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Nanocomposites of Nafion for Fuel Cell Application

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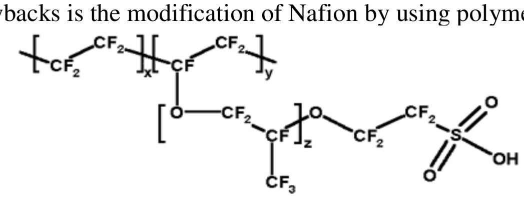
Abstract— **The focus of this paper is to fabricate the membrane and observe the performance of Multi wall carbon nanotubes and functionalized Multi wall carbon nanotubes to Nafion.Nafion is a membrane which is an ionic polymer used in fuel cells. It possesses enormous protons during conduction across the membrane in order to facilitate the oxidation-reduction reactions that take place in a power generating fuel cell. The proton conductivity of Nafion is reduced at high temperatures such as 100 degrees Celsius and low relative humidity such as 50%. There are advantages to operating Nafion at these conditions, such as in real world applications, where the conditions will not always be optimal. Carbon nanotubes have been found to allow water and proton transport through the filled inner confined space. The purpose of this research is to improve the conductivity of proton in fuel cell using additives in Nafion that will help to maintain a consistent saturation level in Nafion at dehydrating condition. In this work, the proton conductivity has been tested of Nafion with various percentage of Multi wall carbon nanotubes (MWCNT) and functionalized Multi wall carbon nanotubes (FMWCNT).The experimental results shows the improved conductivity of proton in functionalised MWCNT.**

Keywords: **Dupont Nafion, PEM fuel cell. Proton conductivity, CNTs, MWCNT, FMWCNT, PNC, MEA.**

I. INTRODUCTION

Fuel cells have received extensive recognition as an alternative method of energy generation. Fuel cells are devices that convert chemical energy into electrical energy using two reactants, a fuel and an oxidant, and an electrolyte. As opposed to traditional batteries, which chemically store a limited amount of electrical energy, fuel cells can operate continuously with the replenished external flows of reactants. Fuel cell technology offers many advantages such as pollution free (no gaseous pollutants like CO or NOx), high efficiency, and simple structure form of energy. Mechanically, fuel cells have no moving parts, thus having high durability, long lifetime, and silent performance. Unlike internal combustion engines using gasoline or diesel, fuel cells are not subject to the second law of thermodynamics or the Carnot maximum cycle efficiency, due to its ability to bypass irreversible thermal steps during the electrochemical conversion process.Scientists have developed many different kinds of fuel cells, including Alkaline fuel cells, Molten carbonate fuel cells, Phosphoric acid fuel cells, Solid oxide fuel cells, Metal hydride fuel cells, direct methanol fuel cells, and proton exchange membrane fuel cells. Each type of fuel cell has its own advantages and drawbacks, yet none is inexpensive and efficient enough to replace conventional ways of power generation. Research in the area of fuel cells has exponentially grown over the last 20 years especially in PEM fuel cells. These are inexpensive to operate and give the highest efficiency compared to other types of fuel cells. They operate at a relatively low temperature of about 80 °C, which makes them ideal to be used in homes and automobile applications. PEM fuel cell uses a polymer membrane as an electrolyte, which conduct protons to the cathode side. The most commonly used polymer for preparation of membrane is Nafion, a per-fluorosulphonyl fluoride copolymer from DuPont[4]. Nafion is the standard by which all new materials are compared. Nafion has also found numerous other applications such as liquid and gas separations, metal ion recovery and the chloro-alkali industry [1]. In the dry state, Nafion is a poor ion conductor, but ionic conductivity increases sharply with water content. Although Nafion is the most suitable entrant for the fabrication of fuel cell membrane, however, Nafion-based membranes have major drawbacks such as high production cost, low conductivity at low humidity and/or high temperature (>100 °C), loss of mechanical stability at high temperature (~100 °C). One of the most commonly used strategies to overcome these drawbacks is the modification of Nafion by using polymer



