High Performance Hydrogen Fuel Cells with Ultralow Pt Loading Carbon Nanotube Thin Film Catalysts†

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Fuel cell membrane electrode assemblies with Pt loading of 0.2 mg Pt/cm² at the anode and ultralow Pt loadings of 6 μg Pt/cm² and 12 μg Pt/cm² at the cathode have been fabricated using thin films of multiwalled carbon nanotube supported Pt catalysts (Pt/MWNTs) at the cathode. The Pt/MWNTs have a Pt weight loading of 26.8 wt % and a uniform and small Pt particle size of 2.1 nm. The MWNTs used are 360 μm long. This thin film cathode catalyst layer with a loading of 6 μg Pt/cm² is about 1.3 μm thick, contains no ionomer, and exhibits surprisingly high performance in a hydrogen proton exchange membrane fuel cell. The peak power density for a membrane electrode assembly with a cathode loading of 12 μg Pt/cm² when tested at 70 °C with hydrogen and oxygen is 613 mW/cm². A mass activity (ampere per milligram of Pt) based on the cathode Pt loading greater than 250 A/mg Pt is achieved with 6 μg Pt/cm², and this is among the highest reported to date.

Introduction

One dominant obstacle to the commercialization of fuel cells is cost. It has been estimated that the fuel cell electrode encompassing the carbon backing layer and Pt precious metal represents about 40% of the total cost of the fuel cell. Therefore, reducing the amount of Pt is intimately related to reducing a major cost contributor of the fuel cell. Consequently, there are numerous studies on a variety of different catalyst supports utilized in the proton exchange membrane fuel cell (PEMFC). The more widely used conventional catalyst support is carbon black. Other catalyst supports range from carbon nanotubes, fibers, and aerogels to nanofibers of an organic pigment. Notably, multiwalled carbon nanotubes (MWNTs) have been shown to be more resistant to corrosion than carbon black under a simulated acceleration of fuel cell operating conditions.

Earlier studies by the authors of this manuscript include different configurations of carbon nanotube (CNTs) in fuel cells. One of these configurations of CNTs used as a catalyst support entailed growth of the CNTs directly onto carbon fiber based paper by chemical vapor deposition (CVD) followed by electrodeposition or impregnation of the Pt nanoparticles onto the CNTs. In this configuration, it was difficult to simultaneously prepare small uniform Pt nanoparticles of less than 5 nm and achieve a high Pt loading. Additionally, the CVD process was also an expensive process to scale up if large areas were needed. Another configuration of CNTs that was investigated involved first depositing small catalyst nanoparticles onto CNTs using ethylene glycol as a reducing agent and solvent to achieve 30 wt % or higher metal catalyst loading and then making a CNT film comprised of the catalyzed CNTs by a filtration method. Alignment of the CNTs was possible by the filtration method. This CNT film was subsequently transferred onto Nafion via a hot pressing method to become a catalyst layer in the fuel cell cathode. A Nafion solution was usually spayed onto the CNT film before the hot press transfer. This filtration technique was successfully applied to hydrogen PEMFCs using MWNTs and to direct methanol fuel cells (DMFCs) using various forms of CNTs. In this study, we use a similar variation of this filtration technique in a hydrogen PEMFC. However, Nafion is eliminated from the catalyst layer, and substantially lower catalyst loadings are used.

Previous work by 3M using nanofibers of an organic pigment to form a nanostructured thin film (NSTF) of less than 1 μm as the catalyst support demonstrates the elimination of Nafion in their catalyst layer. Debe at 3M believes a submicrometer catalyst layer thickness allows for a higher surface area to volume ratio giving smaller distances of travel for protons to percolate to the catalyst surface sites from the proton exchange membrane (PEM) effectively bringing about nearly 100% catalyst utilization. This is in stark contrast to the much thicker conventional catalyst layers of dispersed Pt on carbon black impregnated with Nafion where distances between the catalyst surfaces sites and the PEM can be as high as 15 μm at times. Debe achieves high mass activities with the NSTF catalyst support (Pt/NSTF) and shows small decreases in fuel cell performance with a decrease in Pt loading by a full order of magnitude. Additionally, this high performing Pt/NSTF uses no additional ionomer (e.g., Nafion). In this study, Pt nanoparticles (2.1 nm) supported on 360 μm long MWNTs (Pt/MWNT) form a thin 1.3 μm catalyst layer when using a catalyst loading of 6 μg Pt/cm² via the aforementioned filtration technique. Surprisingly, high fuel cell performance is obtained for such a low Pt loading. The cathode specific mass activities of our Pt/
MWNTs surpass 3M’s reported cathode specific mass activities in the higher mass activity range using a lower operating pressure than that reported by Debe.4

Experimental Methods

MWNT Synthesis. MWNTs were made using a CVD method commonly found in literature.12 The CVD system used is custom built comprised of a 47 mm inner diameter quartz tube and Lindberg Blue single zone tube furnace. Ferrocene dissolved in p-xylene act as the precursors. This mixture is introduced dropwise through a small 1/16 in. flexible stainless steel tube by a solvent resistant peristaltic pump into an upstream region heated at 180 °C where it is evaporated as it is carried by an Ar and H2 mixture (10% H2 by volume) into the MWNT growth region downstream held at 800 °C. The MWNT growth time is 2.5 h resulting in aligned MWNTs of approximately 360 μm in length as measured by scanning electron microscopy (SEM). The MWNTs are collected from the quartz tube after cooling in Ar flow. Typical transmission electron microscope (TEM) images show a range of MWNT diameters mostly from 30 to 80 nm with a few occasional tubes of 100 nm.

