ORGANIC/INORGANIC GUANIDINIUM-BASED HYBRID ANION EXCHANGE

MEMBRANES FOR ALKALINE FUEL CELLS

by

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Presented to the Faculty of the Graduate School of

The University of Texas at Arlington in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE IN MATERIALS SCIENCE AND ENGINEERING

THE UNIVERSITY OF TEXAS AT ARLINGTON

MAY 2015

Acknowledgements

Abstract

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The University of Texas at Arlington, 2015

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Organic-inorganic hybrid membranes are good alternatives to homogeneous ones to overcome the limitations posed by the individual constituent materials. These membranes pose promising applications in fuel cells with the combination of phenomenal functionality of organic polymers and stability of inorganic material. Introduction of inorganic materials into the polymer matrix is usually known to show an increase in mechanical properties of the membrane while, the organic part of the membrane, i.e., the polymer contributes towards the electrochemical properties. The properties of the individual materials combine to enhance the characteristic properties of the hybrid membranes.

In this thesis we attempted to develop guanidinium-based hybrid membranes using inorganic montmorillonite(clay) particles. These layered silicate nanoparticles were discovered to increase the membrane properties such as tensile moduli, toughness at filler content as small as 1%. As widely reported in literature, the clay particles are known to interact with polymer matrix through adsorption, intercalation and cation exchange. Hence, we have tried to form interaction between the clay particles and the guanidinium based polymer (formed through condensation reaction between hexamethylenediamine and guanidinium hydrochloride) through ion exchange. The guanidinium based polymers have

previously displayed high conductivity (nearly 84.7m S cm^{-1} obtained at 20°C in DI water) due to their high basicity and resonance structure. However, they suffer from poor mechanical stability at high ion exchange capacity and tend to become brittle when dry. Hence we have tried to incorporate montmorillonite in the polymer to obtain a hybrid membrane which yields an additional mechanical stability to the material along with the high conductivity. This material is used for casting a hybrid anion exchange membrane for application in fuel cells.

The crux of this thesis focuses on identifying how the properties of the material such as mechanical strength, stability, ionic conductivity, viscosity and texture changes on addition of the clay in different proportions. Specifically, polymer material with different percentage of clay (0%, 1%, 3%) clay were prepared and their properties were thoroughly investigated. Using the FTIR, Raman, Tensile Testing, and AC impedence spectroscopy, we characterized the membranes with different percentages of clay for the aforementioned properties.

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Introduction

1.1 Background and development

Fuel cells are widely considered as one of the environmentally friendly energy

technologies for the 21st century. Their development has undergone successive cycles of

interest and disinterest. Whenever there was a renewed interest in fuel cells, it was usually

a consequence of scientific discoveries, or to fulfill some economic requirement. The

increase in the use of electricity along with the focus on using non-polluting sources of

energy has been one of the major reasons for the development of this technology involving

a direct conversion of chemical energy to electrical energy [2].

Fuel cells are one of the oldest energy conversion technologies yet the origin of this

invention is not very clear. Sir William Grove is widely known as the father of fuel cells

and was one of the first to put forward the concept of fuel cell. It was explained further

(according to the United States department of energy), by Christian Friedrich Schonbein

who first published it in the philosophical magazine in January 1839. Another name

associated with furthering the concept of fuel cell is Francis Thomas Bacon. He

experimented with alkaline electrolytes instead of acid based electrolytes and found that

the KOH electrolytes worked as well as acid ones.

Nowadays, there are 5 major types of fuel cells distinguished by the type of

electrolyte they use: Alkaline Fuel Cells (AFCs), Proton-Exchange Membrane Fuel

Cells(PEMFCs), Phosphoric Acid fuel cells (PAFCs), High temperature fuel cells, and

Direct Methanol Fuel Cells (DMFCs). The AFCs (using aqueous KOH as electrolyte) was

the first type of fuel cell used at the start of the 20th century which ultimately put man on the moon. In 1950s the NASA Apollo space program started using AFC systems and this technology is still in use today. It gave efficiency as high as 70% as well as provided water for the astronauts to drink.

The early alkaline fuel cells used hydrogen as the fuel and liquid KOH as the electrolyte between the anode and cathode at temperatures ranging from 50°C to 200°C. Even though the conductivity of the hydroxyl group was good; this arrangement did not lead to wide-spread applications. Along the issues such as leakage of liquid KOH electrolyte and unavoidable shunt currents, there was also the problem of carbonate precipitation involved in this arrangement. The carbonate formation takes place through the following reactions:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$

$$CO_2 + OH^- \rightarrow HCO_3^-$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

$$CO_3^{2-} + 2K^+ \leftrightarrow K_2CO_3$$
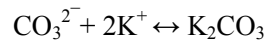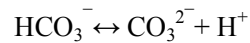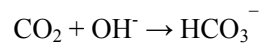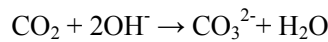
As expressed through the above reactions, the strong alkaline solution will absorb even trace amounts of carbon dioxide due to which the conductivity reduces. Thereby, to avoid the formation of precipitates, highly pure hydrogen and oxygen (devoid of carbon dioxide) was needed. This made the use of alkaline fuel cells a costly process [3] and promoted the development of other type of fuel cells.

1.2 Common Fuel Cells in Use today

1.2.1 Proton Exchange Membrane Fuel Cells

Due to the limitations of the alkaline fuel cells, a major emphasis on the use and development of proton exchange membrane fuel cells was made. Unlike AFCs, these fuel cells utilize a proton conducting polymer electrotyle instead of a liquid one. The hydrogen gas is delivered at the anode where it splits into protons (H^+) and electrons (e^-). A platinum catalyst is used for the splitting of the hydrogen gas. As shown in Figure 1.1, the protons formed at the anode are transferred to the cathode through the proton exchange membrane. The oxygen gas let in through the cathode reacts with these protons (H^+) and electrons to form water molecules. The electrons travel to the cathode through an external circuit. Contrary to the alkaline fuel cell membranes which allow the passage of hydroxyl ions, the proton exchange membranes allows the hydrogen ions to pass through.
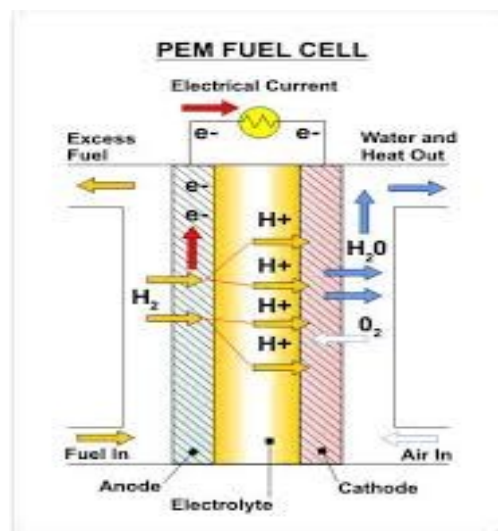
Figure 1.1 General schematic of a typical PEMFC [19]

The reactions and their corresponding electrochemical potentials are listed as follows:

Reaction at anode: $H_2 \rightarrow 2H^+ + 2e^-$ $E^o = 0$ V

Reaction at cathode: $2H^+ + 2e^- + 0.5O_2 \rightarrow H_2O$ $E^o = 1.229$ V

Overall reaction: $H_2 + 0.5O_2 \rightarrow H_2O$ $E^o = 1.229$ V
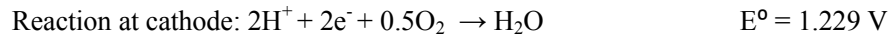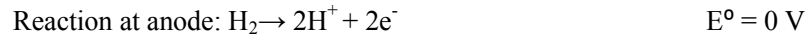
Although the PEMFC is highly efficient, it is a very expensive technology. The use of noble catalysts like platinum is very costly. Also, the use of platinum catalyst on the membrane causes carbon monoxide poisoning. The membrane is sensitive to metal ions (introduced by corrosion of bipolar plates) or contaminants in the fuel.

1.2.2 Direct Methanol fuel cells

This fuel cell is a recent invention in the year 1990 by Dr. Surya Prakash and Dr. George A Olah at the University of Southern California's Loker Hydrocarbon Research Institute. This fuel cell operates in the temperature range from room temperature to nearly 150°C or 200°C and uses methanol as the fuel. The purpose of this fuel cell is for portable applications where the efficiency is not that important, but employment of liquid fuel could boost the over-all energy density. This fuel cell can be classified as a sub-class of proton exchange membrane fuel cells since it also works on the transfer of protons through the membrane to the cathode where they react with oxygen to produce water. This water is consumed at the anode along with the methanol on platinum-based catalyst to produce protons, electrons and carbon dioxide. Methanol on the anode side is usually at low concentration(< 2M) because methanol in high concentrations has a tendency to diffuse through the membrane to the cathode where it is rapidly consumed by oxygen. DMFC shows similar problems as the PEMFCs. Use of platinum as a catalyst is not only costly

but also leads to a reduction in the cell voltage potential (as any methanol present in the cathode chamber will be oxidized). Also, during methanol oxidation reaction, carbon monoxide is formed, which adsorbs onto the platinum catalyst thereby reducing the reaction rate and efficiency of the cell.

1.2.3 Phosphoric acid fuel cell

This type of fuel cell was developed in the mid-1960s. It uses phosphoric acid saturated in a silicon carbide matrix as the electrolyte. These fuel cells use platinum as the catalyst. Just like the PEMFC, hydrogen gas splits up at the anode to give protons and electrons. The oxygen gas at the cathode reacts with these protons and electrons to form water. Unlike the aforementioned DMFCs, the PAFCs are tolerant to a high concentration of CO (around 1.5%) which increases the efficiency. Yet, this is true only in the case of temperatures as high as 150°C to 200°C. At lower temperatures, the CO poisoning is susceptible. Also, phosphoric acid is a poor ionic conductor at lower temperatures. These fuel cells are generally used for stationary power generators.

