AMPHIPHILIC NANOCOMPOSITE PROTON CONDUCTING MEMBRANE
(Vot Number 78098)

Halimaton Hamdan,
Zeolite and Nanostructured Materials Laboratory, Fakulti Sains, Universiti Teknologi Malaysia

Abstract

The major issues limiting the application of Proton Exchange Membrane Fuel Cell (PEMFC) based on perfluorinated membrane (Nafion) is its inefficiency to perform at high temperature and low humidity. The high cost of Nafion which is due to the complicated production process, the swelling problems, and the environmental hazards associated with its disposal are some of the major technology drawbacks. Through the incorporation of nano zeolite as the host material, the proton conductivity may be enhanced because of its moderate proton conductivity, mechanical stability and hydrophilic feature at high temperature. Organosulfonic acid groups (sulfonate $-SO^{-}_3$) are functionalized onto the surface of nano zeolite to further increase the proton conductivities of the bare zeolite, increase the cationic site density in the hydrophilic domains that enlarge hydrophilic domains in the membranes at high temperature. Well alignment of channel structures by the direct chemical bonding between the organosulfonic acid groups and zeolite eases proton and water transport, which consequently produce novel temperature tolerant proton conducting membrane for fuel cells. The synthesized functionalized nanocomposite has proton conductivity in the range of $1x10^{-3}$ S/cm with great properties in mechanical strength, hydrophilic features and chemical stability at high temperature operation. Proton conductivities of zeolites in the operating temperature range of 24-100 °C were enhanced significantly to higher values (about 1-3 orders of magnitude) by loading of sulfonic acids onto the surface of zeolite. Proton conductivities were correlated with the concentration of sulfonic acid groups and increased as follows: sulfonated polystyrene-zeolite composite > propylsulfonic acid functionalized ZSM-5 > phenylsulfonic acid functionalized ZSM-5 > zeolite ZSM-5 which is in line with the ion-exchange capacity and water uptake test.

1.0 Introduction

It is well known how local and global environment issues as well as the consumption and supply of energy are major challenges for the future of our planet. One of the most severe environmental issues today is the rising pollution level as a consequence of internal combustion of motor vehicles. Environmental concerns about global warming and the need to reduce carbon dioxide emission provides the stimulus to seek ways of improving energy conversion efficiency. In recent years, proton exchange membrane fuel cells (PEMFC) have been identified as promising power sources for vehicular transportation and for other applications requiring clean, quiet, and portable power.

Proton Exchange Membrane Fuel Cell (PEMFC) is a viable alternative source of power for both mobile and stationary applications owing to their high-energy efficiency, zero emission and environmental friendly nature. Conventional PEMFC typically operates with Nafion. However, the high cost of Nafion, CO poisoning at the anode and environmental hazards associated with its dispose have induced the development of new membranes and these include organic/inorganic hybrid membranes by using silica as support material. Although hydrophilic, silica particles are poor proton conductor. Nano zeolites are potential candidates to be used as proton conducting membrane instead of silica due to their significant moderate proton conductivity, excellent water retention at high temperatures and molecular sieving capabilities. By considering these properties, functionalized nanocomposite is developed as temperature tolerant proton conducting membrane.

Therefore the objectives of the project are:

(1) To synthesize and ion-exchange mono-dispersed, nano and micro-crystals zeolite

(2) To prepare polymer-zeolite nano-composite membranes

(3) To test proton conductivity and water absorption capacity of polymer-zeolite nano-composite membrane at various temperatures

2.0 Background

Environmental concerns about global warming and the need to reduce carbon dioxide emission provides the stimulus to seek ways of improving energy conversion efficiency. In recent years, proton exchange membrane fuel cells (PEMFC) have been identified as promising power sources for vehicular transportation and for other applications requiring clean, quiet, and portable power [1-2]. Hydrogen-powered fuel cells in general have a high power density and are relatively efficient in their conversion of chemical energy to electrical energy which is more than 40-50%; that is higher than a coal fired power station or any internal combustion engine [3]. Exhaust from hydrogen-powered fuel cells is free of environmentally undesirable gases such as nitrogen oxides, carbon monoxide and residual hydrocarbons that are commonly produced by internal combustion engines. Carbon dioxide, a greenhouse gas, is also absent from the exhaust of hydrogen powered fuel cells. Thus, transportation uses, especially fuel cell electric vehicles (FCEV), are attractive and effective because of its clean exhaust emissions and its high-energy efficiencies. These features also make PEMFCs the most promising and attractive candidate for a wide variety of power applications ranging from portable/ micro power and transportation to large scale stationary power systems for buildings and distributed generation [2].

Despite the promising achievements and prospects of PEMFCs, there are three main challenges that are common including a stable supply of high-purity hydrogen, cost reduction of the system and various technological problems associated with the low performances at high temperature (over 100 °C) and low humidity [4]. Since proton conducting membranes are the key-components in PEMFCs, therefore greater emphasis on research aimed at reducing the cost of proton conducting membranes and overcoming some of the technical problems remaining in a PEMFC system (water management, thermal management and control of CO poisoning of the platinum anode electro catalysts) have been carried out. Conventional PEMFCs typically operate with Nafion membranes. Nafion is the trade mark (produced by DuPont) of a perfluorinated material composed of carbon-fluoride backbone chains and perfluoro side chains with sulfonic acid ion exchange groups. The favourable properties of this polymer lie in the combination of the high hydrophobicity of the perfluoronated polymer backbone and the high hydrophilicity of the sulfonic acid branch [5]. It offers quite good performance below 90°C and possess near ideal physical characteristics for a PEMFC, high ionic conductivity, good thermal stability, adequate mechanical strength and excellent chemical stability [6]. Over the last 40 years, Nafion properties have become a benchmark for comparison with other materials.

The major issues limiting the introduction of PEMFC based on Nafion is its inefficiency to perform at high temperature and low humidity. The poisoning of platinum based anode catalysts by the trace of CO inevitably present in the reformed fuel become apparent when operation of PEMFC is at low temperature. Moreover, the high cost of Nafion which is due to the complicated production process, the swelling problems, and the environmental hazards associated with the disposal of perfluorinated membrane (Nafion) are some of the major technology drawbacks encountered commonly in the application of PEMFC. In addition, Nafion shows considerable methanol permeability when methanol is used as the liquid fuel to generate hydrogen in fuel cells. High methanol crossover not only reduces fuel utilization efficiency, but also decreases cathode performance. Running a cell at temperatures higher than 100 °C is interesting in terms of yield and also for fuel cells because the catalyst poisoning by CO is much less important at high temperatures. Perfluorinated membranes cannot be applied in this temperature range because of swelling and lost of mechanical properties [8]. During operation of a PEMFC, electro-osmotic drag causes dehydration of the membrane of the anode side and consequently a dramatic decrease of the conductivity. Moreover, any change in the water content will result in swelling and shrinkage of membranes, which can lead to the deterioration of the membrane-catalyst interface or even membrane breakage. Careful management of the water balance is therefore one of the key issues for the system design and operation with Nafion [9].

Increasing the temperature above 100 °C is a difficult proposition for PEMFC because of the reliance of Nafion membrane on water for proton conduction. As temperatures increase, the evaporation of water from the Nafion membrane leads to a dramatic drop in conductivity [7]. Environmental considerations have also to be taken into account to use protonated rather than fluorinated polymers especially for the high amounts of membrane potentially necessary for the car application. For these reasons, a material which is cheaper and more environmentally friendly with an operating temperature range up to 100 °C and enhanced humidification conditions would be beneficial. Currently, development of polymer membranes as alternative to Nafion has been an active area in the field. A great number of polymer materials have been prepared and functionalized as membrane electrolytes for PEMFC [9]. Recent developments in the field include new ionomers based on different sulfonated aromatic polymers such as sulfonated polystyrene [10], sulfonated poly(ether ether ketone) [11], sulfonated polyimide [12], sulfonated polybenzimidazole (PBI) [13], and sulfonated poly(arylene ether sulfone) [14] for medium temperature operating PEMFC. Subsequently, considerable efforts have been carried out to modify polymer membrane, aiming at high operating temperatures and overcome the humidification constraints in PEMFC. Accordingly, hydrocarbon polymers based on SiO_2-PEO (polyethylene oxide) [15, 16], SiO_2–PEG (polyethelene glycol) [17], SiO2–PVA (polyvinyl alchohol) [18], SiO_2-PBI [19] and SiO_2-PPO (polypropylene oxide) [20] have been widely used as a host matrix for the preparation of inorganic/organic composites. As a result of the water adsorption on the oxide surface, the back-diffusion of the cathode-produced water is enhanced and the water electro-osmotic drag from anode to cathode is reduced. Despite of improved water retention, the cell performance of these silica-containing membranes is still inferior to the bare Nafion operated at 80°C. Furthermore, the cell performance of organic-inorganic membranes was too low to compete with Nafion membrane.

