Comprehensive studies on polyvinyl alcohol (PVA) doped with MWCNTs and CNFs Nano composite membranes for fuel cells applications

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Abstract: This research work presents a comprehensive review and experimental studies on current trends in the development of proton exchange membrane (PEM) for fuel cell applications. The study focusses on fuel cells, types and their advantages when compared to convention energy conversion devices. Furthermore, research is essential for development of durable membrane resources/materials. Various aspects of PEM fuel cells have been reviewed to realize change in the membrane performance through characterization techniques adopted in this works. This study also focuses on gaps in already published literature which in turn limits our knowledge of characterization mechanism associated and the correlation existing between them. In addition, it needs to understand more appropriately to yield durable mechanisms. Further recent works on polymer electrolyte membrane fuel cells has been critically reviewed and in this direction two case studies have been presented as a part of experimental works carried out. Further Polymer based PEMs were developed using polyvinyl alcohol as a base matrix reinforced with different nano-particles viz., Multi walled carbon nanotubes (MWCNTs) and Carbon nano fibers (CNFs). The membranes were subjected to solubility and swelling tests and were characterized by using Fourier transform infrared (FTIR) spectroscopy, Thermo Gravimetric Analysis (TGA) for feasibility studies on their fuel cell applications.

Keywords: Proton exchange membrane, characterization, Dispersion, Nanoparticles, Polyvinyl alcohol.

1. Introduction:
Energy is an essential input for all developmental activities because it is directly related to the globalization, economic development and social issues which will affect sustainable development. In
today’s life man has entered moon and Mars with necessary energy availability. Magnitude of change in terms of sustainable development through renewable energy requirement is necessary and becoming mandatory. As reported energy produced and consumed nationally and internationally is tremendous. In addition, it is reported that two billion people worldwide are suffering due to lack and lower accessibility to energy resources [1, 2]. Due to increased concern on exhaustion of petroleum based the energy sources and environment change; fuel cell technology has received much concentration in the recent years due to their high results as well as efficiencies and acceptable emission levels.

1.1 Fuel Cell Technology
Figure 1 shows the schematic diagram of a fuel cell developed by Sir. William Robert Grove, W. R. Grove (an English lawyer turned scientist) in the year 1839, which was not in practical usage. In next century the same fuel cell was found in use [2].

In the year 1950, General Electric Company (GE) started manufacture of these fuel cells. In the year 1962 Gemini space mission has given a award to the General Electric company. One kW fuel cell with 35 mg Pt/cm² platinum loading fuel cell was developed by the Gemini. The developed fuel cell was giving the 0.78 volts for 37 ampere per centimeter square area [3]. In the 1960s at that time GE was improved the fuel cell by using the Teflon based catalyst directly to the electrolyte. In the year 1970s considerable progress had been made from catalyst used as Teflon. US department of energy has not given the sufficient grant for the awareness and development of fuel cell. Therefore, the progress of the fuel cell and the improvement also reduced till ten years. Now-a-days, fuel cell technology that plays a very dominant role in the field of automotive due to its easy function, energy economy and pollution free from environment. Fuel cells are electro-chemical devices which directly converts the chemical energy stored in the fuels such as the hydrogen to electrical energy. Its efficiency can attain as high as 60% in the energy conversion. Further about 80% and 90% drop in pollutants of co-generation and thermal energies could happen with their usage [1].

1.2 Fuel Cell Types
They are categorized based on the electrolyte in use and accordingly they are of five categories namely, polymer electrolyte membrane (PEM) fuel cells, solid oxide fuel cells (SOFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), and (5) molten carbonate fuel cells (MCFCs). The achievement of fuel cell (FC) is mainly reliant on electrolyte membrane and its property. Energy conversion through Fuel cell (FC) will be most important energy sources in future [3, 4]. PEM Fuel Cell technology plays a very significant role as a substitute for hygienic energy equipment in different types of energy conversion industries without any emission adding to the environment. Fuel cell technology enabled commercial vehicles are being actively addressed by the manufacturers since from 2017 to till date. The challenges associated with PEMFC’s are their high production cost and
continued effort to improve the activity of the cell to be compatible for automotive applications. Conditioning of fuel cell is usually a long process and costlier for manufacture of PEMFC at higher production rate. A recently assembled PEM fuel cell required to start the membrane electrode assembly (MEA) and permit the cells to reach their planned performances has been reported [4].

