Inorganic-Organic Nano Composite Hybrid Membrane for High Temperature PEM Fuel Cell

By

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THESIS ACCEPTANCE CERTIFICATE

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Dedicated to

To my loving parents whom prayers are always ahead of me.

To my compassionate Professor Mr. Dr. Zuhair S. khan whose constant guidance and regular Motivation’s has led me to complete My MS degree.

Abstract

Low temperature PEM Fuel cells have limitations such as CO catalyst poisoning effect, Water and heat management, etc. These can be reduced by using high temperature PEM fuel cell (>90˚C). Therefore, it is need of hour that high temperature PEMFC must be focused. Inorganic-Organic Nano composite hybrid materials are among the top contenders to be utilized as membranes for high temperature PEMFCs. Vigorous research is continuing using different organic polymers like PEEK, PBI, Nafion along with different nanoparticles like silica and carbon nanotubes, etc. In this thesis, we have investigated the effect of Titania and Nb2O5 nanoparticles on polystyrene-based electrolyte membrane's porosity and thermal stability. We synthesized Titania nanoparticles using TTIP precursor. For hybrid membrane, we have used polystyrene and Poly (styrene-co-maleic anhydride), as polymers and Titanium dioxide and Niobium Pentoxides Nano particles as inorganic filler material. Wet chemistry route is used for Nano particle and hybrid membrane preparation. Synthesized membranes were characterized by using X-ray Diffraction, Scanning Electron Microscopy and Thermogravimetric analysis. The results showed that both Titania and Nb2O5 based impregnated Polystyrene/PS-co-ma blend membranes generated pores of 2-3.5µm and increased thermal stability by 70^{o}C, shows competence for its future utilization as membrane for HT-PEMFCs. SO3H functionalization has negative impact on composite membrane thermal stability however, it has increased carrier mobility many folds as was measured by the Hall effect technique.

Key: *HT-PEMFC; Hybrid membrane; Polystyrene; Nano Particles, Titania,* Nb_2O_5

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1. ***Muhammad Raza shah**, Muzammal Zulfiqar, Dr. Zuhair S. Khan

" Inorganic-Organic Nano Composite Hybrid Membrane Based on Titania and Polystyrene for High Temperature PEM Fuel Cell "

*Annexure I

List of Abbreviations

HT-PEMFC	High Temperature Polymer electrolyte fuel cell.
PS	Polystyrene
PS-co-ma	poly (styrene-co-maleic anhydride)
PS/PS-co-ma	blend of Polystyrene and poly (styrene-co-maleic anhydride)
Functionalized PS-co-ma	sulfonated poly (styrene-co-maleic anhydride)
SEM	Scanning Electron Microscopy
XRD	X Ray Diffraction
TGA	thermogravimetric Analysis
T_{10}	Time required for 10% decomposition
T_{50}	Time required for 50% decomposition
T_{max}	Time required for maximum decomposition
np	Nanoparticles

Chapter 1

Introduction

1.1 Background

Currently the world we live demand for high efficient and environmental friendly energy resources due to the adverse effects of fossil fuel and other hydrocarbon energy sources. A lot of research has been carried out in order to coup the issue specially in solar energy, which has been brought as useful alternative especially for electricity power requirement.

Other sources are also being in hunt for coping this issue, in which fuel cell has become in focus of research and development and can be a useful alternative solution.

1.2 Fuel cell

A fuel cell is an electrochemical device which converts chemical energies of fuel directly into electrical energy. Fuel such as hydrogen, methanol, ethanol and other hydrocarbon are utilized for electricity generation [1]. Basically, in fuel cell a simple chemical reaction occurs at electrodes in which the charges (electron, proton) transfer has been given alternate paths, and there upon electron is capture for energy utilization during reaction completion.

1.2.1 In History

Fuel cell basic principles were described in 1839 by a chemical physicist Sir William Grove of Wales (U.K). Where the term Fuel cell was used by a British chemist Ludwig Mond(1839-1909) and Charles langer for the first time. Ludwig Mond and Charles Langer employed the coal as fuel and obtained the current density of 20Am-2 at 0.73V [1]. The NASA used a PEM fuel cell for the first time in Gemini space shuttle program. Later on Alkaline fuel cell of 12KV was used in space shuttle fuel cell programs [1]. There has been a lot of R&D work carried on Fuel cells at the end of 20th century after due to their utilization capacity for portable as well as stationary power generation [4]. Fuel cell with different power capacities are now used for various applications like [1]:

1-10MW: Power generation

1KW-100KW: Electrical vehicles and public transport.

1W-10KW: for personnel electrical equipment's like Computers.

1.2.2 Fuel cell types

There are five different types of fuel cells varying due to their Electrolyte membrane used and working temperature. They are Solid Oxide fuel cell (SOFC), Molten Carbonate Fuel cell (MCFC), Phosphoric Acid fuel cell (PAFC), Alkaline fuel cell (AFC), Polymer Electrolyte Membrane fuel cell (PEMFC).

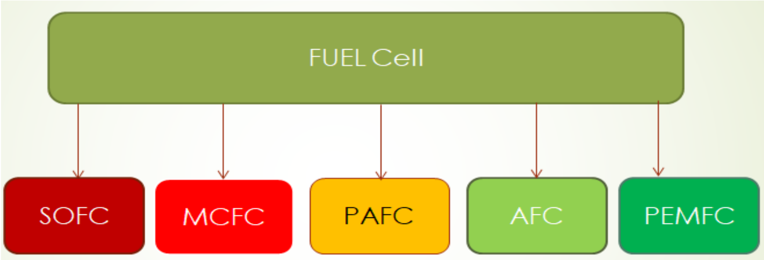
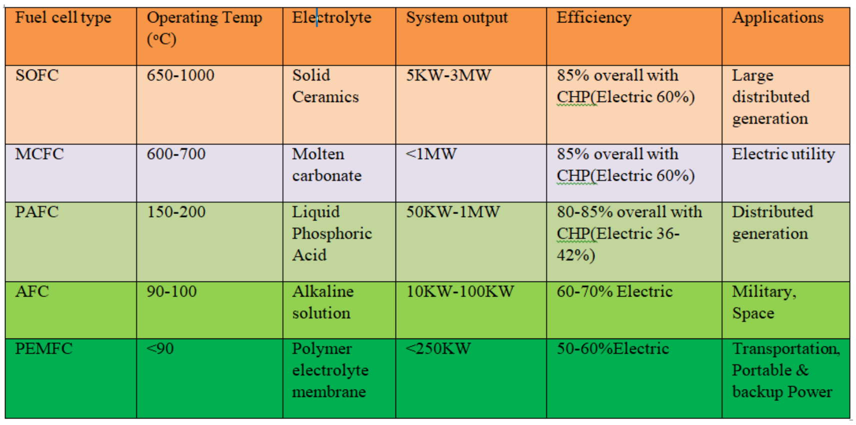


Figure 1 Types of Fuel cell

Table 1 Types of fuel cells characteristics



Fuel cell type	Operating Temp (°C)	Electrolyte	System output	Efficiency	Applications
SOFC	650-1000	Solid Ceramics	5KW-3MW	85% overall with CHP(Electric 60%)	Large distributed generation
MCFC	600-700	Molten carbonate	<1MW	85% overall with CHP(Electric 60%)	Electric utility
PAFC	150-200	Liquid Phosphoric Acid	50KW-1MW	80-85% overall with CHP(Electric 36-42%)	Distributed generation
AFC	90-100	Alkaline solution	10KW-100KW	60-70% Electric	Military, Space
PEMFC	<90	Polymer electrolyte membrane	<250KW	50-60%Electric	Transportation, Portable & backup Power

1.3 Proton Exchange Membrane (PEM) Fuel Cell

Proton exchange membrane fuel cell also called as Polymer electrolyte membrane fuel cell is on the top list of the future R&D in fuel cells due to their uses in transportation and as portable power supply. PEMFC is attracted highly for transportation sector due to its good efficiency, energy density and fast operations. Simpler unit design, low weight and solid electrolyte membrane are addition to its list of preference for transportation manufacturers [2][3].

1.3.1 Working principle:

In PEMFC hydrogen or Methanol is used as a fuel at anode which chemically reacts with oxygen supplied in air at cathode. Water is produced as a byproduct and the transfer of electron is captured for energy generation. The cell reaction which occur at electrodes is

Anode: $2 H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Overall: $2H_2 + O_2 = 4H2O$

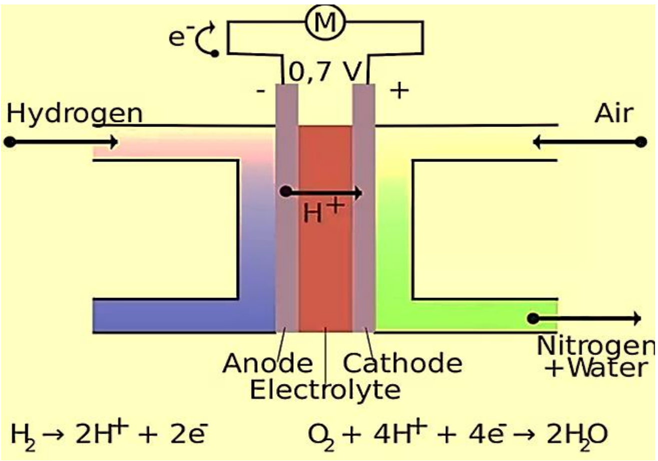


Figure 2 Fuel cell working principle

The proton is transferred through electrolyte membrane from anode to cathode, while electron is given alternate path and is collected as energy source.

1.3.2 PEMFCs Pros and cons

PEMFC is excellent alternate to fossil fuels because it distinguished features as:

Electricity produced directly;

No combustion involved;

No pollution from tailpipe;

Water and Heat only byproduct;

Like batteries producing electricity without combustion.

A lot of R&D work has been done to enhance the power density of PEMFC. For example, electrode assembly methodology when changed from PTFE to thin film transfer method to acquire increased power density from 93mWcm^{-2} to 14793mWcm^{-2} at 0.6V. catalyst loading has been decreased to 100fold since 1980. These improvements have led to overall decrease in PEMFC cost, but still there are some drawbacks associated with PEMFC like pure hydrogen (99.99%) is required due CO poisoning effect, water and heat management; all these drawbacks led to non-favorable availability for commercial utilization.

According to US department of energy, the worldwide fuel cell market will reach $13.830 billion in 2030 projected at CAGR of 28.21%.

1.3.3 Main components of PEM fuel cell

The main components can be divided into following parts,

1. Polymer Electrolyte Membrane (PEM)
2. Electrodes: Anode and Cathode
3. Gas Diffusion Layer (GDL)
4. Current Collector Plates

A symbolic diagram of PEMFC is shown in figure. The hydrogen is supplied via hydrogen flow field at anode and is oxidized to give proton H^+ and electron. The reaction is catalyzed by using platinum Pt catalyst. The proton is allowed to transfer towards cathode via Electrolyte membrane while the electron through alternate path from anode to cathode. At cathode the oxygen is supplied and there at cathode with the help of Pt catalyst it is reduced through electron coming from anode and bond with the proton to produce water and heat. The excess water and heat along with extra air is excreted through oxygen flow field. Similarly, the extra fuel is excreted and recycled at hydrogen flow field. during electron transfer, electron is passed through a load for energy utilization purpose. Thus, the reaction completes and gives us electrical energy. In theory, you can use any material capable of chemical oxidation, which can be fed continuously, as fuel to anode of fuel cell.

Likewise, oxidizer can be any fluid which can be reduced at adequate rate. However, the emphasis in the selection process is to the cost, availability and responsiveness. Hydrogen fuel cell uses H2 gas as fuel and fuel cells provide very high performance and efficiency of pure hydrogen, while using liquid methanol as fuel has relatively low performance and efficiency, Gaseous oxygen or air is the most common option for oxidant because it is readily available and economical. Electrochemical reaction occurs on the surface of electrodes that attach with carbon or carbon fabric paper, referred to as gas diffusion layer (GDL). Carbon connector GDL are full of holes, allowing the flow of Gases and electrons. The catalytic particles are appropriately dispersed in ionomeric materials that support the Proton transfer. Usually the membrane in the cell is Nafion which is solid electrolytes, a perfluoro sulfonic manufactured by DuPont. This membrane allows protons to pass through but prevents electrons from passing through. A Proton moving through the membrane due to the electric field generated across membrane. A fuel cell performance is shown through a plot between current density versus voltage. This provides the steady state performance of given fuel cell system to design, optimization and development. Now we will discuss each component of fuel cell in detail.