Although hydrophilic, silica particles are not proton conductors, inclusion of the hygroscopic silica particles in composite solid electrolytes is primarily single functional, i.e. for water retention. Clearly, bi-functional particles, being both hydrophilic and proton conducting are preferred. The most suitable material with the preferred properties is zeolite. Zeolite is crystalline porous aluminium silicates having uniform pores and cavities. Zeolite is a moderate proton conductor and also hydrophilic which retains more water for efficient proton conduction in the membrane. Because of zeolites microporosity (< 10 Å), zeolites can maintain hydration at very low relative humidity. This feature may be especially helpful for high temperature applications [21]. In addition, molecular sieving capabilities and high surface area of zeolite may be effective at reducing methanol permeability in the case of direct methanol fuel cell. Therefore, zeolite is expected to be a much better material than silica nano particles for the application considered here. Initial attempts to apply zeolite in the preparation of proton conducting membranes include zeolite Zeolon 100 H [22], natural zeolite such a chabazite and clinoptilolite [23], Zeolite Y [24, 25] and mesoporous molecular sieves (MCM-41). The new solid proton conductors were developed based on zeolite loading with heteropolyacids or zeolite-polymer composites. However, the performances of most of the zeolite composite membranes were inferior to that of Nafion membrane with regard to both ion conductivity and transport selectivity. These results were due to the properties of the chosen zeolites, which were proven inadequate for the purpose. The zeolites employed here were mostly in micro sizes which are not size adjustable to match polymer-network dimensions for the development of zeolite polymer nanocomposite membranes. Moreover, during polymer membranes casting and treatment processes, the membranes materials experience strong acidic conditions. These acidic conditions could be detrimental to the survival of these plain zeolites, which generally begins to lose crystallinity at conditions of pH < 4. Furthermore, these efforts for using heteropolyacids as a solid electrolyte suffer from some drawbacks due to their high solubility in water and alcohols. As a result, the problem of high leaching of HPA was found detrimental to long-term use of the composite membranes. Consequently, one of the most promising routes to high temperature performance proton conducting materials is the use of nano zeolite in the preparation of proton conducting membranes. Instead of micro zeolite, nano zeolite with unique physical and chemical properties is a better candidate to be employed in the application considered here.

Nano zeolite is zeolite with discrete and uniform crystals in the dimensions of 100 nm. In general, nano zeolite has higher external surface areas, shorter channels and reduced diffusion path lengths relative to conventional micro zeolite which make them promising proton conducting materials. Brett A. Holmberg *et al.* [26] first reported the proton conductivity analysis of sulfonic acid functionalized nano zeolite BEA. It was shown that sulfonic acid functionalized zeolite BEA nanocrystals showed proton conductivity in the range of 1.2×10^{-3} - 1.2×10^{-2} S/cm at room temperature. In spite of the leaching problem (desulfonation) which might exist at high temperature operation, the proton conductivity data presented here for the acid treated functionalized nano zeolites are promising initial findings.

Great efforts have been and are being made to develop proton conducting membrane for operation at temperatures above 100 °C for fuel cells. It has been demonstrated that the incorporation of hygroscopic and proton conducting zeolite significantly improved the high-temperature performance of proton conducting membranes in many studies. So far, these efforts have not produced solid electrolyte that satisfies all requirements of proton conducting membrane.

Therefore, in this study, three different kinds of organosulfonic acid functionalized nano zeolite ZSM-5, namely propylsulfonic acid and phenylsulfonic acid functionalized nano zeolite ZSM-5 as well as sulfonated polystyrene-nano zeolite ZSM-5 composites are prepared as temperature tolerant proton conducting membranes in fuel cell. Through the incorporation of nano zeolite ZSM-5 as the host material, the proton conductivity can be enhanced at high temperature because of its moderate proton conductivity, mechanical stability and hydrophilic feature at high temperature. Different types of organosulfonic acid groups are functionalized onto the surface of nano zeolite ZSM-5 with the intention to further increase the proton conductivities of the bare zeolite by the introduced charge units (sulfonate $–SO^{-3}$).

2.0 Hypothesis

Novel zeolite materials based polymer composites as solid electrolyte for proton exchange membrane (PEM) is studied to allow a PEM fuel cell to operate at moderate temperature (100-150°C) with comparable or superior performance to that of Silica-Nafion PEM fuel cell operated at 80°C. In this project, amphiphilic zeolite-alkylsulfonic acid nanocomposite is proposed as the temperature tolerant proton conducting membrane as shown in Fig.1.

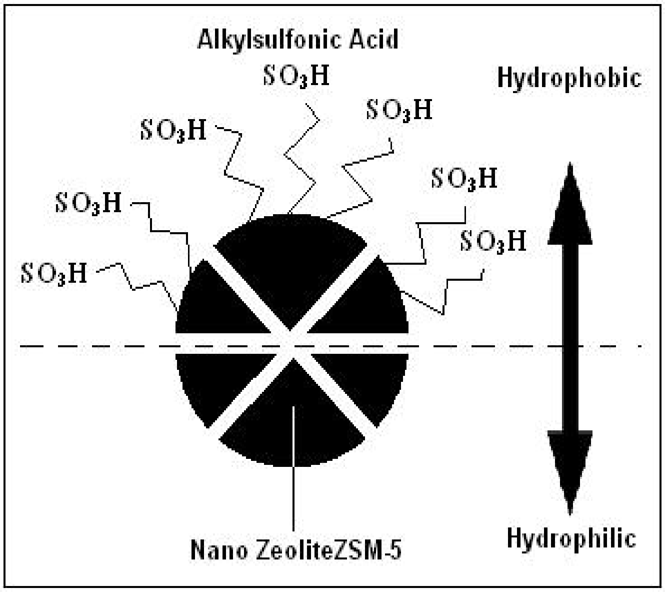


Fig. 1: Molecular level design for amphiphilic zeolite-alkylsulfonic acid nanocomposite.

The surface of the nano-sized zeolite ZSM-5 is partially made hydrophobic by alkylsilylation of the surface with (3-mercaptopropyl) trimethoxysilane (MPTS) as organosulfonic acid precursor followed by the oxidation with [4] as shown in Fig 2. It is notably that the alkylsilane groups are attached on the external surfaces of ZSM-5 since the estimated molecular size of MPTS is larger than the pore apertures of ZSM-5. Thus, the internal pores of the partially modified ZSM-5 surfaces remain hydrophilic.

The concept underlying in this idea is that, the hydrophilic portion will retain water molecules at high temperature which is vital of being the transport medium of proton from anode to cathode, whereas the zeolite surface acid sites and the immobilized bronsted sulfonic acid groups attached on the alkyl chain will be correspond to the proton conductivity of the hybrid material. In addition, hydrophobic alkyl chain will be useful to drive the product water out of the electrode, and thus prevent flooding and blocking of the pores in electrode or gas diffusion layer.

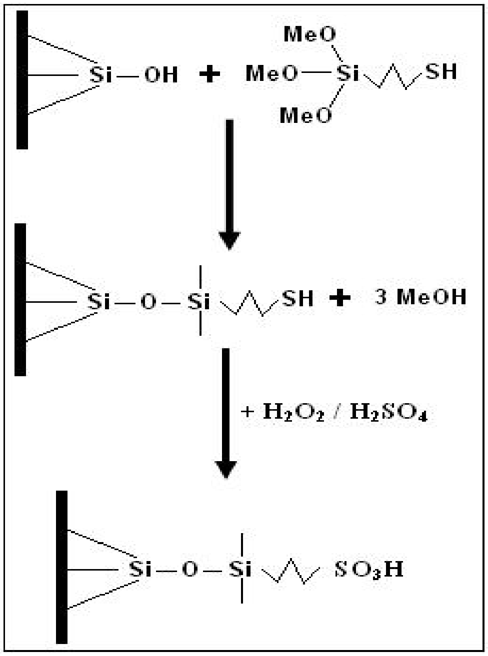


Fig. 2: Modification of zeolite with MPTS followed by oxidation with H_2O_2

Zeolite ZSM-5 is chosen for this study for several reasons.

1. Zeolite is usually synthesized as a high silica zeolite, and is known for its resilience in strong acid environments [5]
2. ZSM-5 is a hydrophilic zeolite which can help to retain more water by hydrogen bonding with its silanol groups.
3. The well-known high solid acidity of zeolite ZSM-5 could also be used to contribute to the overall proton conductivity of the hybrid material.

Nano ZSM-5 zeolite is chosen to be the support because nano particles will provide more external surface areas compared to micro-sized zeolite. Smaller sized zeolites particles are believed to be able to conduct protons more efficiently due to the higher level of interaction between the individual nano particle and their ability to pack closer together. This low void space packing could lead to more continuous proton conduction pathways through the sample and higher overall proton conductivity [6]. Proton conductivity is measured using the following Equation:

Conductivity, $\sigma = L/RA$ ………………………Equation (4)

Where, σ : membrane conductivity, L : thickness of the membrane, R : measured resistance on the membrane, A : cross-sectional area of the membrane perpendicular to current flow.

