Carbon Nanotube Thin Film Based Fuel Cell to Reach DOE Targets

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ABSTRACT

We demonstrate a prototype polymer electrolyte membrane (PEMFC) fuel cell that reaches the technical targets set by DOE for 2015. We show that the Pt required for automotive fuel cells can be reduced by an order of magnitude by utilizing the Pt supported on a thin film of single walled carbon nanotubes (SWNTs). By optimizing the spatial distribution of Pt nano-particles in the catalyst support layer (CSL) we are able to pack more Pt in the active region and reach high power output (1 W/cm^2) with high mass activity (0.54 A/mg_{Pt}). The mass activity of Pt depends on the formation of an efficient triple phase interface for electrons, protons and the reactant gas. In order to maintain the efficient triple phase interface it is essential to optimize both the thickness of CSL and the required Pt loading. Here we show that with the optimum thickness and Pt loading, a SWNT-CSL with an efficient triple phase interface is able to realize high power output and high Pt mass activity.

Keywords: fuel cells, catalyst support, carbon nanotubes, thin films, gas diffusion electrode

1. INTRODUCTION

Carbon nanotubes are one of the promising nanomaterials for energy related applications such as supercapacitors, batteries and fuel cells.[1-3] In particular, carbon nanotubes have attracted the attention of fuel cell scientists and engineers to develop gas diffusion layers (GDL) and catalyst support layers (CSL) based on carbon nanotubes.[4-6] In addition to the extraordinary mechanical, chemical, electrical and thermal properties carbon nanotubes have excellent electrochemical corrosion stability which is attractive to the development of fuel cell electrodes.[7, 8]

Single walled carbon nanotubes (SWNTs) are well characterized[9] and commercially available in highly purified and functionalized forms. Recently, SWNTs gained more attention in fuel cell applications due to their ability to form free standing thin films. The fabrication of GDL and CSL using free standing SWNT thin films had been demonstrated earlier[6,10] and more recently multifunctional SWNT films with integrated GDL and CSL have also been demonstrated as a promising fuel cell electrode.[3] Due to the potential application of SWNT in fuel cells further investigation of SWNT electrode architecture is essential.

The performance of SWNTs in fuel cell electrodes could be further improved as evidenced by the superior performance in hybrid materials.[11] Hybrid materials comprising different types of carbon nanotube can exploit the advantages of both materials and deliver the best performance. In this direction, a hybrid CSL comprised of SWNTs and multiwall carbon nanotubes (MWNT) is reported to outperform the individual SWNT and MWNT based CSLs. The enhanced performance of the hybrid proved to be due to the increased porosity and hydrophobicity which is obtained by the introduction of MWNTs into SWNT-CSL.[11] In order to enable the potential application of SWNT thin films in fuel cell electrode it is important to identify key parameter that affect the performance. In this manuscript we show that with an optimum thickness and Pt loading, a SWNT-CSL reaches high power fuel cell with high mass Pt activity.

2. MATERIALS AND METHODS

Purified SWNTs with carboxylic functional groups (P3-SWNTs, Carbon Solutions Inc.) has been used in this study. P3-SWNT is washed with 0.01 M NaOH solution in order to remove the excess carboxylated carbon fragments by following a published literature.[12] Pt nano-particles are supported on these washed SWNTs using an *in-situ* ethylene glycol reduction method.[11] Thermogravimetric analysis (TGA) was used to estimate the wt% of Pt supported on SWNTs in air at a heating rate of 5 °C/min using a Perkin-Elmer Pyris 1 Thermal Analyzer. We have prepared 29wt% and 51wt% Pt supported SWNTs for this study. The Pt supported SWNTs is dispersed in ethanol and thin film CSL has been prepared by a filtration technique.[11] A carbon paper GDL with microporous layer (SGL Group GDL 25BC) was used instead of a filtration membrane and the Pt-SWNTs dispersion is filtered on the carbon paper GDL under vacuum. The scanning electron microscopy (SEM) image was recorded on a Philips XL30-FEG instrument operating at 10 kV.