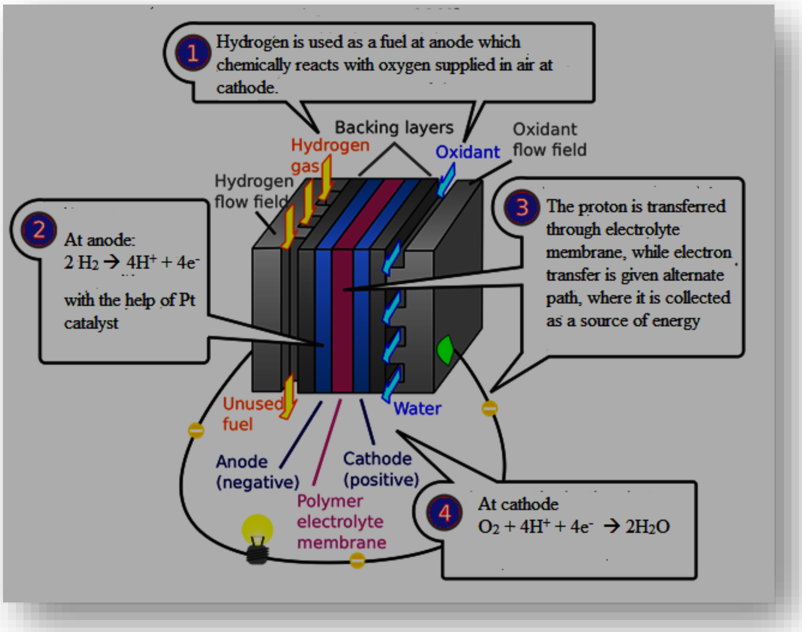
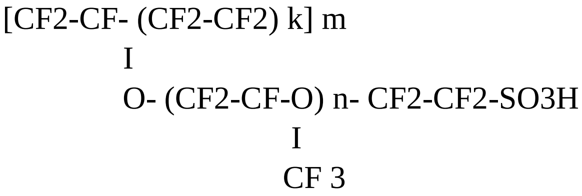


Figure 3 A simplified diagram of PEM fuel cell

1.3.4 Proton Exchange Membranes

Early in 1940s, research scientists have already participated in the development of organic ion exchange membranes. These new ions containing polymers have been described as ionomers. It was thought that these ionic polymers possessed better properties compared to traditional polymers such as nylon or polyester, as they involved the interaction between polymer and ions. Typical applications of these stray compounds, such as thermal plastics, paints, fuel cell membranes and ion-exchange membranes, have been conceived. One of the most important breakthroughs in the area of fugitive ions is the development of the fluorocarbon-based fugitive reactors. It consists mainly of a baseline for each flex fluoride with side strings that are terminated with ionic groups. This type of commercially available ionosphere is the Navon membrane (DuPont), The Dow membrane (DAO Kimkalz, United States of America), Lemon (Asahi Glass Co, Japan) and Aciplex-s (Asahi Chemical Industries Company). Typical thickness of the nafion membrane for fuel cell applications typically ranges between 50 and 175 microns. Nafion is widely used for PEM fuel cell applications. This polymer is based on the spine Polytetrafluoroethylene (PTFE) and has the side strings of the berflorovinil ether pendant, with PFOS collections at the end [1]. It was found that this type of membrane enjoys exceptional stability and possesses properties that can be used in many areas. Consequently, it has been widely used in the chlor-alkali industry because it enjoys the selection of good ions, chemical resistance and ionic conductivity. Since 1966, GE has used naval membranes in fuel cells in protons. At the time, the fuel cell was used to supply energy in space projects by NASA. Although PEMFC was environmentally friendly, it was not considered as a technology for common human. In recent times, however, the need for cleaner and pollution-free energy sources has attracted considerable attention to fuel cells. It is evident from a literary review that Nafion is the main candidate for the PEM fuel cell, although the other membranes mentioned have been investigated. In addition to fuel cell applications, Nafion has been extensively used in recovering metal ions, as a super acid catalyst in organic interactions and various electrochemical devices.



$$\begin{array}{l}
[\mathrm{CF_2-CF-(CF_2-CF_2)\ k]\ m} \\
\qquad\qquad | \\
\qquad\qquad \mathrm{O-(CF_2-CF-O)\ n-CF_2-CF_2-SO_3H} \\
\qquad\qquad\qquad\qquad\quad | \\
\qquad\qquad\qquad\qquad\quad \mathrm{CF_3}
\end{array}$$

Structural formula of the Nafion polymer

1.3.5 Electrodes and catalyst

The electrodes consist of Nano-size platinum (3-5 nm) supported by carbon molecules (30 microns) and mixed with Proton-ionomeric. On top of each layer of the electrode the spread of 100-300µm gas diffusion layer is made of carbon cloth or carbon-based paper. Figure illustrates the typical cross-section of the pole with a carbon black. A tremendous amount of research has been done to develop a high-performance catalyst for fuel cells. In PEM fuel cells, the type of fuel used determines the appropriate type of catalyst required. In this context, tolerance of carbon monoxide (CO) is an important issue, especially when hydrogen consists of the process of fuel reforming. The performance of PEM fuel cell has been shown to decline with CO-concentration of only several parts per million. This is due to a strong chemical absorption force of CO on the catalyst.

1.3.6 Gas Diffusion Layer (GDL)

The GDL which is near the anode and the other side(page) of the cathode is produced often from a pores carbon paper or carbon cloth, as a rule between 100 and 300 µm thickness. The porous state of the GDL materials cares for the effective diffusion of every reactive gas to the catalyst on the membrane and Pole group.

The structure makes possible the propagation of the gas during his(its) propagation, so that the gas stands in regular contact with the whole surface(environment) of the catalyst. The GDL also helps in the water management at the enterprise(operation) of the fuel cell. The GDL makes possible the appropriate amount in steam to reach the membrane / electrodes group.

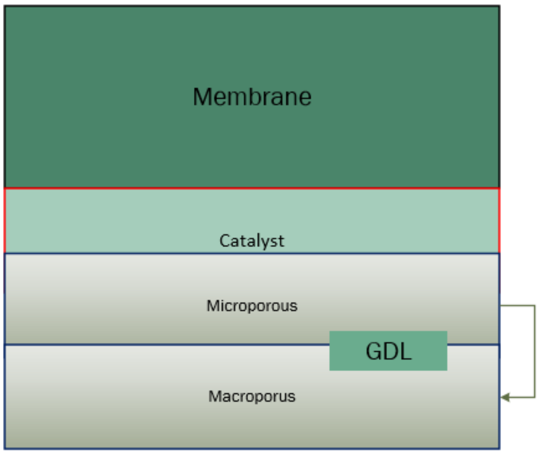


Figure 4 Schematic diagram of a GDL for PEM fuel cell

1.3.7 Flow Field/ Current Collector

The last component on the outside side of unit cell is the current collector plate in which also gas flow field is contained. These both functions of the gas flow field and the current assembly can be fulfilled by two separate components, but in most cells and stakes up to now the flow field is mechanized upon the current collector using different shapes, for example, flow by parallel channels and parallel series groups. The flow field architecture is very important to do justice to the demands of an efficient and uniform(standardized) gas supply and water supply and to remove effective fluid water from the cathode. The current collector's plates in a stake of PEMFC are bipolar plates. It must have high electronic conductivity and high impermeability to fuels as well as non-corrosive in nature. Carbon, stainless steel, titanium all can be considered for current collector plate.

Now with the current collector plate the load containing circuit is attached and hence the PEM fuel cell is completed for operation.

1.3.7 MEA

MEA; this term is used often to represent the part of fuel cell. Actually, the combination of the anode: membrane: cathode is called the membrane electrode assembly (MEA). Original MEA was prepared for GEMINI space program in 1965. 4mg of platinum per cm^2 of membrane area was used there in GEMINI space program. The thickness of MEA depends on type of membrane and how much platinum is used in each electrode. Typical thickness of MEA could be about 200 µ m or 0.2 mm. The electrodes now use less than 0.4 mg Pt/ cm2.

Summary

Fuel cell is an excellent renewable energy alternative to the already depleted conventional fossil fuel and is environment friendly. Fuel cell can be divided into different types, but Polymer electrolyte membrane fuel cell has very promising future due to its versatility from tiny to huge requirements, portability as well as in automobile industry. Also, the fuel it uses is abundant in nature, such as the hydrogen fuel cell uses H2 gas as a fuel and provides excellent fuel cell performance. The half-cell reactions for the hydrogen PEM fuel cell are as follows:

Anode: $H_2 \leftrightarrow 2H^+ + 2e^-$

Cathode: $2/1\ O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$

Overall: $H_2 + 2/1\ O_2 = H2O$

The reaction completes in a cell, to which oxygen/Air and Hydrogen is supplied both at cathode and anode end respectively, which are separated through an electrolyte membrane. Proton is exchanged through electrolyte membrane while an alternative path is provided for electron transfer. This electron transfer provides us with required energy.

In this chapter basic structure of fuel cell, its different components and importance of its electrolyte has been discussed in detail. In this thesis we will be focusing on synthesis novel electrolyte membrane.

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Chapter 2

Literature Review

2.1 Introduction

Since we have studied in previous chapter that due to limitation of PEMFC (<90^{o}C) it cannot be utilized for large scale commercial applications especially due to high cost and pure hydrogen (99.999%) availability issue. Therefore, the demand for High Temperature -PEMFCs are increasing day by day. In this chapter, we will look upon importance of HT-PEMFCs and the different composite hybrid membranes used for this purpose. And at last will discuss upon our choice of polystyrene based composite membrane

2.2 High Temperature PEM fuel cell

Nafion and other fluorinated PEMs have been extensively used because of the excellent conductivity of proton and electrochemical stability due to the backbone of PTFE [1]. However, they are expensive, not as solid as is particularly desirable under the conditions of cycling, humidity, freezing and melting conditions, unstable at temperatures above 85 ° C, and the protons work effectively only when they ansorb sufficient amount of water, which limits the operating temperatures of the cells Fuel PEM to about 80 ° C [2]. On the other hand, for PEMFCs large scale commercialization fuel cell working above 100°c is a highly necessary target. Since the operation of fuel cells at high temperatures increases electrochemical kinetic, improves tolerance of CO, facilitates heat rejection and reduces problems associated with water management. There have been intensive research efforts to find stable substitute membranes at higher temperatures. In fact, PEM should not be the only for the proton transfer under warm and dry conditions, it must be tinny for low resistance and high proton transfer, compatible to form a good connection with electrodes but rigid enough to provide support for assembling the membrane electrode assembly (MEA). Furthermore, it should be stable Thermally and multidimensional, impermeable to gaseous or liquid fuels, as well as electrons, with low voltage clouds and mechanical strength sufficient for several years. This is really hard, and no wonder that success in finding alternatives to Nafion is limited despite extensive research efforts

2.2.1 Advantages of Hight Temperature PEMFC

2.2.1.1 Electrode reaction kinetics

Oxygen deduction reaction has slowest electrochemical kinetics at low temperature so in overall reaction it is rate determining factor. The slow reaction kinetics is responsible for loss of voltages due to slow reaction kinetics. When we move towards the higher temperature, the oxygen reduction rate is significantly improved that consequently improve the performance of PEMFC.

2.2.1.2 Carbon monoxide tolerance

Platinum is the main catalyst in LT-PEMFC. Pt has a high attractiveness for carbon monoxide which is a byproduct of repair [11]. Because of poisoning, the level of tracking of carbon monoxide can lead to a significant decrease in the performance of LT-PEMFC. HT-PEMFC overcomes this problem, at operating temperatures above 150^{o}C, improving its endurance by reducing the carbon monoxide affinity. Below 80 ^{o}C CO absorbs onto the platinum surface and rigorously affects the performance [15], But platinum electrode tolerates 3% carbon monoxide above 160^{o}C [16,17]. This significantly minimized the many stages required in fuel cleaning processes, which increase the cost of whole system.

2.2.1.3 Heat and water management

In the case of PEMFC, 40-50% of total energy is produced in the form of heat. This energy must be quickly removed from the system and not to cause degradation of fuel cell components. On the other hand, when we increase the operating temperature of the fuel cell, the efficiency of energy transmission in the system increased to the environment due to the high temperature of the gradient [17]. The existing technology present in today transport system is not sufficient for the removal of extra heat from the system. For this purpose, a specialized cooling technology is required but it enhances the cost of the system. We can use the existing cooling technology present in vehicles if we increase the operating temperature of PEMFC. Cogeneration [18] and on-board reforming [10] further increases the efficiency of PEMFC.

At a lower temperature (80 ° C or less) and atmospheric pressure water is present at the double stage. Due to the stringent moisturizing requirements of the proton exchange membrane, there is a need for a very tight control water system. If the fuel cell works at high temperatures, the water is in one phase (gaseous) so the water management system is greatly streamlined. Thus, the water transport through the diffusion layer, electrodes and membranes is even easier to simplify the design of the Flow field panel to a large extent. [14] Another important effect of the high temperature fuel cell is that the reactive and produced material is in a gaseous form that is expected to increase the prevalence rate. As in case of high temperature fuel cell there is no water in liquid form so electrochemically reactive surface does not block consequently the efficiency of fuel cell increase due to the increase of reaction rate at electrode surface [12]. The simplified heat and water management system reduces the cost of the stack due to the design of a simpler flow field

.2.2.1.4 Alternative catalysts

As the electrode kinetics is high at higher temperature so it is possible to use catalyst other than platinum which significantly reduce the coat of PEMFC. For example, low cost material like iron [13] can be used as catalyst to facilitate the reaction at electrode surface [19]. Cobalt (Co) can also be used as an alternative catalyst when fuel cell working at high temperature [20].

2.3 Composite materials

Composites are widely used for preparation of efficient and high temperature membranes.

2.3.1 Composites materials

Composite, natural or synthetic, are the materials that are composed of more than 1 components and possessing modified characteristics of both materials. In composite materials, the component with large amount is known as matrix, while the other with less amount is known as filler. This filler modifies the matrix properties.

2.3.2 Nano Composites

Nano composites refers to the composites in which at least one material is in nano meters ranges. It can be classified into following categories

(i) Ceramic matrix nanocomposites
(ii) Metal matrix nanocomposites
(iii) Polymer nanocomposites.

2.3.3 Polymer

Polymer is a large molecule made up repetition of small units called monomers by polymerization process. Their properties like ductility, dielectricity, light weight, process ability and flexibility make them good choice for emerging complex shapes materials.

There are different kinds of polymers that has been in use for hybrid membrane preparation such as Polybenzimidazole PBI, Poly ether ether ketone PEEK, polystyrene. Here we have used Polystyrene as matrix for hybrid membrane, while titania and SiO2 nanoparticles as nano fillers.

2.3.4 Polymer nanocomposites

Polymer composites have attracted a tremendous amount of modern-day consideration because of the enhancement of the properties of the polymer matrix with the addition of reinforcement through fillers. Because of improved mechanical and physical properties by the addition of Nano filler, the fabricated polymer nanocomposites find a wide range of application in new age of electronic, food packing, aerospace, construction and automotive industries [4]. Polymer nanocomposites formed by addition of reinforcement into matrix show superior electrical, mechanical properties, dimensional stability, optical transparency and aging resistance.

2.3.5 Inorganic-Organic Hybrid Composites Membranes for HT-PEMFCs

There are different composites membrane used nowadays for HT-PEMFCs apart from Nafion, around the world with different benefits and drawbacks variations. Following are the essentials material of hybrid composite membrane.

Organic Polymer fiber such as Polybenzimidazole, Poly ether ether ketone, Polystyrene.

Inorganic Nano particles as filler e.g. SiO2, TiO2, ZrP, TiO2, Nb2O5

Acid for proton hopping mechanism such as H2SO4, H3PO4.