It is proposed that the designed membranes would possess a high concentration of sulfonic acid groups to increase the cationic site density in the hydrophilic domains; a high water content created by zeolites to enlarge hydrophilic domains in the membranes at high temperature; and well alignment of channel structures by the direct chemical bonding between the organosulfonic acid groups and zeolite to ease proton and water transport, which consequently produce novel temperature tolerant proton conducting membrane for fuel cells.

3.0 Proton Exchanged Membrane Fuel Cell (PEMFC)

A PEMFC consists of two electrodes and a solid polymer membrane, which acts as an electrolyte. The polymer electrolyte membrane is sandwiched between two platinum-porous electrodes such as carbon paper and mesh. Some single cell assemblies can be mechanically compressed across electrically conductive separators to fabricate electrochemical stacks. In general, PEMFC requires humidified gases, hydrogen and oxygen (on air) as a fuel for their operation. During normal H_2/O_2 PEMFC operation, hydrogen molecules are oxidized at the platinum anode, forming protons and electrons. The electrons produced at the anode travel through the external circuit and arrive at the cathode while protons are transported through the hydrated PEM to the cathode. At cathode, where the reduction of O_2 happens, the oxygen combines with the protons and electrons to produce water.

A fuel cell constantly produces energy by converting fuel into electricity through a chemical reaction in which hydrogen and oxygen are combined to produce water, releasing heat and electrical energy in the process. Proton exchange membranes (PEM) for fuel cells have recently received a great deal of attention for their potential as high efficiency and zero-emission power plants. For instance, A natural gas fueled polymer electrolyte membrane fuel cell system can reach 90% thermal efficiency in a cogeneration configuration. These fuel cell system can also reduce primary energy consumption by 20% while cutting CO_2 and NOx emission, when compared with the conventional combination of grid electricity and gas water heater. The most versatile of PEM can be used in automobiles, laptops and even compact heating systems. But the PEM has some disadvantages; it requires very pure hydrogen fuel. To run on natural gas, gasoline or methanol, the fuel has to be also prepared using a down-steam reformer. An alternative is the direct methanol fuel cell (DMFC), which run directly on liquefied methanol gas. The diagram of basic PEMFC is shown in Fig. 3.

Current PEM fuel cell system based on Nafion still faces significant technology roadblocks that have to be overcome before it can become commercially viable, and these include water management at the electrodes, CO poisoning of the anode catalyst, slow cathode kinetics, and high cost of the Pt electrode catalyst and Nafion. It has been demonstrated that these problems will be eliminated once the operating temperature is increased to above 100°C. To help maintain hydration at high temperatures with promising results, hydrophilic silica nanoparticles have been incorporated into Nafion based membranes. But the cell performance of these silica-containing membranes is still inferior to the bare Nafion operated at 80°C.

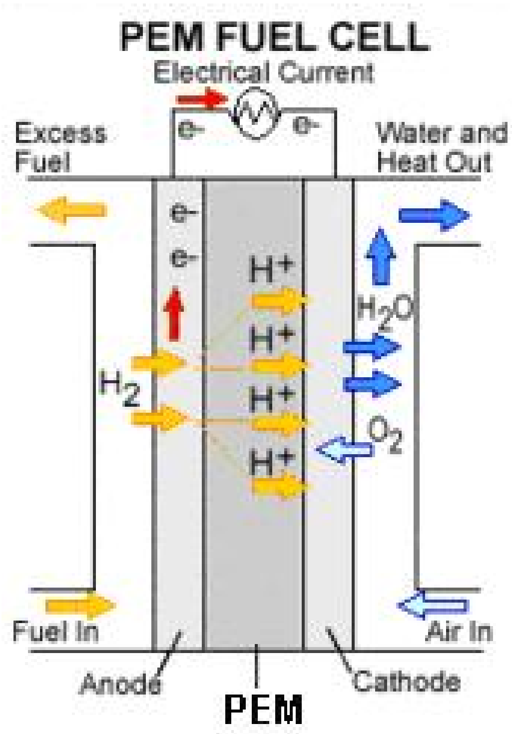


Fig. 3: Diagram of Proton Exchange Membrane Fuel Cell (PEMFC)

The overall electrochemical reactions that occur at the platinum electrocatalyst sites are as follow:

Anode reaction: $H_2 \rightarrow 2H^+ + 2\,e^-$ (Equation 1)
Cathode reaction: $O_2 + 4H^+ + 4\,e^- \rightarrow 2\,H_2O$ (Equation 2)
Overall reaction: $2H_2O + O_2 \rightarrow 2\,H_2O$ (Equation 3)

Generally, there are three main application fields for a PEMFC system such as transportation (fuel cell vehicles), stationary and portable applications. Among the many applications of PEMFCs, transportation is the most competitive and promising. In addition, people could easily see the potential of this promising alternative technology through the development of environmentally friendly vehicles [4].

3.1 Recent Developments in Proton Conducting Membranes

Proton conducting membranes attract considerable attention because they are key-components in PEMFCs. The primary demands on the hydrated PEM are high proton conductivity (at least 0.01 S cm-1), low fuel and O_2 permeability, lowcost (less than USD 10 kW-1 in a PEMFC), and high chemical, thermal and mechanical stability [32]. The current well-developed PEMFC technology is based on perfluorosulfonic acid polymer (Nafion) as electrolyte. Nafion encounters several technology shortcomings in the commercial use of PEMFC. Therefore, extensive researches have been carried out for alternative proton conducting membranes that can satisfy all the requirements of a PEM.

The developed membranes are classified into four groups: modified Nafion membranes; all polymeric heterocycle electrolytes; acid-base polymer membranes; and alternative sulfonated polymers and their organic/inorganic hybrid composites membranes. Great efforts have been carried out to modify Nafion membranes in order to achieve high temperature operation. Impregnation and recast of the Nafion membrane with hygroscopic oxide nano silica and titania particles and solid inorganic proton conductors (for example heteropolyacids) provide an effective way to overcome the humidification constraints in PEMFC.

PWA and silica into the Nafion membrane has resulted in enhanced thermal stability and water uptake, besides retaining its inherent property. The second approach investigated is the development of all-polymeric electrolytes that rely entirely on structure diffusion of the protons. Several researchers have reported the synthesis of proton conducting polymeric systems based on nitrogen-containing heterocycles, such as imidazole, benzimidazole and pyrazole. These heterocycles form hydrogen bonded networks similar to that found in water, and also their transport properties are similar to that found in water with proton transfer occurring via structure diffusion. Notably, these levels of conductivity were obtained in the complete absence of water. The acid-base hybrid materials were prepared by mixing strong phosphoric acid polymer of PVPA with the high proton exchange capacity and inorganic base of heterocycle, such as imidazole, pyrazole and 1-methylimidazole. As a result, PVPA- heterocycle composite materials showed high proton conductivity of approximately 10-3 S/cm at 150 °C under anhydrous condition.

In the third approach studied, different complexation of basic polymers with oxo-acids, which are characterized by excellent thermal, chemical and mechanical properties, have been studied extensively. Several researchers have developed high-temperature PEMs based on complexes of oxo-acid, such as phosphoric acid, H_3PO_4 and sulfuric acid with different basic polymers, especially sulfonated poly(ether ether ketone) [11], sulfonated polyimide [12], sulfonated polybenzimidazole (PBI) [13], and sulfonated poly(arylene ether sulfone) [14].

Polymers bearing basic sites such as ether, alcohol, imine, amide and imide groups react with strong oxo-acids. The basicity of the polymers enables the establishment of hydrogen bonds with the acid. In other words, the basic polymers act as a solvent in which acid undergoes to some extent of dissociation. The fourth approach investigated is the use of alternative sulfonated polymers and their hybrid membranes (organic-inorganic composite membranes) containing inorganic nanoparticles (e.g. silica, zeolite, ZrO_2, TiO_2, and silica supported tungstophosphoric acid). In addition to Nafion, a great number of polymer components have been used for preparing organic-inorganic composite, including those with and without functional groups such a polyethylene oxides (PEO) [15, 16], polyethelene glycol (PEG), polyvinylalcohol (PVA), sulfonated poly(ether-sulfone), polydimethylsiloxane and many others. The incorporation of various hygroscopic and often proton conducting, inorganic nanoparticles has been shown to significantly improve the high-temperature performance of several types of PEMs. Several reasons have prompted extensive development of the inorganic-organic composite membrane for fuel cells [9], particularly to:

- improve the self-humidification of the membrane at the anode side by dispersing hydrophilic inorganic components homogeneously in the polymer.
- reduce the electro-osmotic drag and therefore the drying-out of the membrane at the anode side.
- suppress the fuel crossover, e.g. methanol in DMFC.
- improve the mechanical strength of the membranes without sacrificing proton conductivity.
- assist the improvement of the thermal stability.
- enhance the proton conductivity when solid inorganic conductors are used.

Flexibility of organic polymer and stability of inorganic have been mixed to have both beneficial properties, while a doping of acidic molecules or acidic inorganic solid clusters provides for protonic conducting pathways for the hybrid membrane. Thus, the organic/ inorganic interfaces are structurally controlled to enable the membranes to become a remarkable family of protonic conducting hybrids.

