

TiO₂-CNT composite as novel corrosion resistant PEMFC catalyst support

by

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ABSTRACT

There is a need for novel materials to replace carbon black as platinum catalyst support in PEMFC that are more resistant to corrosion by electrochemical oxidation. The novel material investigated in this effort was Titania/multiwall carbon nanotube composite. TiO_2 -MWCNT was synthesized using a surfactant assisted wet chemical technique. The TiO_2 -MWCNT composite was obtained from chemical reaction between TiCl_4 and hydroxyl functionalized MWCNT. D.C electrical conductivity vs. CNT content profiles showed adverse effects on conductivity beyond 17%. The addition of CNT conferred a maximum electrical conductivity of 0.87 S/cm, a value less than the target of 1 S/cm but sufficient for the intended function. XRD scans revealed the effective formation of anatase titania while the presence of CNT was indicated by the black color in the final TiO_2 composite and SEM. Cyclic voltammetry scans at 8 hour-intervals, after oxidation at 1.2V vs. Ag/AgCl by chronoamperometry technique, demonstrated the superior resistance to corrosion of the synthesized TiO_2 -CNT as compared to commercial carbon black.

Chapter 1

1.1 BACKGROUND

Polymer exchange membrane fuel cells (PEMFC) are low temperature electrochemical cells that directly convert the chemical energy in hydrogen into electricity without combustion. The release of electrical energy in a PEMFC, as opposed to widespread combustion-based systems, produces only water as by-product. A traditional fuel cell operates as follows (Larminie, 2003):

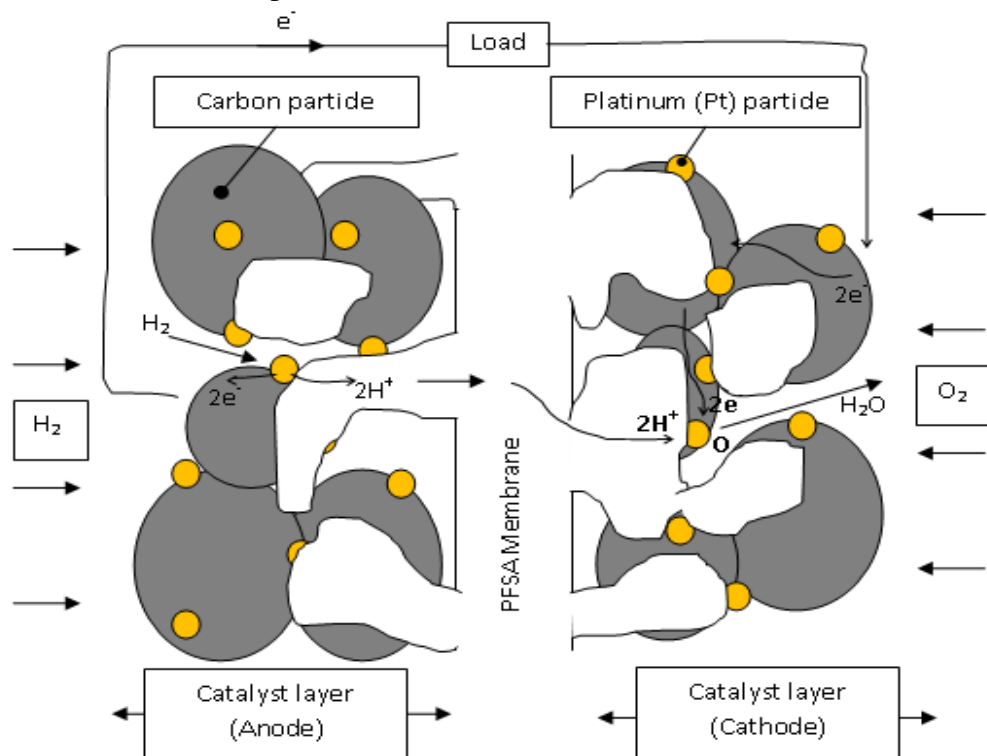
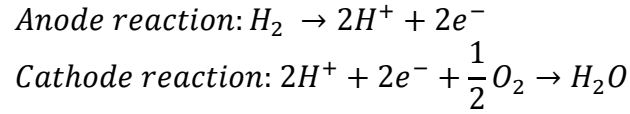


Figure 1- Schematic of PEMFC

Note: All reactions occur at three phase contacts: Gas/Platinum/Ionomer. The ionomer is solid state perfluorosulfonic acid (PFSA). As an acid, PFSA is capable of protons conduction from the anode to the cathode of the fuel cell.



At the anode, hydrogen gas splits into protons and electrons under the catalytic effect of platinum in the catalyst layer. The generated protons cross over to the cathode through the proton exchange membrane (usually NafionTM PEM). Electrical current is produced when the electrons generated in the anode reaction traverse the external circuit to the cathode. At the cathode, protons and electrons combine with oxygen gas on platinum catalyst to produce water.

1.2 INTRODUCTION

PEMFC for transportation application has been of particular interest to the DOE since the 1980s as a candidate solution in reducing the growing dependence of the United States on foreign oil (DOE, 2009). This particular interest has spurred intense research to improve the overall viability (efficiency, durability, affordability) of PEMFC. In terms of durability, commercial PEM fuel cell stacks come with very limited warranties. For example, Ballard Inc. warranted the University of Delaware fuel cell bus stack for only 100 hours of operation which is less than 5 days of continuous driving. A major reason for such a short commitment from fuel cell manufacturers is a relatively quick degradation of cell catalyst layers (CL) during cycling. A recent quantitative study (Zhang et al., 2009) reports the following changes in the CL structure after 300 hours of operation:

- ✓ Decrease in fluorinated compounds (synonymous with a decrease in ionic conductivity)
- ✓ Increase in graphitic carbon (+17.9 % after 300h operation)
- ✓ Decrease in metallic platinum content (-10.1%)
- ✓ Agglomeration of metallic platinum (decrease in active surface area detrimental to activation)
- ✓ Increase in oxidized forms of carbon (+7.2%)
- ✓ Increase in oxidized forms of platinum (+10.1%)
- ✓ Migration of platinum to sub-surfaces of the catalyst layer (reduces catalyst site occupancy)

The CL structure change is corroborated by distinct fall in the performance curves of the cells. Janssen et al. (2009) made similar findings: they observed a steady decrease in electrochemically active surface area (ECSA) and increase in transport losses as a result of cycling. Carbon corrosion is hereby proven to be an important obstacle to the economic viability of PEMFC and commands investigation of different materials as platinum support in the CL. Metal oxides such as Al_2O_3 , MgO , and TiO_2 are proven to withstand the corrosive environment (high acidity, electrochemical potential, water presence) of electrochemical cells (Hsieh et al., 2009). TiO_2 in particular carries further desirable properties summarized below:

- ✓ Hypo-d-electronic configuration which enhances the catalytic activity of Pt (Rajalakshmi et al., 2008) (Jaksic, 2001)
- ✓ CO stripping properties of metallic titanium (Hassan et al., 2009)

- ✓ Excellent dispersion of platinum, resulting in ECSA comparable to carbon support

Altogether, TiO_2 is an excellent candidate towards extending the cyclability of the catalyst support in the fuel cell environment. Unfortunately, TiO_2 is an electrical insulator, a feature which impedes its function as the catalyst support. Anatase TiO_2 has DC conductivity of the order of $10^{-6} \text{ S.cm}^{-1}$ as compared to 0.1 up to 0.3 S.cm^{-1} for the protonic conductivity of the perfluorosulfonic acid (PSFA) membrane (Kraemera et al., 2008). Used alone, the extremely low electrical conductivity of TiO_2 would be a limiting factor in the reactions and species transport involved in the fuel cell operation. Kraemera reports that the conductivity of the CL needs to be approximately 10 times higher than the protonic conductivity so as not to be a limiting factor to species exchange in the PEMFC reactions. As a consequence, an electron conducting backbone is required in the structure of the TiO_2 -based CL in order to make the novel catalyst support a viable alternative to carbon-based catalyst supports.

- Capacity to form a stable structure with TiO_2
- Excellent electrical conductivity
- Resist corrosion in the fuel cell environment

Table 1- Selection guidelines for the TiO_2 electrically conductive reinforcement

Carbon nanotubes (CNT) have received significant scientific interest since their discovery for their unique and opportune combination of properties. They incorporate high mechanical modulus of the order of 1 TPa for multi-walled CNTs (Salvetat et al., 1999), high electronic conductivity, excellent thermal (peak rate of destruction on TGA at 650°C (Pang et al., 1993)) and chemical stability. A strong correlation exists between thermal stability and electrochemical stability (Kraemera et al., 2008), which suggests that the high thermal stability of CNT is an asset for this application. Using a combination of high potential chronoamperometry and cyclic voltammetry, the superior stability of CNTs over carbon black in the simulated conditions of a fuel cell was confirmed (Li, 2008). Furthermore, CNTs have been successfully used to move metal oxides (Al_2O_3 and ZnO) from electrical insulators to electrically conductive composites (Kumari et al., 2009) (Sameera et al., 2010). Using sintered ceramic techniques and direct deposition of CNT on Al_2O_3 , Kumari et al. achieved conductivities up to 33.4 S/cm in CNT- Al_2O_3 composites containing only up to 19.1 wt% CNT. On the other hand, using a chemical wet technique similar to the

one presented herein, Sameera et al. achieved a maximum conductivity of 0.55 S/cm using up 83.3 % by weight of multiwall carbon nanotubes (MWCNT) in ZnO. In our study, we investigate the use of electrically-reinforced TiO₂-MWCNT as the catalyst support material in PEMFC. The objective is to obtain a corrosion resistant CL with performance comparable or superior to current carbon supports.

Chapter 2

2.1 MATERIAL SYNTHESIS PROCEDURE

TiO₂-CNT composites were synthesized using a surfactant assisted wet chemical technique. Hydroxyl-functionalized MWCNT (CNT-OH) were purchased from BuckyUSA Corporation. In a beaker, deionized water (DI-water) of about 5000 times the mass of CNT-OH was taken. The necessary quantity of CNT-OH and a mass of surfactant (dodecylbenzenesulfonic acid-sodium salt from Aldrich®) equal to 0.3% of water weight was then added. The mixture of DI-water, CNT-OH and surfactant was pulse-sonicated (5 second ON, 3 second STANDBY) using a tip sonicator (750 W SONICS® VibraCell™) for 2 hours to disperse the CNT-OH in water. The dispersed mixture was placed on a hot plate and magnetically stirred. The necessary volume of titanium tetrachloride (TiCl₄ from Fluka®) was added dropwise to the mixture using a syringe. Theoretically, 1.372 mL of TiCl₄ is required to produce 1g of TiO₂. Nonetheless, to compensate for the loss due to the volatility of TiCl₄, it was assumed that 1.4 mL of TiCl₄ would produce 900 mg of TiO₂. Note however that the concentrations of MWCNT in the final composite TiO₂-CNT were calculated based on the theoretical correspondence of 1.374 mL TiCl₄ for 1 g of TiO₂. The formation of titania was assumed from the onset to guide the chemical procedure. This procedure was developed by Palanichamy (2010).



Figure 2 - TiO_2 -CNT synthesis setup and steps

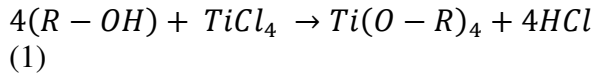
The addition of TiCl_4 to the mixture produced an immediate black precipitate (Fig. 2), as opposed to the white color of pure TiO_2 , testifying of an interaction between TiCl_4 and CNT-OH. The beaker content was then heated to 80°C for about 3 hours to ensure complete reaction. Water was removed from the product precipitate by multiple filtrations through filter papers. The product composite TiO_2 -CNT was heated at 100°C in an oven to remove any remnant water. Finally, the

composite was heated to 450°C in experiment 1 and 400°C in experiment 2 (LUCIFER® Furnaces Inc. Model 6033CT 8810) for 2 hours to burn off any remaining surfactant material. High temperature heating also leads to phase change in TiO₂ to form anatase TiO₂.

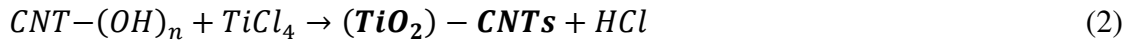
2.1.1 RATIONALE OF PROCEDURE

2.1.1.1 TiCl₄ reaction with CNT-OH

TiCl₄ is known to react with the hydroxyl group of alcohols to produce alkoxides according to the formula:



This feature of TiCl₄ is being exploited to force a reaction between TiCl₄ and CNT-OH according to the following unbalanced equation:



TiO₂-CNT is a polymer structure schematically represented in Fig. 4.