2.3.5.1 Poly benzimidazole PBI based composite membranes

PBI is synthetic fiber which has high melting point, and extraordinary chemical and physical properties with higher grade stability and toughness at higher temperature. Because of its higher characteristics, it is utilized usually for protective material such as in astronomer space suit, firefighter's gear and elevated temperature gloves [5]. Due its exceptional characteristics it has been in utilization to investigate as potential hybrid membrane for HT-PEMFC. Silicon dioxide, ZrP nano particles along with other are used as inorganic filler and resulted in good durability up to 5000 hours above 100 oC and with better conductivity [6].

2.3.5.2 Poly ether ether ketone base composite membrane

PEEK is organic thermos plastic polymer which has outstanding chemical and mechanical resistive properties at high temperature. Due to strong characteristics, it has application in bearings, piston, pump parts etc. [7].

2.3.5.3 Polystyrene based composite membrane

Polystyrene is a synthetic aromatic hydrocarbon polymer made of styrene monomer. It is an inexpensive, is a weak barrier to oxygen and water vapor and has a relatively low melting point. As a thermoelectric polymer, the polystyrene is in a solid state (glass) at room temperature. Its glass transition temperature is 95oC [7].

2.3.5.4 Titania nanoparticles as inorganic filler

Titanium di-oxide is one of the most attractive materials in nanotechnology [8][9]. It has a wide application from sun screen to pigments, and as utilization of filler, it can exhibit good characteristic due to its high thermal stability.

2.3.5.5 Niobium pentoxide Nano particles

Niobium pentoxide is the inorganic compound with the formula Nb_2O_5. It is a colorless insoluble solid that is fairly unreactive. Nb2O5 is mostly used for niobium precursor for niobium preparation. It is insoluble in water and has high melting point temperature of 1512^{o}C.

2.3.5.6 SO3H group

Sulfonic acid is used in organic chemistry for functionalization R-SO3H. functional groups are substitutes responsible for characteristics chemical behavior of molecules. The functional groups show their characteristics, irrespective of molecule size and type. So, one can predict the chemical behavior of these compounds with confirming its functional group.

SO3H is used to facilitate proton transfer in membrane via proton hoping mechanism. Water is continuously supplied through membrane which facilitate H+ proton transfer through membrane by forming hydronium ion $H3O^+$, $So3^-$. Sulfonic acid. Proton hopping mechanism is explained clearly in diagram below.

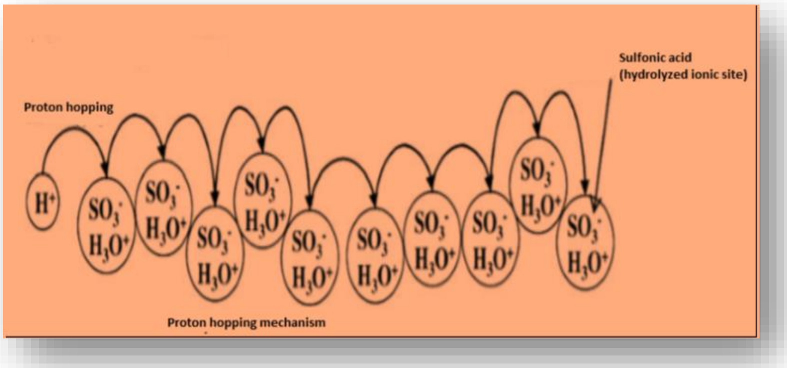
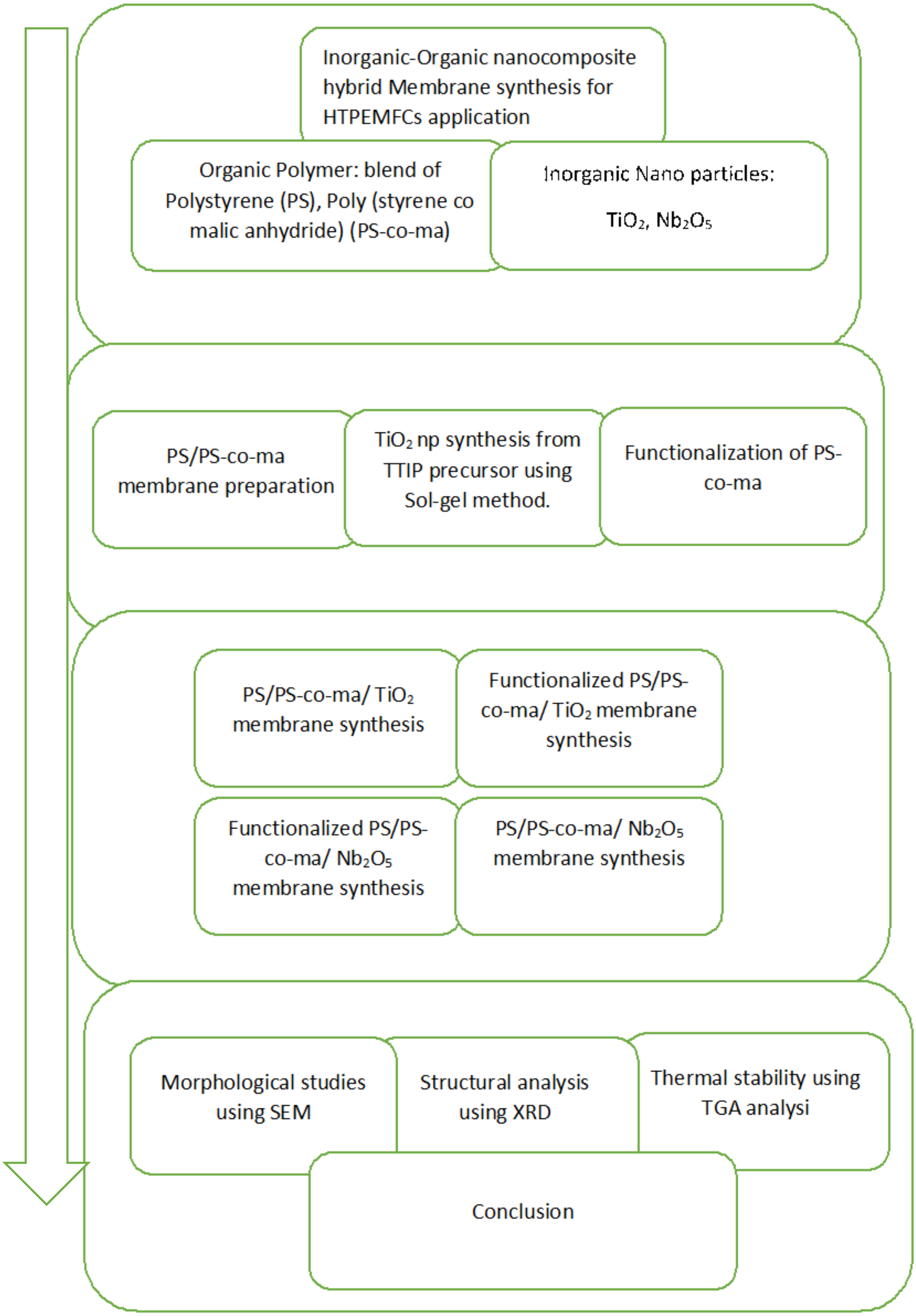


Figure 5 Proton Hopping through membrane

Summary

High temperature PEMFCs has become the demand of the time due to its high advantages over others. It can be achieved using a polymer electrolyte membrane which can operate above 90^0C. polymer membrane thermal stability can be increased using inorganic Nano filler like SiO2, Titania and Nb2O5 nanoparticles. Different polymers such as PBI, PEEK etc. are among top choice polymers for this contest. Polystyrene is another easily available polymer. To study Nb2O5, Titania nanoparticles impregnation impact on polymer, we are using Polystyrene as our primary polymer.

Thesis flow-chart



Objectives

- To synthesized Titania Nano particles using TTIP precursor.
- To synthesize novel inorganic-organic composite hybrid membrane using polystyrene (PS) and Poly (styrene-co-maleic anhydride) (PS-co-ma) as organic polymer, TiO2, Nb2O5 Nano particles as inorganic fillers.
- To study the impact of Titania, Nb2O5 Nano particles on polymer membrane.
- To investigate the impact of SO3H group doping
- To compare the results of different membranes.

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Chapter 3

Synthesis Methods and Characterization Techniques

Since the overall object of this work is to develop better membranes for fuel cell application, the required experimental procedures to make or modify electrolyte membranes followed by vital characterization tests including chemical, physical, thermal and electrochemical analysis are described in this chapter.

3.1 Synthesis techniques

There are different techniques used for synthesis of organic inorganic nanocomposite membrane. Which are discussed below.

3.1.1 Solution Casting Process

Solution casting process is a simple and low-cost technique for isotropic membrane preparation [1]. In this method, first, a solute is dissolved in a solvent to generate a casting solution and according to the desired membrane thickness the weight of the casting solution can be varied. Then the prepared solution is poured into a membrane-casting plate which is horizontally adjusted such that the casting solution is uniformly spread out into the plate. After, the top of the plate is covered with a watch glass and put into the convection oven to perform the heat treatment until the solvent in the casting solution is completely evaporated.

The casting plate is then removed from the oven to be cooled down. After cooling, deionized water (DI H2O) is poured in the plate to loosen the membrane for being peeled off from the glass. Finally, the edges of the casted membrane are trimmed and by applying a standard preparation technique, the membrane is treated before starting any performance characterization tests.

3.1.2 Melt blending

Melt blending is another frequently used method for the preparation of polymer nanocomposites. Thermoplastic polymers, such as polystyrene [2], polypropylene [3] poly (ethylene 2,6-naphthalate) [4], can be used as matrix materials in this method. This method is superior then solution casting because solvent does not require for the dispersion of nanofiller. Melt blending uses high shear force and high temperature to disperse nanofiller in a polymer matrix, and it is well-matched with current industrial practices. Special equipment, such injection machine, extruder, which are able to operate at high temperature producing high shear force to disperse the nanofiller. In comparison with the solution mixing, this method is mostly considered less efficient to disperse nanofiller in polymer matrix and its application is also restricted to low filler concentrations in matrix (thermoplastic).

3.1.3 In situ polymerization

In-situ polymerization is a well-organized method for the uniform dispersion of nanofiller in a thermosetting polymer matrix. In this method, nanofiller are first mixed with monomers and then these monomers are polymerized through condensation or addition reactions. One of the basic benefit of this method is that the covalent bond formed between the polymer matrix and functionalized nanofiller which results in much Improve mechanical properties of nanocomposites through strong interfacial bonding.

3.2 Characterization Techniques

3.2.1 X Ray Diffraction (XRD)

XRD is an analytical tool for identification of phases and orientations in crystalline compounds. XRD is a non-destructive technique that provides crystallographic information of the specimen. It is useful in determining structural properties like crystal size, lattice parameters, lattice strain etc.
Working principle When crystalline materials are irradiated by X-rays, they interact with atoms of the material and refract X-rays of characteristic energy. An individual pattern is generated by each material. In a mixture of materials, each substance gives its own pattern independently [5]. XRD works on the principal of constructive interference of refracted X-rays. Fig.3.1 shows working of XRD machine. When X-rays interact with matter, three phenomena may occur, Ionization, fluorescence and diffraction. In XRD, when X-rays hit atoms, the electrons in atoms start vibrating with frequency same as the frequency of striking X-rays. Bragg's law is used to describe the working of XRD $\sin(\theta) = n\lambda / 2d$ (3.1)

Where:

θ = Incident angle

d = Spacing between the planes and

λ = wavelength of the X-rays

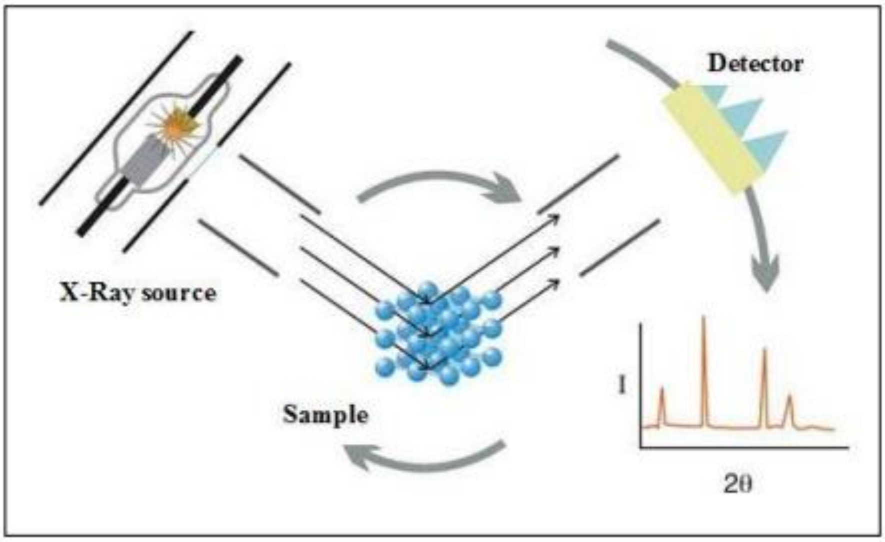

Figure 6 working of XRD

After striking on the sample, these X-rays are detected by a detector that makes a diffractogram. A diffractogram is a graph which is plotted between 2θ on x-axis and intensity on y-axis. The detector records intensities of the diffracted beams and angles. This pattern is a fingerprint of the material. Miller indices define the interplanar spacing and orientation. Number and position of peaks (2θ values) enable to determine lattice type, cell parameters and crystal class. Intensity of peaks gives information about position and types of atoms in the specimen [6]. It is to be noted, however, that XRD cannot detect amorphous materials. Amorphous structures with poorly defined characteristics yield diffuse patterns, compared to the distinct intensity peaks obtained with crystalline materials.

3.2.2 Scanning Electron Microscopy (SEM)

SEM is an imaging tool that is used to study surface morphology of the samples. The surface of the prepared substrate is analyzed in three dimensions with high resolution and magnification. SEM provides magnification up-to 300,000X and has an effective probing depth of 10 nm to 1 µm.

Working principle

A focused electron beam is kept over the sample that results excitation of electrons presents in the sample. An Image is produced on the display of computer connected to the machine. The magnification depends on the relationship of size between the display and the area of the surface being scanned. Samples being scanned in SEM may face damage problems, but it rarely happens. During high magnification, some polymers plastic-based materials may be transformed. This damage can be prevented using the machine at low voltage [6].

