HETEROGENOUS CATION EXCHANGE MEMBRANE: FABRICATION, CHARACTERIZATION AND PERFORMANCE STUDIES USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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by

NOR ADIBAH BT AHMAD

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LIST OF SYMBOLS

SYMBOL	DESCRIPTION	UNIT
R_2	Polarization resistance	Ω
R_1	Ohmic resistance	Ω
$\|Z\|$	Modulus impedance	Ω
ΔZ	Difference in impedance	Ω
$-Z_{img}$	Imaginary impedance	Ω
Z_{real}	Real impedance	Ω

LIST OF ABBREVIATION

IEMs	Ion Exchange Membranes
CEM	Cation-Exchange Membrane
AEM	Anion-Exchange Membrane
CER	Cation-Exchange Resin
PVC	Polyvinyl Chloride
MWCNT	Multi-walled Carbon Nanotube
ECM	Equivalent Circuit Model
EIS	Electrochemical Impedance Spectroscopy

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KATION HETEROGEN PERTUKARAN MEMBRAN:

FABRIKASI, PENCIRIAN DAN PENGAJIAN PRESTASI MENGGUNAKAN ELEKTROKIMIA IMPEDANS SPEKTROSKOPI

ABSTRAK

Dalam kajian ini, novel PVC kation pertukaran membran dan matrix campuran membran berasaskan PVC telah dibuat pada komposisi resin pertukaran kation dan bahan tambahan yang berbeza, ciri-ciri dan prestasi mereka telah diuji dengan menggunakan kaedah elektrokimia impedans spektroskopi. Karbon tube nano telah digunakan sebagai bahan tambahan dalam campuran pembuatan matriks campuran membran. Kepekatan resin yang digunakan dalam matrix campuran membran ditentukan dari pencirian dan prestasi resin polimer tulen. Ia telah didapati bahawa pengambilan air daripada membran polimer tulen telah dipertingkatkan manakala pengambilan air matrix campuran membran bertambah baik dengan peningkatan nanopartikel tetapi pada komposisi tertinggi, pengambilan air telah dikurangkan. Sudut sentuhan air telah dikurangkan apabila komposisi resin dan bahan tambahan meningkat tetapi pada komposisi resin dan bahan tambahan yang paling tertinggi, sudut sentuhan air telah meningkat. Kapasiti pertukaran ion telah dipertingkatkan apabila kepekatan resin meningkat, tetapi hanya sehingga peratusan 8%. Membran dengan peratusan 8% komposisi resin memiliki kapasiti tertinggi pertukaran ion yang dengan itu ia telah dipilih untuk menjadi asas kepada komposisi resin dalam pembuatan matrix campuran membran. Kapasiti pertukaran ion telah dikurangkan apabila kepekatan bahan tambahan meningkat kerana jumlah yang tinggi bahan tambahan yang memenuhi ruang di sekitar zarah resin. Kekonduksian ion telah dipertingkatkan apabila komposisi resin dan bahan tambahan meningkat, tetapi tiba-tiba menyebabkan pengurangan apabila resin dan kepekatan bahan tambahan adalah

di komposisi yang tertinggi. Kekonduksian ion meningkat daripada ((2.99 to 4.72) Ω^{-1}cm^{-1}) dengan meningkatnya komposisi bahan tambahan kepada membran. elektrokimia impedans spektroskopi ialah alat yang sangat baik untuk mengkaji sifat elektroimia of ion pertukaran membran.

ABSTRACT

In this study, novel PVC cation exchange membrane (CEM) and PVC-based mixed matrix membrane were fabricated at different cation exchange resin (CER) and additive concentration, characterized and their performance were tested by using Electrochemical Impedance Spectroscopy (EIS) method. Multi walled carbon nanotubes (MWCNT) was employed as additive in mixed matrix membrane fabrication. CER concentration used in the mixed matrix membranes were determined from the characterization and performance of pure polymeric CER. It was found that water uptake of the CER-CEM was enhanced while the water uptake of MWCNT-CEM was improved with the increasing of nanoparticles but at the highest loading of MWCNT, the water uptake was reduced. Water contact angle was reduced as the CER and MWCNT concentration increases but at high loading of CER and MWCNT, water contact angle was increased. Ion exchange capacity was enhanced as the CER concentration increased, but only up to 8%wt. Membrane with the 8%wt CER loading possessed the highest ion exchange capacity thus it was chosen to be the base of amount of CER in the fabrication of mixed matrix membrane. Ion exchange capacity was reduced as the MWCNT concentration increased due to the high amount of MWCNT that occupied the spaces around CER particles. The ion conductivity was enhanced when the CER loading and MWCNT increased, but suddenly resulting in reduction when CER and MWCNT concentration were at their highest. Ionic conductivity increased from (2.99 to 4.72) $\Omega^{-1}\mathrm{cm}^{-1}$ with the addition of MWCNT to the membrane. ElS is an excellent tool to investigate the electrochemical properties of IEM.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Separation membranes have become crucial material not only in industries, but also in day-to-day life (Kariduraganavar et al., 2006). Nowadays, ion exchange membrane (IEMs) are one of the most advanced separation membranes that are used in a large variety of application as represented in Figure 1.1. Since the application of IEMs has become more diverse, the requirements for membrane with extraordinary properties has increased. These requirements have led to the development of various types of newly functionalized IEMs.