1.2.4 High-Temperature Fuel Cells

High-temperature fuel cells include solid oxides fuel cells (SOFCs) and molten carbonate fuel cells (MCFCs). They operate at a very high temperature typically between 600°C to 1000°C and do not require a platinum catalyst like majority of the fuel cells in use today. Due to the high temperature of operation of the fuel cells, the fuel is converted to hydrogen through internal reforming. One of the most attractive aspects of this type of fuel cell is the resistance to carbon monoxide poisoning. Instead, these fuel cells can use carbon oxides as fuel, thereby making the system attractive for fuelling with gases made from coal. A SOFC uses a ceramic electrolyte to transport the negative oxygen ion from

the cathode to anode. The electrolyte used in a MCFC comprises of molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix of beta-alumina solid electrolyte. Non-precious metals can be used as catalysts at the anode and cathode thereby reducing the cost of the entire system.

1.3 Renewed interest in Anion Exchange Membrane Fuel Cells

It is not certain that there is enough platinum in the world today to sustain the continued use of PEMFC's. Hence scientists all over the world are showing renewed interest in AEMFC's in development of solid anion exchange membranes unlike the liquid electrolyte used earlier for transport of hydroxyl ions from the cathode to anode. In this new design, the membrane plays the dual roles of separator and conductive medium (for hydroxyl ions only) between the anode and cathode. The membrane electrode assembly (MEA), sandwiches the solid membrane between the two electrodes, which include the catalyst layer and the gas diffusion layer. The reaction scheme for the solid electrolyte fuel cell is the same as for the liquid cell.

1.4 Operation of the anion exchange membrane fuel cell (AEMFC)

The mechanics of a traditional AEMFC (Figure 1.2) is simple to understand. Oxygen reduction takes place at the cathode and produces the hydroxyl ions which are the most important species in the anion exchange membrane fuel cell. These OH^- ions are transported to the anode through an anion exchange membrane where they combine with hydrogen gas to form water. The electrons generated at the anode during oxidation of hydrogen gas travel through an external circuit towards the cathode where they participate in the electrochemical reduction of oxygen.

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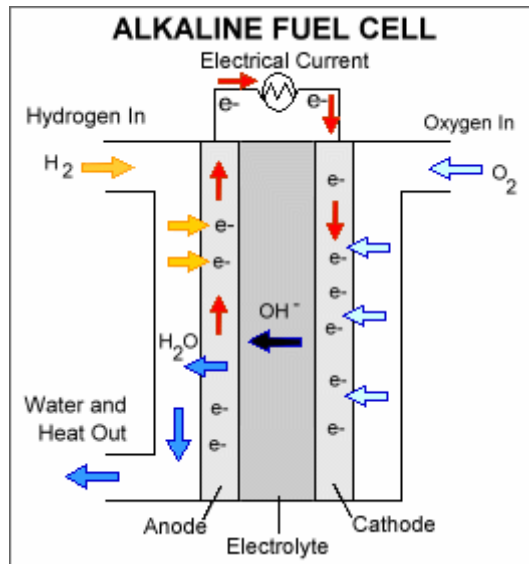
Figure 1.2 Anion Exchange Membrane Fuel Cell [19]

The half-cell and overall reaction are as follows:

At anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

At cathode: $0.5O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Overall: $H_2 + 0.5O_2 \rightarrow H_2O$
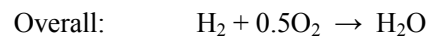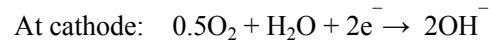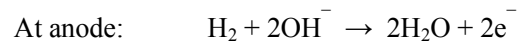
The role of an AEM is to conduct hydroxyl ions at very high rates from the cathode to anode. The AEM and its integration with the electrodes form the heart of the membrane electrode assembly in an alkaline fuel cell. If the transport of OH^- ions is not sufficiently high, and highly selective, then the membrane will not find any application in an AFC.

1.5 Membrane Electrode Assembly

The membrane electrode assembly (as shown in Figure 1.3) is the heart of a fuel cell. It is the core component of a fuel cell that produces electrons from the electrochemical

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reactions. It is composed of a polymer membrane sandwiched between the catalyst layers

and diffusion layers on either side. There are two approaches for applying the catalyst layer

for the MEA depending on which the configuration can be three layered or five layered.

One is the combination of the catalyst and diffusion layer that forms an electrode. This is

known as the five layered configuration. Another arrangement is coating of the catalyst

layer on the surface of polymer electrolyte membrane commonly referred as catalyst

coated membranes (CCM). The CCMs are then sandwiched between two gas diffusion

layers. This is typically known as a 3 layer membrane electrode assembly configuration.

Membrane electrode assembly depends mostly on catalyst, loading, size, shape, and type of

the gas diffusion layer.
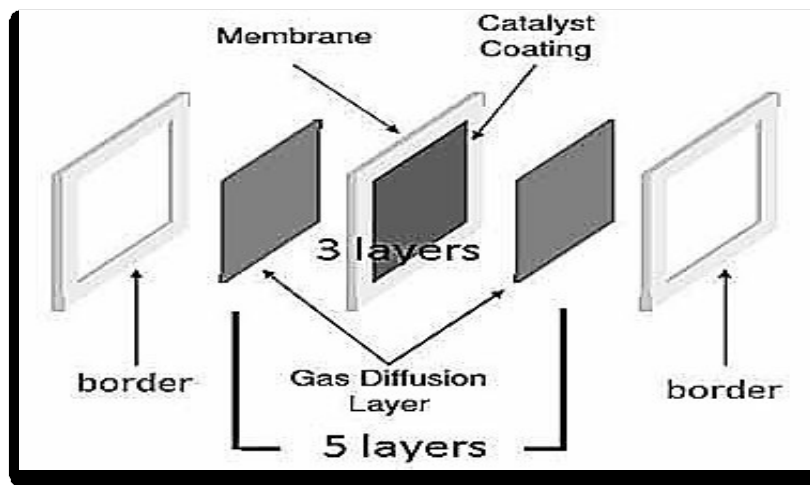
Figure 1.3 Membrane Electrode Assembly [19]

1.6 Type of Anion Exchange Membranes

The anion exchange membranes are primarily presented in 3 categories (Figure 1.4),

i.e., heterogeneous membranes, interpenetrating polymer networks, and homogeneous

membranes.
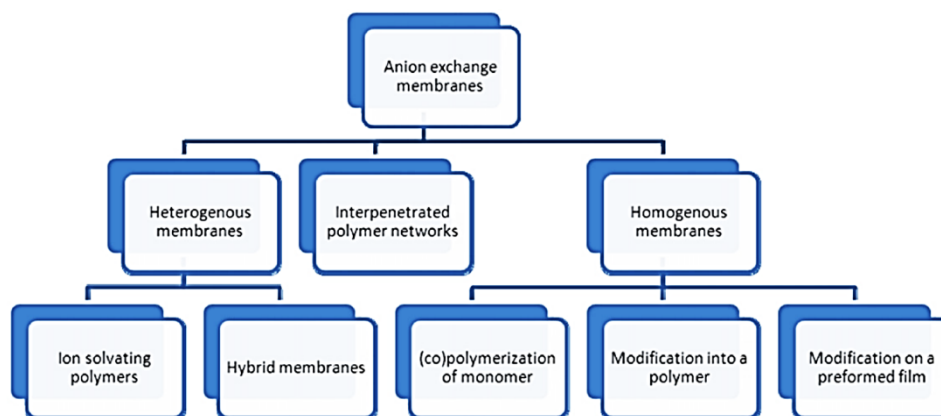
Figure1.4 Tree diagram of different alkaline anion exchange membranes [4]

1.6.1 Heterogeneous Membranes

The general definition of this type of membrane is an anion exchange material embedded in an inert compound. This type of membrane is further divided into two types of membranes depending on the nature of the inert compound, i.e., ion solvating membrane and hybrid membrane.

The ion solvating membrane has the inert compound in the form of a salt. They usually comprise of a matrix (water soluble polymer), a hydroxide salt (mostly KOH) and some plasticizer. The polymer matrix will contribute towards the mechanical properties, while the alkaline salt is responsible for the electrochemical properties and ionic conductivity of the anion exchange membrane. The ionic conductivity mostly depends on the interactions between the hydroxide salt and cations although mobility of amorphous polymer chains also plays an important part. Ionic conductivity of the membrane is capacitated through the binding energy between the cations and anions and the segmental

motion of the polymer hosts. The polymer property is further increased if the polymer backbone used is highly flexible and possesses low glass transition temperature [4][5].

Meanwhile, the hybrid membrane has the inert compound in the form of an inorganic material. These types of membranes are usually composed of organic and inorganic segments. The organic part provides the electrochemical properties and the inorganic part (silane or siloxane) contributes to the mechanical properties of the membrane. These membranes are mostly formed through the sol-gel process; although, other methods like intercalation, blending, in-situ polymerization and molecular self-assembly can also be used [6],[7].

1.6.2 Interpenetrating Polymer Network

The second type of AEM used is the Interpenetrating Polymer Network (IPN) which is a combination of two polymers in network form of which at least one polymer is synthesized or cross-linked in the immediate presence of the other without any covalent bonds between them. One of the polymers is conductive while the other is hydrophobic (therefore non-swelling upon being in contact with water). The membranes using these polymer blends usually swell in solvents without dissolving in them. Most of the IPN's are heterogeneous systems. They possess an excellent combination of electrochemical and mechanical properties. The hydrophobic polymer usually provides good thermal, chemical and mechanical properties while the conductive polymer functions in the transport of anions. Special properties are obtained due to the interlocking of polymer chains. The IPN exhibits a low electrical resistance due to the presence of the polyelectrolyte, good mechanical strength, chemical stability and durability (due to stable polymer matrix) at a reasonable cost. Although, there is a slow extraction taking place over time since the

polyelectrolyte is not attached to the other polymer. This leads to a loss in conductivity and ion exchange capacity [8].