Nanocomposite (PNC) technology. PNCs have recently shown a worldwide growth effort especially in the fabrication of high temperature PEM for fuel cells[9].In principle, Nano composites are the extreme case of composites in which the interfacial interactions between two or more phases are maximized to obtain the superior performance as compared to any of the pure solid component. In PNCs,[12] nanometre-size particles of inorganic or organic materials are homogeneously dispersed at a Nano scale level in a polymer matrix .There is a wide variety of nano particles, of different natures and sizes that are blended with Nafion to generate new generation materials to improve its properties for PEM fuel cell applications. Among them, carbon nanotubes (CNTs) are attracting great research interest as a Nano reinforcing material in PNCs because of their extraordinary high strength and high modulus, their excellent electrical conductivity along with their important thermal conductivity and stability, and their low density .This paper will focus on the chemical aspect of Nafion. Through experimentation, the goal is to improve the proton conductivity improvement by forming Nafion composite in a porous matrix with additives for property improvement i)Nafion -MWCNT composites ii)Nafion - Functionalised MWCNT composites. It has been shown before that carbon nanotubes (CNT) interact well with water. A fuel cell requires transport of protons across the Nafion membrane, making the carbon nanotubes a good choice as an additive. This paper will discuss the methods of preparing the cast of our own membrane with Multiwall carbon nanotube [8] and Sulphated Multi wall carbon Nano tubes and the fabricated membrane is tested and data analysis used on the membranes. Normally CNT's is one has to naturally consider the effect of electronic conductivity of CNTs. Certain type of functionalization[11] indeed enhances the electronic conductivity and it is always important to consider the risk of electrical short- circuiting despite the use of very low amounts of CNTs (1%,2%,3%). Proper dispersion is essential for ensuring uniform behaviour and the normally reported value of percolation threshold for CNTs. The proton conductivity is tested through the Electrochemical Impedance Spectroscopy(EIS). The degree of dispersion of CNT sin the Nafion matrix was studied by scanning electron microscope(SEM).

II. METHODOLOGY

A. Making MWCNT Nafion Solution

Multiwall Carbon Nanotubes was added by weight percentages. In this experiment three different amount of (1%,2%,3%) [6] MWCNTs. Materials: Nafion per fluorinated resin solution (5 wt%) in a mixture of lower aliphatic alcohols and water, isopropyl alcohol (≥ 99.5%) and Ethanol.

MWCNTs was mixed with Ethanol and stirred for fine dispersion for 12 hrs .

↓

Solution was stirred and heated at 80°c for 2hrs

↓

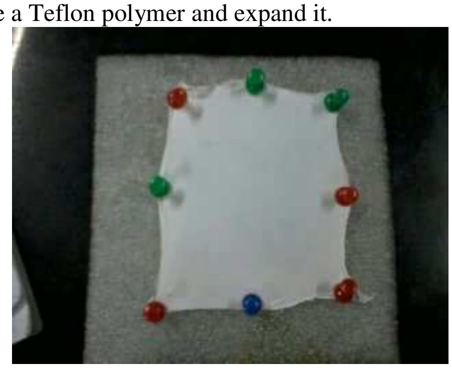
5ml Nafionsolution(5%) is added in MWCNT solution and stirred and heated for 8hrs

↓

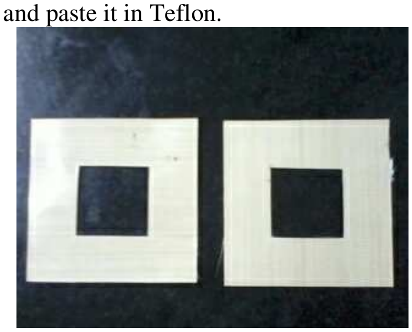
Dimethylform amide is added and stirred

Preparing MWCNTs Nafion membrane-Sample preparation

- **Step 1**:
  Take a Teflon polymer and expand it.



- **Step 2**:
  Take a square gasket 7x7m length and cut 3x3 m inside and paste it in Teflon.



- **Step 3:**
  Prepare solution for coating (using brush

Pristine MWCNT +Sulphuric acid is stirred and boiled at 250°C for 18hrs

↓

After cooling down the product was rinsed in distilled water until sulphated ions

↓

Dried in an air oven 393k for 12hrs to obtain sulphated CNT

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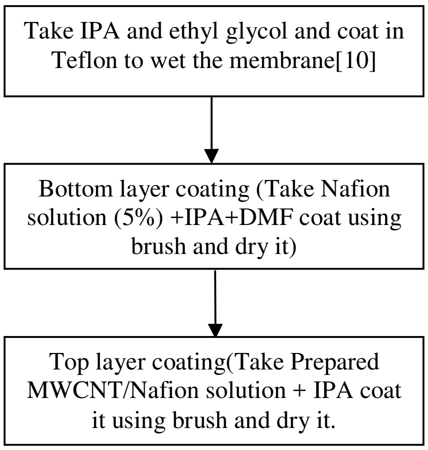
After the membrane is prepared it was hot pressed using Hydraulic press. Then it was put in to acid was bye using 0.5% molar sulphuric acid and boiled in water for one hour then it was cooled in normal water.

