

Nitrogen Doped Carbon Nanotube Thin Films as Efficient Oxygen Reduction Catalyst for Alkaline Anion Exchange Membrane Fuel Cell

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Nitrogen doped carbon nanotubes (N-CNTs) were synthesized from three different aliphatic diamine compounds. Ethylenediamine based N-CNTs (ED-CNTs) were found to have the highest nitrogen content and displayed significant oxygen reduction reaction (ORR) activity. ED-CNTs were fabricated into a thin, free standing film for use as cathode layer in an alkaline anion exchange membrane electrode assembly (MEA). These thin films displayed significantly higher performance in the alkaline MEA setup when compared with commercial carbon supported platinum (Pt/C). The increase in performance was attributed to the distinct structural properties of N-CNTs and enhanced electronic properties resulting from a high degree of nitrogen incorporation.

Introduction

Low temperature fuel cells offer significant advantages over current energy generation technologies, including high conversion efficiencies and low environmental impacts (1). Alkaline fuel cells (AFCs) were the first devices used to generate electricity from hydrogen and oxygen, however low power density and electrolyte durability are ongoing challenges facing the commercialization of these products (2). Alkaline anion exchange membrane (AAEM) fuel cells offer a significant advantage over traditional AFCs in that the electrolyte membrane is not prone to poisoning by CO₂ that may be present in gas fuel streams (3, 4), leading to significantly higher durability. AAEM fuel cells also offer several distinct advantages over their counterparts, proton exchange membrane (PEM) fuel cells, including significantly lower activation overpotential in alkaline conditions (2, 5), less corrosive operating environments (3, 4, 6) and no need to humidify the fuel gas streams (6). The oxygen reduction reaction (ORR) taking place on the cathode of AAEM fuel cells requires a highly active electrocatalyst most often consisting of expensive platinum materials (2-4, 7). Developing an inexpensive, non-noble alternative to these materials without sacrificing performance or durability is essential for realizing AAEM fuel cell commercialization. Recently, comparable ORR catalytic activity of nitrogen doped carbon nanotubes (N-CNTs) in alkaline solution compared with traditional platinum loaded carbon black (Pt/C) has been reported (8, 9), however the performance of N-CNTs as a cathodic catalyst has not been investigated in an actual AAEM fuel cell setup.

In the present study N-CNTs were synthesized from three different aliphatic diamines with varying carbon chain lengths, using a simplistic single injection CVD setup. Ethylenediamine based N-CNTs were found to possess the highest nitrogen content and ORR activity in alkaline conditions, thus were fabricated into a thin, free standing film by a filtration method for use as a cathode for AAEM fuel cells. The novelty of this work lies in the fabrication and testing of these thin films as an ionomer

free cathode catalyst layer in an AAEM fuel cell membrane electrode assembly (MEA). Utilizing N-CNT thin films as a cathode catalyst offers several advantages over commercial Pt/C towards AAEM fuel cell technologies: (i) N-CNT thin films are inexpensive and readily produced, while displaying high catalytic activity towards ORR, (ii) their porous nature allows for good oxygen diffusion, while their thin structure allows adequate hydroxide access, eliminating the requirement for an ionomer in the catalyst layer, (iii) N-CNT thin films are free standing and do not require any bonding agents that might interfere with catalytic performance, and (iv) N-CNTs have significant stability under operating conditions (9).

Experimental methods

N-CNTs were synthesized by injecting a single source solution of either ethylenediamine (ED), 1,3 diaminopropane (DAP) or 1,4 diaminobutane (DAB) into a chemical vapour deposition (CVD) setup under nitrogen gas flow at 800 °C. Ferrocene was dissolved in the source solution at 2.5 wt.% as growth catalyst. Synthesized N-CNT materials (ED-CNT, DAP-CNT and DAB-CNT, respectively) were treated with sulphuric acid to remove any residual iron growth catalyst or amorphous carbon impurities.

ORR half cell testing was carried out using a rotating ring disk electrode (RRDE) setup. The loaded working electrode was immersed in a 0.1 M KOH electrolyte and the potential was swept from 0.2 V to -0.95 V versus a Ag/AgCl reference electrode. Steady state linear sweep voltammetry readings were taken under electrolyte oxygen saturation and nitrogen induced deaeration conditions to evaluate ORR activity and obtain a background reading, respectively.

