 nm to 8 nm. The single PEMFC displayed the maximum power density 720 mW/cm² and 350 mW/cm² with the O₂ and air oxidant introduced into cathode, respectively.

ACKNOWLEDGE

The authors are grateful to the National Science Foundation Center of Research Education in Science and Technology (HRD-0734850) and MRI acquisition at the Texas A&M University-Kingsville; the support from Department of Energy, the Office of Science and the host by the Divisions of Educational Programs and Chemical Science and Engineering are also duly acknowledged. Authors are also thankful to the assistance and support from the fuel cell group members at Argonne National Laboratory; The use of TAMU Materials Characterization Facility and Dr. Liang and Dr. Young's suggestion and discussion are acknowledged. Dr. Linda Washington (the former program coordinator of Faculty and Student Team (FaST) from Argonne National Laboratory) is specifically acknowledged for her dedication to promote faculty and student to engage in the fields of Science Technology Engineering and Mathematics.

REFERENCES

- [1] J. Larminie, A. Dick, *Fuel cell systems explained*, 2nd ed., John Wiley & Sons Ltd., UK, 2003.
- [2] X. Yu, S. Ye, *Journal of Power Sources*, 172: 133-144, 2007.
- [3] T.W. Ebbesen and P.M. Ajayan, *Nature*, 1, 358 (16), 1992
- [4] V. Kamavaram, V. Veedu, and A.M. Kannan, *Journal of Power Sources*, 188: 51-56D, 2009.
- [5] M. Snow and L. Green, *Microelectronic Engr.*, 30, 969, 1996.
- [6] Cooper, *Fuel Cells*, 103, 24, 2007.
- [7] D.J. Liu, *ECS Trans.*, 16, 1123, (2008).
- [8] J. Yang, *Chem. Comm.*, 3, 329, (2008).

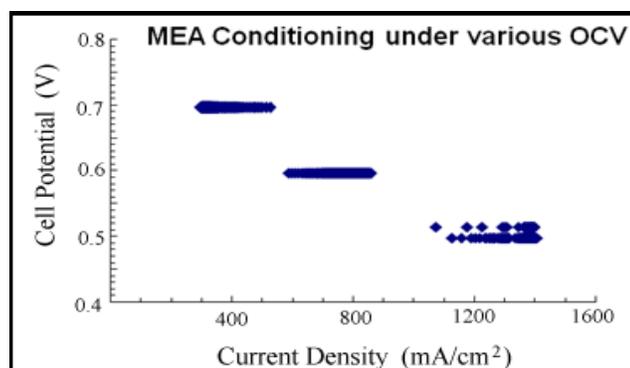


Figure 4: The conditioning of PEMFC device at OCVs.

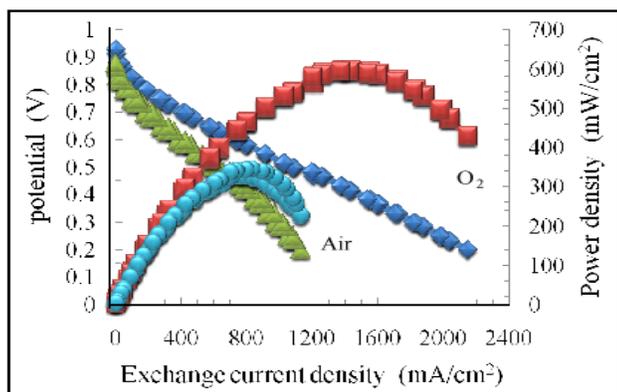


Figure 5: The electrochemical performance of PEMFC device with H₂ as fuel and O₂/air as oxidant, (Red: Power density in O₂, Blue: Current density in O₂; Gray: Power density in air, Green: Current density in air).