2. Performance study of fuel cell
Numerous methods for fabricating Proton Exchange Membranes to meet the exact design to meet industrialized challenges have been reported in the literature. The methods used further depend on the materials used, and the part design or end users or applications. This section presents the results obtained on the use of PEMs for fuel cell applications.
In the observation of novel based PEMs fuel cells with high-quality resistance for heat and mechanical properties are the need of the hour [5, 6, 7]. Polybenzimidazole (PBI) being excellent warm up resistant material having good mechanical properties could be on such candidate for PEMs. However, it has poor process capability, and lower proton conductivity. Efforts to improve its process capacity and proton conductivity, acid doping, sulfonation and blending have been proposed. With this method long time immersing in the process adopted tends to decrease the mechanical properties of PEMs developed. He suggested Proton Exchange Membrane (PEM) fuel cell technology against old alkaline fuel cell technology, used at present in the Shuttle, for space missions [8].
The study has been involved Five-year improvement program that begin under the 2nd Generation Reusable Launch Vehicle (RLV) Program, transitioned through the Next Generation Launch Technologies (NGLT) Program, continual under gathering Systems in the Exploration Technology Development Program (ETDP). The study of mechanical and water transport property of Nafion membranes, completely fluorinated ion conducting type polymer membrane material in proton exchange membrane fuel cells (PEMFCs) [9]. Effects of temperature and hydration on the mechanical properties of Nafions have been obtained with link to microstructure and molecular stage interactions. The investigation of the proton-exchange membranes (PEM) for a direct methanol fuel cell equipped by modifying the chemical structure of the poly (vinyl alcohol) (PVA) by means of the sulfonation [10].
The mixture of the new proton-conducting polymer membrane along with the poly (vinyl alcohol) and diamine-containing the organic molecules were immobilized to PVA. Sulfonation was carried out by means of 4, 4-diaminodiphenyl ether-2 and 2-disulfonic acid (ODADS). The chemical structure and the thermal stability of the sulfonated PVA were studied y using FTIR and thermo gravimetric analysis technique, respectively. The Thermal stabilities of the membranes were characterized by using TGA and found that PVA-ODADS membranes were thermally steady up to 220°C. The investigation of polyvinyl alcohol reinforced with MWCNTs and suggested an improved compatibility between modified CNTs and Nafion matrix [11]. The PVA-functionalized carbon nano tube (CNT-PVA) have been characterized using Fourier transform infrared (FTIR) spectroscopy, Thermo gravimetric analysis (TGA), and solubility test and found that FTIR spectroscopy, TGA analysis, and solubility test were persuasive for confirmation of the attachment of PVA on CNT surfaces and Instron test verified the hypothesis that CNT-PVA/Nafion composite membranes possessing better mechanical properties than Nafion 212 and recasted Nafion membranes.
From the exhaustive literature survey conducted on the development of PEM based membranes for fuel cell applications it is found that continued research is required for sustained feasibility of their use in real time applications. The main objectives of the present research work are to present detailed review on the developments in the fuel cell membrane technology and to identify the research gaps in this area. Further development of proton ion exchange membranes for fuel cell applications has been highlighted in detail. As part of the experimental works PEM membranes were developed using B2SA grafted plain PVA with varied concentrations of MWCNTs/CNFs incorporated in the holding matrix of PVA.

3. Materials and Methodology adopted:
This section highlights the material selected and the methodology adopted in the development of Proton Conducting Membranes for fuel cell application. PVA (Polyvinyl Alcohol) was used as the
holding matrix while MWCNTs (Multi-walled Carbon Nano Tubes) and CNFs (Carbon nano fibers) were used as the filler material. In addition to this HCL (Hydrochloric Acid) and B2SA (Benzaldehyde-2-Sulphonic Acid Sodium Salt) were also used. Table 1 and 2 shows the Specifications of MWCNTs, CNFs respectively.

**Table 1. Specification of MWCNTs**

| Characteristic Property         | Inferences                                      |
|--------------------------------|-------------------------------------------------|
| Manufacturing Process          | Chemical Vapor Deposition (CVD)                 |
| Diameter                       | 10-30 nm                                        |
| Length                         | 1-2 microns                                     |
| Purity                         | >95% (MWCNT)                                   |
| Amorphous carbon               | < 3%                                            |
| Residue (Calcination in air)   | <2%                                             |
| Average interlayer distance    | 0.34 nm                                         |
| Special surface area           | > 350 m²/g                                      |
| Bulk density                   | 0.05-0.17 g/cm³                                 |
| Real density                   | 1.2 g/cm³                                       |
| Charging                       | 2180 (capacity: mA h/g)                        |
| Discharging                    | 534 (capacity: mA h/g)                         |
| Volume Resistivity             | 0.1-0.15 ohm.cm (measured at pressure in powder) |

**Table 2. Specification of CNFs**

| Characteristic Property         | Inferences                                      |
|--------------------------------|-------------------------------------------------|
| Product Number                 | 719811                                          |
| Pyrograf Product Number        | PR-25-XT-PS                                     |
| Bulk Density of Product (lb/ft³), Kg/m³ | (0.5 – 3.5) 8.00 – 56.06                   |
| *Nanofiber Density             | 1.4 - 1.6                                       |
| (including hollow core) (g/cm³) |                                                 |
| Nanofiber Wall Density (g/cm³) | 2.0 - 2.1                                       |
| Catalyst (Iron) Content (ppm)  | < 14,000                                        |
| Outer Diameter, (nm)           | 125 - 150                                       |
| Inner Diameter, (nm)           | 50-70                                           |
| Specific Surface Area, m²/g    | 54                                              |
| Average pore volume (cm³/g)    | 0.120                                           |
Average Pore Diameter (angstroms Å)  89.30

Figure 2 and Figure 3 shows the casting process and casted plain PVA and NPs reinforced polymer membranes respectively.