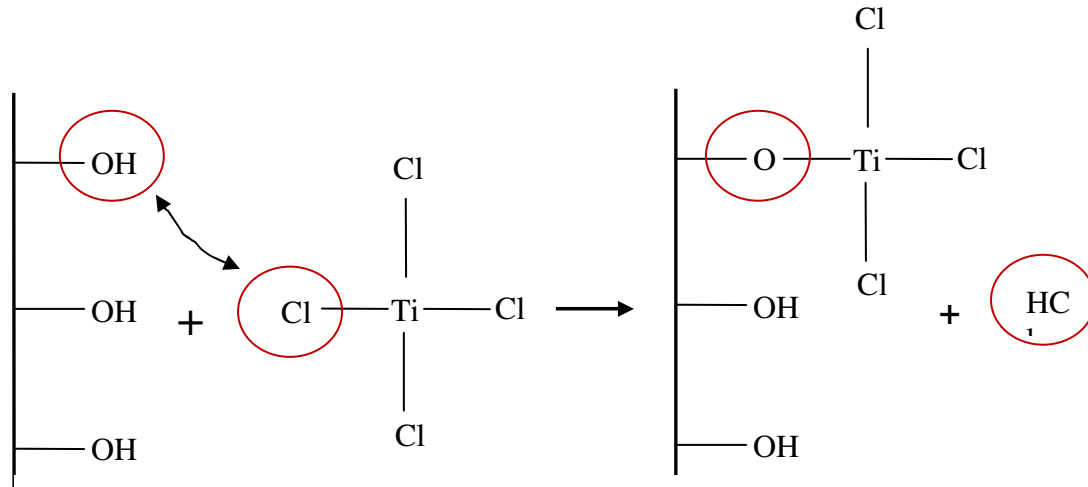


Figure 3 - Expected reaction between the hydroxide function on CNT and the Chloride of the TiCl₄

The high propensity of hydrogen and chlorine atoms to react and produce hydrochloric acid is utilized in the above procedure. The dispersed CNT-OHs at the encounter of TiCl_4 are expected to lose the hydrogen in the hydroxide group to the chlorine on titanium tetrachloride for the formation of hydrochloric acid. Meanwhile, the titanium atom is free to exchange a covalence with the oxygen left on the CNT.

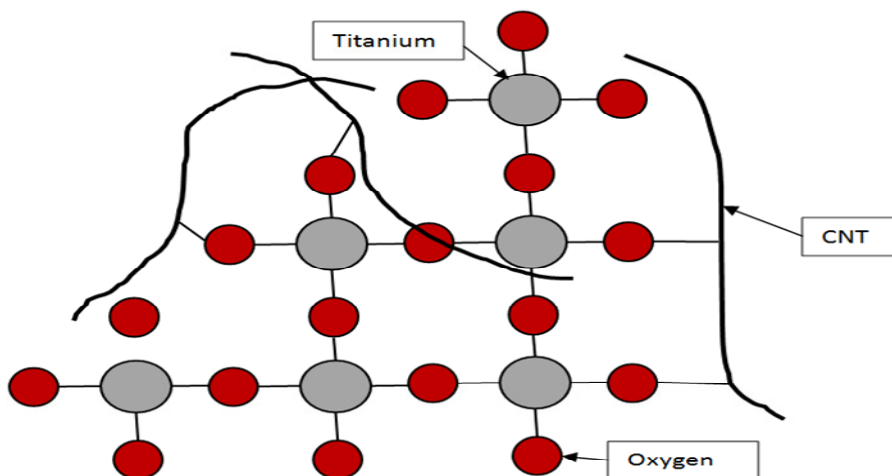


Figure 4 - Structural diagram of expected final material

The elementary step described in Fig. 3 replaces the chlorine on TiCl_4 with $[-\text{O}-\text{CNT}]$ at the encounter of TiCl_4 and $\text{CNT}-\text{OH}$ molecules. In addition to the substitution of $[-\text{O}-\text{CNT}]$ for chlorine, the aqueous media promotes the formation of a polymeric TiO_2 crystalline structure from TiCl_4 (the most prevalent reaction). The final material is then an oxide of titanium bonded to the CNT (Fig. 4). The exact crystalline structure is revealed via X-ray diffraction. The MWCNT in the composite is the conducting backbone while the TiO_2 particles support and disperse the platinum catalyst particles to form an optimal catalyst layer.

2.1.1.2 Why use a surfactant?

Forms of carbon such as MWCNT and graphene are hydrophobic, favoring agglomeration and suspension in aqueous solutions. Titania, as other metal oxides, is highly hydrophilic. The use of anionic surfactants such as dodecylbenzenesulfonic acid-sodium salt allows dispersion of CNT in water for a more uniform chemical interaction between TiCl_4 and CNT during synthesis (Wang et al., 2009). The homogeneous dispersion increases the probability of encounter between TiCl_4 and CNT-OH to maximize the occurrence of the reaction described in Fig. 3. A surfactant such as the one used in our synthesis offers micelles with dual hydrophobic and hydrophilic ends. The hydrophobic tail of the micelle binds to the hydrophobic CNT reactant while the hydrophilic region promotes dispersion of the captive CNT in the aqueous media (Fig. 2, addition of TiCl_4). The uniformity of the distribution of CNT in the final composite is likely due to the optimal dispersion obtained prior to the chemical reaction between CNT-OH and TiCl_4 (Wang et al., 2009).

2.1.1.3 High temperature surfactant removal

High temperature burning of the surfactant need not affect the structural integrity of the components of interest in the synthesized composite. Thermal degradation of CNTs occurs above 650°C , and TiO_2 can withstand temperatures above 750°C suffering only phase changes (Huang et al., 1997). The degradation temperature of dodecylbenzenesulfonic acid-sodium salt was approximated at 300°C (Tsotra, 2004). Within this configuration, temperatures between 400°C and 450°C safely burned off the surfactant without any major degradation neither in TiO_2 nor CNT.

Chapter 3

3.1 MATERIAL STRUCTURE

3.1.1 X-Ray Diffraction (XRD)

The crystalline structure of the material was elucidated using X-ray diffraction. The measurements were carried out using a 3 kW Philips® XPERT-MPD diffractometer with copper anode.