1.6.3 Homogeneous Membrane

Homogeneous Membranes are among the most highly studied membranes. Extensive research has been carried out on this type of membranes since 1970. These comprise of anion exchanging material forming one phase system. The cationic charges are covalently bound to the polymer backbone as sidegroups. To maintain the electro-neutrality of the polymer a mobile counter ion is associated with each ionic functional group. The stability of the electrolyte depends on the alkalinity as well as temperature of media. The homogeneous membranes are synthesized through 3 ways-

a) Polycondensation of a monomer containing a moiety that can be turned into anion exchange groups, which can be copolymerized with non-functionalized monomers and eventually cast into anion exchange membranes.

b) Introduction of cationic characters on a preformed film either directly by grafting of a functionalized monomer or indirectly by grafting a non-functional monomer followed by a functionalization reaction.

c) Introduction of cationic moieties by chemical modification into a polymer (or polymer blends), followed by dissolution of a polymer and casting it into a film [7],[9] .

1.7 Major Anion Exchange Membrane Systems

Table 1.1 Well-developed Anion Exchange Membrane Systems
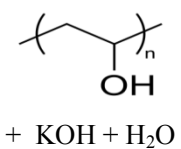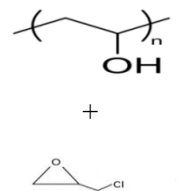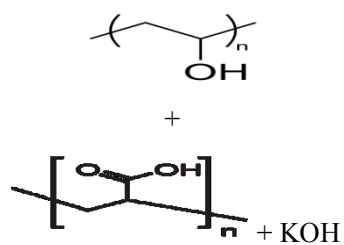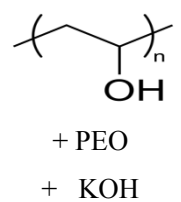
Type of Membrane	Membrane System	Scope for Performance
Heterogeneous Ion-Solvating Membrane	Polyether Oxide/KOH/Water	Good ionic conductivity (10^{-3} S cm^{-1}). Although with increasing salt concentration, PEO tends to crystallize resulting in a decrease in ionic conductivity
	 + KOH + H$_2$O	Chemical Stability, hydrophilicity, Ionic conductivity nearly 0.047 S cm^{-1}. Although, membrane gets damaged with use of high conc. Of KOH
	+	Conductivity as high as 0.02 S cm^{-1}, amorphous region increased
	+ + KOH	Ionic Conductivity of 0.30 S cm^{-1} , excellent mechanical Strength and ductility, Wide temperature range(25-90°C)
	+ PEO + KOH	When PVA is greater than 50%, electrolyte converts to amorphous phase, ionic conductivity increases to 0.01 S cm^{-1}

Table 1.1 Continued
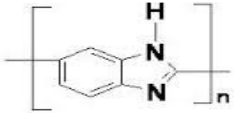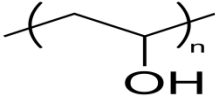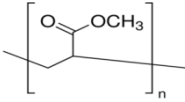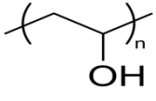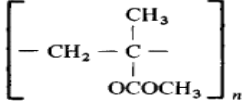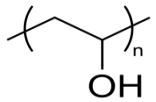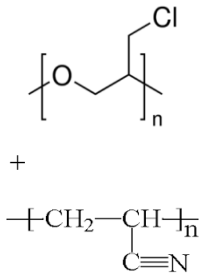
	+ KOH	Thermal/chemical stability, water insoluble, ionic conductivity nearly 0.1 S cm^{-1} at KOH conc. as high as 6M.
Heterogeneous - Hybrid	+ ZrO$_2$ + KOH	Excellent ionic transport (0.98- 0.99), Conductivity (0.267 S cm^{-1}), high thermal properties
	+ SiO$_2$	Anion exchange capacity as high as 0.19 X 10^{-3} mol/g
	+ TiO$_2$ + KOH + H$_2$O	Enhanced chemical property, ionic conductivity 0.170 S cm^{-1}, TiO$_2$ served as solid plasticizer
	+ SiO$_2$	High Anion Exchange capacity (0.19-1.20 X 10^{-3} mol/g)
	PPO-Si(OCH$_3$)$_3$	OH$^-$ conductivity as high as0.008 S cm^{-1} with favourable tensile strength
Interpenetrating network	+ Cationic polyelectrolyte like polyethyleneimine	Best ion exchange capacities obtained is nearly 0.0006- 0.0007 eq/g

Table 1.1 continued

		High ionic conductivity of 0.002 S cm^{-1} with good mechanical properties
Homogeneous Membrane	Styrene based: Styrene +Chloromethyl ether/bischloromethyl ether (for chloromethylation) + Quaternization by diethyl-2-hydroxyethyl amine	Ionic conductivity nearly 0.001 S cm^{-1} Excellent mechanical strength, low electrical resistance yet exhaustive method of preparation
	Epichlorohydrin based: - Add allylglycidyl ether (c/s linking) + 2 cyclic diamines - Polyether + DABCO / DABCO + Trimethyl ammine	Ionic conductivity nearly 0.02 S cm^{-1}
	PP based Chlorinated PP+ Ethylene diamine	Ionic conductivity nearly 0.004 S cm^{-1}
	PVA based PVA + Quaternary Ammonium(as charge carriers)+ Glutaraldehyde (c/s linking)	Ionic conductivity nearly 0.007 S cm^{-1}
	Chitosan based c/s linked quaternized PVA + Chitosan blend + trimethyl ammonium chloride cross-linked by glutaraldehyde	Ionic conductivity nearly 0.01 S cm^{-1}
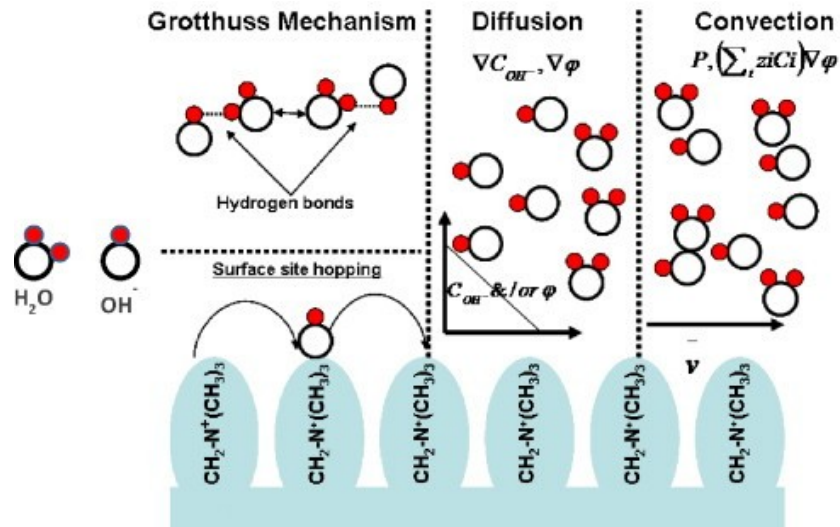
Figure 1.5 Comparison of different mechanisms for hydroxyl ion transportation [4].

1.8 Transportation mechanism of Hydroxyl ions through alkaline membrane

Due to the early developmental stages of the alkaline anion exchange membrane fuel cells, the transportation mechanism of the hydroxyl ions is not very clear. There are various theories on the transportation mechanism (as shown in Figure 1.5) which are derived based on the understanding of transport of ions in PEMFCs.

1.8.1 Grotthuss Mechanism

One of the most dominant mechanism theories is the Grotthuss mechanism. Majority of the OH^- ions exhibit Grotthuss behavior in aqueous solution (comparable to protons). The mechanism however is different than transfer of protons. Hydroxyl ions diffuse through the hydrogen-bonded network of water molecules through cleavage of covalent bonds. Many scientists claim that the hydroxyl anions tend to have stable solvation shells that re-organize the solvent molecules and disturb the hydrogen bond network (whereas the hydrogen ions are naturally integrated into the hydrogen bonding network of water). This

theory explains the mechanism of transport of the hydroxyl ions through membrane along a chain of water molecules through formation and breaking of the hydrogen bond. Various theories have proposed that the movement of the hydrated hydroxyl ion is accompanied a hyper coordinating water molecule [10]. The arrival of an electron-donating water molecule leads to the re-arrangements in the hydrogen bond, reorganization, accompanied by hydrogen ion transfer, and the formation of fully tetrahedrally co-ordinated water molecule.

1.8.2 Diffusion Transport

Hydroxyl ion transport in this type of mechanism is through diffusion which takes place in the presence of concentration or electrical potential gradient. A notable feature of this type of transport is that it results in a mass transport without requiring bulk motion.

1.8.3 Convection

Convection is one of the dominant ways through which the hydroxyl ion transportation is proposed to take place across the membrane [11],[12]. The hydroxide ions moving across the membrane drag water molecules with them thus generating a convective flow of water molecules within the membrane.

1.9 Transport Properties

Even though the transport coefficients for protons and hydroxides are equal and the dominant mechanisms for transport through the membrane are same, there are fundamental discrepancies between the PEM and AEM conductivities. According to Grew and Chiu [13], these discrepancies may arise due to insufficient OH^- ion dissociation and solvation, morphology of the structure, interactions between the OH^- ions in solution [14], [15].

Another reason for the discrepancy in ionic conductivity may be due to contact with air during measurement. When the cell is not completely isolated and air penetrates the hydroxyl ions may react with CO_2 from the air and convert to carbonates/ bicarbonates which will lead to decrease in ionic conductivity [15]

1.10 Fuel Cell performance losses

During operation, fuel cell efficiency could continuously decrease due to a couple of reasons. Prime amongst them is the activation losses. To reduce these losses, roughness in the electrodes has to be created and catalysts have to be employed. Secondly, fuel cell suffers losses due to fuel cross-over or the internal shorting of the fuel cell. It is caused due to small molecules like hydrogen or methanol which permeate through the polymer membrane. The internal current is calculated as the product of gas usage, number of electrons and Faraday's Constant. The efficiency of the fuel cell is also majorly lost due to Ohmicresistance and can be controlled by tailoring the thickness of the membrane. Lastly, another major reason for loss of efficiency is mass transport or concentration losses.