B. Synthesis of Functionalized MWCNTs



III. RESULTS AND DISCUSSION

A. SEM Analysis

SEM was used to study the dispersion of the CNTs in the membrane and also to find the morphological changes as a result of functionalization. No morphological changes were found as a result oxidative treatment of the CNTs. The carbon nanotubes were not harmed at all as a result treatment and length of the tubes remained > 1µm. Thus it can be concluded that the oxidative treatment does not harm the nanotube and purified material can be obtained by the method. The Nafion-MWCNT structure shows carbon nanotubes dispersed in the Nafion matrix. The CNT seem to be uniformly distributed in the matrix and the concentration of the CNTs increase with increase in percentage of CNTs in the matrix. The SEM pictures thus confirm the formation of CNT- Nafion composite.

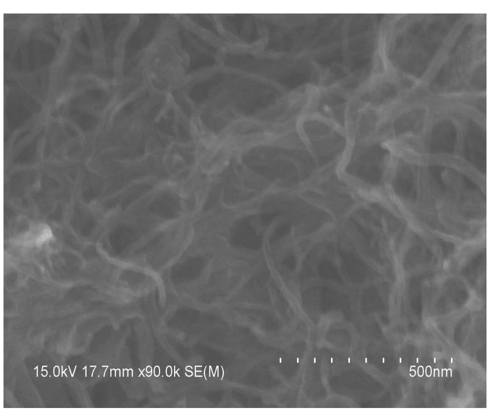


Fig. 1: SEM image of PMWCNT

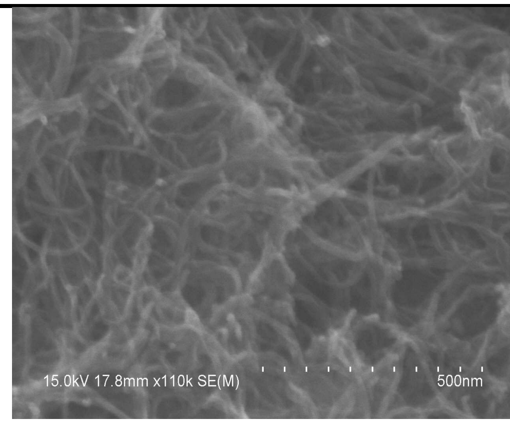


Fig. 2: SEM image of FMWCNT

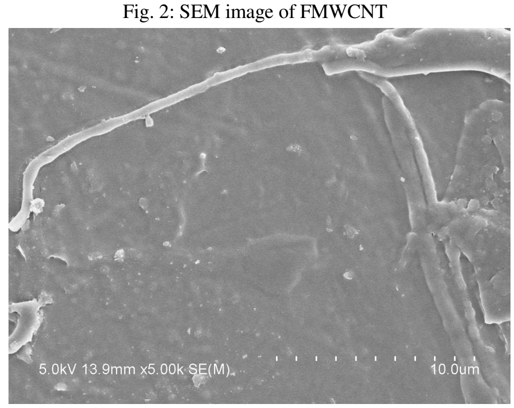


Fig. 3: SEM Image of 1% FMWCN innafion membrane

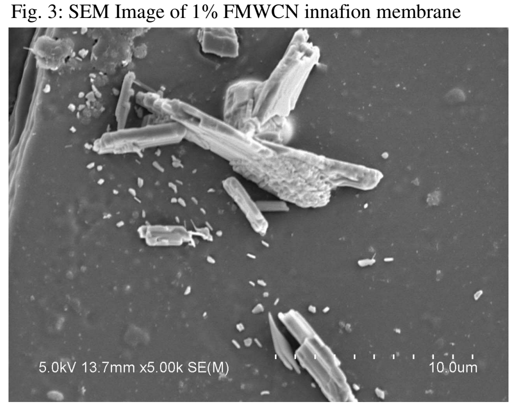


Fig. 4: SEM Image of 2% FMWCN innafion membrane

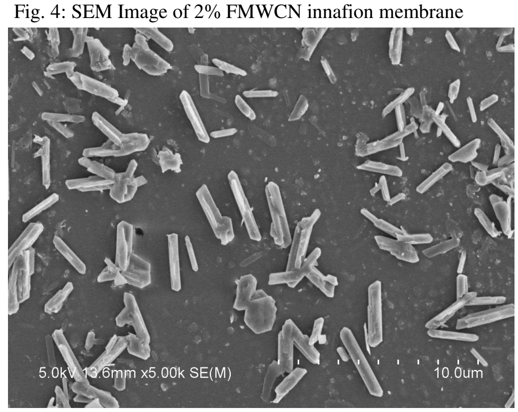


Fig. 5: SEM Image of 3% FMWCN innafion membrane

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B. XRD Analysis

XRD Analysis: XRD analysis usually involves the identification of a phase in a specimen. XRD patterns of MWCNT sample and MWCNT are shown in Fig. 6 and 7.It is clear from Figure 21 that beside the MWCNT peak at 64.8° ($Al_2 O_3$) and 77° ($CO_{(101)}$) there are strong peak at 44.2° (Fe), .and in 37.9° indicating the presence of $Al_{(111)}$.