Table 3 shows the designation and detailed composition of membranes of MWCNTs, CNFs.

| Designation | Composition                      |
|-------------|---------------------------------|
| M0          | 4g of PVA                       |
| M1          | 4g of PVA + 0.01g of MWCNT/CNFs |
| M2          | 4g of PVA + 0.02g of MWCNT/CNFs |
| M3          | 4g of PVA + 0.03g of MWCNT/CNFs |
| M4          | 4g of PVA + 0.04g of MWCNT/CNFs |

4. Characterization Techniques used:
FTIR and TGA analysis of the developed membranes were carried out. Figure 4 shows the FTIR spectroscopy setup. Figure 5 shows the thermo gravimetric analysis instrument used.
5. Results And Discussions:
To check the suitability of the membranes for the intended fuel cell applications, the following tests of solubility, swelling, FTIR and TGA were carried out and the results and discussions are presented as below.

5.1 Solubility Test
As proton conductivity is directly proportional to the water content in the PEFMC at the cathode and keeps the electrolyte at the correct level of hydration. For this membrane developed should be insoluble in water. Plain PVA membranes were soluble in water but membranes developed using PVA and nano-particles (NPs) of both MWCNTs and carbon nano-fibers were insoluble. It should be noted that the insolubility increased with increase in dosage of nano-particles in the holding matrix. Increasing the weight of the Nps dosage membranes will not dissolve and form non-homogeneous mixture. Table 4 shows the solubility results of the membranes developed with two NPs used.

| Composition with MWCNTs | Composition with CNFs | Duration | Result |
|-------------------------|-----------------------|----------|--------|
| Plain PVA               | Plain PVA             | 24 hrs   | Dissolved |
| PVA+0.01g MWCNTs        | PVA+0.01g CNFs        | 24 hrs   | Not dissolved |
| PVA+0.02g MWCNT         | PVA+0.02g CNFs        | 24 hrs   | Not dissolved |
| PVA+0.03g MWCNT         | PVA+0.03g CNFs        | 24 hrs   | Not dissolved non homogeneous mixture |
| PVA+0.04g MWCNT         | PVA+0.04g CNFs        | 24 hrs   | Not dissolved non homogeneous mixture |

5.2 Swelling Test
Swelling tests were carried out by submerging the developed membrane in various concentrations of Ethanol and water (100%, 95%, 90%, 85%, 80%). The weight of the membranes is found out at several period of 24, 48, 72 hrs, respectively and average swollen rates was calculated. Figure 6 shows the swelling tests carried out on PVA+MWCNTs polymer membranes. It is found that from figure...
increased concentration of MWCNTs in the holding matrix decreases the degree of degradation of the membrane because of increased hydrophobic action.

Figure 6. Swelling tests carried out on PVA+MWCNTs polymer membranes

5.3 Fourier Transform Infrared Spectroscopy Analysis (FTIR)

Figures 7 shows the FTIR Spectra of Membranes incorporated with both MWCNTs and CNFs. FTIR spectra of Benzaldehyde grafted PVA membranes and MWCNTs, CNFs incorporated membrane were depicted. A characteristic strong band exhibited at around 3400 per cm in membranes because of stretching of O-H of hydroxyl groups. The actual peak of benzaldehyde is 1700 range. From the graph it may be noted that the peak has not appeared. This concludes the Aldehyde group of Benzaldehyde is involved in the result forming ether linkage so no peak has appeared at 1700. The carve at 3500 is increasing downwards from M0 to M4 because of the increase in aromatic ring content.

5.4 Thermo Gravimetric Analysis (TGA)

Figure 8 shows the Thermo gravimetric Analysis of polymer membranes incorporated with both MWCNTs and CNFs. From the figure it follows that the TGA of the Plain PVA polymer showed that thermal stability up to 40°C. A membrane containing 0.01g of MWCNT showed better thermal degradation property. Compared to plain PVA and NPs incorporated membranes viz, M1, M2, M3 membrane 0.04g of MWCNT and CNFs (M4) showed better thermal degradation property. In temperature range of 478 to 554 °C the weight loss varied from 33% but remains constant 28% in range of 554 to 600°C.
6. Conclusions:
Comprehensive review on fuel cell membranes showed that several researchers have mainly concentrated on improving the performance of membranes developed using various nano-particles, bonding chemicals.

   a. The developed membranes using PVA and NPs showed encouraging results in terms of improved solubility, swelling degradation as well.
   b. Increasing the concentration of MWCNT/CNFs showed improved degree of degradation of the membrane due to increased hydrophobic action.
   c. From TGA analysis it was found that increasing the concentration of NPs for the combinations of PVA+0.04g MWCNT/CNFs (M4) thermal stability increased.
   d. FTIR Spectroscopy results showed confirmation of NPs with PVA surfaces and the attachment increased with the increase in concentration of NPS in PVA Membrane.

Overall PVA incorporated with 0.04g (M4) MWCNTs/CNFs membrane showed promising results for fuel cell applications.

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