1.11 Scope of Work

Much work reported in the literature has been done on the development of hybrid membranes using different type of particles like ZrO_2, TiO_2 etc. In this thesis we are trying to explore the impact of another type of inorganic particle (montmorillonite) on a certain guanidinium based polymer material which has high ionic conductivity due to high basicity and resonating structure. The montmorillonite by themselves are known to possess high mechanical properties. The incorporation of these moieties into a guanidinium based polymer was done with the intention of producing a membrane with good electrochemical properties along with excellent mechanical properties.

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This thesis focuses on identifying how the properties of the material such as mechanical stability, chemical stability, ionic conductivity and texture changes on addition of the clay in different proportions. Specifically, polymer materials with different percentage of clay (0 wt%, 1 wt%, 3 wt%) clay were prepared and cast into membranes. Their properties were thoroughly investigated. Using the FTIR, Raman, tensile Testing, Ionic conductivity testing, we characterized the membranes with different percentages of clay for the aforementioned properties.

Chapter 2

Design Rationale and Experimental Details

2.1 Desirable Properties of Membranes for Fuel Cells

For a membrane to function with maximum efficiency, it must fulfill certain criteria. Some of the essentialities for good functioning of the membrane are:

i. Low resistance – This ensures the low electrical resistance which the membrane offers to the flow of ions. The cross-linked structure having guanidinium groups as the main chain in the structure will enhance the membrane stability and increase hydroxide ion conductivity. This polymer structure will also suppress chemical degradation due to the chemical attack of hydroxide ions (either by Hoffman elimination or direct nucleophilic substitution).

ii. High permselectivity – Referring to the preferential permeation of certain ionic species (OH$^-$ in this case) through the anion exchange membrane with the retention of ions of the opposite charge.

iii. High Ion Exchange Capacity- Referring to the number of ionic sites which participate in the exchange process. High ion exchange capacity (IEC) is desirable to achieve a good conductivity. Yet, as we increase the IEC, a fully hydrated membrane will result in a high degree of dimensional swelling causing loss of mechanical properties. Brittleness will result when the membrane is partially or fully dry; therefore, a compromise between high IECs and mechanical strength needs to be achieved.

iv. Low degree of dimensional swelling- Swelling in this context implies the changes in shape of the membrane on removal from the activation solution. The stability of the membrane reduces and the membrane becomes weak with the increase in swelling. Membranes which swell have a tendency to form cracks when drying out of any system. Swelling here does not refer to the water uptake from the solution.

v. Thickness- The membrane should be as thin as possible. Yet, a very thin membrane is not usually mechanically strong enough to be used in a fuel cell.

2.2 The Proposed Polymer Clay Interaction

(Guanidinium based polymer)   +   (Montmorillonite Clay)
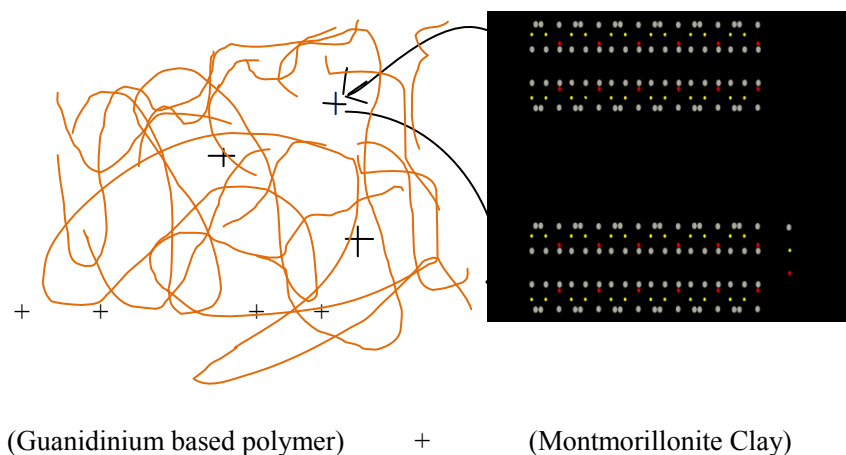
Figure 2.1 The Proposed polymer-clay Interaction

As demonstrated in the reaction schematics in Figure 2.1, the main idea behind the use of montmorillonite in the synthesis of the polymer is to induce physical cross-linking between the fixed opposite charges in the clay and the guanidinium polymer.A crosslinked

polymer offers obvious advantages like stability of the membrane and decrease in the swell ratio, while IECs of the polymer itself could be independently controlled.

The pure guanidinium polymer we have synthesized is known to possess fixed strong guanidinium groups in its structure. The clay is known to carry strong anion exchanging groups in its structure. An ion exchange between the organic polymer and the inorganic clay particles would create some bonding between the two species and integrate the structure, through the electrostatic interactions. The integration of the structure will further contribute towards higher mechanical properties of the membrane like the load carrying capacity, and ultimately the tensile strength. Inorganic filler like montmorillonite is widely known to increase the mechanical properties of the composite system as well as improve the thermal stability. Also, due to the integration of the structure, the dimensional stability of the structure is expected to improve (due to the ability of the clay particles to hold the polymer more firmly).

Depending on the nature of the components used, the method used for the preparation, and the reaction conditions, three types of nanocomposite structures could be obtained. If the polymer used is unable to intercalate between the silicate sheets in the clay, a phase separated micro-composite is obtained whose properties will stay in the same range as a traditional micro-composite. The second type of composite is obtained when a single extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating layers from both the species. This is known as the intercalated structure. The third type of structure known as exfoliated structure is obtained where the silicate layers are uniformly dispersed in the polymer matrix.

2.3 Background of the reactants

2.3.1 Montmorillonite (Clay)

Montmorillonite [18],[19] (Figure 2.2) was discovered in 1847 in France and is composed of inorganic particles belonging to the 2:1 (two tetrahedral sheets sandwiching one octahedral sheet) phyllosilicate group of minerals.It is specifically a subclass of Smectite group.

Figure 2.2 Montmorillonite clay [19]
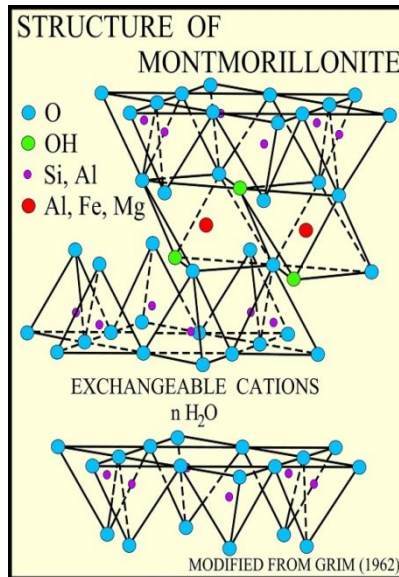
Figure 2.3 Structural chemistry of montmorillonite [19]

The typical structure of montmorillonite (Figure 2.3) specifically comprises of aluminium or magnesium hydroxide octahedral sheet sandwiched between two silicon oxide tetrahedral sheets. It is a di-octahedral clay of smectite group and composed of stacked alumino-silicate layers. Chemically the structure of this clay is $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. The Na^+/Ca^+ ions act as exchangeable cations.

The clay is layered in stacks and the gaps created between these layers are known as galleries. The water content in montmorillonite varies and the clay increases greatly in volume when it absorbs water. The inorganic clay particles have the ability to disperse into the polymer. This dispersion usually occurs in cases when the interaction between the organic (polymer) and inorganic particles (clay) is strong. The interaction can be increased through the modification of the surface chemistry through ion exchange reactions.

Additionally, we can observe that if the weight of polymer being formed is high there is more interaction of the polymer with the clay particles.

The addition of clay to the polymer could cause an increase in the overall swelling ratio. There is an increase in the interlayer spacing between the constituent elements. This property is useful especially when we want to remove the polymer from the flask after synthesis. The clay will swell highly on addition of water thus making it easy to remove the polymer from the flask.

The design rationale primarily is based on the following three reasons:

1. Firstly, these montmorillonite particles have a very high mechanical strength. The use of clay nanolayers in polymers, because of their strong interaction and the formed physical crosslinking sites, can improve the tensile modulus, stiffness, and toughness of the hybrid material. Due to the coupling between the polymer matrix and the clay particles, the applied stress is shared which can give the material higher mechanical properties.

2. Secondly, the impermeable montmorillonite clay layers enhance the barrier properties of the membrane. Gas permeability in the anion exchange membrane is estimated to decrease even with small loadings of clay in the polymer. A good membrane will show higher conductivity of hydroxyl ions, lower permeability of hydrogen and oxygen gases.

3. Lastly, the montmorillonite will increase the heat resistance of the system when compared to pristine polymers. We can use a higher working temperature with the anion exchange membrane when blended with clay.

A major drawback with addition of clay may be the increase in brittleness or opacity especially at higher fractions.