Free standing ED-CNT films were fabricated by a filtration method. ED-CNTs were suspended in ethanol solvent and ultrasonicated to ensure adequate dispersion. The mixture was then filtered through an aluminum oxide membrane (Whatman, Anodisc 47, 0.02 mm) and annealed overnight at 100 °C. The filter membrane was immersed in 1 M sodium hydroxide solution for several minutes, after which the free standing thin ED-CNT film could be collected and was ready for use after drying. MEAs with an active area of 5 cm² were prepared by pressing the anode, 70 µm thick FAA commercial anion exchange membrane (Fuma-Tech GmbH) and cathode together. Catalyst ink was sprayed onto carbon paper in order to prepare the anode (0.5 mg_{Pt}cm⁻² Pt/C, E-TEK) electrode. The cathode electrode consisted of either the N-CNT thin film (0.2 mgcm⁻²), or carbon paper sprayed with Pt/C (0.2 mg_{Pt}cm⁻²) for comparison. The MEA cell temperature was kept constant at 80 °C and flow rates of 0.3 Lmin⁻¹ at a back pressure of 3 atm were utilized for both H₂ and O₂.

Scanning electron microscopy (SEM) images were obtained using a LEO FESEM 1530. X-ray photoelectron spectroscopy (XPS) imaging was obtained using a monochromatic Al K_α X-ray source to provide surface elemental compositions.

Result and discussion

The half cell ORR activity of synthesized N-CNTs and commercial Pt/C (E-TEK) was investigated in 0.1M KOH in order to demonstrate the ORR activity of the pristine materials using RRDE voltammetry. Comparative steady state polarization curves are displayed in Figure 1. The electrocatalytic activity of N-CNT materials towards ORR was found to be directly related to their overall nitrogen contents displayed in Table 1, as

determined from XPS analysis. ED-CNTs possessed significant nitrogen content (4.74 at. %) along with high ORR activity, superior to that of Pt/C. The higher nitrogen content observed for ED-CNTs was attributed to the highest nitrogen to carbon atomic ratio present in ED, compared with the DAP and DAB aliphatic diamine compounds with longer carbon chains. Thus, a higher nitrogen presence during growth resulted in higher nitrogen concentrations observed for N-CNT samples and enhanced ORR activity.

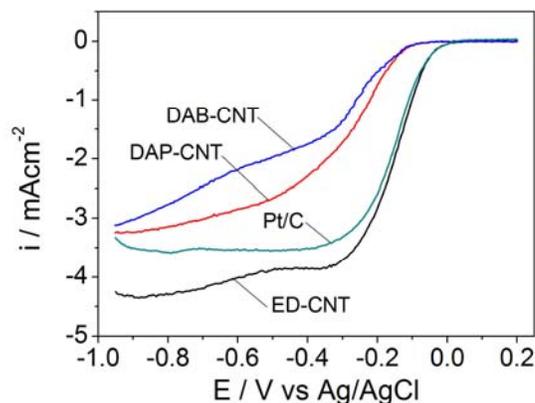


Figure 1. ORR polarization curves for N-CNT samples with Pt/C for comparison. Curves taken in 0.1M KOH at 900 rpm with a scan rate of 10 mVs^{-1} in the cathodic direction.

TABLE I. Nitrogen contents of N-CNT samples determined by XPS analysis

Sample	% at. N
ED-CNT	4.74
DAP-CNT	2.48
DAB-CNT	1.20

Due to their high inherent ORR activity and significant nitrogen content, ED-CNTs were selected as ideal candidates for fabrication into thin films using a filtration method, followed by heat treatment. An image of the thin film is displayed in Figure 2a, clearly demonstrating its free standing nature without any bonding agents. SEM images of the ED-CNT thin film were taken to investigate the microstructure of the material. A top view image is shown in Figure 2b displaying an interlaced mat of ED-CNTs with a highly porous bulk structure. The ED-CNTs are well dispersed creating a homogenous thin film.