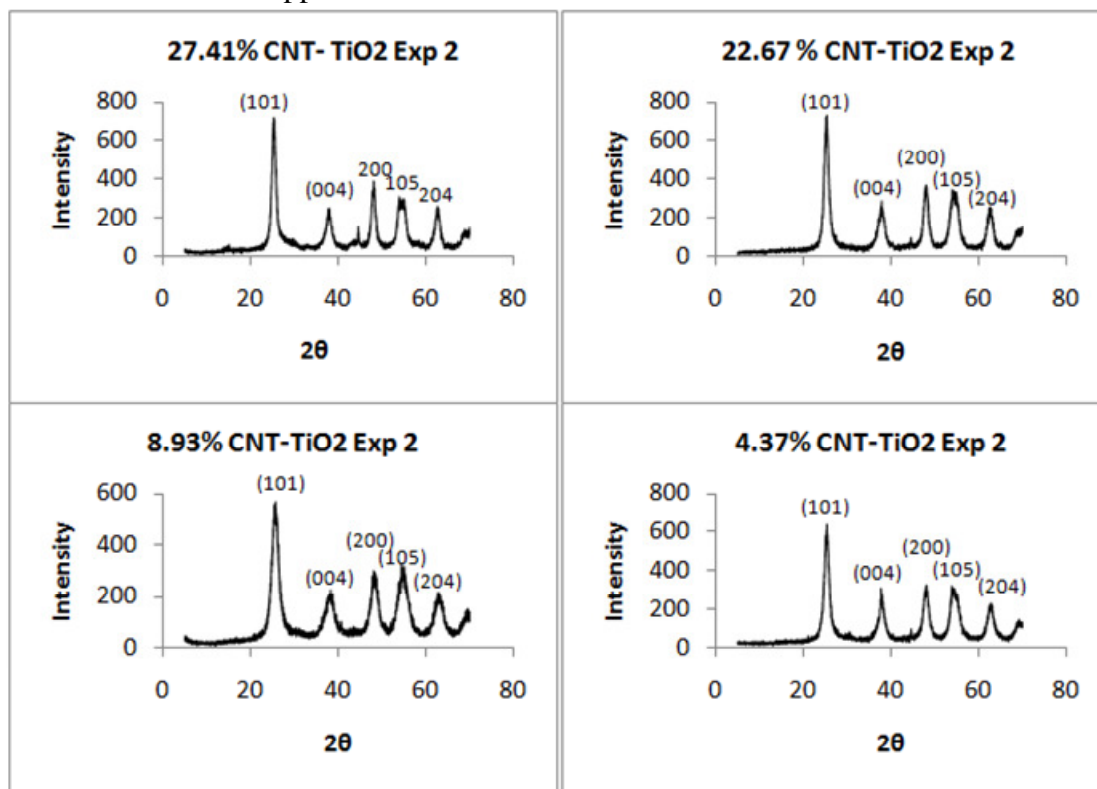


Figure 5 - XRD scans of TiO₂-CNT composites with different CNT contents (percentage CNT indicated in titles)

The representative peaks of anatase phase TiO_2 occur at scattering angles (2θ) of 25.3° , 36.6° , 48.0° , 55.0° , and 62.6° , which corresponds to (101), (004), (200), (105), and (204) crystallographic planes (Hsieh et al., 2009). The peaks as seen in Fig. 5 signal the definite presence of anatase TiO_2 . The pronounced peaks show highly crystalline structures in all samples. The relatively low concentrations of CNT used (27.41% maximum) has had a low impact on the crystallinity of titania. The presence of CNT is not revealed in these scans due to their amorphous nature.

3.1.2 Scanning Electron Micrograph (SEM)

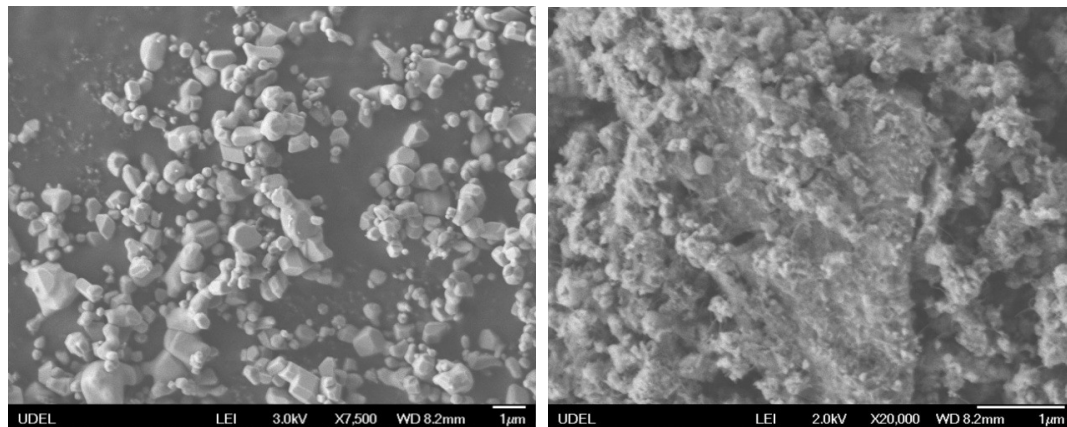


Figure 6- SEM of Pristine TiO_2 (left) vs. TiO_2 -CNT composite (right) (Palanichamy, 2010)

SEM scans in Fig.6 demonstrate the uniform distribution of carbon nanotubes in the composite TiO_2 -CNT. Though the scans were made at different magnifications, there is a clear structural difference between the pristine TiO_2 and the composite TiO_2 -CNT. In the scan of TiO_2 -CNT, strands of CNT are observed throughout the material.

The crystal structure of the final composite is altered by the incorporation of CNT. Carbon nanotubes are known to agglomerate; our preparation technique has prevented such agglomeration and successfully distributed the carbon nanotubes in the whole TiO_2 matrix, thereby providing good electrical conductivity.

Chapter 4

4.1 CONDUCTIVITY OF SYNTHESIZED TiO_2 -CNT

In order to find the optimal concentration of CNTs in TiO_2 , two sets of five different concentrations of TiO_2 -CNT composites were synthesized and tested for DC conductivities. The final composite being a powder, a two-block chamber with electrode contacts was used to compress the material into a pellet under a press.