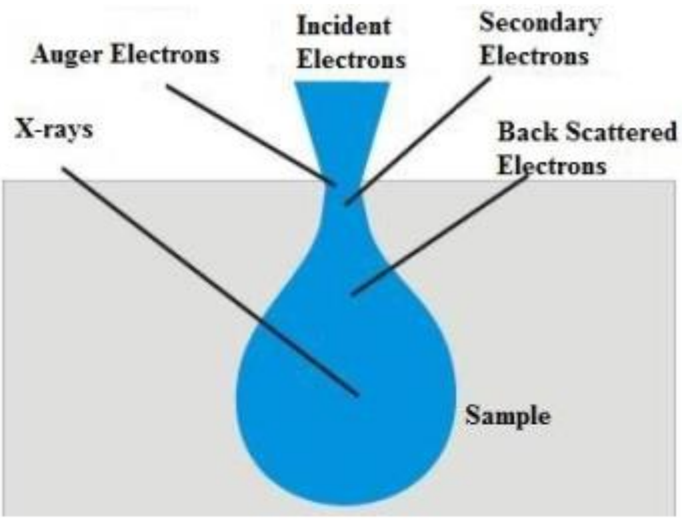

Figure 7 working principle of scanning SEM

Imaging with SEM is fast and easy, but the resolution is typically lower. In addition, SEM produces no direct height information of the surface structures and is sometimes difficult to use with insulating samples.

3.2.3 Thermal Gravimetric Analysis (TGA)

TGA is a continuous process to study the thermal degradation of polymeric materials which involves the measurement of sample weight as the reaction temperature is changed by means of a programmed rate of heating. Mass is lost if the substance contains a volatile fraction. Thus, the sample weight decreases slowly as reaction begins, then decreases rapidly over a comparatively narrow temperature range, and finally levels off as the reactant becomes spent. So, in thermal gravimetric analysis basically weight change of material is determined as a function of temperature in a controlled atmosphere. Thermal gravimetric measurements are also used to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can be used to characterize materials that display weight loss or gain due to oxidation, decomposition, or dehydration. Thermal gravimetric analysis (TGA) analysis relies on a high degree of accuracy in three measurements: temperature, weight, and temperature change. The most apparent weight loss is determined by taking the derivative of TGA curve. To determine composition and purity, the mass of the substance is taken first in the mixture by using thermal gravimetric analysis. TGA also used to determine the composition, purity and mass of a substance.

3.2.4 Hall Effect Technique

It is the potential difference developed across an inductor/ insulator when a current is passed through it along with magnetic field applied perpendicular to current. It was discovered by Edwin Hall in 1879.

The hall coefficient is defined as the ratio of the induced electrical field to the current density output and the applied magnetic field. It is a characteristic of the material that the connector consists of, whose value depends on the type, number and characteristics of the cargo vectors that make up the current.

The effect of the hall is due to the nature of the current in insulator. The current consists of the movement of many small charge carriers, usually electrons, holes, ions or altogether. When there is a magnetic field, these charges test a force called Lorentz force ($F=qE+qV+B$), which induce a voltage in it. This is hall voltage difference generated.

Since hall effect equally work on Electron and proton therefore, it can be used to calculate the proton mobility and concentration in proton dominant membrane.

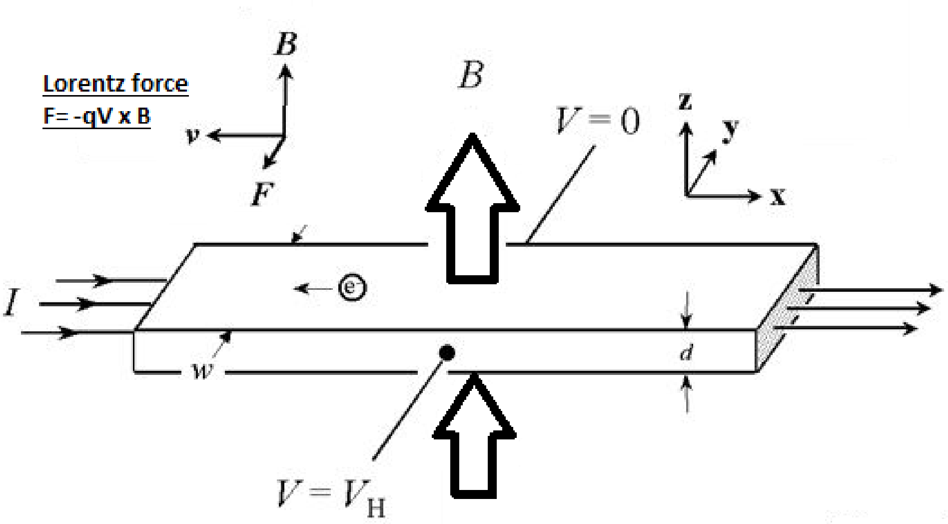

Figure 8 Schematic of Hall effect.

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Chapter 4

Experimentation

Several experiments were carried out to achieve the objectives, which are discussed accordingly.

4.1 TiO2 Nanoparticles preparation

TiO_2 nanoparticles powder were prepared via sol gel method using titanium tetra Isopropoxide TTIP, ethanol ETOH, distilled water and hydro chloric acid HCL as starting material. TTIP was added dropwise to solution of distilled water, Ethanol and HCL with continuous magnetic stirring in ratio of 1: 15: 60: 0.2 accordingly. The white solution obtained was kept on slow stirring for 48 hours at room temperature. The precipitated TiO2 was filtered and dried at 50c. the dried crystals obtained were then converted into powder. The powder obtained was calcinated at 400 C for 3 hours [1].

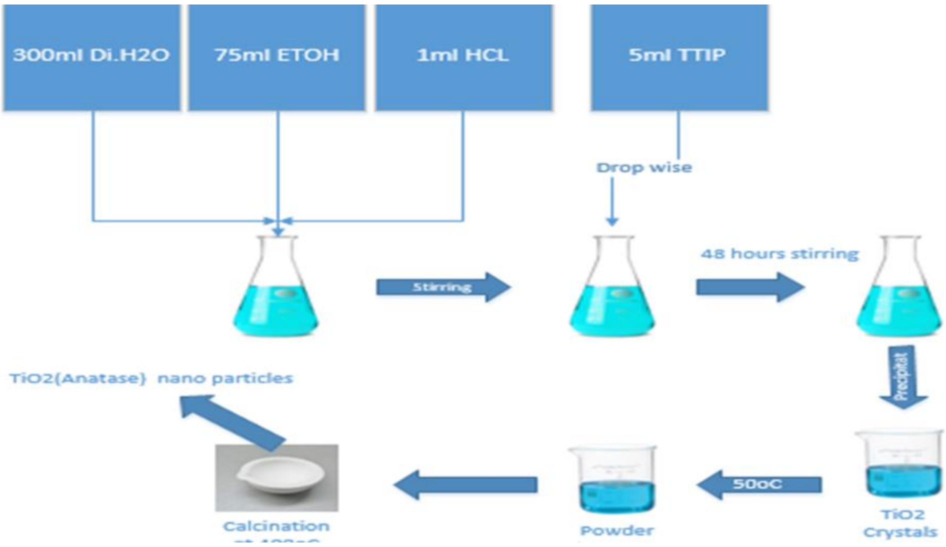

Figure 9 Titania nanoparticles Synthesis

4.2 PS-co-ma functionalization with H2SO4

4gram PS-co-ma was dissolved in 40ml THF and stirred for 1 hour. Concentrated H2SO4 2ml was added slowly into solution. After continuous stirring for 5 hours at room temperature light yellow solution was obtained. Add distilled water and neutralize the solution by 10% NaOH solution. Finally Heat the solution in oven at 60C [3].

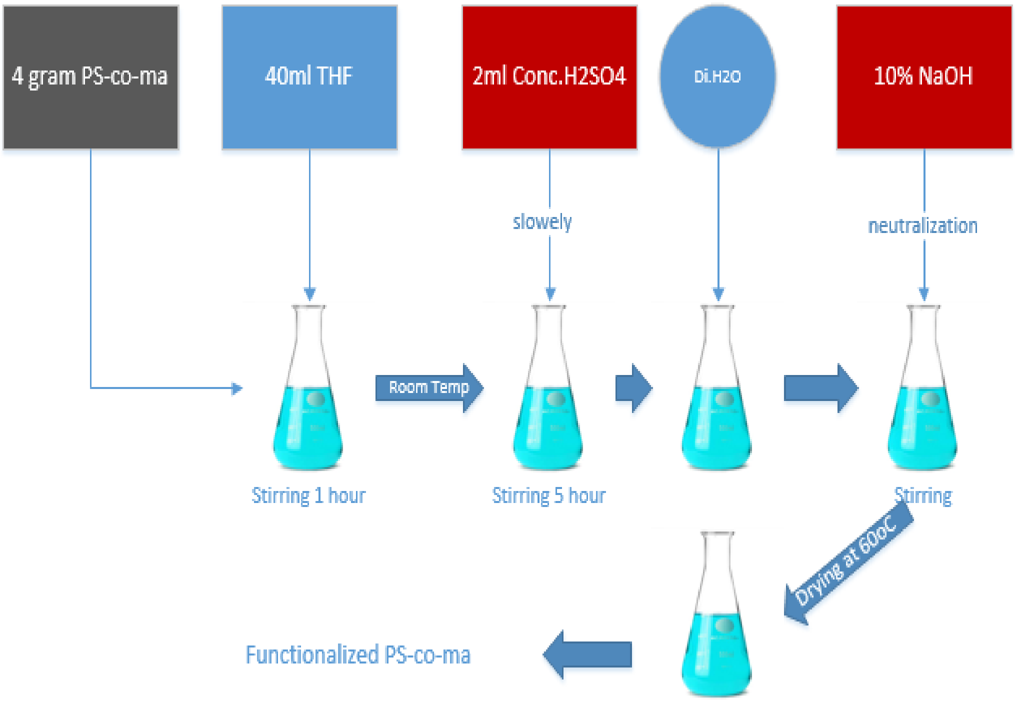

Figure 10 Functionalization process of PS-co-ma

4.3 PS/PS-co-ma membrane preparation

0.5gram Polystyrene 10%wt solution in THF tetra hydro furan and 1.5gram PS-co-ma 10%wt solution in THF were prepared by continuous stirring for 3 hours. Then both solutions were mixed together and continuously stirred for further 3 hours at room temperature. Then the solution is poured into glass petri dish and kept at room temperature for drying. The dried membrane is obtained by placing petri dish in distilled water [2].

4.4 PS/PS-co-ma/ TiO_2 membrane preparation.

0.5gram Polystyrene 10%wt solution in THF tetra hydro furan and 1.5gram PS-co-ma 10%wt solution in THF were prepared by continuous stirring for 3 hours. Then both solutions were mixed together and continuously stirred for further 3 hours at room temperature. Dispersed the tiO2 nanoparticles in THF (10%wt) and apply sonication for 1 hour. The dispersed TiO2 in THF is then poured into polymer mixture and stirred for 12 hours at room temperature. The mixture is the cast on glass petri dish and at room temperature the THF can evaporate. The membrane is separated from glass by dipping into distilled water.

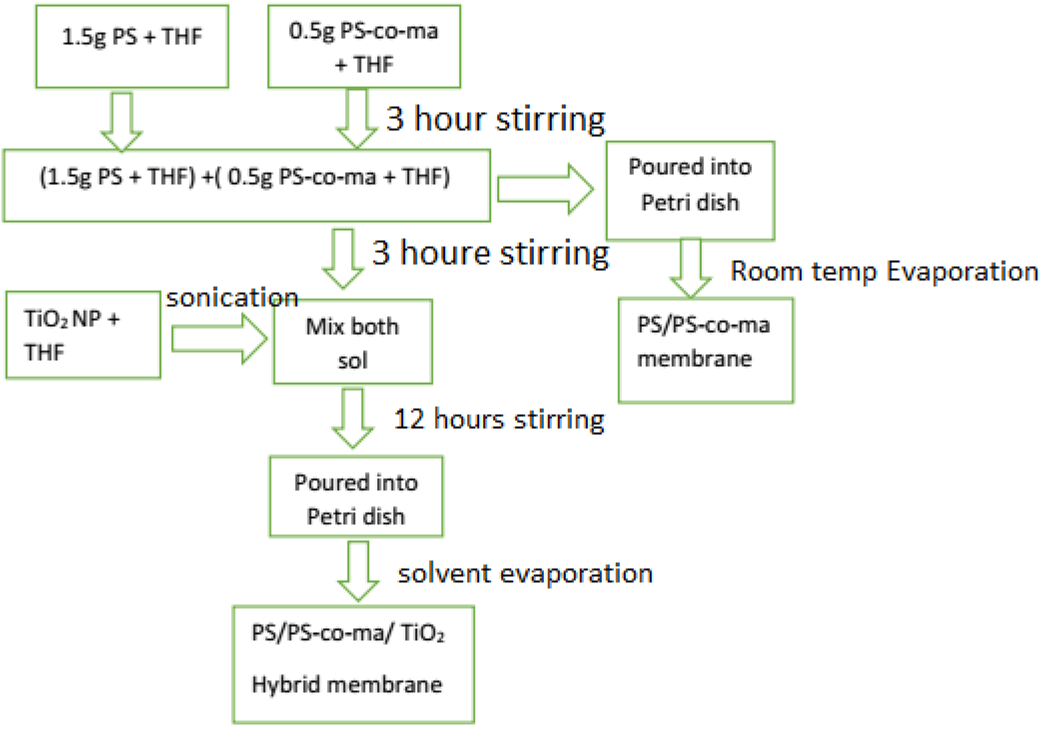

Figure 11 PS/PS-co-ma/TiO2 membrane synthesis

4.5 PS/ Functionalized PS-co-ma/ TiO_2 membrane preparation.

0.5gram Polystyrene 10%wt solution in THF tetra hydro furan and 1.5gram Functionalized PS-co-ma 10%wt solution in THF were prepared by continuous stirring for 3 hours. Then both solutions were mixed together and continuously stirred for further 3 hours at room temperature. Dispersed the TiO2 nanoparticles in THF (10%wt) and apply sonication for 1 hour. The dispersed TiO2 in THF is then poured into polymer mixture and stirred for 12 hours at room temperature. The mixture is the cast on glass petri dish and at room temperature the THF is allowed to evaporate. The membrane is separated from glass by dipping into distilled water.