Nano zeolite is zeolite with discrete, uniform crystals with particles dimensions of less than 100 nm. Changes in the molecular properties of zeolites at nanoscale greatly enhance their physical and chemical properties. Nano zeolite has unique properties relative to conventional micro zeolite. Compared with the conventionally micro zeolite, nano zeolite has more external surface area, higher surface energy and shorter channels. The ratio of the atoms on their surface and in the bulk increases dramatically with the decreasing of the particle size. Thus, nano particles with unique physical and chemical properties will outperform micro-sized particles in the catalytic reactions.

Among all zeolites, medium pore-sized ZSM-5 represents a continuing area of interest for several applications. Zeolite ZSM-5 is a highly siliceous zeolite, widely employed as a catalyst in organic synthesis, petroleum refining and petrochemical industries because of its high solid acidity, hydrophilicity and its resilience in strong acidic environments.

3.2 Applications of Zeolite as Proton Conducting Membrane

In recent years, zeolites have been applied in proton conducting membrane for fuel cells because of their potential conductivity, hydrophilicity, and thermal stability. Generally, zeolites exhibit no electronic conductivity, since they reveal a wide electronic band gap of several electron-volts. Whereas, zeolites contain exchangeable non-framework cations to compensate for the negative charge of the framework caused by the difference in the valence between Si(IV) and Al(III). In general, these may be any alkali, alkaline-earth or rare earth cation as well as organic cations such as the tetramethylammonium ion. The exchangeable cations, which are electrostatically bound to the polyanionic host lattice, can move along the pore and channel structure of the crystal's interior. Therefore, zeolites can potentially be a candidate for novel proton-conducting materials, since the cation is mobile in the framework structure, which has been materialized as ion exchangers in an aqueous phase [55]. Furthermore, because of zeolites microporosity (< 10 Å), zeolites can maintain hydration at very low relative humidity. This feature could be especially helpful for high temperature applications.

A few studies were carried out to apply zeolites in the preparation of proton conducting membranes, such as zeolite Beta [27], Y-Zeolite [24, 25], mordenite, zeolon 100 H [22] and natural zeolite such a chabazite and clinoptilolite [23] The initial attempt was tried by Poltarzewski, Z. *et. al.* [22]. Proton conducting composites electrolytes based on zeolite (Zeolon 100 H) dispersed in poly(tetrafluoroethylene) matrix was synthesized and characterized. The composite membranes exhibit relatively high ambient temperature ionic conductivity (10^{-2} S/ cm) and a wide thermal stability range. The highest current and power densities obtained were approximately equal to 50 mA/ cm^2 and 4 mW/ cm^2.

Composite membranes formed of zeolitic fillers embedded in Nafion were made by evaporating the solvents from a suspension of small zeolite crystals in a Nafion solution [23]. Two natural zeolites were selected as filler: chabazite and clinoptilolite. This work was carried out in order to exploit the molecular sieving properties of the natural zeolites to improve selectivity of Nafion ion conducting membranes. However, the performances of chabazite-Nafion and of clinoptilolite- Nafion composite membranes were inferior to that of zeolite-free recast Nafion membranes with regard to both ion conductivity and transport selectivity. These results were due to the properties of the chosen zeolites, which proved inadequate to the authors' purpose. Besides, a new solid inorganic proton conductor was developed based on Yzeolite [24] and mesoporous molecular sieves (MCM-41) [26] loaded with tungstophosphoric acid and molybdophosphoric acid. These new materials combine the high thermal and structural stability of Y-zeolite and MCM-41 with outstanding conductivity of heteropolyacids, which places them among the one of the most promising solid proton conductors. The highest proton conductivity of around 0.01 S/cm was obtained at room temperature for fully hydrated 50 wt% heteropolyacids loaded Y-zeolite and MCM-41.

Another effort was tried by mixing the Y-zeolite loaded heteropoly acids into sulfonated polyetheretherketone (SPEEK) polymer matrix [25]. These composite membranes demonstrated a maximum of 10^{-2} S/cm at 140 °C. In addition, synthesis and proton conductivity of sulfonic acid functionalized zeolite BEA nanocrystals has been prepared and determined by Brett A. Holmberg *et. al.* [27]. Phenethyl functionalized zeolite BEA nanocrystals were synthesized using a mixture of fumed silica and phenethyltrimethoxysilane as silica source. A concentrated sulfuric acid treatment of the Pe-BEA nanocrystals is effective in simultaneous removal of the organic structure-directing agent and addition of sulfonic acid. Sulfonic acid functionalized zeolite BEA nanocrystals show proton conductivity in the range of 1.2×10^{-3} - 1.2×10^{-2} S/cm compared to 1.5×10^{-4} S/cm for unfunctionalized zeolite BEA, which is comparable with conventional proton conductive Nafion (10^{-1} S/cm) [15].

4.0 Methodology

Through the incorporation of nano zeolite as the host material, the proton conductivity may be enhanced at high temperature because of its moderate proton conductivity, mechanical stability and hydrophilic feature at high temperature. Polystyrene has been functionalized onto the surface of nano zeolite as membrane electrolytes for PEMFC, principally to lower the material cost for high-temperature operation as the used polymer components represent a large group of polymers that are low in cost and commercially available. Organosulfonic acid groups are functionalized onto the surface of nano zeolite with the intention to further increase the proton conductivities of the bare zeolite by the introduced charge units (sulfonate $–SO^{-}_{3}$). It is proposed that the designed membranes would possess a high concentration of sulfonic acid groups to increase the cationic site density in the hydrophilic domains; a high water content created by zeolites to enlarge hydrophilic domains in the membranes at high temperature; and well alignment of channel structures by the direct chemical bonding between the organosulfonic acid groups and zeolite to ease proton and water transport, which consequently produce novel temperature tolerant proton conducting membrane for fuel cells.

The preparation of functionalized nanocomposite proton exchange membrane in this study involves three steps: the synthesis of nano zeolite; the preparation of organosulfonic acid functionalized zeolite nanocomposite; and the sulfonation of the produced nanocomposite.

Nano zeolite (particles size in the range of 100 nm) is synthesized via hydrothermal crystallization of clear supersaturated homogeneous synthesis mixtures free of Na^{+} ion. The nano zeolite surface was then silylated by using 3-mercaptopropyltrimethoxysilane, followed by grafting polymerization of styrene and divinylbenzene onto the modified zeolite surface. After that, the prepared polymer-zeolite nanocomposite would be sulfonated by using acetylsulfate. The preparation of sulfonated polystyrene-zeolite composite is illustrated in Fig. 4.

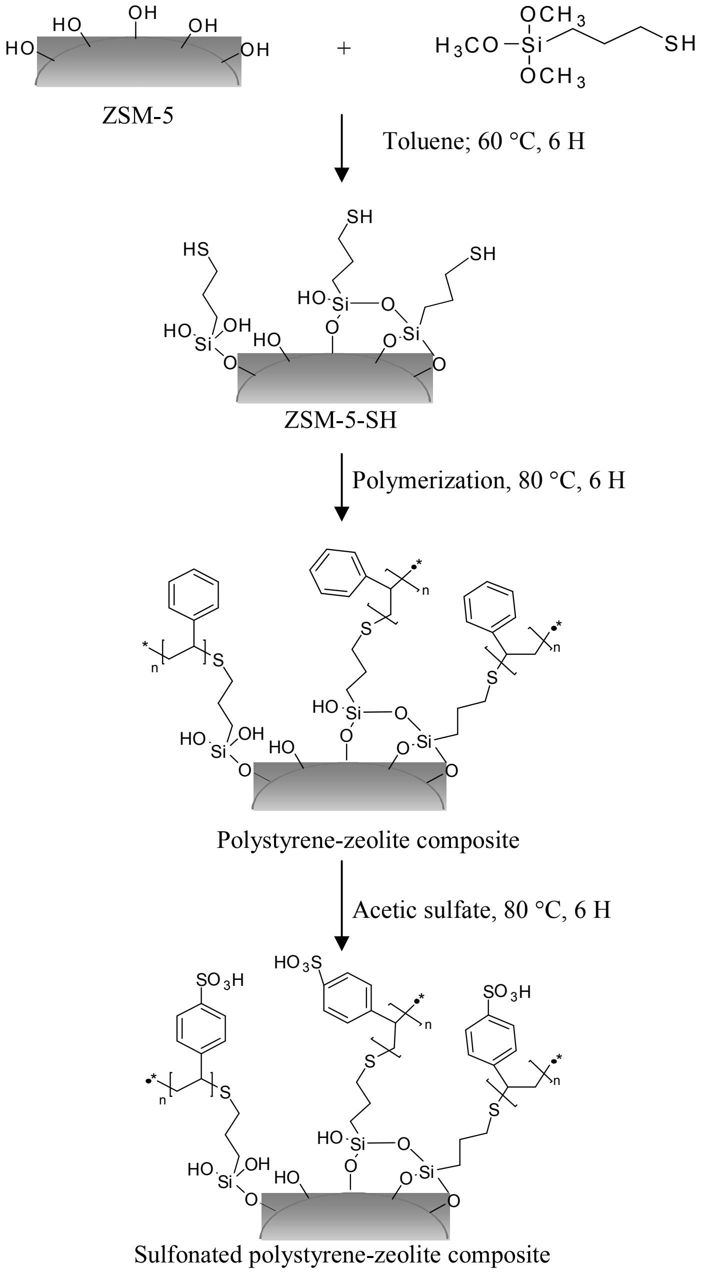


Figure 4: Preparation of sulfonated polymer-zeolite nanocomposites.