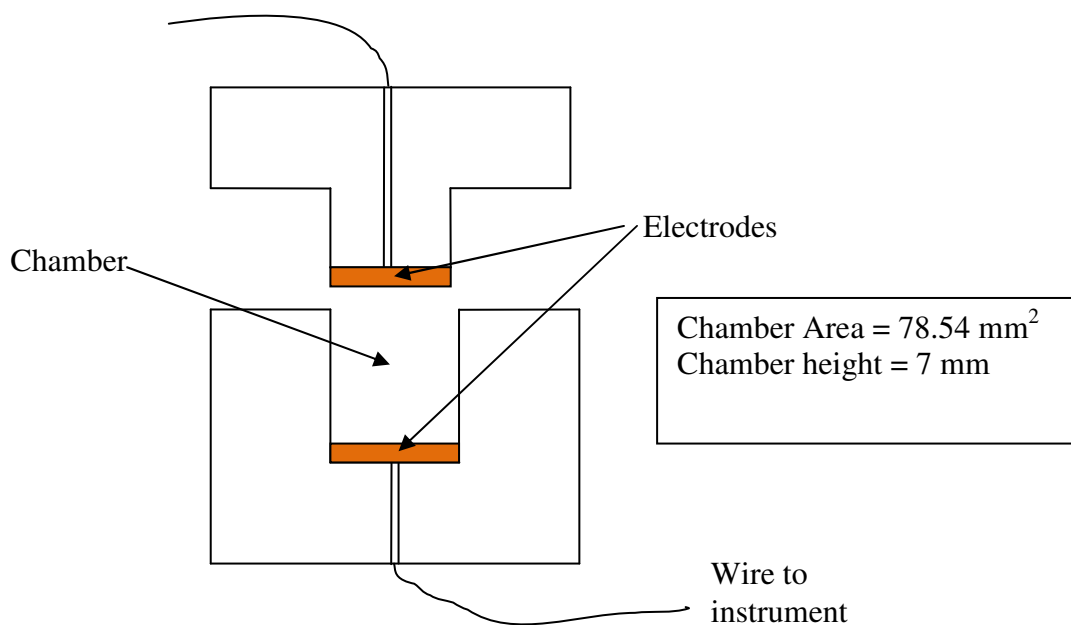


Figure 7- Schematic of the conductivity cell

The pellets were fabricated by compressing 0.5 g of TiO_2 -CNT material under 1500 psi (CARVER® Hydraulic press model #3912). The conductivity was then measured with the conductivity cell under pressure using VersaSTAT3™ by AMETEK® in

linear voltammetry mode. The results are presented in Table 2 and 3. *Composition* stands for the percentage by weight of MWCNT in the composite TiO₂-MWCNT.

Comp osition	Pellet height (cm)	Pellet Resistance (Ω)	Conductivity (S.cm ⁻¹)
3.71%	0.405	2.00E+06	2.58E-07
7.52%	0.417	8.8445	0.060030488
15.46 %	0.402	0.9113	0.561660375
23.87 %	0.437	2.4581	0.22635547
32.79 %	0.472	1.7909	0.335567402

Table 2 - Conductivity results: Experiment 1

Compo sition	Pellet height (cm)	Pellet Resistance (Ω)	Conductivity (S.cm ⁻¹)
4.37%	0.42	6857.1	7.80E-05
8.93%	0.39	18.567	0.026744345
18.00 %	0.383	0.5606	0.869870862
22.67 %	0.41	0.7188	0.726247903
27.41 %	0.45	1.1089	0.516689021

Table 3 - Conductivity results: Experiment 2

Experiment 1 (Table 2) and experiment 2 (Table 3) differ only in the high temperature surfactant removal stage. The surfactant in the samples of experiment 1 was burned off at 450°C while the same was done at 400°C in experiment 2.

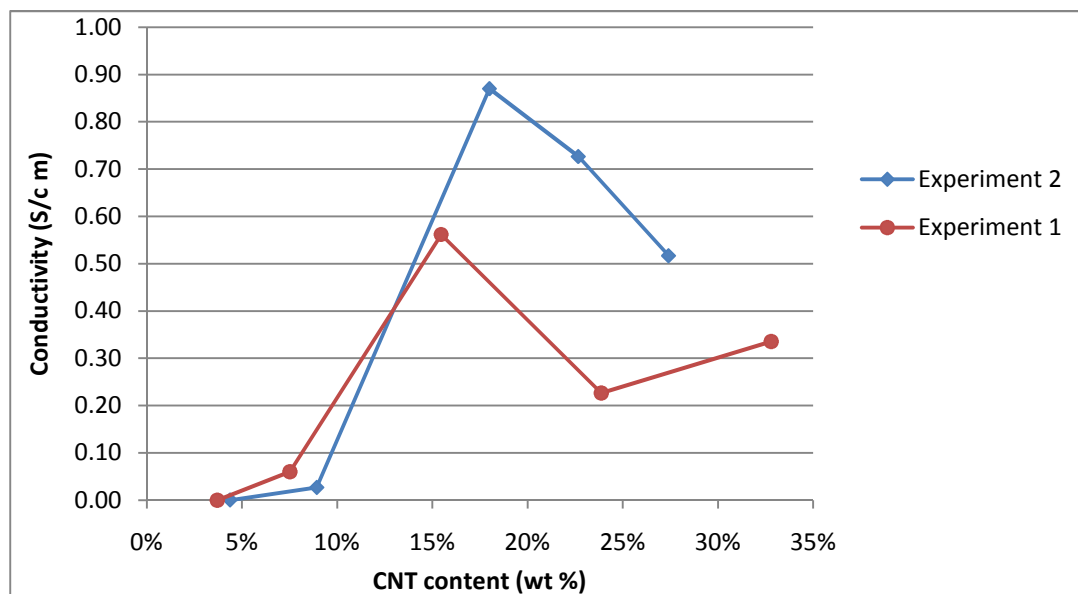


Figure 8 – Conductivity trends as a function of CNT content observed in TiO₂-CNT

In general, conductivities of samples in experiment 2 are superior to conductivities in experiment 1. The trend can be explained by the exposure of the samples in experiment 1 to higher temperature (450⁰C in exp. 1 vs. 400⁰C in exp. 2). The higher temperature is likely to have caused more oxidation damage to the CNT and breakage of TiO-CNT bonds in the composite leading to overall lower conductivities. The initial weights of the products after water evaporation at 100⁰C are significantly larger than the expected weights of the composite (Table 4), suggesting that the surfactant is not entirely removed by the filtration process. High temperature surfactant removal brings the final weights within expected ranges; remnant surfactant ash is partly responsible for the final weights being over the initial target of 1000 mg.