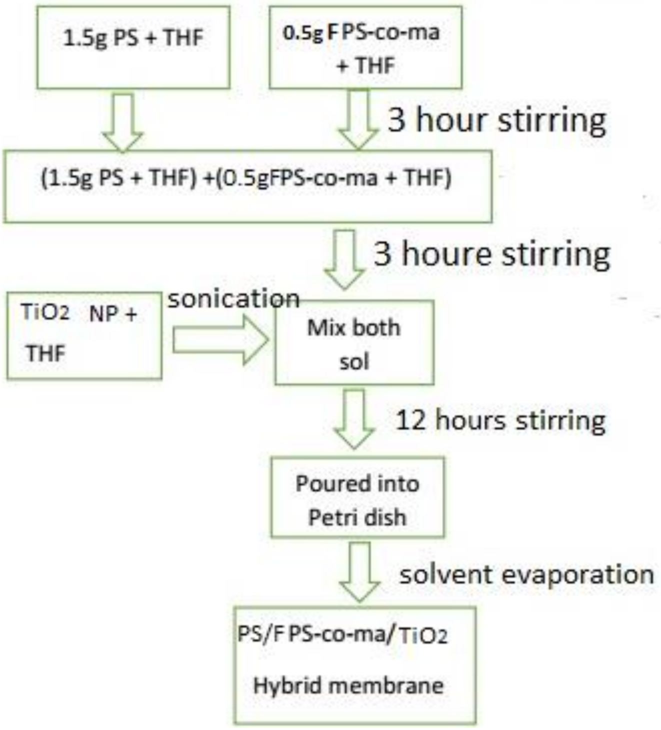

Figure 12 functionalized PS/PS-co-ma/TiO2 hybrid membrane

4.6 PS/PS-co-ma/ Nb_2O_5 membrane preparation

0.5gram Polystyrene 10%wt solution in THF tetra hydro furan and 1.5gram PS-co-ma 10%wt solution in THF were prepared by continuous stirring for 3 hours. Then both solutions were mixed together and continuously stirred for further 3 hours at room temperature. Dispersed the Nb2O5 nanoparticles in THF (10%wt) and apply sonication for 1 hour. The dispersed Nb2O5 in THF is then poured into polymer mixture and stirred for 12 hours at room temperature. The mixture is the cast on glass petri dish and at room temperature the THF is allowed to evaporate. The membrane is separated from glass by dipping into distilled water.

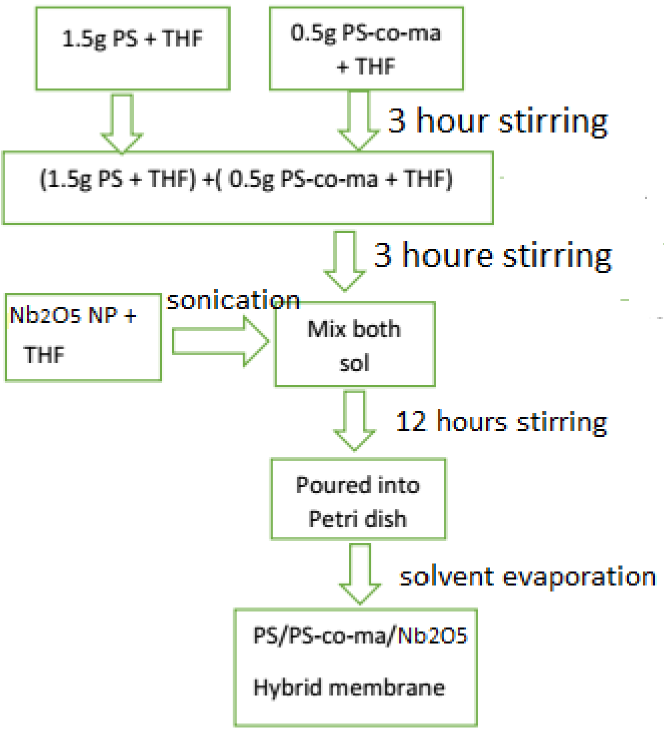

Figure 13 PS/PS-co-ma/Nb2O5 hybrid membrane

4.7 PS/ Functionalized PS-co-ma/ Nb_2O_5 membrane preparation.

0.5gram Polystyrene 10%wt solution in THF tetra hydro furan and 1.5gram Functionalized PS-co-ma 10%wt solution in THF were prepared by continuous stirring for 3 hours. Then both solutions were mixed together and continuously stirred for further 3 hours at room temperature. Dispersed the Nb2O5 nanoparticles in THF (10%wt) and apply sonication for 1 hour. The dispersed Nb2O5 in THF is then poured into polymer mixture and stirred for 12 hours at room temperature. The mixture is then cast on glass petri dish and at room temperature the THF is allowed to evaporate. The membrane is separated from glass by dipping into distilled water.

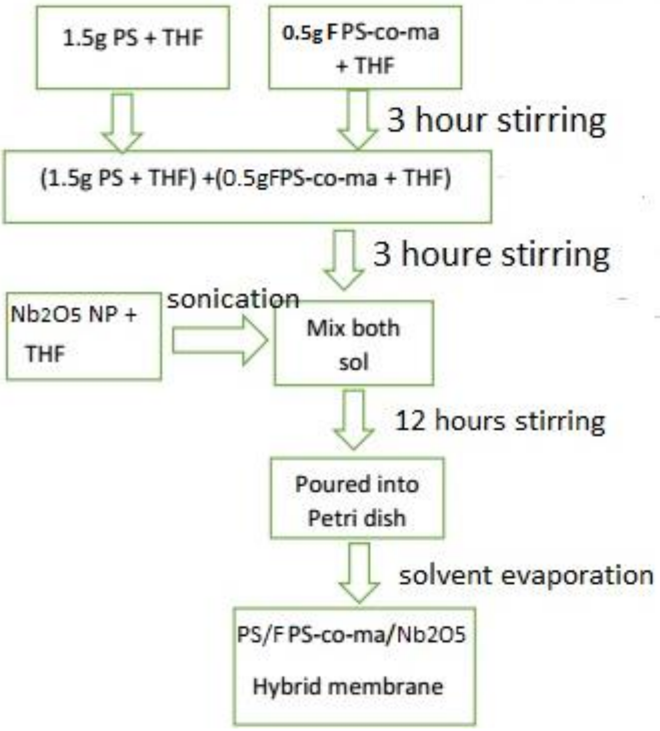

Figure 14 Functionalized PS/PS-co-ma/Nb2O5 hybrid membrane

Summary

Different Nano composite hybrid membrane such were successfully synthesized using wet chemistry rout methodology. Polystyrene and Poly(styrene-co-malic) blend was used as organic polymer and Nb_2O_5 and Titania nanoparticles as inorganic fillers. TiO2 nanoparticles were synthesized using TTIP precursor. PS/PS-co-ma simple blend membrane was also prepared for comparisons analysis. Some PS-co-ma was also doped with small amount of concentrated H_2SO_4 for functionalization and hence for preparation sulfone group functionalized membrane synthesis.

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Chapter 5

Results and Discussion

In this chapter the results and detailed analysis of experimentation of chapter 4 will be discussed. 5 different types of membrane and TiO2 Nano particles were synthesized and will discuss it results in detail in this chapter.

5.1 XRD analysis

XRD analysis for different synthesized membrane were done and discussed as following.

5.1.1 TiO2 Nanoparticle and PS/PS-co-ma/TiO2 composite membrane.

XRD studies were conducted to study the crystallinity of composite membrane. Fig 10. shows the pattern of TiO2 Nano particles Maximum Peak for pure Titania dioxide Nano particles were observed at $2\theta = 25.6^\circ$ (anatase. (1 0 1)) while other peaks were observed at 27˚, 37˚, 38˚ and 48,˚ which confirms Titania successful synthesis. All intensity peaks of Titania nano particles were matched with PDF card # 75-1537. The broader peaks of Titania is due to smaller crystallite size [1]. Pure Titania shows the tetragonal structure and anatase form. Fig.10 also shows the pattern of sample blend of PS/PS-co-ma membrane which has broad peaks at $2\theta = 10^\circ$ and at $2\theta = 20^\circ$.

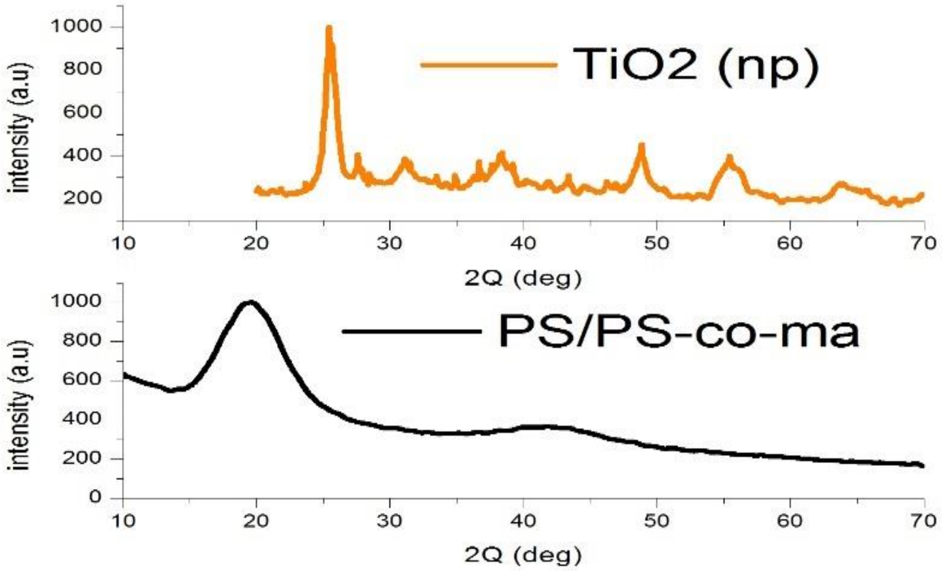


Figure 15 XRD pattern of TiO2 Nano particles and PS blend membrane

5.1.2 PS/PS-co-ma/TiO2 composite membrane.

The pattern of composite hybrid membranes of Titania Nano particles with simple and functionalized Polystyrene are shown in figure 11. The maximum peaks for simple and functionalized composite membrane were observed at 2θ =25.45˚ and at 2θ=25.06˚ respectively, these peaks correspond respectively to reflection from (002) and (100) planes. Other peaks are at 2θ = 27.5, 30.93˚, 37˚, 38˚. Similarly, polymer peak was observed at 2θ = 19˚. The peaks are in correspondence with that of anatase Titania Nano particles and Polystyrene and shows composite synthesis successful. The composite membrane peaks were like the PDF card # 13-0843.

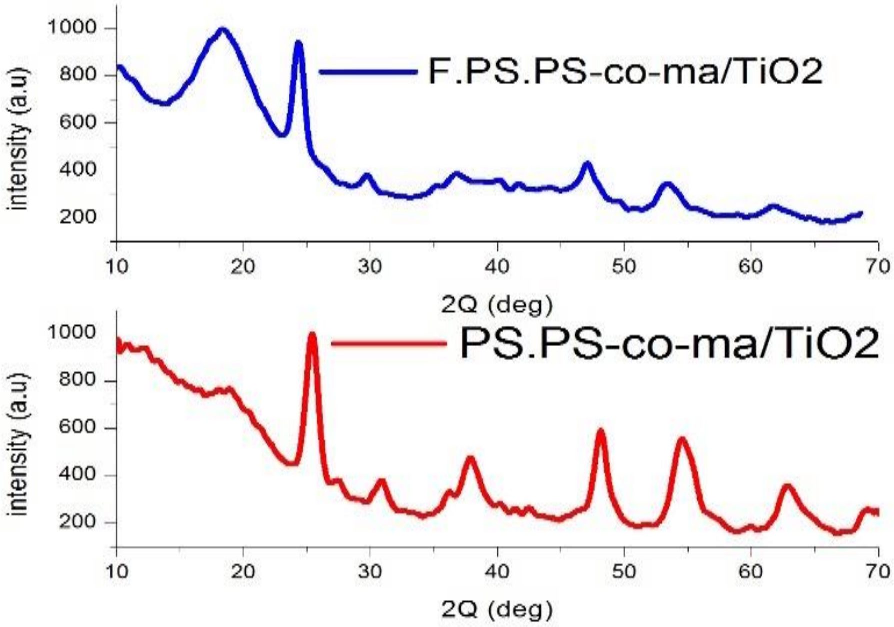


Figure 16 XRD pattern of PS/PS-co-ma/TiO2 composite

5.1.3 PS/PS-co-ma/Nb_2O_5 composite membrane.

The crystallinity of Nb_2O_5 composite membrane were studied through XRD. It is shown in the pattern in figure 12 that along with Polystyrene peaks there are intensity peaks of Nb_2O_5 Nano particles. The intensity peaks of simple Nb_2O_5 are at 2θ = 22.6˚ (0 0 1), 28.3 ˚ (1 8 0) , 28.9 ˚ (2 0 0) and 36.6 ˚ (1 8 1) while that of functionalized PS/PS-co-ma/ Nb_2O_5 has peaks at 2θ = 23.3˚ (0 0 1), 29.0 ˚ (2 0 0) , 29.6 ˚ (2 2 0) and 37.2˚ (2 1 1). The slight shift in peaks is due to functionalization. The obvious difference in peaks is due to effect of sulfonate group. In case of Functionalized composite hybrid membrane, the intensity of peaks decrees as compared to simple composite hybrid membrane. The decrease in intensities is due to decrease in crystallinity. Thus, functionalization decreases the crystallinity of composite membrane [2]. The introduction of SO3H groups into the Polystyrene alters the chain conformation and packing, and thus causes loss of crystallinity [2]. The composite membrane peaks were like the PDF card # 71-0336.