5.0 Results and Discussion

Nano-ZSM5 and micro-ZSM-5 both in powder form were synthesized. Nano-ZSM-5 was produced as a white fluffy solid, while the micro-ZSM-5 sample appeared as an off-white solid.

5.1 X-Ray Diffraction

The XRD patterns for nano zeolite ZSM-5 and sulfonated polystyrene-zeolite ZSM-5 nanocomposite obtained are depicted in Figures 5. XRD diffractograms of all the samples synthesized show characteristic patterns for zeolite ZSM-5. They are pure and highly crystalline as proven by intense and narrow peaks without elevated baseline and extra peaks. Thus, the formations of nano zeolite ZSM-5 is successful based on both of the methods. XRD patterns of all of the modified zeolites contain amorphous phases at 2θ of 10°- 20°. However, the polymer-zeolite nanocomposites still show characteristic patterns for ZSM-5, which indicates that ZSM-5 is stable during the polymerization and sulfonation process. There is no appreciable change in the framework structure of the zeolites even after modification.

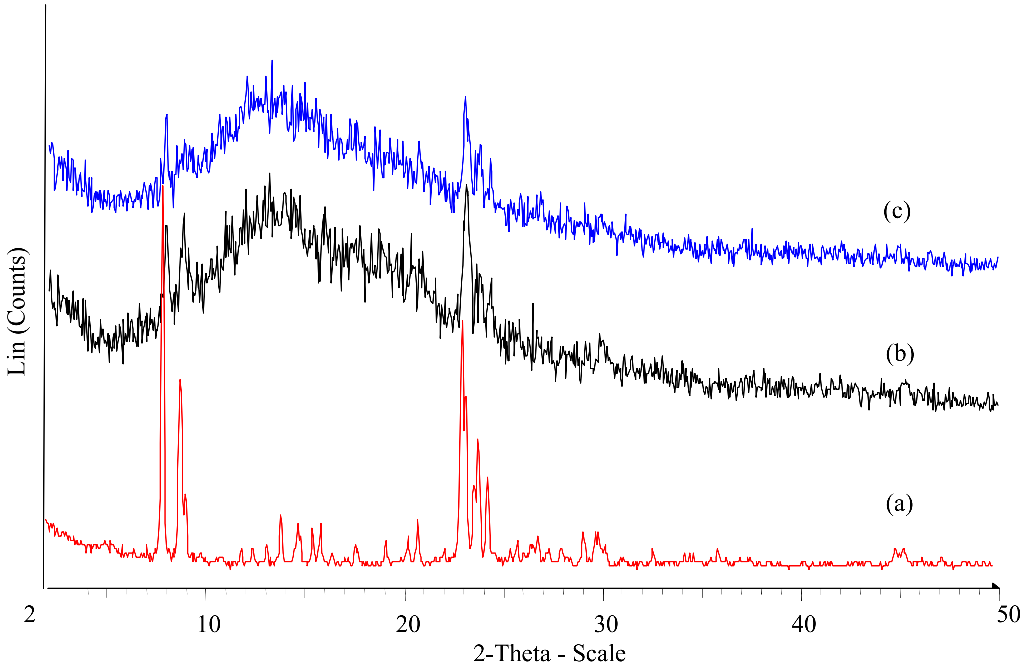


Figure 5: X-ray diffractograms of polymer-zeolite composites: (a) nano zeolite ZSM5, (b) polystyrene-nano ZSM-5 composite, (c) sulfonated polystyrene- ZSM-5 nanocomposite

5.2 Fourier Transformed Infrared (FTIR) Spectroscopy

Lattice vibration spectra of nano zeolite ZSM-5 and sulfonated polystyrene-zeolite ZSM-5 nanocomposite are shown in Figure 6.

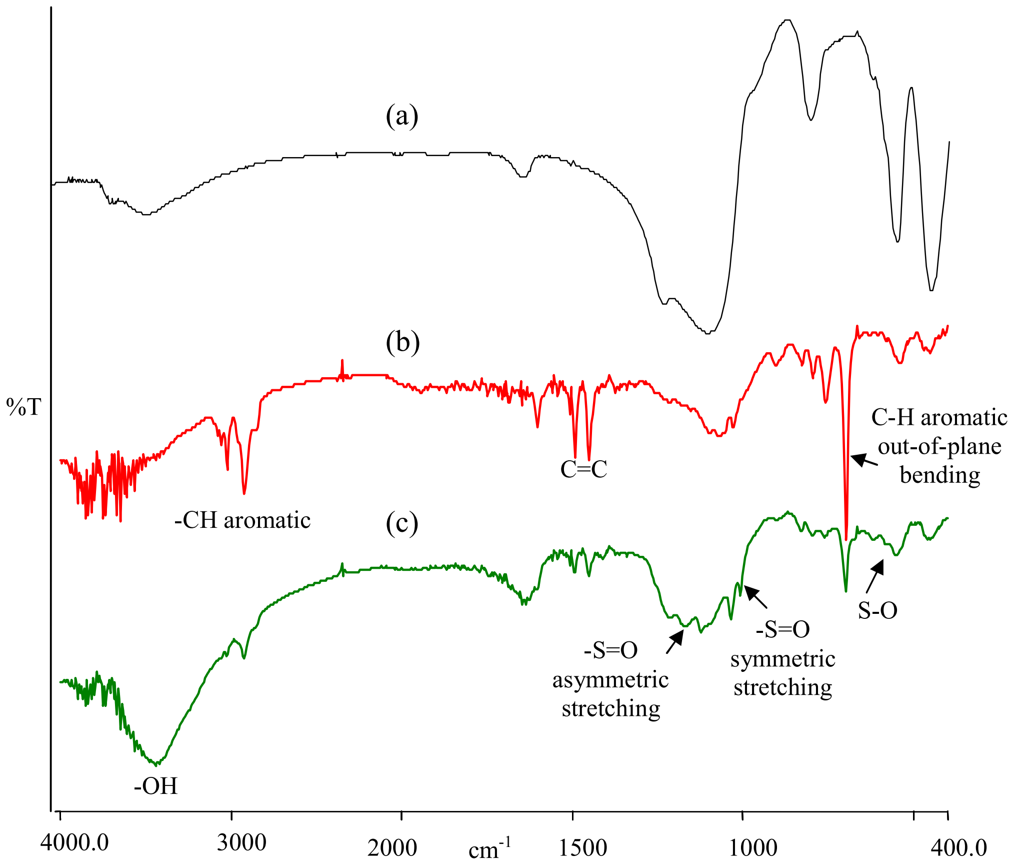


Figure 6: IR spectra of polymer-zeolite composites: (a) nano zeolite ZSM-5, (b) polystyrene-nano ZSM-5 composite, (c) sulfonated polystyrene-zeolite ZSM-5 nanocomposite.

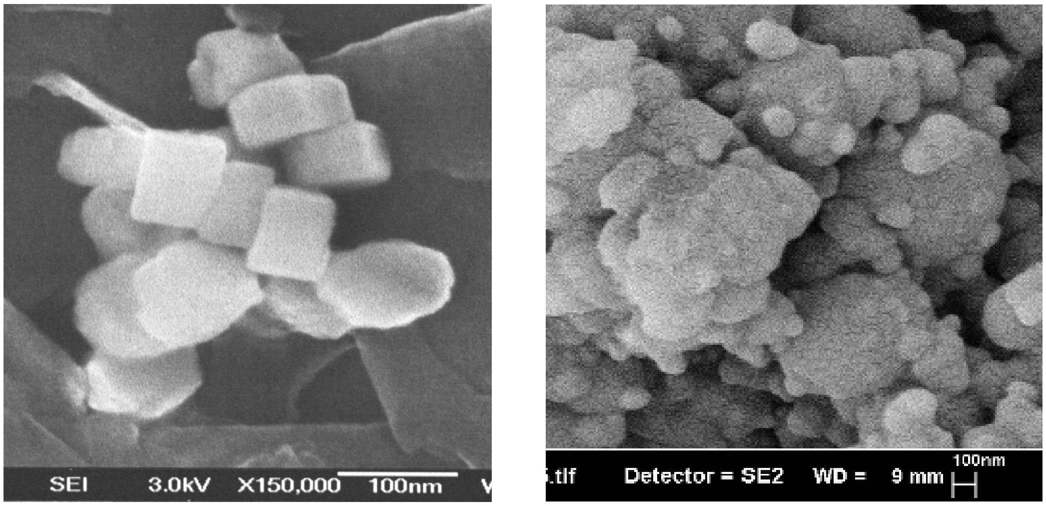
All the samples show 6 similar bands at around 3440, 1635, 1223, 1091, 792, 543 and 451 cm^{-1}. The broad peak around 3440 cm^{-1} is due to O-H stretching of water absorbed in the cavities and channels of zeolites while the peak at around 1635 cm^{-1} corresponds to the bending mode of O-H of water. Besides that, the broad band at around 1091 cm^{-1}, the most prominent in the IR spectra, corresponds to asymmetric stretching of the internal vibration bands of SiO_4 or AlO_4 while the small bands observed at around 1223 cm^{-1} is assigned to asymmetric stretching of the external vibration bands of SiO_4 or AlO_4. On the other hand, the bands at around 792 cm^{-1} and 543 cm^{-1} are due to the symmetric stretching of SiO_4 or AlO_4 and double ring vibration respectively. The small band observed at around 451 cm^{-1} is assigned to Si–O–Si bending modes.