The gas diffusion electrode with SWNT-CSL is cut into 5 cm^2 for fuel cell testing. Nafion membrane (DuPont NRE-212) was sandwiched between anode and cathode by hot pressing at 140°C for 3 min at a pressure of 40 Kg/cm^2. The anode was made with a Pt loading of 0.03 mg_{Pt}/cm^2 while the Pt loading on the cathode was varied between 0.03 to 0.075 mg_{Pt}/cm^2. Hydrogen and oxygen were used at the anode and cathode, with a flow rate of 0.2 SLM under a pressure of 35 psig. Anode and cathode humidifier temperatures were held at 70 (or) 80°C and the cell temperature was maintained at 70 (or) 80°C. Polarization curves were measured on a University Model fuel cell test station (Fuel Cell Technologies, Inc.). Cyclic voltammetry (CV) and accelerated stability experiments were carried out using a three electrode system on a CH Instrument potentiostat (model# 1140). The working electrode is fabricated to expose 1 cm^2 active area of the CSL by covering other parts with Teflon tape. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively, and all experiments were carried out under nitrogen atmosphere in 0.5 M H_2SO_4 at a 50 mV/s scan rate.

3. RESULTS AND DISCUSSION

The Pt supported SWNTs samples were characterized by TGA to estimate the wt% of Pt supported on the SWNTs. Figure 1 shows the TGA weight loss curves recorded in air. The starting SWNT material shows 7wt% residue and after the *in-situ* reduction method Pt supported SWNTs record a weight loss of 36% and 58%. After correcting for the 7wt% residue, the wt% of Pt is estimated to be 29 and 51 wt% respectively for these samples.

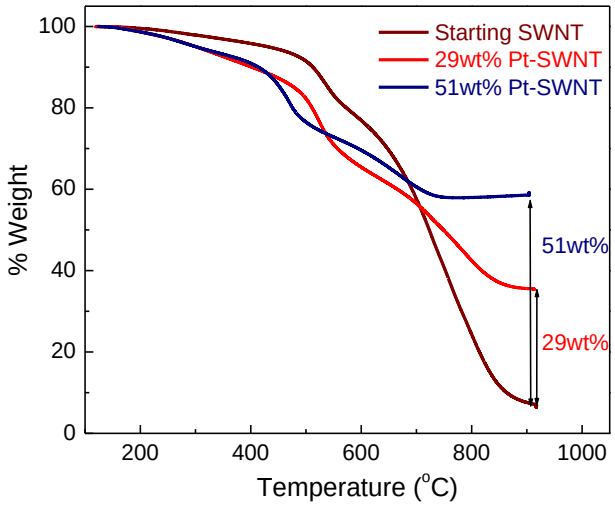

Figure 1: TGA of Pt supported SWNTs

Figure 2 shows the photograph and SEM image of SWNT-CSL prepared by filtration technique. The photograph shows the uniform coating of SWNT thin film on the carbon paper GDL, similar to commercial electrodes. The SEM image shows that the SWNT coating is porous in nature and it is suitable for gas diffusion and water management. The random network of SWNT is interconnected and acts as channels for collecting the electrons. The filtration technique allows the uniform formation of highly conducting SWNTs random network as opposed to casting and air-brushing techniques.