2.3.2 Hexamethylenediamine

Hexamethylenediamine (HMDA, Figure 2.4) can be defined as a hexamethylene hydrocarbon terminated by an amine group on both ends. It is an organic compound in the form of white/colourless crystalline powder with the general formula $H_2N\text{-}(CH_2)_6\text{-}H_2N$ and a molecular weight of 116.21g/mol. The boiling point of HMDA is nearly 201°C at atmospheric pressure. HMDA is found to be readily soluble in water.

$$H_2N\diagdown\diagup\diagdown\diagup\diagdown\diagup NH_2$$

Figure 2.4 Chemical structure of hexamethylenediammine

2.3.3 Guanidinium Hydrochloride

The structure of this compound (Figure 2.5) comprises of network of guanidinium cations and chloride anions. Its molecular formula is CH_6ClN_3 and molecular mass is 95.53g/mole. It has a melting point of around 182.3°C and is highly soluble in water. The guanidine hydrochloride exists in a solid state and needs to be heated to change it into a liquid thereby making it feasible for use. The guanidinium based polymer was chosen since it is known to obtain conductivity as high as 84.7m S cm^{-1} as well as enhanced the mechanical stability [23] when it was reinforced in an expanded porous PTFE substrate, as demonstrated by our prior study. We tried to understand how the properties would change

when the guanidinium based polymer is used as a part of the main chain when incorporated with an inorganic filler.
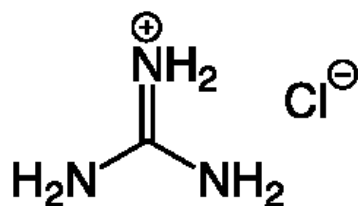
Figure 2.5 Chemical structure of guanidinium hydrochloride

2.4 Synthesis of the Guanidinium Based Polymer

The synthesis route for the Guanidinium based polymer was derived from references [16],[17],[23]. The condensation reaction between GHCl and HMDA was used for the formation of guanidinium based polymer. Equimolar quantities of both the reactants were added into a three necked flask. The first neck held a reflux condenser to allow for the dissipation of the heat produced during the polymerization process. The reaction temperature was as high as 180°C which makes the use of reflux condenser necessary for easy removal of heat. The second neck held a mechanical stirrer which facilitates the mixing and managing viscosity increase encountered during polymerization. A magnetic stirrer was also attempted to control the viscosity in place of the mechanical stirrer. However, in this arrangement the magnetic stirrer was not able to overcome the high viscosity after a certain time and stopped stirring. The third neck carried a thermocouple for the purpose of maintaining constant temperature. All the three necks were closed with the help of rubber corks to prevent the fumes from going out of the flask.

Figure 2.6 Experimental setup for synthesis of the polymer

The mixture was stirred at 100°C for 1 h, 140°C for 4 h and 180°C for 4 h as shown

in an experimental setup in Figure 2.6. A PID temperature controller was used for the

temperature control. The temperature was increased slowly to counter the increase in

viscosity with temperature. It was found that if the temperature increase was gradual we

could get a high molecular weight, highly cross-linked polymer. Alternatively, if the

temperature of the mixture was not high enough, or the time for which the reaction took

place is not optimum, a polymer with a very low molecular weight would be obtained.

Contrarily, decomposition and burning of the polymer may take place if the temperature is

not well controlled. Hence, we need to maintain a balance between the temperature and

time for obtaining a polymer with high molecular weight. The polymer solution formed

was allowed to cool down naturally before its extraction from the flask.

The same procedure was followed for synthesis of the hybrid polymers containing clay. We added clay (montmorillonite) in 1% or 3% by weight as required in addition to the reactants mentioned earlier. The set-up of the experiment was the same as the one used for synthesis of the pristine polymer. A low rate of reaction was beneficial to allow more clay particles to interact with the polymer and form the desired physical cross-linking sites between the polymer and clay. Hence, the temperature was increased more gradually. If the temperature is increased suddenly, the viscosity will increase rapidly and decrease the reaction time (thereby reducing the possibility of higher number of clay particles interacting).

2.5 Extraction of the Polymer

Extracting the polymer from the three necked flask is a big challenge. The polymer starts cooling down rapidly as soon as the heat supply is off. When the polymer cools it starts to harden. Removing this hardened mass from the beaker is a challenge (as shown in Figure 2.7).

Figure 2.7 Polymer after synthesis

Primary method of removal of the polymer from the flask was the addition of water to the polymer while temperature was still high. The polymer was highly hydrophilic. On addition of water, the polymer tends to swell up (as shown in Figure 2.8). Due to this, it becomes easier to remove the polymer from the flask. The higher the percentage of clay added to the polymer, the higher was the degree of swelling observed. We kept the synthesized polymer in DI water for a few hours (nearly 2h) to allow the effortless extraction and removal from the flask. The polymer can also be removed from the flask by dissolution in a suitable solvent. Methanol was found to dissolve in the polymer to a good extent with the help of external mechanical stirring and simultaneous heating on a hot plate.

Another option for removal of the polymer from the flask was to scoop it out as soon as the polymer is synthesized. Yet, this is the most inconvenient method since the polymer tends to harden in the air inside the flask itself when we try to scoop it out. Another disadvantage of this method is that even if we are successful in scooping out a certain amount of polymer, the entire amount synthesized cannot be extracted from the flask. Also, as polymer tends to get disoriented and we cannot use this tangled, hard mass for casting a thin film membrane.
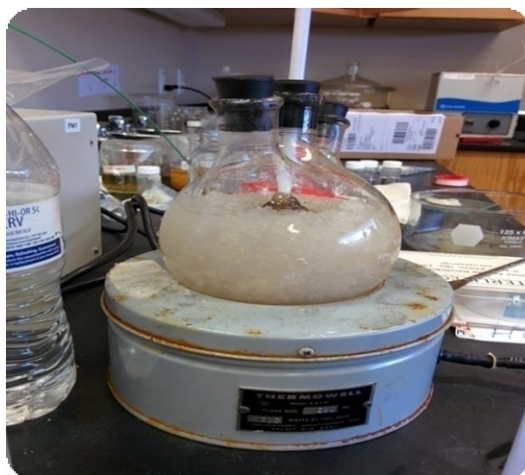
Figure 2.8 Polymer after swelling with water

General 2.6 General Sample Calculations

2.6.1 Synthesis of a pure guanidinium polymer

Weight of Guanidinium Hydrochloride taken = 30g

→1 Mole of Guanidinium Hydrochloride =95.53 g

→30 g of Guanidinium Hydrochochloride = 0.31 Moles

→1 Mole of HexamethyleneDiamine = 116.21g

→0.31 Mole of HexamethyleneDiamine = 36.49g

Hence, total weight of ingredients = 30 + 36.49 = 66.49g

2.6.2 Synthesis of polymer with 1% clay

Weight % = weight of solute/(weight of solute + weight of solvent)

$$1= \frac{x}{x+66.49}X100$$

x + 66.49 = 100x

99x = 66.49

x = 0.67g (weight of clay)

2.6.3 Synthesis of polymer with 3% clay

Weight % = weight of solute/(weight of solute + weight of solvent)

$$3= \frac{x}{x+66.49}X\ 100$$

3x + 199.47 = 100x

97x = 199.47

x = 2.05g (weight of clay)

2.7 Casting of the Membrane

The polymer synthesized was cast into membrane in two ways: direct evaporation and using a doctor blade.

2.7.1 Direct Evaporation

This method involved casting the membrane directly with the polymer dissolved in the solvent without any treatment for extraction of solvent. The polymer was cast into a flat glass petri-dish and kept in an oven for around 10 h. The temperature was gradually increased in steps until 90°C such that the solvent (water in this case) evaporated from the polymer as uniformly and gradually as possible. The membrane starts setting due to the heat provided by the oven. We have to make sure the polymer did not dry too much and become too hard to remove from the petri-dish. The petri-dish was then transferred into a vacuum oven for two purposes, i.e., any remaining traces of moisture were removed. Secondly, the membrane is strengthened mechanically by heat treatment in the vacuum oven.

The disadvantage of using this technique is that we usually do not get a membrane of uniform thickness due to un-uniform rate of evaporation from different parts of the cast membrane. Also, for the same reason, the film tends to be hard in one part than the other.

2.7.2 Method of Using Doctor Blade

The method involved is similar to the evaporation method aforementioned except for the technique of casting the membrane. We used a doctor blade to cast the membrane of desired thickness onto a glass plate. In this method the amount of solvent used to extract the polymer from the flask was very little. Hence, the initial heat treatment in the oven for

32

6 hours was used effectively to set the membrane after which the membrane is subjected to treatment in the vacuum oven for around 7 hours. Figure 2.9 shows the evaporation of the water from the polymer solution for ease in casting the polymer membrane. In this method the membrane we obtain has a much higher strength primarily due to majority of heat being utilized for the cementing of the membrane rather than evaporation of solvent. This method is preferred for two reasons. Firstly, we obtain a membrane which was made purely of polymeric material and devoid of any traces of a solvent. Secondly, we can obtain a membrane of the desired uniform thickness without the thickness variation due to uneven rate of evaporation.

Figure 2.9 Vaporization of solvent from polymer solution

2.8 Membrane Removal

Removal of the polymer membrane from the glass plate is a delicate task which requires a lot of skill and patience. A small sharp blade was used to remove the membrane

from the glass plate. Three situations were generally encountered during membrane formation:

a) Overheating: After the heat treatment, the membrane has hardened firmly on to the glass plate. If it has been hardened beyond a certain limit, then it will tend to break as we try to remove it. It becomes too brittle and does not come off as a single piece. Deficiencies like pin-holes are encountered due to overheating or low toughness of the specimen.

b) Under-heating: If it has not received enough heat treatment then it will be very sticky and tend to stick to the blade. The polymer has not set properly and cemented firmly in this case to be able to stand on its own as a membrane. When we try to take out such a membrane from the glass plate it usually distorts the specimen. Usually water bubbles are observed due to incomplete loss of water during heat treatment in such cases.

c) Precise Heating: The most desirable scenario is one where the polymer material receives precise amount of heat treatment. Such membranes are generally mechanically strong to stand on their own as well as soft enough to come off the glass plate easily. The polymeric mass will not be sticky in this case and will not disorient or break in the process of removal.

2.9 Membrane modification through heat treatment

The polymer membranes are subjected to heat treatment after drying for the sole purpose of strengthening the membrane. Heat treatment of the membrane causes the chains to be packed together (forming crystalline polymers, thereby decreasing the plasticity of the membrane) and increasing the compactness of the membrane. The most important advantage of heat treating a polymer membrane is the increase in the density of the

polymer matrix. A higher density implies a lower value of the free volume and improvement in the packaging of the polymer chains. Compared to the as-cast membranes, the heat treated membrane is known to show higher density (and thereby having a low fractional free volume).