As shown in Figures 6.3 (b) and (c), grafting of polystyrene on thiols functionalized zeolite ZSM-5 was confirmed by the presence of benzene ring features: C-H aromatic symmetric stretching vibrations at 3025 and 2922 cm^{-1} and skeletal C=C in plate-stretching vibrations at 1493 and 1601 cm^{-1}. It can also be seen that the prominent peaks at 756 and 697 cm^{-1} in polystyrene-zeolite composite are due to –C-H out of plane bending.

After sulfonation, the new peaks identified in the spectra in Figures 6.3(c) at around 650, 1008 and 1177 cm^{-1} are due to the symmetric stretching of sulfonate groups (S=O), asymmetric stretching vibrations of S=O and S-O stretching band respectively. In addition, the O-H stretching bands at 3445 cm^{-1} are more intense for sulfonated polystyrene-zeolite composite samples which originate from sulfonic acids (-SO_3H). The IR data proved that the sulfonation of polystyrene-zeolite composites with acetyl sulphate were successful.

5.3 FESEM Analysis

FESEM micrographs of nano zeolite ZSM5 and sulfonated polystyrene-zeolite ZSM-5 nanocomposite are shown in Figure 7 .



(a) (b)

Figure 7: FESEM micrograph of: (a) nano-ZSM5 (b) sulfonated polystyrene-zeolite ZSM-5 nanocomposite

FESEM image of nano-ZSM5 in Figure 7 (a) shows that single crystals mostly with spherical shape are formed which exhibit smooth faces and edges. The synthetic zeolite has fine and uniform structure with average particles size of 100. FESEM micrographs prove that the synthesis of nano-sized ZSM-5 (sample nano-zsm5) via hydrothermal crystallization of clear supersaturated homogeneous synthesis mixtures was successful as the particles size of sample nano-ZSM5 is in the range of 1-100 nm. From Figure 7 (b), polystyrene in this case agglomerates to form larger particles with size between 100-500 nm. A ‘raspberry-like’ morphology of composites was obtained with the nano particles ZSM-5 being dispersed throughout the particles of polystyrene.

5.4 BET Surface Area Analysis

Nano-ZSM-5 presents a higher BET surface area than the micro ZSM-5 sample, which indicates that the surface area of zeolite (especially external surface area) is enhanced when the particle size decreases. As proven in SEM micrograph, nano-ZSM-5 possesses average particles size of 100 nm while the average particle size of micro-ZSM-5 is 3 µm. By restricting ordered atomic arrangements to increasingly small volumes, materials begin to be dominated by the atoms and molecules at the surfaces, often leading to properties that are strikingly different from the bulk material. As the zeolite size gets smaller, the surface area-to-volume ratio gets larger. In other words, if a big chunk of material was broken down into small pieces, the smaller the pieces become, the larger is the surface area for the same amount of material which is commonly called the surface-to-volume ratio.

5.5 Ion Exchange Capacity Measurement

In general, the ion capacities of the samples (Table 1) increase as follow: sulfonated polystyrene-zeolite composites > propylsulfonic acid functionalized ZSM-5 > phenylsulfonic acid functionalized ZSM-5 > zeolite ZSM-5. These prove that sulfonated polystyrene-zeolite composites contain the highest content of sulfonic acid groups as the proton content is proportional to sulfonic acid amount.

Table 1: Ion-exchange properties

Types of Zeolite ZSM-5	Sample	Ion-exchange Capacity (mmol H+/g)
Micro ZSM-5 samples	ZSM-5	0.01
	ZSM-5-SH-SO3H	0.04
	ZSM-5-SH-PS-SO3H	1.00
	ZSM-5-PTCS-SO3H	0.05
Nano ZSM-5 samples	ZSM-5	0.04
	ZSM-5-SH-SO3H	0.25
	ZSM-5-SH-PS-SO3H	0.89
	ZSM-5-PTCS-SO3H	0.14

Propylsulfonic acid and phenylsulfonic acid functionalized nano ZSM-5 samples have higher ion-exchange capacities compared with the corresponding micro ZSM-5 samples. However, in contrast, sulfonated polystyrene-micro ZSM-5 composite has higher ion-exchange capacity compared to the corresponding nano ZSM-5 composite. These are mostly because of the higher amount of organosulfonic acid groups attached on the external surface of the zeolite ZSM-5 as proven by IR and TG analyses.

5.6 Water Uptake Test

It is very important to characterize the behaviour of proton conducting membranes in contact with water, since the presence of water in the membrane is a prerequisite for reaching high proton conductivity. Generally, sulfonated polystyrene-zeolite composites show the highest water adsorption capacity followed by propylsulfonic acid functionalized ZSM-5, phenylsulfonic acid functionalized ZSM-5 and zeolite ZSM-5. These indicate that water sorption increased with sulfonic acid content due to the strong hydrophilicity of the sulfonate groups. Sulfonic acid in this context is capable to increase the hydrophilicity of the membranes.

It was observed that propylsulfonic acid and phenylsulfonic acid functionalized nano ZSM-5 samples show higher water uptake capacities compared with the corresponding micro ZSM-5 samples. However, in contrast, sulfonated polystyrene-micro ZSM-5 composite has higher water uptake compared to the corresponding nano ZSM-5 composite. These results are in good agreement with ion-exchange capacity test, FTIR and TG analyses that probably higher amount of organosulfonic acid groups were attached on the external surface of the corresponding zeolite ZSM-5. Besides, nano zeolite ZSM-5 has higher water uptake compared to micro zeolite ZSM-5. This is in line with IR and BET surface area analyses as the nano zeolite ZSM-5 possesses higher surface area and more silanol groups on its surface which play a significant role in the water adsorption. The higher preference of nano zeolite ZSM-5 for water is also due to the presence of polar groups such as cations and hydroxyls in the intracrystalline void space and of electric field gradients brought about by the presence of aluminium in the tetrahedral framework.

5.7 Proton Conductivity of Sulfonic acid Functionalized ZSM-5

Zeolites are ionic conductors, since the exchangeable cations (H+, Na+, etc.), which are electrostatically bound to the polyanionic host lattice, can move along the pore and channel structure of the zeolites by hopping diffusion under the influence of the applied electric field. As the temperature increases, the activation energy of the charge transport increases. Therefore, the protons bound to the polyanionic host lattice can overcome the electrostatic binding energy more easily by thermal activation to hop from its equilibrium site to a neighbouring site, which as a result lead to higher proton conductivities.

The results of the proton conductivity measurements of the above samples are shown in Table 2.

Table 2: Proton conductivity of sulfonated polystyrene-ZSM-5 composites.

Sample	24°C	50°C	75°C	100°C
Nano Zeolite	5.43×10^{-6}	5.85×10^{-6}	8.80×10^{-6}	1.48×10^{-5}
Sulfonated polystyrene – zeolite nanocomposite	2.32×10^{-5}	2.67×10^{-4}	3.14×10^{-4}	1.26×10^{-3}

The general trend observed is the increase of proton conductivity with temperature up to 100 °C. Besides, the conductivity of zeolite was enhanced considerably to higher values by loading of sulfonic acids onto the surface of zeolite. The synthesized functionalized nanocomposite has proton conductivity in the range of 1×10^{-3} S/cm which is comparable with the commercial Nafion with great properties in mechanical strength, hydrophilic features and chemical stability at high temperature operation.