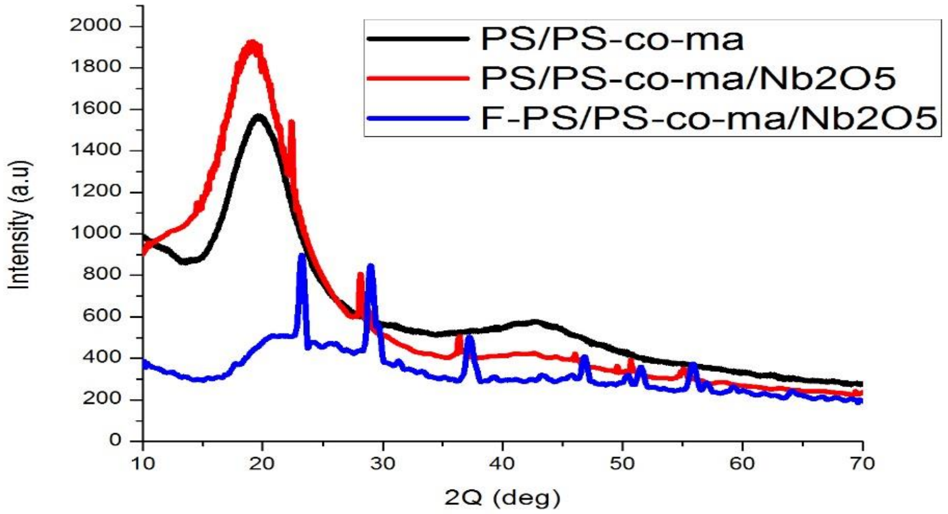


Figure 17 XRD pattern of Polystyrene and Nb2o5 composite

5.2 Morphological studies (SEM)

Morphology of the prepared blend and composite membrane has been studied via Scanning Electron Microscopy(SEM).

5.2.1 SEM analysis of PS/PS-co-ma, PS/PS-co-ma/TiO2, Functionalized PS/PS-co-ma/TiO2

Both pure and hybrid membranes were examined for morphological analysis via SEM. Morphology of Pure PS/PS-co-ma, Titania doped PS/PS-co-ma and Titania doped functionalized PS/PS-co-ma has been shown in fig (13) and (14), (15) respectively. Fine looking morphology was observed for pure PS/PS-co-ma membrane which shows smooth surface with almost no pores, thus non-favorable for proton exchange purpose. On the other hand, irregular morphology of simple

PS/PS-co-ma/TiO2 shows good porosity, thus favorable for proton exchange throughout the electrolyte membrane between the electrodes. While the functionalized PS/PS-co-ma membrane irregular morphology has been distorted and with non-uniform distribution shows nanoparticles junks and fever holes.

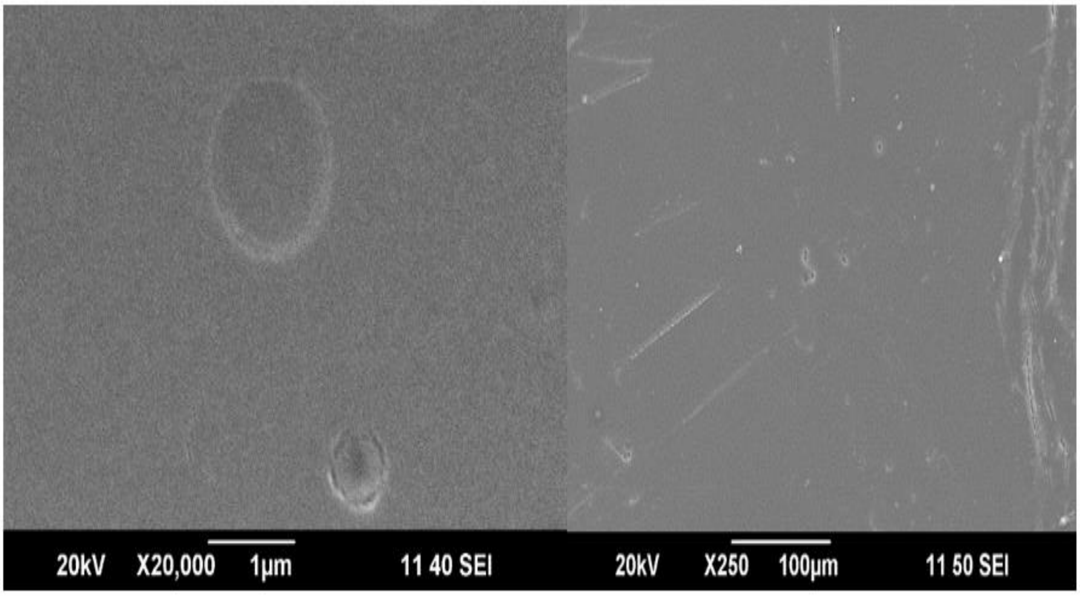


Figure 18 PS/PS-Co-Ma membrane

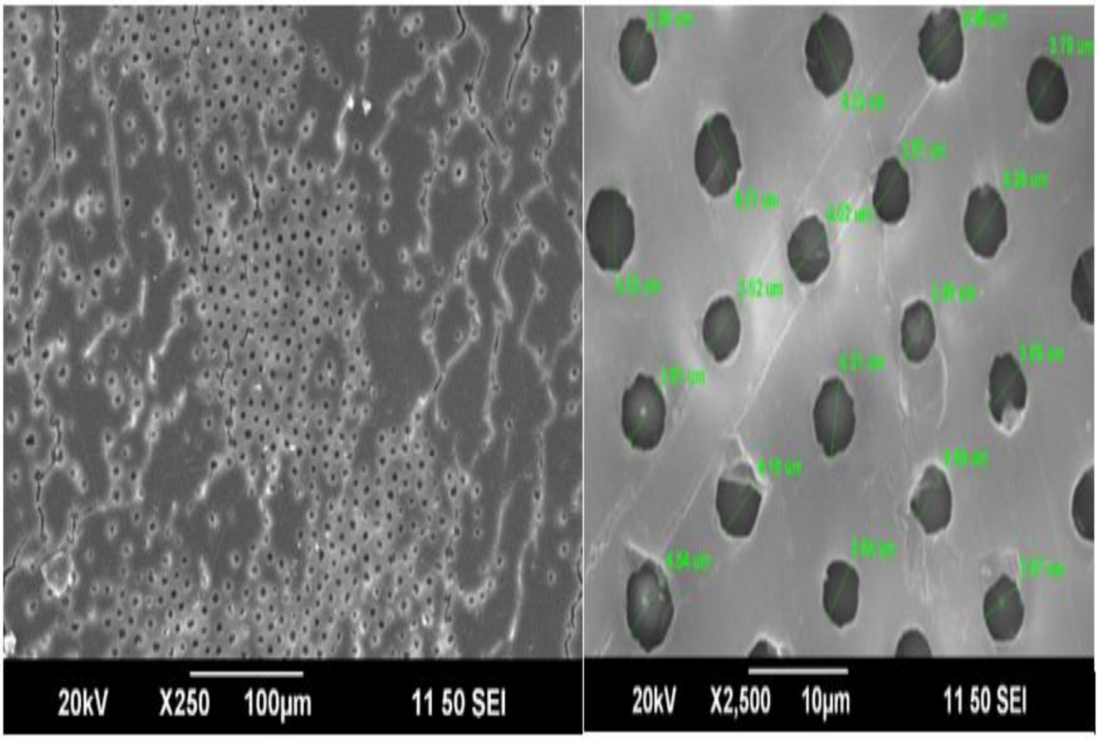


Figure 19 PS/PS-co-ma/TiO2 np hybrid membrane

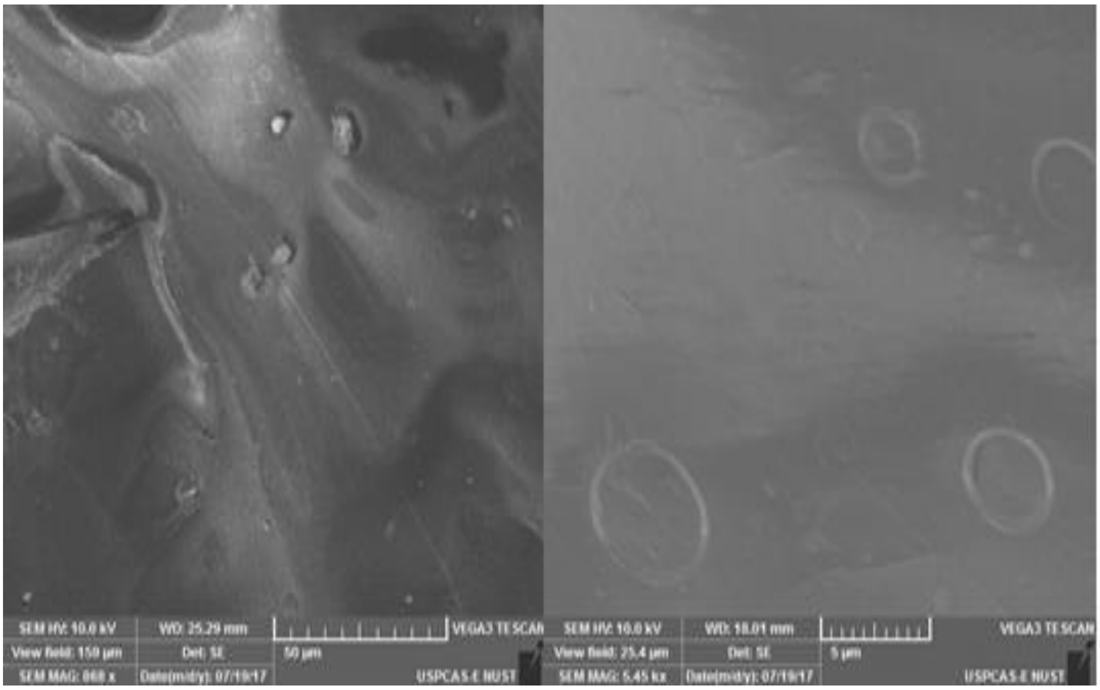


Figure 20 Functionalized PS/PS-co-ma/TiO2 np hybrid Membrane

5.2.2 SEM analysis of PS/PS-co-ma/Nb2O5, Functionalized PS/PS-co-ma/Nb2O5.

The morphology of the functionalized nonfunctionalized Nb2O5 impregnated membrane has been shown in the figure (16), (17) respectively. Which shows irregular morphology. It can be studied that niobium pentoxide nanoparticles have been impregnated successfully. The porous surface is highly visible in simple hybrid composite membrane while in functionalized membrane with similar resolution the pores are less visible and with particles junks protuberant visibility.