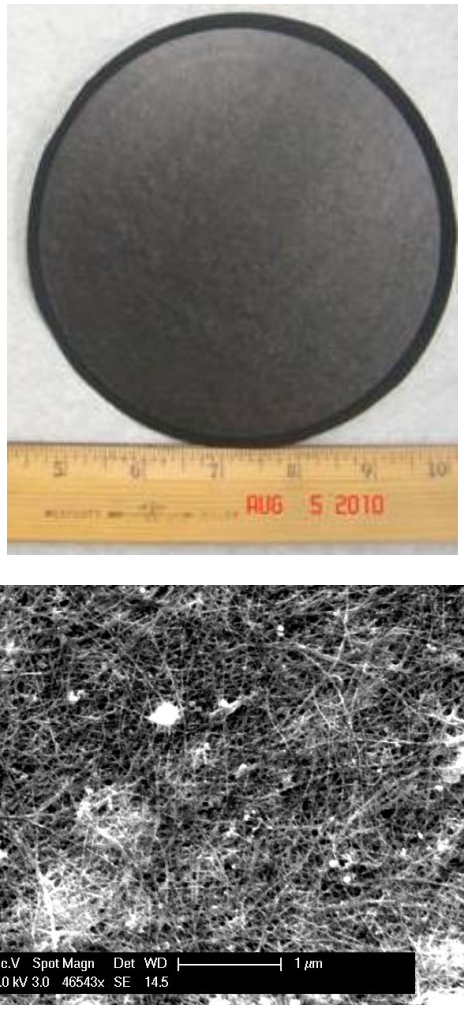

Figure 2: Photograph and SEM image of SWNT-CSL

We have prepared three different CSLs (A, B and C) using 29wt% Pt supported on SWNTs with a Pt loading of 0.03, 0.05 and 0.075 mg_{Pt}/cm^2 respectively. In order to pack more Pt into the CSL we have utilized 51wt% Pt supported on SWNTs and prepared a CSL (D) with a Pt loading 0.075 mg_{Pt}/cm^2 (Figure 3). Due to the rough profile of the carbon paper it was difficult to measure the thickness of the CSLs using cross sectional SEM. For thickness estimation we have prepared a reference thin film of Pt supported SWNT on an alumina filter and measured the thickness using cross section SEM. We have estimated the thickness of the A, B, C and D to be 0.6, 1.0, 1.5 and 0.8 μm respectively based on the amount of SWNT used (Figure 3).

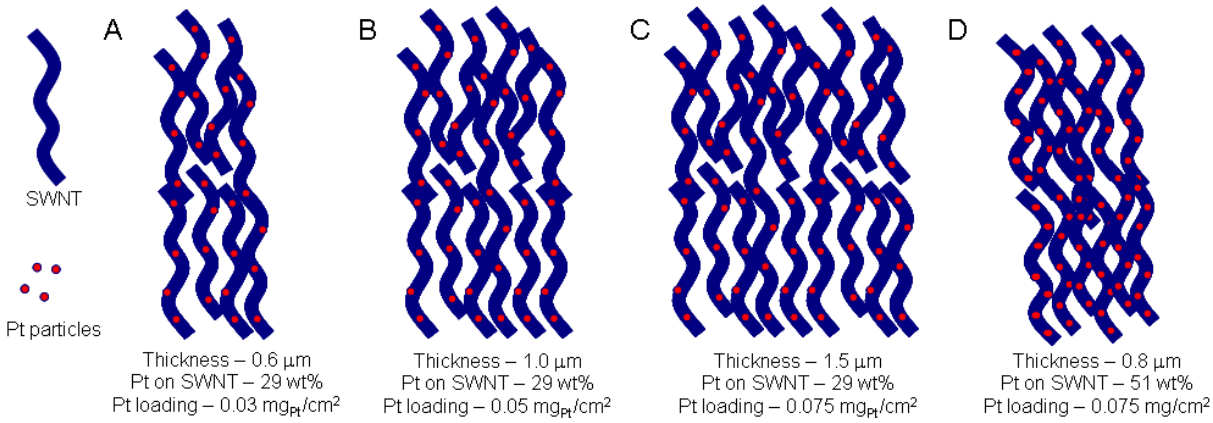

Figure 3: Schematics of cathode CSLs fabricated and their estimated thickness and Pt loading.

We have fabricated membrane electrode assemblies (MEAs) by using the SWNT-CSL (A to D) as cathode and their fuel cell performance was evaluated using hydrogen and oxygen (Figure 4) at 70 °C under 35 psig back pressure.

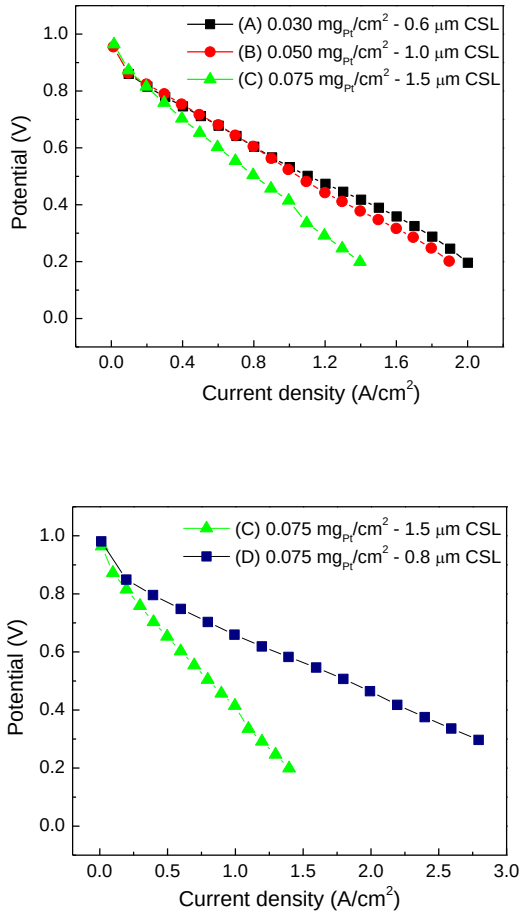

Figure 4: Comparison of fuel cell performance of cathode CSL (A, B, C and D) at 70 °C and 35 psig.