Catalyst Preparation. Prior to Pt deposition onto the MWNTs, the MWNTs were surface oxidized by refluxing in a 1.0 M H2SO4/2.0 M HNO3 mixture for 6 h. The Pt/MWNTs were prepared by depositing platinum in an ethylene glycol solvent. The MWNTs were suspended into ethylene glycol by ultrasonication for 13 h. The pH was adjusted to 10 as measured by litmus paper by addition of a 1 M NaOH mixture in ethylene glycol. A mixture of dihydrogen hexachloroplatinic acid (H2PtCl6·6H2O) and ethylene glycol were slowly added dropwise with stirring. This mixture of MWNTs, hexachloroplatinic acid, NaOH, and ethylene glycol was heated at 140 °C for 3 h under refluxing conditions while stirring to facilitate Pt reduction. Upon cooling to room temperature, the pH of the mixture was slowly brought down to 2 by the dropwise addition of an aqueous solution of 0.1 M HCl. A Pt loading of 26.8 wt % was achieved after filtration, washing with water, and drying. This loading was determined by thermogravimetric analysis (Pyris 1 TGA) after adjusting for MWNT iron precursor catalyst content (1.3 wt % after surface oxidation).

Pt/MWNT Characterization. The Pt/MWNT catalyst was imaged by transmission electron microscopy (TEM) using a Philips Tecnai 12. Mean Pt nanoparticle size was measured by X-ray diffraction (XRD) using a Bruker AXS D8 Advance. Cross sections of the thin films of the Pt/MWNT after hot pressing onto the Nafion membrane were imaged with a scanning electron microscope (Philips XL30-FEG) to estimate the thickness of the resulting thin films.

Membrane/Electrode Assembly Fabrication and Testing. The carbon backing layers used in the membrane/electrode assembly (MEA) were purchased from SGL Carbon Group (Model GDL 25CC). The GDL 25CC comes with the hydrophobic microporous layer (MPL) deposited onto the carbon fiber based carbon backing layer by the manufacturer. The GDL 25CC were used on both the anode and cathode. Anodes used in this study were prepared in a conventional manner by airbrush spraying a sonicated catalyst ink mixture of 20 wt % Pt/XC-72 (E-TEK, HP C1-20), 5 wt % Nafion solution (Ion Power, Inc.), water, and isopropyl alcohol onto the GDL 25CC. The resulting loadings on the GDL 25CC are 0.2 mg Pt/cm2 and 35 wt % Nafion loading with respect to total dry weight of the ink.

Thin films were prepared before the final hot pressing of the MEA. The thin films were prepared by sonication a dilute suspension of 26.8 wt % Pt/MWNTs in ethanol. The suspension was then filtered through a 90 mm 0.4 μm pore size polycarbonate filtration membrane (Millipore, HTTP) using a standard glass microfiltration apparatus. The resulting thin film was cut into 5 cm2 squares along with the underlying filtration membrane.
using a razor blade. A Nafion NRE-212 membrane (Ion Power, Inc.) was used as the proton exchange membrane (PEM). The MEA components are assembled in the following order before hot pressing: 5 cm² anode electrode with 0.2 mg Pt/cm² and 35 wt % Nafion on GDL 25CC, Nafion NRE-212 PEM, and Pt/MWNT thin film on top of filtration membrane (see Figure 1). The Pt/MWNT on the cathode and Pt/XC-72 on the anode are in contact with the PEM during hot pressing. Hot pressing occurs at a pressure of 140 atm at 145 °C for 3 min. After cooling, the filtration membrane is peeled off of the thin film of Pt/MWNTs and a GDL 25CC is placed on top of the thin film of Pt/MWNTs with the MPL in contact with the Pt/MWNTs. The resulting MEA is 5 cm² and is placed inside a fuel cell assembly designed for 5 cm² MEAs with serpentine flow channels machined into graphite bipolar plates (Electrochem, Inc.). The MEA was tested using a Scribner Associates fuel cell test station (Model 890B) providing the simulated load. Humidifiers are custom built. Cell temperature is maintained at 70 °C. Anode and cathode are operated at identical conditions of 35 psig, humidifier temperatures are set at 80 °C, and H₂ and O₂ flow rates are at 0.2 standard L/min. MEAs were activated over a period of about 6 to 8 h by cycling the voltage between open circuit voltage and 0.2 V.