Composition	Theoretically calculated final weight (mg)	After 100°C evaporation (mg)	After surfactant burn-off (mg)	Percentage deviation of final weight from theoretical weight
4.37%	1143.29	1850	1347	17.82%
8.93%	1120.41	2256	1340	19.60%
18.00%	1111.08	2760	1340	20.60%
22.67%	1102.77	3910	1260	14.26%
27.41%	1094.46	5130	1181	7.91%

Table 4 - Weight changes through processing steps: Experiment 2

The bell-shape of the conductivity curves (Fig.8) cannot be rigorously explained but is certainly a consequence of the method used in the synthesis of the samples. The chemical formula of the surfactant is $C_{18}H_{29}NaO_3S$. High temperature burning of the composite causes the formation of CO_2 , H_2O and SO_x that consume the surfactant. Any remainder of the surfactant is probably a sodium compound. Noticeably, the conductivity profile follows the pattern of deviation from theoretically calculated weights. There is a possibility that the surfactant ash is a conductive sodium compound that is dominating over the expected effect of the CNT. Further investigation is required to accurately determine the cause of the bell-shape observed in the conductivity. Initially, we intended to obtain a final composite weight of 1000 mg. The high percentage deviation of the final composite weight from initially intended 1000 mg is a combination of remnant surfactant ash and the fact that a surplus of $TiCl_4$ was used to compensate for losses due to volatility of $TiCl_4$. The peak conductivities in both experiments occur between 15% and 20% using the material synthesis procedure described above. The highest conductivity achieved (0.87 S/cm) is

below the target of 1 S/cm but still 3 to 9 times higher than the proton conductivity of the PFSA membrane. Additionally, deposition of metallic platinum during use will certainly raise conductivity above the required value.

Chapter 5

5.1 DURABILITY OF SYNTHESIZED TiO₂-CNT

The synthesized composite of TiO₂-CNT is intended to replace carbon black (CB) as a more corrosion resistant support of platinum catalyst in the cell. Henceforth, the resistance to electrochemical oxidation of the optimally conductive composite (20wt% CNT in TiO₂-CNT) as compared to carbon black was studied in a 3-electrode electrochemical cell. The electrochemical cell was made of a glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode immersed in 0.5 M H₂SO₄. 10 mg of the material under test (TiO₂-CNT or CB) was dispersed by sonication in 5 mL isopropyl alcohol (IPA). A 10 μ L sample of the suspension was then pipetted onto the glassy carbon electrode surface. Upon evaporation of the IPA, 5 μ L of Nafion Ionomer solution (5 wt% LiquionTM solution) was pipetted onto the deposited test material to act as a binder and electrolyte. Argon purging gas was bubbled through the sulfuric acid during the experiment. Electrochemical oxidation was induced at the working electrode by successive 8 hours exposures to anodic 1.2V potentials via chronoamperometry. Cyclic voltammetry scans (0 to 1.2 V at scan rate of 0.1 V/s) were performed after each 8 hours of chronoamperometry to reveal the charging currents as well as the formation of surface oxides as redox peaks on the CV curves (Li, 2008). Results are presented in Fig. 9 and Fig. 10.

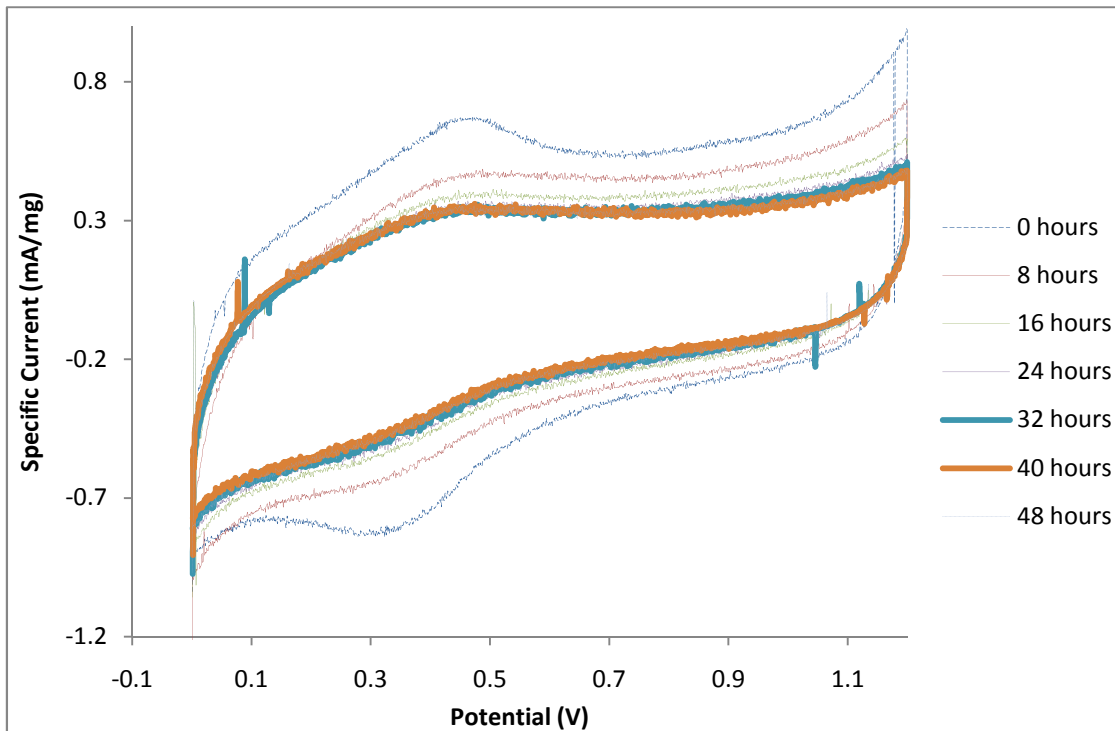


Figure 9 - CV scans of $\text{TiO}_2\text{-CNT}$ after successive 8 hours 1.2V chronoamperometry

The CV scans of the synthesized $\text{TiO}_2\text{-CNT}$ start with visible oxide peaks at 0 hour. The double layer charging area shrinks with time until no significant oxidation current peaks are visible. Stabilization is a result of the removal of the impurities with time which results into reduced oxidation currents. Any later oxidation occurring in $\text{TiO}_2\text{-CNT}$ composite will certainly be due to the presence of CNT and remnant organics from the surfactant. The initial surface oxides evidenced by the peaks on the 0 hour scan of the composite are explained by oxidizable species leftover from high temperature burning of the organic surfactant (dodecylbenzenesulfonic acid-sodium salt). Equation (3) is proposed to quantify the rate of oxidation as a function of time in carbon compounds.

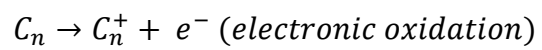
$$I = \frac{k}{t^n} \quad (3)$$

where I is the specific rate of oxidation, t the electrochemical oxidation time, k and n constants. The following values as summarized in Table 5 are found for the time exponential decay constants n for CB and CNT at 80°C under conditions similar to the present experiment (Li, 2008).