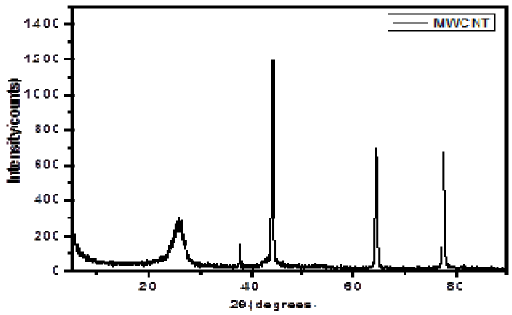

Fig. 6: X ray pattern of MWCNT

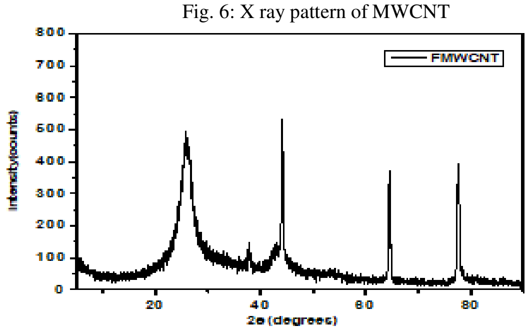

Fig. 7: X ray pattern of FMWCNT

The XRD pattern FMWCNT sample (Fig.7) shows that the peak at 26° has decreased compare to MWCNT because of the Oxidation process and that the Fe peaks also decreased. And carbon was presence higher in Functionalized Multiwall carbon Nano tube compare to Pristine MWCNT

C. Comparison of Impedance

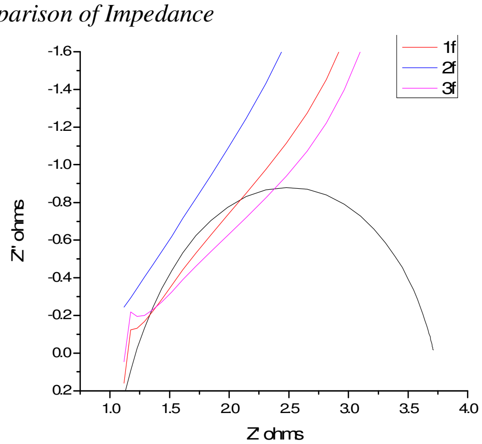

Fig. 8: Comparison of impedance curves

TABLE I

S. No	Material	Z´	Conductivity(ρ)
1	MWCNT 1%	2.6817	0.55244 ms
2	MWCNT 2%	2.626	0.564158ms
3	MWCNT 3%	0.88975	0.166505ms

TABLE II.

S.No	Material	Z´	Conductivity(ρ)
1	FMWCNT 1%	1.1193	0.302211ms
2	FMWCNT 1%	0.91381	0.2467287ms
3	FMWCNT 2%	0.91381	0.2467287ms
4	FMWCNT 3%	0.90105	0.2432835ms

Comparing the impedance of the FWCNT in Table II(1%,2%,3%) from pure Nafion membrane without MEA[11] there is an improvement in impedance ,but in Table I 2%MWCNT 3% MWCNT has the improvement in impedance [5]comparing to pure Nafion

D. Power density and V-I Characteristics:

The Polarization curves obtained in ambient conditions are reported in Fig. 9. As it is expected, the curve for MWCNT exhibits an insulating behavior, while even with the lowest MWCNTs content (2%) an electrical current (≈1.5mA at 1V) is obtained. The slope of the curves increases with increasing MWCNT%, with a non-linear behavior, indicating non-ohmic conductivity. Electrons conductivities were calculated from the slopes of the linear portions of the Polarization curves and are given in Fig.9 were also the values obtained from FMWCNT.