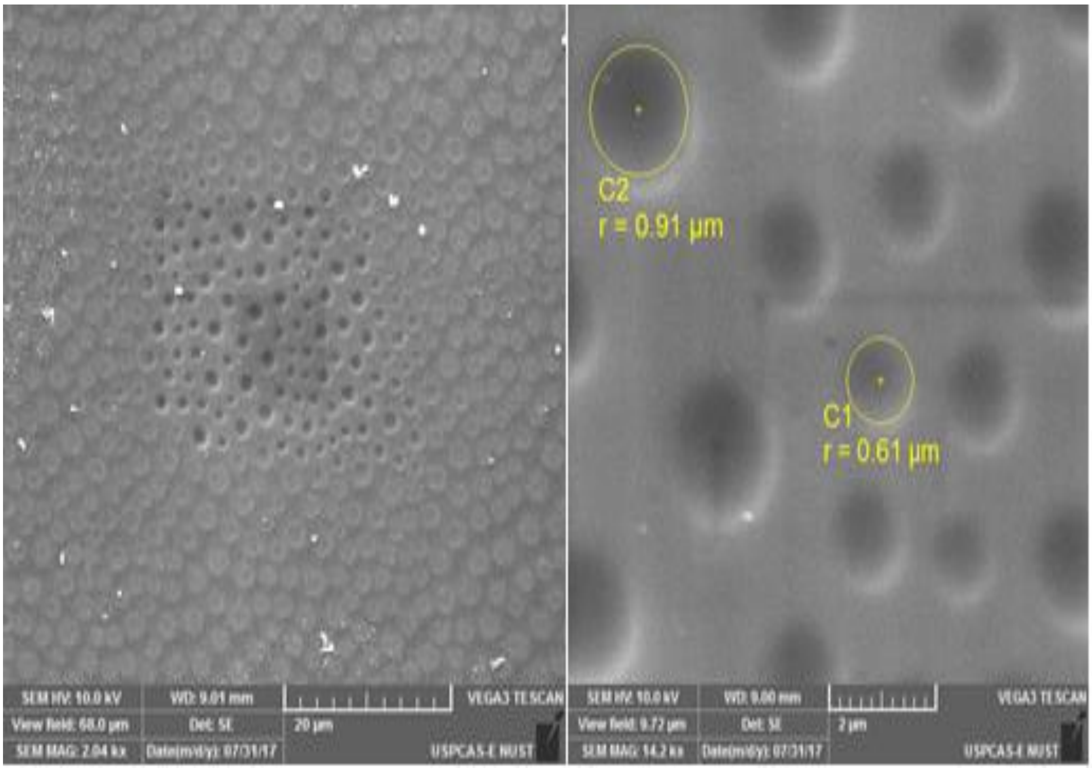


Figure 21 PS/PS-co-ma/Nb2O5 np hybrid membrane

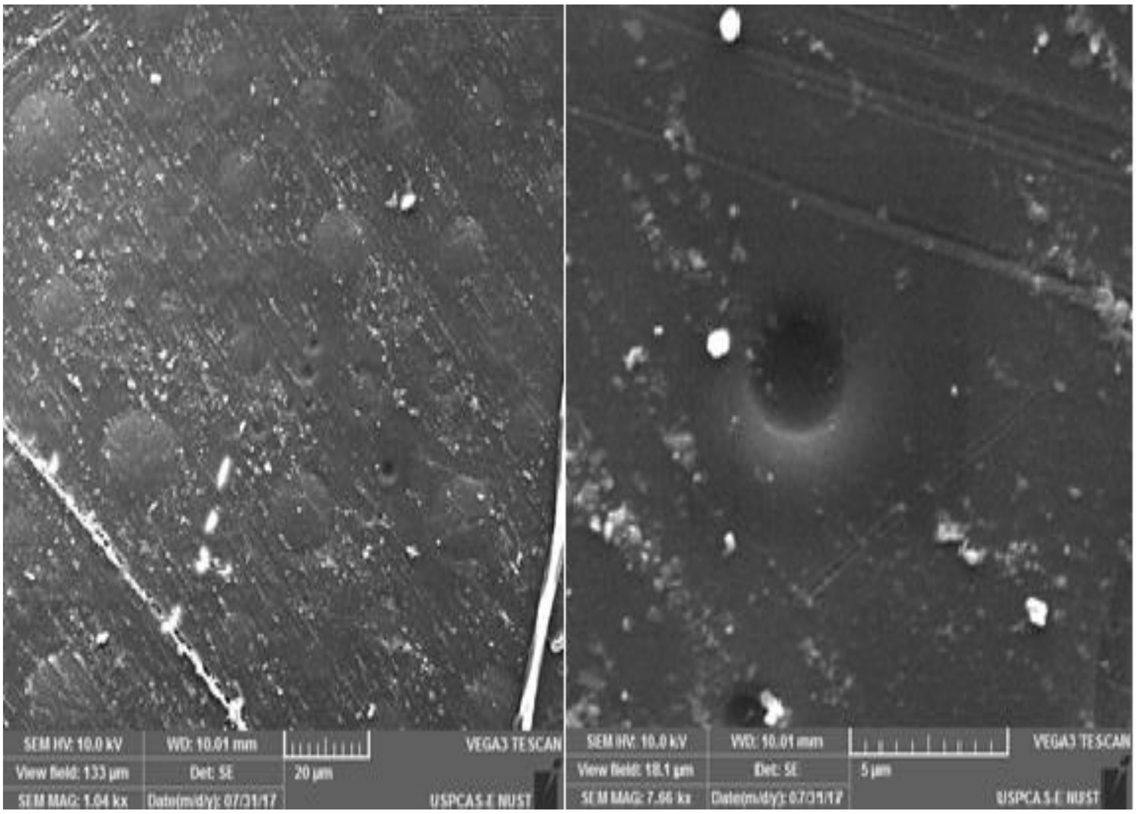


Figure 22 Functionalized PS/PS-co-ma/Nb2O5 np hybrid membrane

From SEM analysis the non-uniform distribution of nanoparticles can be observed, which increase with SO3H group functionalization.

5.3 Thermogravimetric analysis

The thermal stability of the prepared nanocomposites membrane samples was determined using TGA, which is an important factor to stability of MEA. Weight changes of the prepared nanocomposite sample with constant increase of temperature was recorded using TGA. At high temperature the sample was reduced due to formation of volatile substances. Samples were heated from room temperature to 500°C with constant increase of 10°C in a minute and nitrogen environment.

5.3.1 TGA of TiO2 nanocomposite PS/PS-Co-Ma

The thermal stability of TiO2 nanocomposite Polystyrene blend membrane was found using TGA. The thermogram is shown in fig 18. The thermogram shows impregnated Titania membrane in comparison to simple polystyrene blend membrane, which clearly shows the enhanced thermal stability of Titania composite membrane over simple polystyrene blend membrane. The thermos gram shows three stages of degradation, first (<100°C) is due to loss of water, second stage (180-

250^{o}C) is degradation of SO_3H and the last stage (>400) is degradation of main polymer chain.

It can be seen from the thermograms that polystyrene simple blend membrane has a maximum rate of decomposition at 375 ^{0}C. while Titania impregnation has increased membrane thermal stability. Simple Titania impregnated polystyrene blend membrane start its decomposition at 410^{0}C while functionalized Polystyrene blend impregnated with Titania nanoparticles has a bit decreased maximum decomposition i.e. at 400^{0}C. different decomposition temperature has been shown in table 1.

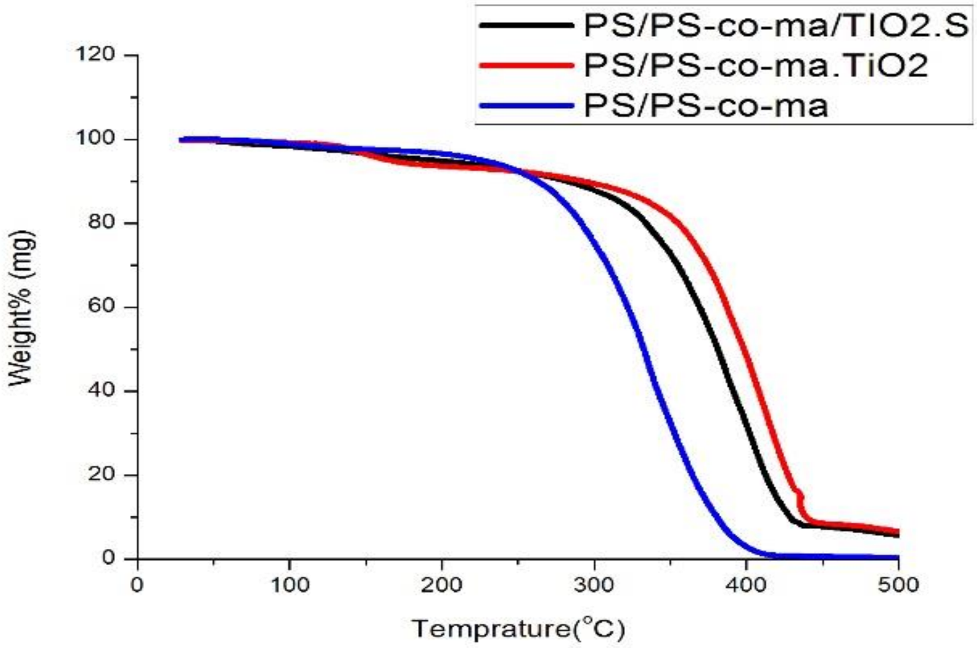


Figure 23 TGA pattern PS blend TiO2 np hybrid membrane

Table 2 TGA PS blend TiO2 np hybrid membrane

Sample	T_{10}	$T_{1/2}$	T_{max}
PS/PS-co-ma	260	332	338
PS/PS-co-ma/TiO2	294	395	410
Functionalized PS/PS-co-ma/TiO2.	283	382	400

5.3.2 TGA of Nb2O5 nanocomposite PS/PS-Co-Ma

The thermal stability of Nb_2O_5 nanocomposite Polystyrene blend membrane was found using TGA. The thermogram is shown in fig 19. The thermogram show impregnated Nb_2O_5 membrane in comparison to simple polystyrene blend membrane, which clearly shows the thermal stability of Nb_2O_5 impregnated blend over simple polystyrene blend membrane. It can be seen from the thermograms that polystyrene simple blend membrane has maximum decomposition at 375 ^{0}C. while Nb_2O_5 impregnation has increased its thermal stability. Simple Nb_2O_5 impregnated polystyrene blend membrane start its decomposition at 418^{0}C while functionalized Polystyrene blend impregnated with Nb_2O_5 nanoparticles and has a bit decreased maximum decomposition i.e. at 385^{0}C. The strange behaviour of Functionalized composite hybrid membrane Is due to SO3H functional group, which has led to increase non uniform distribution of fillers as well as decrease in thermal stbailty of composite membrane[3]. The different decomposition temperatures have been shown in table 2.

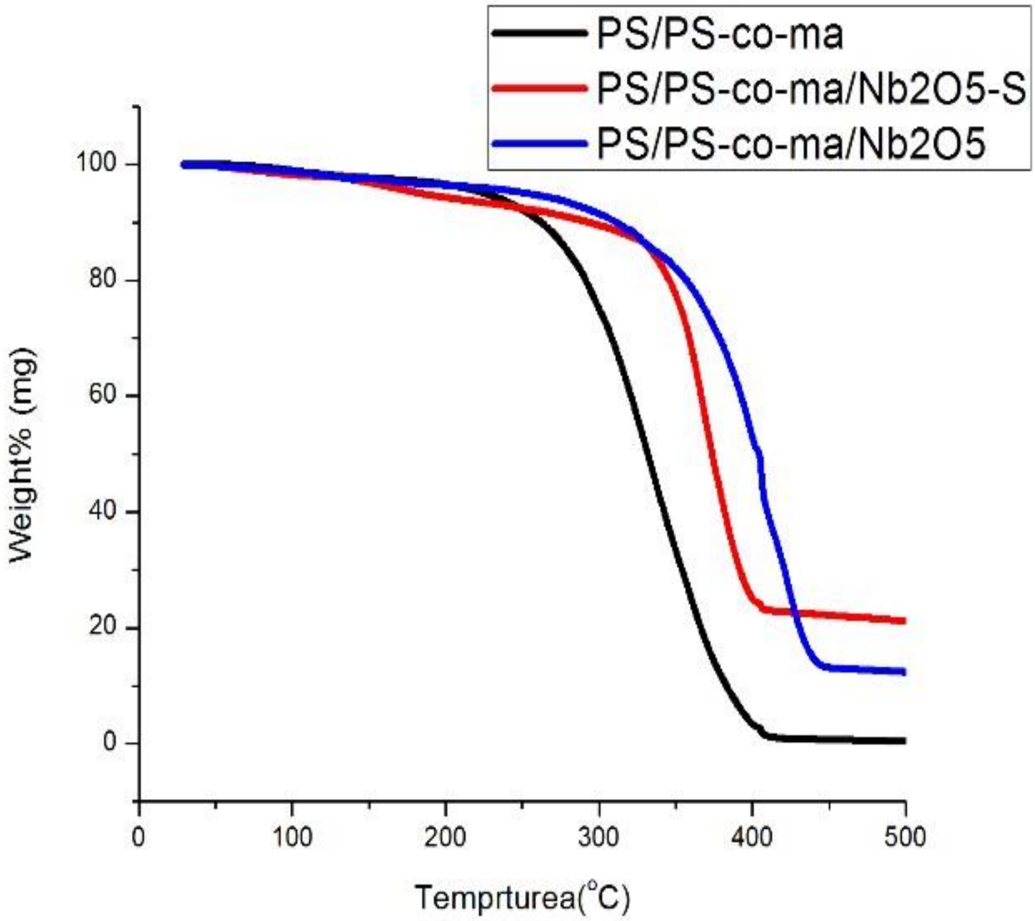


Figure 24 TGA PS blend Nb2O5 np hybrid membrane

Table 3 PS blend Nb2O5 np hybrid membrane

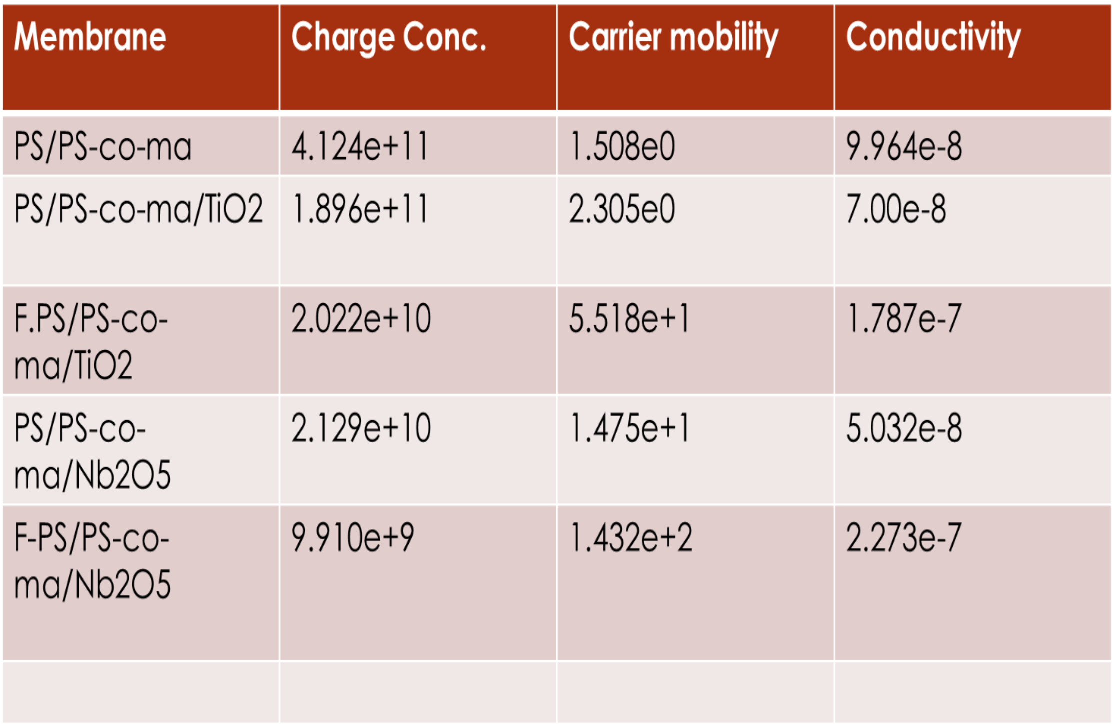
Sample	T_{10}	$T_{1/2}$	T_{max}
PS/PS-co-ma	260	332	338
PS/PS-co-ma/Nb_2O_5	380	405	418
Functionalized PS/PS-co-ma/ Nb_2O_5.	293	373	385

The difference in residue shows the non-uniform distribution of Nano particles. From both pattern it can be concluded that both Titania and Nb_2O_5 nanoparticles impregnation has increased polymer membrane thermal stability.

5.4 Charge mobility via Hall effect.

Since hall effect detect hall voltage with any charge transfer, irrespective of electron or proton. Therefore, hall effect can be utilized to detect the effect of sulfonation with respect to carrier mobility, concentration and conductivity [4]. Known All prepared membrane with known width were put to hall effect process one after another. Due to higher insulation properties of membranes only 20nA maximum current is applied to detect the hall effect phenomenon. The results are shred through table below.

Table 4 SO3H functionalization effect on carrier mobility



Membrane	Charge Conc.	Carrier mobility	Conductivity
PS/PS-co-ma	4.124e+11	1.508e0	9.964e-8
PS/PS-co-ma/TiO2	1.896e+11	2.305e0	7.00e-8
F.PS/PS-co-ma/TiO2	2.022e+10	5.518e+1	1.787e-7
PS/PS-co-ma/Nb2O5	2.129e+10	1.475e+1	5.032e-8
F-PS/PS-co-ma/Nb2O5	9.910e+9	1.432e+2	2.273e-7

From table with the addition of SO3H functionalization the mobility of charge carrier increases by 10fold. Hence SO3H functionalization increased mobility cause to higher proton mobility through membranes.