Over the whole range of temperature tested, data in Table 1 shows that nano ZSM-5 gives higher proton conductivity (5.4×10^{-6} - 1.5×10^{-5} S/cm) as compared with micro ZSM-5 (2.8×10^{-6} -5.9×10^{-6} S/cm). This can be explained as a consequence of 4 factors. First, nano ZSM-5 particles possesse higher surface areas which were proven via BET surface area analysis. The increase in surface area to volume of materials provide larger amount of accessible protons on the active sites which are exchangable to move along the polyanionic host lattice of zeolite. Secondly, the ratio of the atoms on the surface of ZSM-5 to those in the bulk increases dramatically with decreasing the particle size. Therefore, larger portion of hydrophilic silanol groups are located on the surface of nano ZSM-5 which is in line with FTIR spectroscopy and TGA results. This helps to maintain higher level of hydration necessary for the efficient proton conduction. Thirdly, smaller sized zeolites particles are believed to be able to conduct protons more efficiently due to the higher level of interaction between the individual nano particle and their ability to pack closer together. This low void space packing could lead to more continuous proton conduction pathways through the sample which resulted in higher proton conductivity.

Moreover, nano ZSM-5 has reduced diffusion path lengths, which make them better proton conduction materials.

Despite the presence of high number of extraframework cations for ZSM-5 zeolite, shows that the conductivities of both of the ZSM-5 zeolites were surprisingly poor, which are in the range of 2×10^{-6}- 2×10^{-5} S/ cm. The ionic conductivity of several common zeolite framework types with alkali ions has been investigated in the past. Although the high number of extraframework cations present implied them to be good ionic conductors, to date, there is no clear rationale behind this observation.

The proton conductivities of ZSM-5 zeolite were increased significantly due to the presence of sulfonic acid groups in the composite because of a few reasons. In all cases, proton transfer is obviously associated with acid sites (sulfonic acid groups) bounded to the support materials. Hydration allows bridging acidic sites assisting ion hopping and providing additional charge carriers as the sulfonic acid groups dissociate into SO_3^- (fixed charge) and H^+ (mobile charge) upon the addition of water. The protons, which are responsible for the ion conductivity, thus, encounter a lower resistance to hop from one water molecule to the next or from one cluster of water molecules to the next under a potential gradient. In its simplest form this can be represented as:

$$R\text{-}SO_3H + H_2O \rightarrow R\text{-}SO_3^- + H_3O^+$$

$$H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$$

Apart from the hopping mechanism helped by the presence of sulfonic acid groups, ZSM-5 zeolite in this context plays a significant role in the diffusion of the hydronium and dimmer ions which are formed. Generally, zeolite is known to be capable to retain water molecules in their cavities especially up to high temperature. Thus, proton attached to a water molecule could be transmitted through a chain of water molecules from one electrode to the other, providing a fast route for conductivity, corresponding to a low specific resistance of the membranes. Figure 8 shows a postulated picture of the proton conduction mechanism in sulfonated polystyrene-zeolite ZSM-5 nanocomposite.

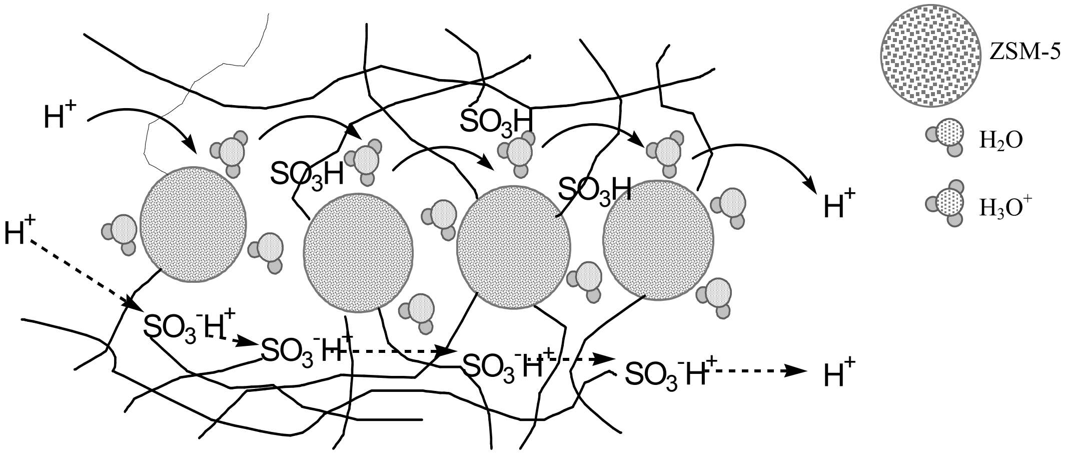


Figure 8: Proton transport mechanism in sulfonated polystyrene-zeolite composite

5.8 The effects of particle size of ZSM-5 zeolite in proton conductivities of propylsulfonic acid and phenylsulfonic acid functionalized ZSM-5.

For both the propylsulfonic acid and phenthylsulfonic acid functionalized ZSM-5, higher proton conductivities were observed in modified nano ZSM-5 samples. In the earlier discussion, FTIR, TGA, ion-exchange capacity test and water adsorption capacity results showed that higher content of propylsulfonic acid and phenylsulfonic acid were loaded onto the surface of nano ZSM-5. Proton conductivity is in general proportional to the concentration of sulfonic groups bonded to the support materials. A high concentration of sulfonic acid groups would assist in ion hopping and provide additional charge carriers. Consequently, sulfonic acid functionalized nano zeolite ZSM-5 consists of higher proton conductivity because of the higher degree of cationic site density in the hydrophilic domains in the membranes. Moreover, the proton conduction of sulfonic acid functionalized nano zeolite ZSM-5 is assisted by the novel characteristic of nano zeolite ZSM-5 due to its higher water retention especially at high temperature, low void packing between the individual particles and shorter diffusion pathways which enhance proton migration in the membrane.

The comparison of proton conductivities between the nano and micro zeolite ZSM-5 with attachment of sulfonated polystyrene are presented in Figure 9 which indicates that higher proton conductivities, however, were observed in modified micro zeolite ZSM-5 samples, which may be explained by the morphology and the content of sulfonic acid in the systems. Sulfonated polystyrene-zeolite composite consists of two phases: the hydrophobic region which is composed of the polymer backbone; and the hydrophilic region which contains the ZSM-5 particles, sorbed water, ionic groups and their counter ions, as illustrated in Figure 2.

As a result of electrostatic interaction, the ionic groups (sulfonic groups) tend to aggregate to form tightly packed regions or clusters. Hydration makes the adjacent clusters to be interconnected through channels; that enhances ion and water transport. From this fact, the clusters arrangement has a marked influence on the proton conductivities. The reorganization of the structural pattern is important for an uninterrupted trajectory for proton diffusion. Figure 8 demonstrates that sulfonated polystyrene was dispersed more evenly on the surface of ZSM-5 and almost the entire external surface of micro ZSM-5 was covered by sulfonated polystyrene.

Thus, micro ZSM-5 sample show fewer phases separated morphology of discrete hydrophobic and hydrophilic region. As a result, the protons can diffuse more effectively from one active site to another which is helped by the water molecules retained in ZSM-5. Moreover, higher amount of sulfonic acid was attached on the surface of micro zeolite ZSM-5 which was proven by FTIR, TGA and ion-exchange capacity test. The higher content of sulfonic acid may enhance the hydrophilicity in the membrane which would assist in more continuous proton diffusion. As a consequence, higher proton conductivities were observed in sulfonated polystyrenemicro ZSM-5 samples.

Chemically bonded sulfated polystyrene-ZSM-5 contains higher proton conductivity compared with the physical mixtures of sulfated polystyrene/ZSM-5 and bare sulfated polystyrene (sample PS-SO_3H). The properties of zeolite polymer nanocomposites are greatly influenced by both the degree of dispersion of the particles of ZSM-5 zeolites in the base polymers and the interfacial adhersion between the inorganic and organic components. Although nanocomposites can be prepared by simply blending of ZSM-5 particles with base polymers via high shear stirring, the degree of dispersion of the particles and the interfacial adhesion, these methods were obviously insufficient to create the desirable material properties of proton conductors. By introducing silane coupling agents, which create strong covalent bonds between the polymer and zeolite, a good interfacial adhesion and good dispersion of ZSM-5 particles in the base polymers is achieved. Therefore, chemically bonded sulfated polystyrene-ZSM-5 provides a direct contact between the sulfonic acid groups of polystyrene and zeolite particles. As a result, protons can move more continuously which lead to higher proton conductivity.

Furthermore, bare sulfonated polystyrene faces a more serious problem of swelling indicating that the presence of zeolite in the composite material may increase the mechanical strength of the proton conducting membranes.

6.0 Performance of Functionalized Nanocomposite Proton Exchange Membrane in a Model Fuel Cell

A model fuel cell as shown in Figure 9 was built up in order to test the availability of our synthesized functionalized nanocomposite proton exchange membrane. The model fuel cell consists of a single stack proton exchange membrane, a hydrogen generator, a motor mounted on a stand with a plastic fan and a load measurement box. The model fuel cell which was run on our functionalized nanocomposite proton exchange membrane produced current about 0.85 volts at 350 mA. The performance data presented here is promising initial finding to prove the availability of our functionalized nanocomposite to replace the current commercial Nafion in fuel cell application which is cheaper and environmentally friendly with high operating temperature and enhanced humidification conditions.

Figure 9: Model fuel cell run on our functionalized nanocomposite proton exchange membrane.