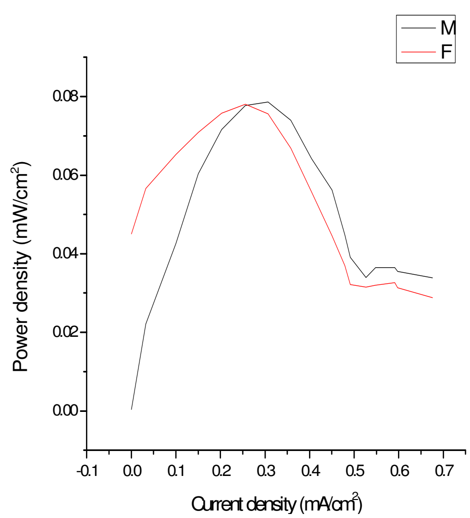

Fig.9: Polarization curve of the Membrane

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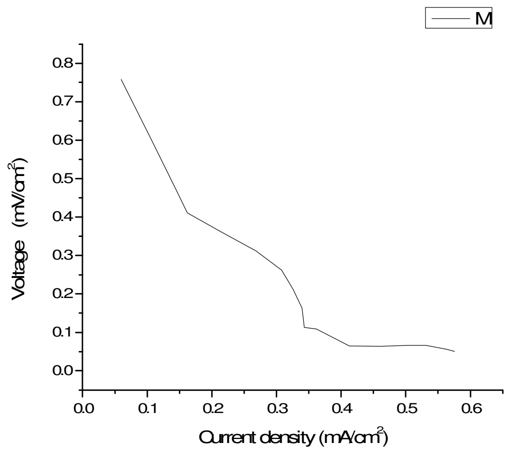

Fig. 10: I-V curve of MWCNT

The efficiency of the fuel cell was measured in terms of the voltage generated when the cell is fed with the reactant gases. The cell with only Nafion membrane generated a voltage of 0.900 V under open circuit conditions. The open circuit voltage of the 2% MWCNT and FMWCNT based composites are 0.751 V and 0.904 V respectively. As the primary function of MWCNT is to conduct electrons there is a decrease in voltage for the MWCNT incorporated membrane. When the functionalization of CNT takes place some of the surface groups are replaced with carbonyl, hydroxyl and sulphonic acid functionalities. As a result the conductivity of FMWCNT decreases. It results, in higher voltage of the functionalized MWCNT incorporated Membrane electrode assembly (MEA). I-V plot and the power density plot for 2% MWCNT and 2% FMWCNT based membrane electrode assembly is shown in the fig.11.

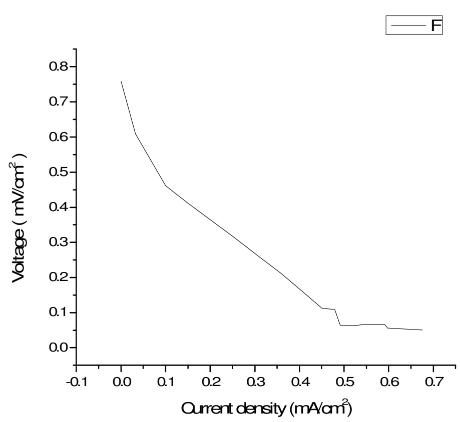

Fig. 11: I-V curve of MWCNT

IV. CONCLUSION

PEM Fuel cells are widely considered to be the best alternative to the fossil fuels for power generation but the overall cost factor associated with it needs to be improved further. The current study is focused to improve the cost efficiency of fuel cell by integrating nanotechnology into fuel cells. Since Nafion used as a proton conductor, this study is aimed to develop a Nano composite Nafion membrane using a porous matrix concept that can address the issue of cost and performance together. In order to achieve this MWCNTs and functionalized MWCNTs (0-3%) were used to reinforce the nafion membrane. Different weight percentage of the additive was added into Nafion solution and subsequently test were conducted to check for the variation in proton conductivity. It was found that among the various composites prepared 2% functionalized MWCNT composite gave the highest conductivity. This membrane was used to prepared membrane electrode assembly and performance of this was compared with that of MWCNT composite. The performance of functionalized MWCNT composite was higher that of Non-functionalized composite.

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