Results and Discussion

XRD patterns for the Pt/MWNT catalyst are shown in Figure 2. The mean particle size of the Pt nanoparticles was estimated from the isolated Pt(220) peak with the Scherrer equation. The mean particle size is approximately 2.1 nm which is consistent with typical TEM images of the Pt/MWNT samples (see Figure 3). Typical TEM images show uniform and small diameter Pt nanoparticles from 2 to 3 nm well dispersed on the surface of the MWNT at a loading of 26.8 wt % Pt.
thin films of Pt/MWNTs supported on the polycarbonate filtration membrane. After hot pressing this thin film of Pt/MWNTs supported on the polycarbonate filtration membrane onto the PEM, the polycarbonate filtration membrane is easily peeled off with what visually appears to be nearly 100% transfer. The differential mass of the polycarbonate membrane with Pt/MWNTs before and after peeling is about 0.1 mg in the case of 6 µg Pt/cm², which approaches the detection limit of the mass balance itself. Therefore, the differential mass before and after peeling was not used in estimating the Pt loading as is typically done for making conventional fuel cell electrodes with typical Pt loadings of 0.2 mg Pt/cm². Assuming uniform distribution of the Pt/MWNTs over the 7.5 cm diameter of deposition onto the polycarbonate membrane, the Pt loading is estimated knowing the amount of Pt/MWNT originally dispersed into ethanol. The cathode Pt loadings used were 6 µg Pt/cm² and 12 µg Pt/cm² assuming 100% transfer of the Pt/MWNT to the PEM. The filtration method of Pt/MWNT transfer onto the PEM is much easier than spraying a catalyst ink onto a GDL before hot pressing and significantly less labor intensive. Of course, at these low Pt loadings, a spraying technique for catalyst layer application would introduce many inaccuracies from either overspray or the use of a mass balance to measure the differential weight before and after spraying. Furthermore, the filtration method of Pt/MWNT transfer would also ensure a more intimate contact with the PEM.

Traditional fuel cell performance curves were measured after allowing for a steady reading at each point during the current scan as controlled by the Scribner Associates fuel cell test station (see Figure 4). At a loading of 6 µg Pt/cm², a peak power density of 431 mW/cm² occurs at a current density of 1.15 A/cm². For a loading of 12 µg Pt/cm², a peak power density of 613 mW/cm² occurs at a current density of 1.65 A/cm². These peak power densities are astonishingly high for the ultralow Pt loadings used. A useful analysis is to convert the traditional performance curve data to a more meaningful comparison where the data reflects the cathode Pt loading. Hence, mass activity curves were derived from the fuel cell performance curves by normalizing the current density (ampere per square centimeter) to the Pt mass loading (milligram of Pt per square centimeter). Mass activity curves from the Los Alamos National Lab (LANL) and 3M Corporation were extracted from Figure 13 of chapter 45 in Handbook of Fuel Cells: Fundamentals, Technology, and Applications. Cathode specific mass activities are shown in Figure 4 for a Pt loading of 0.12 mg Pt/cm² for the Pt/C (Pt supported on carbon black) LANL curve and 26 µg Pt/cm² for the 3M Pt/NSTF curve. All of the mass activity curves use a Nafion NRE-212 membrane “C” that LANL used is believed to be similar to Nafion NRE-212 that the 3M Pt/NSTF curve used. The LANL black) LANL curve and 26 µg Pt/cm² for the 3M Pt/NSTF curve. All of the mass activity curves use a Nafion NRE-212 membrane “C” that LANL used is believed to be similar to Nafion NRE-212 that the 3M Pt/NSTF curve used. The LANL curve and 26 µg Pt/cm² for the 3M Pt/NSTF curve. All of the mass activity curves use a Nafion NRE-212 membrane “C” that LANL used is believed to be similar to Nafion NRE-212 that the 3M Pt/NSTF curve used. The LANL curve and 26 µg Pt/cm² for the 3M Pt/NSTF curve. All of the mass activity curves use a Nafion NRE-212 membrane “C” that LANL used is believed to be similar to Nafion NRE-212 that the 3M Pt/NSTF curve used.

Pt is known to have six orders of magnitude lower activity for the four electron process of the cathode oxygen reduction reaction when compared with the two electron one for the anode hydrogen oxidation reaction. Therefore, modifications were only made to the cathode in this study to observe the effects on performance of using this novel Pt/MWNT thin film catalyst layer architecture. It is expected that significant reduction of Pt use in the anode side and thus the reduction in the total amount of Pt use in a fuel cell are possible while maintaining the same level of performance while using the low Pt loading Pt/MWNT thin film catalyst layer.14,15

Conclusions
A promising design has been demonstrated for a membrane electrode assembly that is simple and can dramatically reduce the amount of Pt needed while maintaining a high level of performance. This work has significant implications for solving the cost issue of fuel cells, which is one of the most significant obstacles in the quest for commercializing hydrogen fuel cells for automotive transportation.

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References and Notes