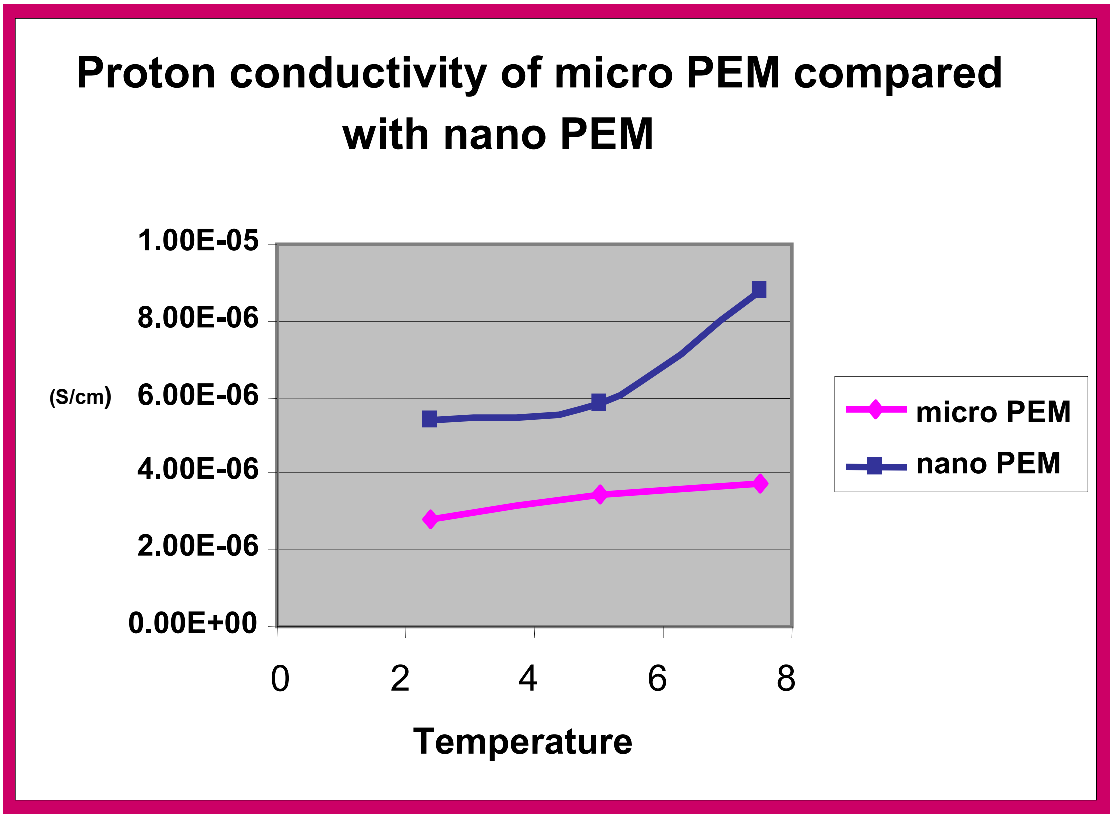


Figure 10: Proton conductivity of micro PEM and Nano PEM

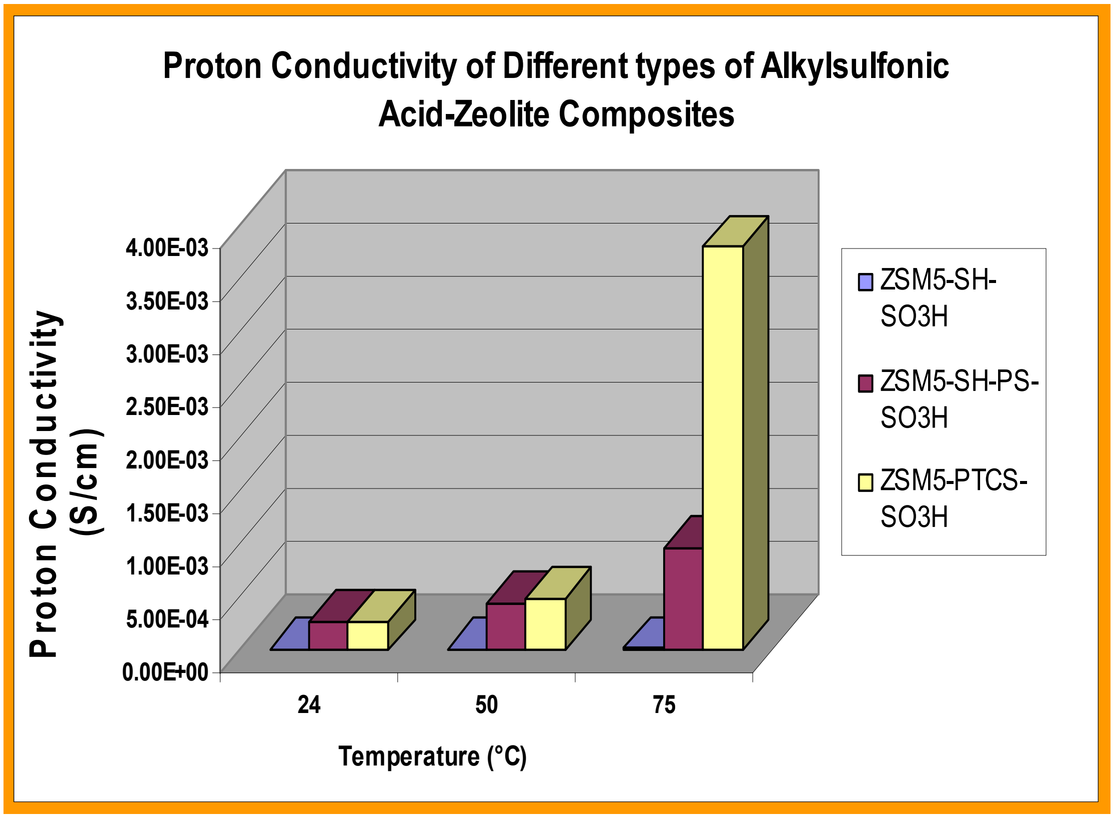


Figure 11: Proton conductivity of different types of alkylsulfonic acid – zeolite composites

7.0 CONCLUSIONS

Nano ZSM-5 zeolite with particles size of ~100 nm was successfully synthesized via hydrothermal crystallization of clear supersaturated homogeneous synthesis mixtures free of Na+ cations in just 24 hours at 170 °C with the following composition: 1 Al_2O_3: 60 SiO_2: 21.4 TPAOH: 650 H_2O. It was confirmed by XRD and FTIR results that the synthesized zeolites ZSM-5 were pure and highly crystalline while FESEM micrographs proved that the average particles size of the nano zeolite ZSM-5 sample is in the range of 50-100 nm. The surface investigation performed by BET method supports the hypothesis that the surface area of nano zeolite ZSM-5 is increased considerably when the particle size of zeolite becomes smaller.

Three different kinds of sulfonic acid functionalized zeolite nanocomposites were successfully synthesized in this study, namely propylsulfonic acid functionalized ZSM-5, phenylsulfonic acid functionalized ZSM-5 and sulfonated polystyrene-zeolite ZSM-5 composites. Characterization by XRD, FTIR and TGA indicate that the functionalized zeolites comprise of amorphous regions due to the organosulfonic acid groups attached onto the external surface of zeolites.

Impedance spectroscopy results showed that the proton conductivities of zeolites in the operating temperature range of 24-100 °C are enhanced significantly to higher values (about 1-3 orders of magnitude) by loading of sulfonic acids onto the surface of zeolite. Proton conductivities correlated with the concentration of sulfonic acid groups and increased as follow: sulfonated polystyrene-zeolite composite > propylsulfonic acid functionalized ZSM-5 > phenylsulfonic acid functionalized ZSM-5 > zeolite ZSM-5; in line with the ion-exchange capacity results and water uptake test which indicates that sulfonated polystyrene-zeolite composites show the highest loading of sulfonic acid and water adsorption capacity. Impedance spectroscopy results also showed that nano zeolite ZSM-5 and its corresponding propylsulfonic acid and phenylsulfonic acid functionalized samples display higher proton conductivities as compared with micro zeolite ZSM- 5 samples; correlated with the novel characteristics of nano ZSM-5 and enhanced attachment of sulfonic acid on its surface.

Sulfonated polystyrene-micro zeolite ZSM-5 composite however shows slightly higher proton conductivity than the corresponding nano zeolite ZSM-5 nanocomposite which may be explained by the morphology and the higher loading of sulfonic acid in the systems, as proven via FESEM, ion-exchange capacity and water uptake test.

In conclusion, through the incorporation of nano and micro zeolite ZSM-5 as the host material, the proton conductivities of the composite materials were enhanced at high temperature because of the hydrophilic feature of the surface sulfonic groups and the novel characteristic of nano and micro zeolite ZSM-5. Therefore, it is evident that organosulfonic acid functionalized zeolite ZSM-5 systems are potentially excellent alternatives of temperature tolerant proton conducting membranes.

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