Heat treatment tends to increase the overall mechanical and chemical stability of the membrane. Another advantage of heat treatment is the reduction in the intra-membrane layer delamination.

2.10 Activation of the Membrane

The membrane which was mechanically strong was activated by putting it inside 1 M KOH solution for nearly 48 h to allow sufficient time for hydroxide ion to be exchanged and functionalization of membrane [1]. KOH solution is chosen for the activation of the membranes since it possesses one of the highest alkalinity among all solutions available as well as highly soluble in water.

The membrane was then washed with and kept in DI water for another 24 h, then extracted and dried by wiping it with a soft tissue. The membrane was thus activated and ready to be tested for different properties. We shall discuss and compare the properties of membranes with no clay, 1% clay and 3% clay in later chapters.

Chapter 3

Characterization, Results & Discussion

The characterization of a hybrid membrane is intimately related to two parameters, namely the polymer matrix and the nature and concentration of cationic charges. In case of hybrid membranes mostly the organic polymer matrix is responsible for the electrochemical properties are responsible for the anion exchange capacity, transport number, and ionic conductivity. While, the inorganic particles like montmorillonite are responsible for the mechanical property of the membrane. [4].

To confirm the correct incorporation of the clay into the polymer matrix, we employed Fourier Transform Infrared Spectroscopy and the Raman Spectroscopy. The peaks appearing are characterized for specific bonds using the wavelength - absorption/transmission frequencies data as available widely in literature.

The mechanical strength of the membrane is calculated using the tensile testing to measure properties like toughness, tensile strength, yield Strength. We want to understand how these properties vary with different proportions of clay induced into the polymer. While, the Ionic conductivity was tested using the electrochemical Impedence Spectroscopy to measure how the conductivity in the polymer varies with increase in the percentage of clay.

The stability of the membrane is one of the most important factors in fuel cell operation. It is the evaluation of resistance of the membrane to highly alkaline solutions. In this study, the dry membrane was subject to a concentrated solution of 1 M KOH for a certain time. After exposure, the sample was visually inspected and compared with the dry un-activated membrane for any change in the physical, mechanical properties. Usually, a

membrane will show sign of mechanical failure on exposure to KOH and water. It is essential for the membrane to have good stability to withstand the membrane electrode assembly fabrication process and the compression in a fuel cell stack as it is the weakest component in a fuel cell [20].

3.1 Raman Spectroscopy

Most of the interactions between the photons and the molecules of the sample are elastic. That is, the photons on interaction with the sample molecules are scattered without change in energy or frequency. A small amount of photons on interaction with the sample molecules are emitted with an energy/frequency which is higher or lower than the energy/frequency of the incoming photons due to the tendency of sample molecules to give energy to the incoming photons [19]. If the final vibrational state of the molecules is less energetic than the initial state, then the inelastically scattered photon will be shifted to a higher frequency, and this is designated as an anti-Stokes shift (Figure 3.1). This technique offers detailed sample characterization by probing individual chemical bond vibrations in the sample to characterize the composition of the system.
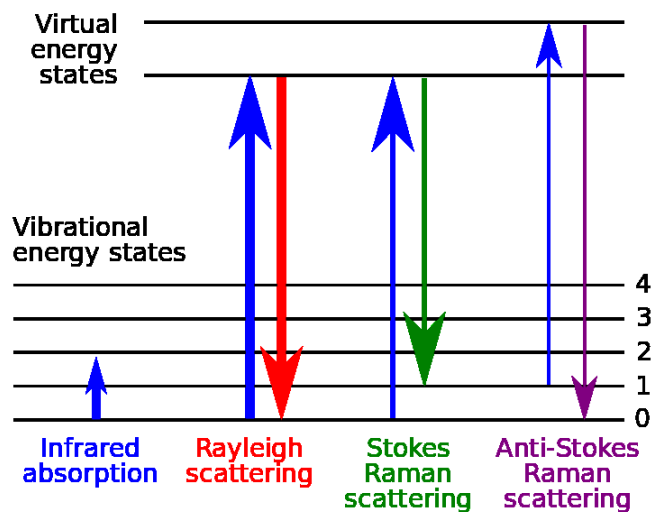
Figure 3.1 Pictorial representation of the Raman Scattering [19]

3.1.1 Variation in Raman Spectra on addition of clay

A thermo scientific DXR microscope with a 780 nm filter was used for carrying out Raman spectroscopy study. The OMNIC software was used to collect dispersive spectra. The full range for the laser source is from 450-3396 cm^{-1}. The number of scans (32) and the photobleaching time (4 minutes) decided the time required for the testing. A pinhole sized small and sharp edged aperture was selected to obtain a good depth of field. All the specimen samples tested were kept as dry as possible as a precautionary measure to obtain wavelengths corresponding to the polymer only and not of the solvent. Raman testing is not destructive to the polymer sample unless a laser of too much power is focused on a very small area for a very long time. Figure 3.2 gives us Raman spectra of specimens loaded with different proportion of clay. The characteristic Raman peaks and the corresponding chemical groups are listed in Table 3.1.
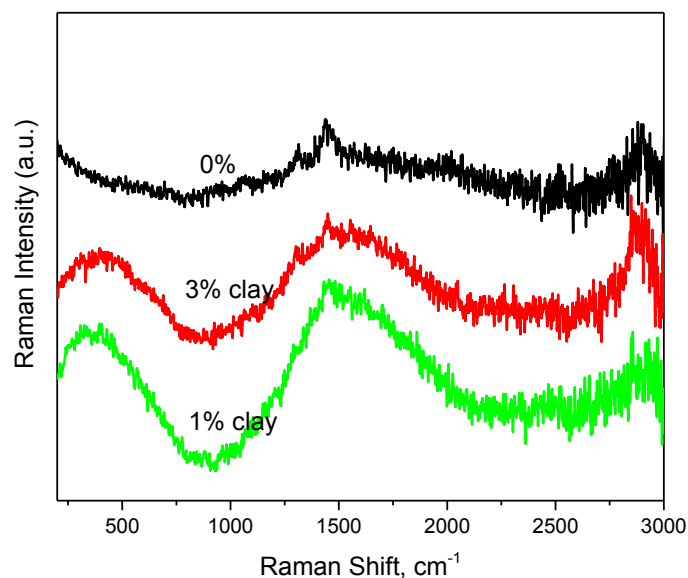
Figure 3.2 Raman Spectra with varied proportion of clay

Table 3.1 Different peaks labeled according to Raman Shift

Group	Raman Shift cm^{-1}
Aliphatic C-H	2910
-CH$_2$	1450
Si-O	470

In agreement with the literature [4], Figure 3.2 clearly indicates the peaks for montmorillonite against the underlying guanidine based polymer. The peak at 2910 cm^{-1} denotes aliphatic C-H stretching band. The peak at 1450 cm^{-1} is due to the bending vibrations of the –CH$_2$ group on the alkyl chains. The peak at 470 cm^{-1} corresponds to the Al-O-Si vibrations from the montmorillonite clay. This peak is absent from the pure guanidinium polymer due to the absence of the Al-O-Si group. As we can observe, this

peak intensity increases with the addition of clay, i.e., the peak for polymer with one percent clay shows a lesser intensity than the polymer with three percent clay. The peak intensity can be attributed to the difference in molecular weight of the sample.

Table 3.2 Variation in peak intensity with proportion of clay

Wave Number	% Clay	Intensity
470	0%	4
	1%	9
	3%	13
1500	0%	9
	1%	12
	3%	15

Table 3.2 and Figure 3.3 show the peak intensity for samples with different amount of clay. Here, the peak intensity ratio (at 520 cm^{-1} and at 1500cm^{-1}) was calculated:

0% clay: 4/9 = 0.44

1% clay: 9/12 =0.75

3% clay: 13/15= 0.86

This indicates an almost linear relationship between the peak intensity ratio and the clay weight fraction, indicating uniformly distributed clay in the polymer matrix.
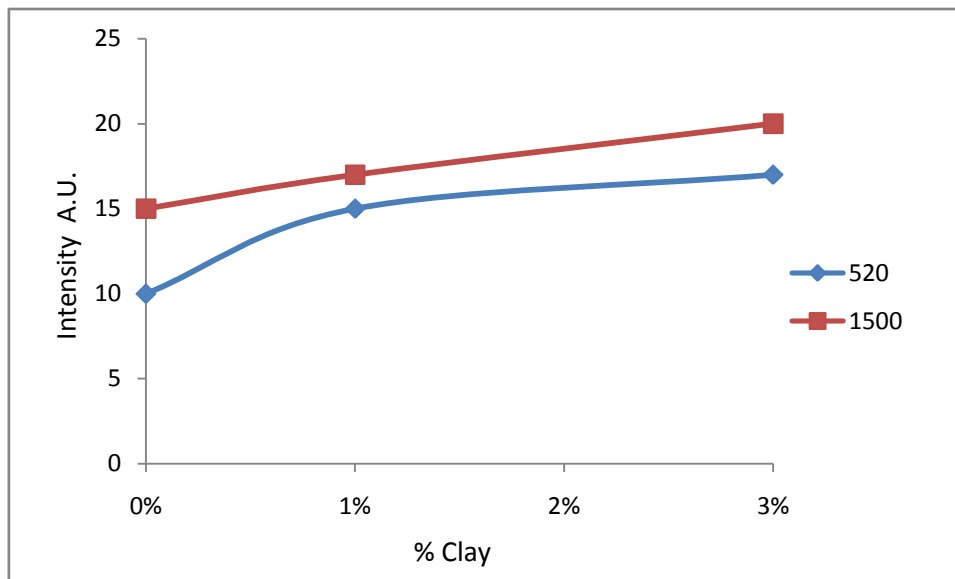
Figure 3.3 Variation of peak intensity for samples with different amount of clay

3.2 Fourier Transform Infrared Spectroscopy

FTIR is widely used in the confirmation of proper incorporation of clay moieties inside the polymer substrate. When exposed to infrared radiation, the sample molecules selectively absorb radiation of specific wavelength, causing change in dipole moment. Hence, vibration energy levels of sample molecules transfer from the ground state to excited state. The number of absorption/transmission peaks and the intensity of these peaks are related to the change in dipole moment and possibility of transition of energy levels.