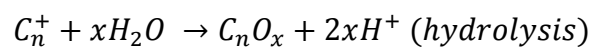
	No platinum	Platinum functionalized
CB	0.34	0.61
CNT	0.44	0.73

Table 5- Time exponential decay constants of CNT and CB

The time decay exponents are generally higher for CNT suggesting that oxidation rate of CNT in TiO₂-CNT is likely decrease faster with time compared to CB. The synthesized composite is anticipated to be more stable than CB in the electrochemical environment of a fuel cell. The prediction is confirmed by pronounced oxidation peaks on the CV scans of CB. The experimental CV profiles of CB widen with time. Surface oxide peaks are much higher than TiO₂-CNT and appear to become more defined after prolonged exposure to anodic 1.2 V. This result signals steady increase in surface oxides formation with no signs of stabilization past 48 hours. Oxides formation on carbon species is described as electronic oxidation step followed by hydrolysis. The chemical mechanisms are detailed in equations (4) and (5):



(4)



(5)

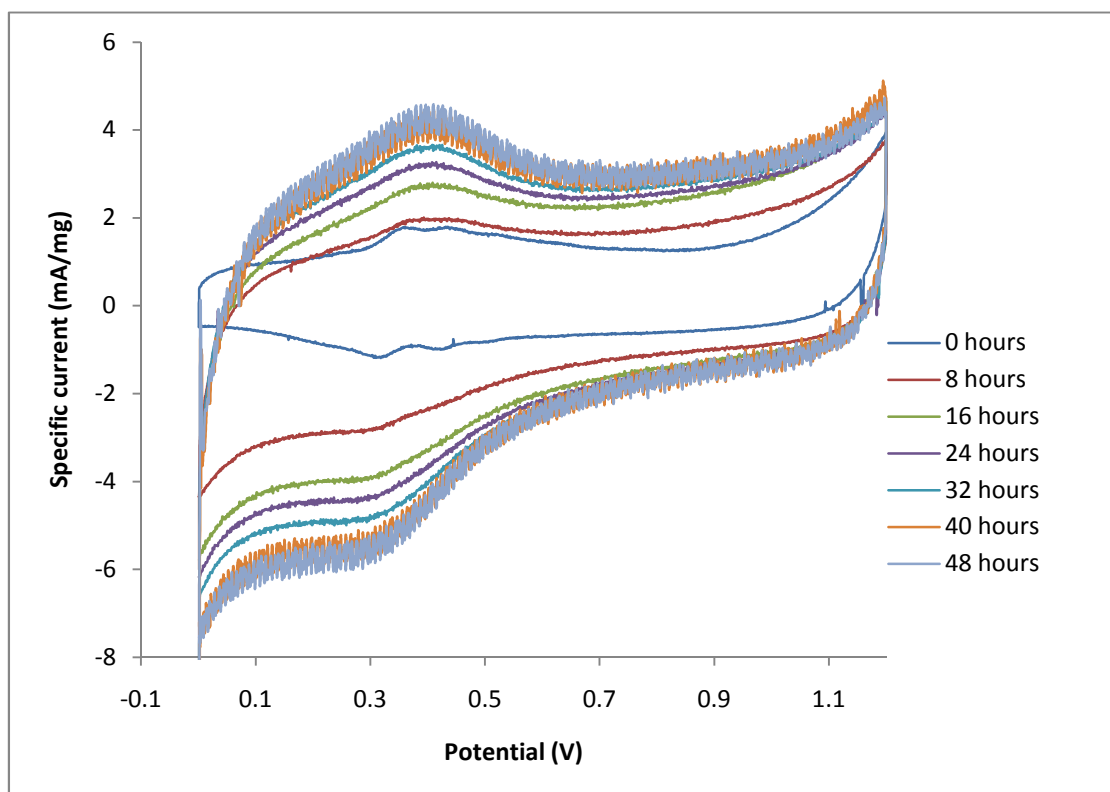


Figure 10 - CV scans of CB after successive 8 hours 1.2V chronoamperometry

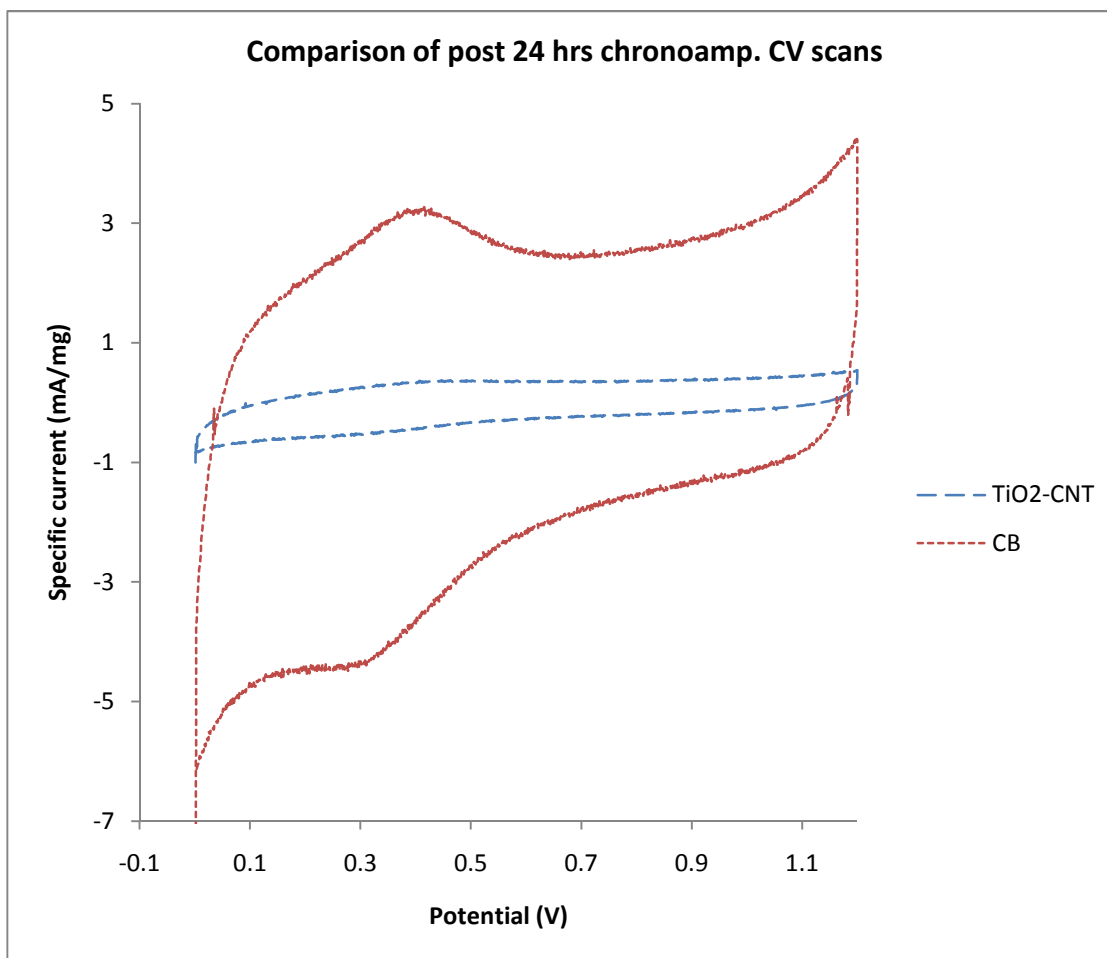


Figure 11 - Graphical comparison of CV scans post 24 hours chronoamperometry

The multilayer structure of MWCNT allows only the formation of oxides on the outermost layers, which in turn protect the inner tubes from further oxidation (Li, 2008). In the case of CB, the heterogenous structure allows access to any carbon clusters even after neighboring particles have been oxidized and acquire passivating properties. This mechanistic explanation is in agreement with the experimental behavior of CNT and CB taken alone (Li, 2008). Moreover, only a small proportion of

CNT is present in the composite under study, the remainder being titania, an oxide proven very stable in the fuel cell environment. The combination of rapid stabilization and low quantity of the oxidizable component in TiO_2 -CNT is responsible for the superior stability observed. Fig. 11 shows the relative scale of the oxidation peaks detected on CB and TiO_2 -CNT after 24 hours of electrochemical oxidation. It is apparent that the composite of interest is devoid of surface oxides when compared to commonly used carbon black. Overall, TiO_2 -CNT as synthesized is undeniably more resistant to corrosion via electrochemical oxidation than carbon black currently used for catalyst support in proton exchange membrane fuel cells.

Chapter 6

6.1 CONCLUSIONS

Proton exchange membrane fuel cells are promising alternatives to portable energy generators to be used in vehicles and other stationary applications. A number of challenges still need to be resolved to justify the economic and technical viability of fuel cells. In this work, a composite of titania and CNT was investigated as an alternative corrosion-resistant catalyst support for PEM fuel cells using a relatively simple and inexpensive chemical procedure.

Under our chemical wet synthesis method, the proportion of CNT in TiO_2 for optimal electrical conductivity was found to be in the range of 15 and 20 % by weight. The highest conductivity found was 0.87 S/cm. Though this value is below the target of 1S/cm, it is still up to 9 times higher than the proton conduction, and should not be an obstacle to cell performance.