Summary

Different characterizations were carried out for composite hybrid membrane analysis. The impregnation of polymer with Nano particle has certainly increased its thermal stability and porosity of composite membrane. The functionalization with SO3H group has resulted both decrease in crystallinity and thermal stability of composite membrane.

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Conclusions

Five novel composite membranes of polystyrene and poly (styrene-co-maleic anhydride) blend were prepared using nanoparticles of Titania and Niobium pentoxides as fillers. TiO_2 nanoparticles were also synthesized in lab. It can be concluded after characterizations that:

- Addition of Nano particles has increased the number of pores of size 2um to 3.um in the membrane.
- Nanoparticles have improved thermal stability of composite membranes over simple membrane by approximately 70°C.
- SO3H functionalization has negative impact on thermal stability and crystallinity of composite membrane however, SO3H functionalization has increased charge mobility by 10 times.
- TiO2 and Nb2O5 Nano particles can be used successfully as filler for synthesis of Organic-inorganic composite membrane for HT-PEMFC.
- TiO2 nanoparticles are better choice for nanoparticles than Nb2O5 because ,it can be synthesis easily in lab with different procedures, can be mixed easily with polymer membrane, give more thermal stability and porosity.

Recommendation

Several studies can be conducted in continuation to this study, however, there are certain studies that would validate/invalidate the conclusions of the study. This work demands that the findings presented here must be critically explored and meaningfully employed to help commercialize the economical membrane synthesis. To carry this work further, we recommend

To study the behavior of synthesized membrane in a model fuel cell and validate its working there.

The incorporation of Nb2O5, TiO2 Nanoparticles should be employed in promising hydrocarbon polymers such as PBI, PEEK and Poly imidine base simple or blend membranes and their corresponding results should be compared accordingly.

Annexure I

Inorganic-Organic Nano Composite Hybrid Membrane Based on Titania and Polystyrene for High Temperature PEM Fuel Cell

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[2]Abstract

Low temperature PEM Fuel cells have limitations such as CO catalyst poisoning effect, Water and heat management, etc. These can be reduced by using high temperature PEM fuel cell (>90˚C). Therefore, it is need of hour that high temperature PEMFC must be focused. Inorganic-Organic Nano composite hybrid materials are among the top contenders to be utilized as membranes for high temperature PEMFCs. In this research, we have synthesized titania nanoparticles using TTIP precursor. For hybrid membrane, we have used polystyrene Mw 35000 and Poly (styrene-co-maleic anhydride), cumene terminated as polymers and Titanium dioxide Nano particles as inorganic filler. Wet chemistry route is used for Nano particle and hybrid membrane preparation. Synthesized membranes were characterized by using X-ray Diffraction and Scanning Electron Microscopy. The results showed that Titania based impregnated Polystyrene/PS-co-ma blend membranes exhibited good characteristics for its utilization as membrane for HTPEMFCs.

Keywords: *HT-PEMFC; Hybrid membrane; Polystyrene; Nano Particles;*

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1. Introduction

Proton exchange membrane / polymer electrolyte membrane Fuel cell (PEMFC) is the promising fuel cell, which has application in portable devices, transport vehicles as well as in stationary power generations[1]. Power is generated in PEMFC through an electrochemical reaction in which oxygen reacts with hydrogen.

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[2] The paper was presented in EESD 2016 conference held in Mehran engineering university of technology.

At anode: $2H_2 \rightarrow 4H^+ + 4e^-$

At cathode: $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

Overall reaction: $2H_2 + O_2 \rightarrow 2H_2O$

The transfer of electron in this reaction is given an alternate path and which is collected as source of power while the H^+ is passed through electrolyte membrane from anode to cathode. The membrane plays an important role, that it may let pass maximum of protons through itself while blocking the passage of electron.

Currently Nafion is used as PEMFC membrane which has high durability and operate well at temp below 90˚C, but it has some disadvantages like water and heat management, CO catalyst poisoning effect, high cost of membrane as well as Platinum Pt catalyst [2-4]

PEMFCs which can operate between 100˚C to 200˚C are known as HT-PEMFCs. HT-PEMFC can overcome above mentioned issues and it can also utilize the waste heat for cogeneration process[3]. Advantages of HT-PEMFC[2] includes fast reaction fast reaction kinetics, where Oxygen Reduction Reaction (ORR) is slow in LT-PEMFC which results in power losses due to the over potential at cathode, but in HT-PEMFC ORR reaction rate is high which results in improved efficiency.

Carbon monoxide CO tolerance issue is a serious issue in operation of LT-PEMFC. LT-PEMFC uses Platinum catalyst, which has strong affinity for CO, thus a little amount CO can cause degradation. The CO poisoning effect decreases with increase in temp, thus HT-PEMFC can overcome this effect. Heat management is another issue with LT-PEMFC operation, as half of energy produced is heat, which require its removal continuously because such heat above operating temp causes degradation of cell and require special costly management for its removal. HT-PEMFC can overcome these issues. the increased temperature can be controlled by existing Colling systems available in vehicles or in cogeneration as well as on-board reforming facility. Water management also remain a striking issue when operating at low temp, as both gaseous as well as liquid phase of water is present at low temperature. which cause it difficult to maintain the membrane humidification level maintained for efficient process. At high temperature operation only gaseous phase of water is present thus simplifying water management.

At high temperature the simpler heat and water management along with more CO tolerance and fast reaction kinetics made possible a simpler design of flow field and thus decreasing the overall cost of cell.

Currently Research is carried to develop electrolyte membrane for HT-PEMFCs which can operate above 100˚C near 120˚C as in accordance with US department of Energy guidelines for automotive applications[1]. Different polymers as well as organic-inorganic composite membranes had been developed and studied as alternate membrane for HT-PEMFC electrolyte applications[2,5].

Research work has also been carried on polystyrene and titania interaction like polystyrene encapsulation of TiO_2 nanoparticles[6] and Titania impregnation into polystyrene resulted in better mechanical properties[7],also its interaction for photo catalyst environment resulted better[8]. In this research we have synthesized cost effective novel inorganic-organic composite membrane in which polystyrene and Poly (styrene-co-maleic anhydride), cumene terminated has been selected as polymers while titania TiO2 nano particles as inorganic fillers. For structural characterization XRD has been successfully performed, morphological study of membrane has also been performed using SEM.

2. Materials and Methods

2.1. Materials

The materials used in this experiment are Polystyrene Mw 35000 and Poly (styrene-co-maleic anhydride), cumene terminated M_n 19000 from Sigma Aldrich, THF (Tetra hydro Furan) from Fisher Scientific, TTIP Titanium (IV) Isopropoxide from Sigma Aldrich.

2.2. Methodology

Wet chemistry route has been used for TiO_2 nano particles as well as membranes.

For synthesis of TiO_2 nano particles 5ml of TTIP was slowly added into solution of 75ml ETOH, 300ml deionized water and 1ml HCL. Kept the solution on slow stirring for 48 hours at room temperature. The precipitated TiO2 was filtered and dried and after grinding it the powder were calcinated at 400˚C for 3 hours in furnace.

For membrane preparation 1.5gram Polystyrene (PS) and 0.5gram PS-co-ma 10% solutions were prepared respectively in THF. After stirring for 3 hours, both solutions were mixed and kept further for 3hour at magnetic stirring. Prepared PS/PS-co-ma solution was then poured into glass petri dish and let the solvent to evaporate at room temperature. PS/PS-co-ma blend membrane was obtained by placing the petri dish in distilled water.

For PS/PS-co-ma/TiO2 membrane preparation, 10% solution of Titania nano particles in THF is kept for 1-hour sonication. Mix titania solution with PS/PS-co-ma solution prepared earlier and keep it for two hours at magnetic stirring. Prepared PS/PS-co-ma solution was then poured into glass petri dish and let the THF to evaporate. Smooth composite membrane was obtained after placing Petri dish in distilled water.

3. Results and Discussion

3.1. X-Ray diffraction (XRD) analysis

XRD studies were conducted to study the crystallinity of composite membrane. Fig.1(a). shows the pattern of TiO2 Nano particles Maximum Peak for pure Titania dioxide nano particles was observed at 2θ= 25.6˚ while others peaks were observed at 27˚, 37˚and 48˚. All peaks of titania nano particles were matched with PDF card # 75-

1537. The broader peaks of titania is due to smaller crystallite size. Pure titania shows the tetragonal structure and anatase form. Fig.1(b) shows the pattern of composite hybrid membrane. The maximum peak for composite membrane was observed at $2\theta = 20^\circ$ and at $2\theta = 24.66^\circ$. The composite hybrid membrane peak at angle 20˚ shows the polystyrene peak while that at 24.6˚ is of impregnated Titania nano particles. The composite membrane peaks were similar to the PDF card # 13-0843.

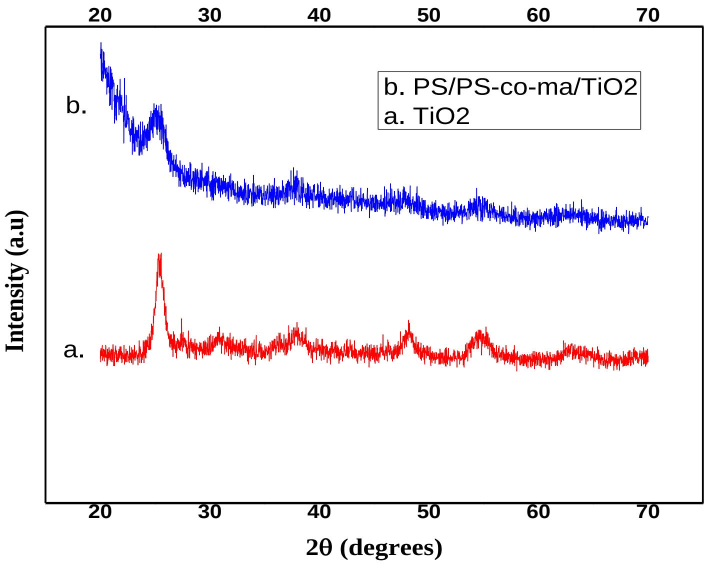

Figure 1. XRD pattern of TiO_2 Nanoparticle and PS/PS-co-ma/TiO_2 composite membrane

3.2. Surface Morphology

Both pure and hybrid membranes were examined for morphological analysis via SEM. Morphology of Pure PS/PS-co-ma and titania doped PS/PS-co-ma has been shown in fig 2(a) and 2(b) respectively. Fine looking morphology was observed for pure PS/PS-co-ma membrane which shows smooth surface with almost no pores, thus non favourable for proton exchange purpose. On the other hand, morphology of composite membrane surface reveals that hybrid membrane has irregular morphology and Titania nano particles has been successfully impregnated. The morphology at high resolution shows very fine and dense distribution of nano sized pores in surface of composite membrane. The average pore size found to be 3-4µm. This distribution of fine pores provides a good pathway for conduction of protons throughout the electrolyte membrane between the electrodes.

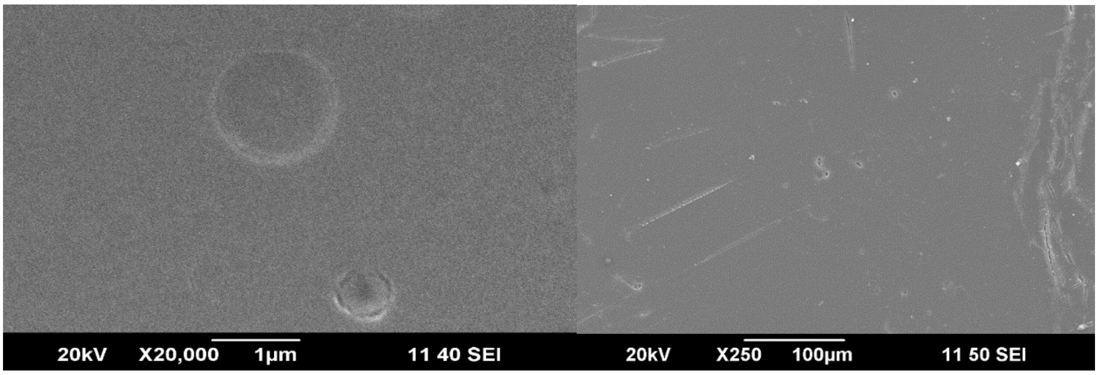

Figure 2(a): SEM morphology of PS/PS-co-ma blend membrane

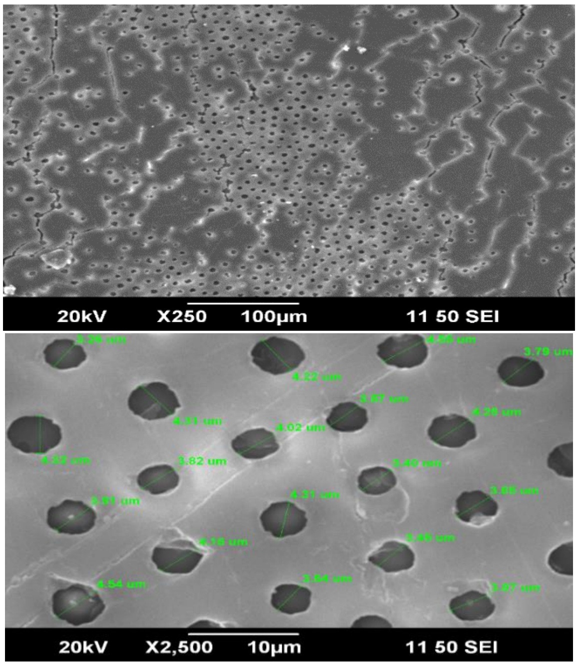

Figure 2(b) SEM morphology of PS/PS-co-ma/TiO_2 composite hybrid membrane

4. Conclusion

TiO_2 nano particles and Organic-Inorganic composite hybrid electrolyte membrane for PEM fuel cell were successfully synthesized. From XRD analysis it was found that impregnation of inorganic Titania nano particles to the polystyrene blend has been done successfully. From SEM analysis it was concluded that The impregnation of titania has resulted in very fine and increased number of holes on surface of composite membrane for H+ transfer. The average hole size was found to between 3-4µm.

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