It is observed that the performance of B and C is decreased even though the Pt loadings are higher than A (Figure 4 - top). The reason for this decrease is the increase in the CSL thickness and it should be noted that the optimum thickness is for a SWNT-CSL of less than 1.0 μm. In the case of D we are able to pack the same amount of Pt as C (0.075 mg$_{Pt}$/cm^2) but at a reduced thickness of 0.8 μm. On comparing C and D the power output is significantly improved for D due to the placement of an efficient triple phase interface closer to nafion membrane (Figure 4-bottom). At an operating temperature of 80 °C and a back pressure of 35 psig CSL-D is able to reach a peak power of 1 W/cm^2 (Figure 5) and to reach all of the DOE targets (Table 1). The Tafel measurement at 80 °C with a back pressure of 35 psig shows a slope of 80 mV/decade which is close to the theoretical slope of 70 mV/decade.

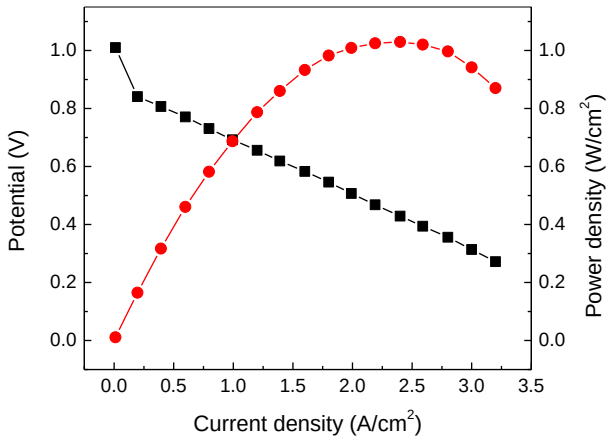

Figure 5: Fuel cell performance of CSL-D (cathode: 0.075 mg$_{Pt}$/cm^2) at an operating temperature of 80°C and 35 psig.

The Pt surface area of 29wt% Pt supported SWNT (*i.e.* CSL-A) is measured to be 59 m^2/g from CV measurements and it also showed excellent stability during the accelerated stability test with less than 5% reduction in the Pt surface area for more than 5000 cycles as shown in the Figure 6.

Parameter	Units	2015 DOE Targets	Present work
Pt Specific power density	g_{pt}/kW	0.200 (or) lower	0.130
Pt group metal (PGM)	mg_{PGM}/cm^2	0.200 (or) lower	0.105
Mass activity (iR-free)	A/mg_{Pt}@0.9V	0.44 (or) Higher	0.54
Specific activity	$\mu A/cm^2$@0.9V	720 (or) Higher	981
Rated power	W/cm^2	1.0 (or) Higher	1.0
¼ rated power at 0.8V	W/cm^2	0.250 (or) Higher	0.300
Current density at 0.8V	A/cm^2	0.300 (or) Higher	0.380

Table 1: DOE 2015 technical targets and the results obtained from the present work
(note: The present work is carried out at 80°C with 35 psig back pressure)

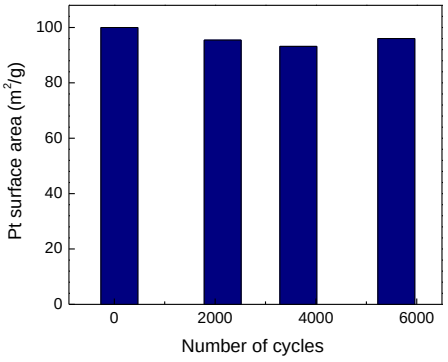

Figure 6: Accelerated stability test of SWNT-CSL (A)

4. SUMMARY

This promising wet-chemistry thin film technology together with the reduced Pt loading can be easily scaled and adapted to automotive fuel cells. This technology represents a promising application of nanotechnology that will benefit a broad range of industries interested in the successful implementation of hydrogen based power sources in order to further the penetration of clean technologies in the energy sector.

5. ACKNOWLEDGEMENT

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