The initial objective of offering a material more resistant to corrosion by electrochemical oxidation in the cell environment was achieved. CV scans after anodic 1.2V chronoamperometry unequivocally demonstrated the superior performance of the composite TiO_2 -CNT compared to commonplace carbon black. Almost no oxides were detectable on the surface of the composite past 8 hours of electrochemical oxidation while pronounced redox peaks signaled continuous formation of surface oxides on CB. In the fuel cell environment, particularly at the cathode where oxidizing potentials are encountered, TiO_2 -CNT would outperform CB in stability. Optimal ECSA and cell performance would be preserved for prolonged

cycling. Furthermore, the composite as synthesized would be relatively cost effective, and as such, improves durability for very small added cost.

Further investigation is required to elucidate the fall in conductivity observed past 17 wt% CNT content. Though proof of the superior performance TiO_2 -CNT has been obtained, quantitative study of durability is necessary to assign definitive degradation rates, evaluate economic merits and guide later improvement work.

REFERENCES

- DOE. (2009, April). *Multi-Year Research, Development and Demonstration Plan*. Retrieved March 13, 2010, from DOE, Energy Efficiency & Renewable Energy: <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/introduction.pdf>
- Hassan, F.; et al. (2009). Functionalization of electrochemically prepared titania nanotubes with Pt for application as catalyst for fuel cells. *Journal of Power Sources* .
- Hsieh, C.-T.; et al. (2009). Electrochemical capacitance from carbon nanotubes decorated with titanium dioxide nanoparticles in acid electrolyte. *Journal of Physics and Chemistry of Solids* , 916–921.
- Huang, P.; et al. (1997). Phase transformation of YiO_2 monitored by Thermo-Raman spectroscopy with TGA/DTA. *Thermochimica Acta* , 85-92.
- Jaksic, M. (2001). Hypo–hyper-d-electronic interactive nature of interionic synergism in catalysis and electrocatalysis for hydrogen reactions. *International Journal of Hydrogen Energy* , 559–578.
- Janssen, G.; et al. (2009). Proton-exchange-membrane fuel cells durability evaluated by load-on/off cycling. *Journal of Power Sources* , 501–509.
- Kraemera, S.; et al. (2008). Evaluation of TiO_2 as catalyst support in Pt- TiO_2/C composite cathodes for the proton exchange membrane fuel cell . *Journal of Power Sources* .
- Kumari, L.; et al. (2009). Synthesis, microstructure and electrical conductivity of carbon nanotube–alumina nanocomposites. *Ceramics International* , 1775-1781.
- Larminie, J.; Dicks, A. (2003). *Fuel cells explained*. Wiley.
- Li, Liang; Xing, Y. (2008). Electrochemical durability of carbon nanotubes at 80°C. *Journal of Power Sources* , 75–79.
- Palanichamy, Krishnan. (2010). Post-doctorate Research Associate. University of Delaware Fuel Cell group

- Pang, L.; et al. (1993). Thermogravimetric Analysis of Carbon Nanotubes and Nanoparticles. *The Journal of Physical Chemistry* .
- Rajalakshmi, N.; et al. (2008). Nano titanium oxide catalyst support for proton exchange membrane fuel cells. *International Journal of Hydrogen Energy* , 7521-7526.
- Salvetat, J.; et al. (1999). Mechanical properties of carbon nanotubes. *Applied Physics A: Materials Science & Processing* , 255–260.
- Sameera, I.; et al. (2010). Preparation, characterization and electrical conductivity studies of MWCNT/ZnO nanoparticles hybrid. *Physica B* , 1709–1714.
- Tsotra, P.; Friedrich, P. (2004). Thermal, mechanical, and electrical properties of epoxy resin/polyaniline-dodecylbenzenesulfonic acid blends. *Synthetic Metals* , 237–242.
- Wang, D.; et al. (2009). Self-Assembled TiO₂–Graphene Hybrid Nanostructures for Enhanced Li-Ion Insertion. *ACS NANO* , 907-914.
- Zhang, F.-Y.; et al. (2009). Quantitative characterization of catalyst layer degradation in PEM fuel cells by X-ray photoelectron spectroscopy. *Electrochimica Acta* , 4025–4030.