The FTIR spectra of the polymer samples were obtained on the thermo-electron corporation Nicolet 6700 machine. The range used for this experiment was between1000-4000 cm^{-1}. The number of scans used was 32.
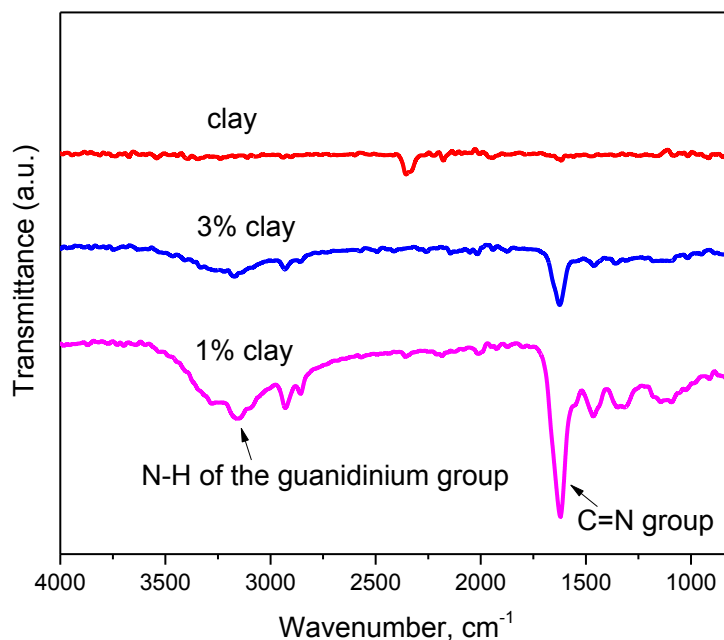
Figure 3.4 FTIR spectra comparison of clay and the hybrid membranes with different composition

Comparing the FTIR spectra for the clay and clay incorporated guanidinium polymer membranes (as shown in Figure 3.4), in the range of the scanned wave number, two major peaks are observed for the clay induced polymer membrane at 1630 cm^{-1} and 3320 cm^{-1}. The peak at 1630 cm^{-1} corresponds to C=N vibration from guanidine groups [23], while the one around 3320 cm^{-1} corresponds to the stretching vibration from N-H bond in the polymer [23]. The FTIR spectra for the clay do not show any peaks from the polymer, except a small one at around 529 cm^{-1} (Al-O-Si bending vibrations, not shown) [27]. The result shows that incorporation of the clay into the polymer matrix may not impact the functional groups of the membrane materials.

3.3 Mechanical testing

Tensile testing is by far the most common methodology for the measurement of the tensile/mechanical strength of a material. The membrane samples were evaluated under a controlled strain rate until failure (Figure 3.5). The ultimate tensile strength, toughness, Young's modulus values were the major source of interest in this test. Figure 3.6 (stress vs. strain) was obtained on carrying out the tensile test for the pure polymer, 1% and, 3% clay induced polymer membranes.

Figure 3.5 Necking in pure polymer during tensile testing
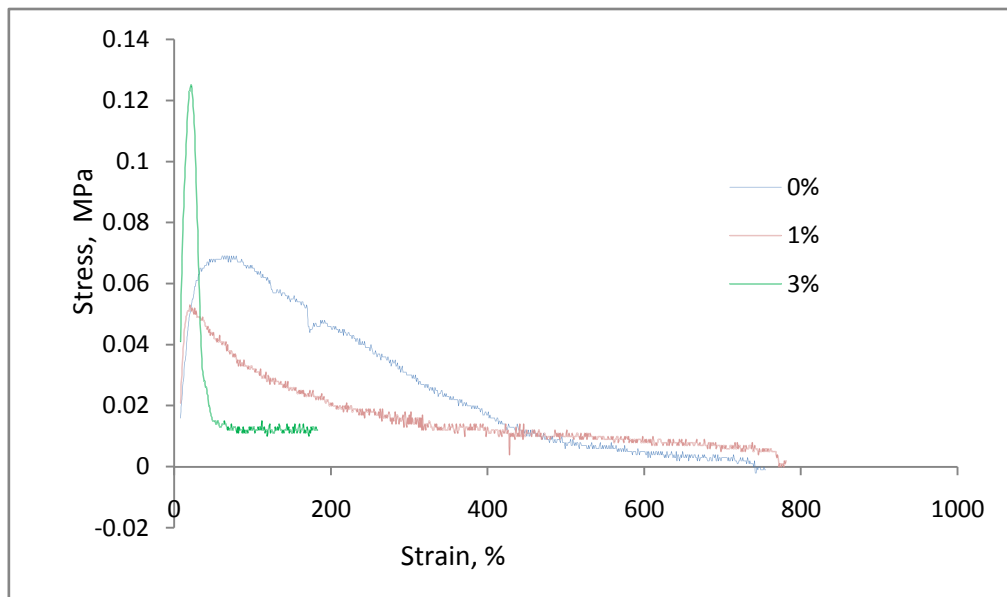
Figure 3.6 Variation of tensile strength for guanidine polymer with different fractions of clay (wt %)

The pure polymer shows a modulus (slope of the initial elastic region) of around 0.740 MPa, the polymer with 1% clay gives a modulus of 10.054 MPa, while a specimen with 3% clay gives a modulus of 12.254 MPa, as illustrated in Figure 3.7.As we can observe from Figure 3.7, we get a relatively higher value of the tensile modulus with addition of the clay. There is a variation in the nature of break which took place. Considerable necking (as shown in Figure 3.5) occurs in case of the pure polymer. This can be attributed to the fact that in a pure polymer, the individual chains can slide against each other with ease. This increases the elongational property of the polymer. Addition of the inorganic clay particles in higher proportion causes polymer to become highly cross-linked (physically). The cross-linking causes resistance to the movement of the chains against each other. Hence, the chains move against each other with lot of difficulty; therefore, the

clay incorporated polymer did not show lot of elongation. Besides, the tensile strength of the membrane with 3% of clay is almost twice of those of the membranes with less amount of clay.
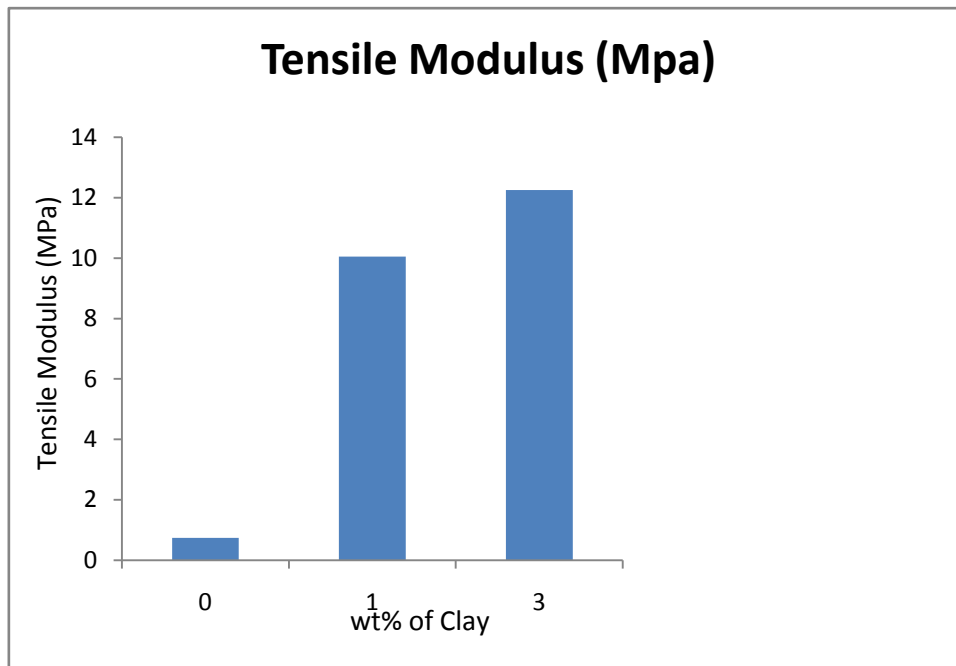
Figure 3.7 Variation of tensile modulus with different amounts of clay

The toughness of the specimens can be obtained by calculating the area under the stress-strain curve. The toughness is seen to vary with the amount of clay added (Figure 3.8). It is seen that the pure guanidinium polymer without any clay shows a toughness of $18.79 \text{J} \cdot \text{m}^{-3}$. As is seen in Figure 3.8, addition of a small amount of clay to the polymer causes the toughness to decrease to 9.36. Hence, we see a remarkable decrease in toughness by $9.43 \text{J} \cdot \text{m}^{-3}$ with the addition of only 1% clay by weight. Adding clay beyond a certain value will increase the brittleness of the membrane very drastically and thereby reduces the toughness of the membrane. For a polymer with 3% clay, the toughness was

calculated to the value of around $0.37 J \cdot m^{-3}$. As we can observe from the graph, addition of clay up to one percent will give a fairly tough membrane.
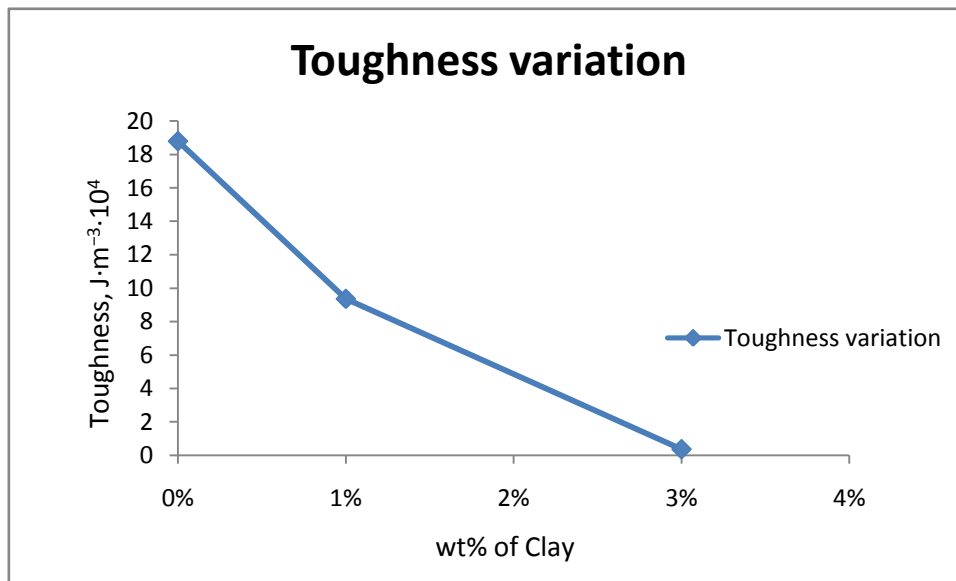
Figure 3.8 Variation of toughness for membrane samples with different amounts of clay

The above graph shows the general trend in the toughness of the membranes on addition of the clay in various proportions. As we can observe, the addition of clay from 1% to 3% gives an optimum value toughness and tensile strength.