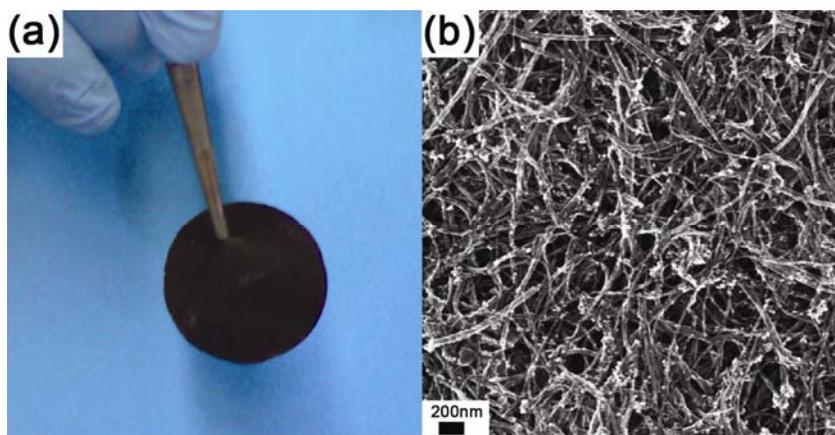


Figure 2. a) ED-CNT thin film displaying free standing nature and b) top view SEM image of ED-CNT thin film displaying homogeneous dispersion, resulting in highly porous, interlaced arrangement.

The performance of an ED-CNT thin film was tested as an ORR cathode in an alkaline MEA setup and compared with the performance of commercial Pt/C catalyst under identical conditions. Results from MEA analysis are displayed in Figure 3. Maximum power densities of 25.5 mWcm^{-2} and 19.1 mWcm^{-2} were determined for the ED-CNT film and Pt/C, respectively, corresponding to a 34 % increase in performance for the ED-CNT film. At a cell potential of 0.6 V, current densities for the ED-CNT film and Pt/C were determined to be 37.5 mAcm^{-2} and 27.5 mAcm^{-2} , respectively, a 36 % increase in performance for the ED-CNT film. These results indicate that ED-CNT thin films act as an efficient cathode in AAEM fuel cell MEAs, with performance superior to that of traditionally used Pt/C. The increase in performance observed for ED-CNTs can be attributed to their high inherent catalytic activity resulting from the significant nitrogen incorporation. Nitrogen doping has been shown to result in increased electronic conductivities (10, 11) and electron donor behavior (12, 13) of N-CNT materials. Moreover, high nitrogen concentrations have been reported to result in increased edge plane exposure resulting in active sites that serve to facilitate the adsorption and reduction of reactants and intermediates (1, 14). Combined with ideal structural properties of the thin film, specifically a high surface aspect ratio and a highly porous structure, a logical explanation for the enhanced alkaline MEA performance is formulated. Thus, nitrogen rich N-CNT thin films are established as non-noble ORR electrocatalyst materials for use as a cathode layer in AAEM fuel cells. They offer the distinct advantages of high inherent catalytic activity and a facile, relatively inexpensive synthesis procedure.

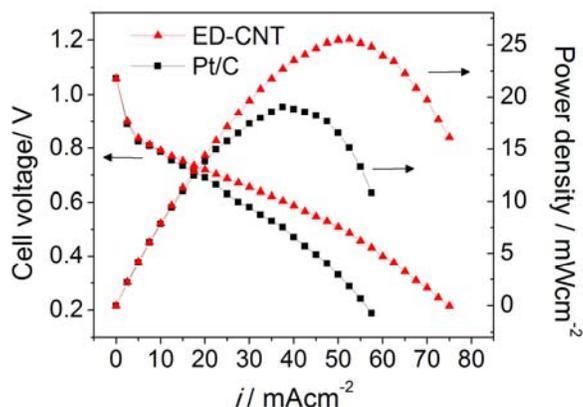


Figure 3. MEA performance displaying polarization curves (filled symbols) and power density curves (empty symbols) for 0.2 mg cm^{-2} ED-CNT thin film (red triangles) or $0.2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ commercial Pt/C (black squares) cathode catalysts, commercial FAA anion exchange membrane and $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ commercial Pt/C anode catalyst.

Conclusions

In summary, thin, free standing ED-CNT films were synthesized and tested as an ORR cathode catalyst for use in AAEM fuel cells. Electrochemical testing confirmed the catalytic activity of ED-CNTs prior to film fabrication, attributed to the presence of nitrogen atoms in the graphite lattice of the material. Using the ED-CNT thin film as a cathode catalyst in an AAEM fuel cell MEA resulted in a significant increase in peak power density and current density under normal operating conditions (cell voltage of 0.6 V) compared with commercial Pt/C. This work confirms the potential of utilizing nitrogen doped N-CNT thin films as cheap, effective ORR catalyst alternatives for use in AAEM fuel cells.

Acknowledgments

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