3.4 Ionic Conductivity of the membrane

The ionic conductivities of the AEM strip with one percent clay (approx 4cm X 1.35 cm) was estimated using AC impedance spectroscopy and the commonly employed four point probe technique. The machine used was Princeton Applied Research PARSTAT 2273 frequency response analyzer. Electrochemical Impedance Spectroscopy (EIS) was performed using a small sinusoidal voltage, 10 mV, across the membrane sample at

frequencies between 10 milliHz and 1 KHz. The bode plot was used to determine the frequency region over which the impedance has constant value and the real impedance value at the highest frequency measurement in the Nyquist plot (Figure 3.9) was taken as the resistance of the membrane. This was then used to calculate the membrane conductivity, i.e.,

$$\sigma = \frac{L}{Z_{re}XA}$$

where L is the length between sense electrodes (1.2 cm), Z_{re} is the real impedance response at high frequency, and A is the membrane area available for conduction. The impedance calculated from the Nyquist plot gives a value of nearly 141 ohms. Therefore, the conductivity value is calculated as:

$$\sigma = \frac{0.4}{141X0.08X0.45} = 78 \text{ mS cm}^{-1}$$

The pure guanidinium based polymers are known to give conductivities as high as 67 mS cm^{-1} at 20°C and 74 mS cm^{-1} at 60°C [23].

It can be concluded from the values in table 3.3 that the addition of clay particles in small proportion in the polymer does not tend to affect the conductivity of the membrane very substantially. We can observe from table 3.3 that the ionic conductivity of the membrane is nearly 71 mS cm^{-1} which is nearly equal to the value of ionic conductivity for pure polymer.

Table 3.3 Average Ionic Conductivity for polymer with 1wt% clay

Specimen	Conductivity (mS cm^{-1})		Error %
Specimen 1	65	Average Conductivity =71 mS cm^{-1}	6%
Specimen 2	70		1%
Specimen 3	78		6%

However, on addition of clay in larger proportions decreases the conductivity. As can be seen in table 3.4, addition of 3% clay to the polymer makes the ionic conductivityto decrease by nearly three times. The average ionic conductivity for polymer drops to 21.66 mS cm^{-1}. The decrease of ionic conductivity with a higher percentage of the clay is believed to result from an impeded charge transport network due to higher degree of physical crosslinking.

Table 3.4 Average Ionic Conductivity for polymer with 3 wt% of Clay

Specimen	Conductivity (mS cm^{-1})		Error %
Specimen 1	26	Average conductivity =21.66 mS cm^{-1}	4.34%
Specimen 2	19		2.66%
Specimen 3	20		1.66%
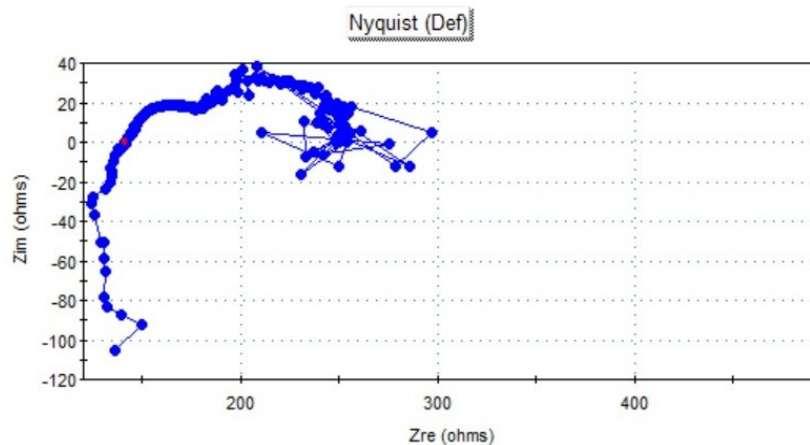
Figure 3.9 Nyquist Plot of the polymer sample with 1 wt% clay

3.5 Viscosity

The viscosity of the polymer will tend to increase as the synthesis proceeds (Figure 3.10). It was observed that the addition of clay to the polymer enhances this increase in viscosity. A pure guanidine polymer will show a lesser increase in viscosity as synthesis proceeds. When the polymer was induced with one percent clay, there was a slight increase in the viscosity of the polymer at the beginning. Towards the end of the synthesis reaction, the mechanical stirrer was found to stir the mixture with lot of difficulty. A polymer with induction of 3% clay was observed to have an even higher viscosity increase as the reaction proceeded. Polymers induced with clay can be reasoned to show a higher increase in the resistance due to the physical cross-linking caused due to exchange between fixed opposite charges in the clay and polymer. Pure guanidinium polymer has fixed guanidinium groups in its structure while the montmorillonite clay is known to carry strong anion exchange groups. An ion exchange between the organic polymer and inorganic clay will create strong bonding between the two species through electrostatic interactions. Due

to this bonding, the resistance to the movement of polymer chains increases causing an increase in viscosity.

Figure 3.10 Viscosity rise in polymer (3% clay)

3.6 Stability of the membrane

To estimate the stability of the polymer, the dry membrane was activated by exposing it to highly alkaline KOH solution for 36 h. Later the same membrane was washed, wiped with a tissue and kept in clean distilled water for 24 h. The polymer membranes were not observed to be very stable. The pure polymer is highly soluble in water and does not sustain for long in the water while polymers with some proportion of clay in them will take a longer time to dissolve. Compared to a pure polymer, the membrane induced with higher amount of clay will not dissolve in water due to the tendency of the clay to hold the polymer together because of the physical cross-linking between clay and polymer. The membrane with 3% clay was the strongest one amongst all the 3 specimens tested. It stayed

strong after 36 hours in the 1M KOH solution. Also, it was reasonably strong after staying in distilled water after 12 h.

Secondly, if the polymer is synthesized for a longer time frame we will get a polymer which is higher in molecular weight. A polymer membrane with high molecular weight dissolves slowly compared to a polymer membrane with low molecular weight. Also, the membranes which were heat treated to a higher temperature were more stable than the membranes which were subjected to lesser heat treatment.

Chapter 4

Conclusion and Future Work

From the experiments carried it has been found that addition of inorganic montmorillonite particles to the guanidinium based polymers creates a substantial difference in most of the properties of the membrane material. The mechanical properties of the polymer material like the Young's Modulus, the toughness of the polymer membrane increased to a great extent even with addition of the clay in small proportions.

The ionic properties of the membrane also vary substantially with the incorporation of the montmorillonite clay particles in the polymer material. A smaller proportion of clay does not affect the properties of the membrane very highly. Yet, incorporation of clay as high as 3% by weight will drastically reduce the ionic conductivity, possibly due to impeded ionic transport path caused by the clay. Further study needs to be conducted to confirm this.

Also, during the synthesis it was observed that the viscosity tends to increase significantly as the percentage of clay incorporated in the polymer increases. This mostly happens due to the resistance the polymeric chains face in their movement due to thephysical cross-linking of the organic polymer with inorganic clay particles.

In the future, the thermal properties of the pure polymer with and without the clay should be studied. Montmorillonite is known to greatly increase the thermal properties of the membrane. The study of thermal properties involving membrane stability at high temperatures will vary on proportion of clay particles incorporated. Also, the texture of the membranes should be studied more closely and accurately to see if the polymer clay interaction forms an intercalated/exfoliated structure etc. Furthermore, we should try

incorporation of montmorillonite in different guanidinium polymers to study if they behave

in the same way as with the polymer discussed in this thesis. We can try the synthesis of

polymer membranes using materials which will continue to give us the excellent

mechanical properties along with a good ionic conductivity and the stability in KOH and

water system.

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Shambhavi Sakri received her bachelor degree in polymer Engineering from the University of Pune, India in August 2013. During her bachelors she worked on a project involving the synthesis and mechanical evaluation of polypropylene-polypropylene symmetric cross-ply laminates for application in packaging for the University of Pune. She has pursued an internship at Tata Autocomp Systems Ltd. during her bachelors. In January 2014, she joined the department of materials science and engineering at the University of Texas, Arlington to pursue her masters. Her primary research interest has always been in polymers. Hence she joined the electrochemical research group in the MSE Department and worked in the development of hybrid guanidinium based polymer membranes using montmorillonite clay for application in the anion exchange membrane fuel cell. Her academic career displays her deep interest in the development of polymer materials for different applications. She has also given seminars during her undergraduate studies on the development and widespread use of polymer materials in different spheres of life, biopolymers.....

She plans on joining industry after her graduation to pursue a job which will offer her challenging opportunities in research and development along the lines of her interests.