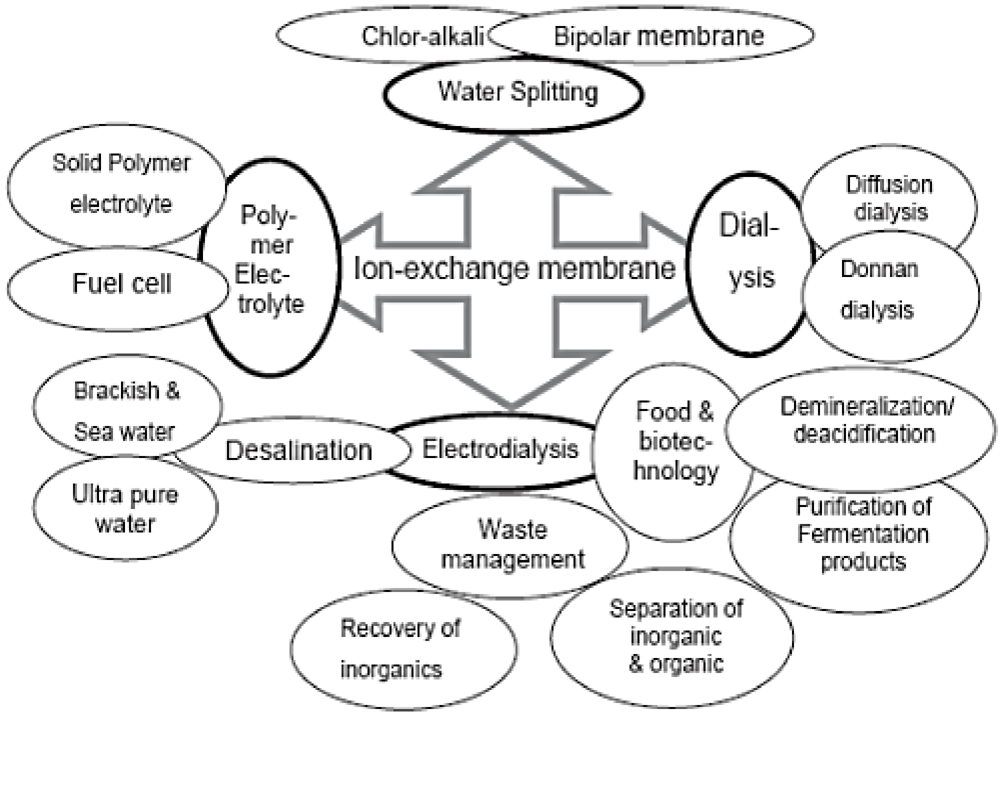

Figure 1.1 Industrial applications of IEMs (Nagarale et al., 2006)

Generally, IEMs exist as thin sheets or film of ion exchange material, which allow the separation of ions by permitting the preferential transport of cation or anions (Inamuddin and Luqman, 2012). Ions, along with the solvents which is water molecule, are permeated through the membranes by driving forces. IEMs can be found in two types of structure; homogenous and heterogeneous membranes and it can be functionalized into cation exchange membranes (CEM) and anion exchange membranes (AEM). CEM allows the passing of cations which contain negatively charged functional groups and repel anions while AEM is just the opposite (Jaroszek and Dydo, 2016).

Polymer is one of the common material involved in the preparation of membrane. Polymeric materials such as poly-vinyl-chloride (PVC), poly-vinylidene fluoride (PVDF), polysulfone (PS), polyethersulfone (PES) and polybenzimidazole usually act as base polymer and can be applied in different methods (Nagarale at al., 2006). Besides polymer, IEMs can also be made from inorganic material such as clay, zeolites, betonites, or phosphate salts. However, these type of membranes are not significant due to their high cost, bad electrochemical properties and large pores (Xu, 2005).

Pure polymeric IEMs have weaknesses that limit their industrial applications. Excessive fouling and low resistance to chlorine and oxidants are several causes that restrict the performance of polymeric membranes (Mohanty, 2012). This leads to the growing of new initiative, the development of mixed matrix membrane (MMM) by dispersing inorganic materials in polymer matrix. The inorganic particles might be zeolite, carbon molecular sieves, carbon nanotubes or nano-sized particles (Chung et al., 2007). Besides enhancement in the efficiency, mixed matrix membranes show significant changes in IEMs' properties, such as mechanical strength, thermal stability, electrical and magnetic compared to pure organic polymeric membranes (Parvizian et al., 2014).

A numbers of research has been reported that the membrane conductivity depends on the ion concentrations of the external solutions (Długołecki et al., 2010) (Choi et al., 2001) (Nagarale et al., 2004). Recently, an attractive method that can be used to study the membrane conductance is electrochemical impedance spectroscopy (EIS). This technique can give an understanding of what is happening at the membranes and thus with the aid of this knowledge, more enhancements can be made to increase the performance of IEMs. Therefore, in this study, EIS is used as a tool to provide information and understand the performance of fabricated IEMs with different structure and properties.

1.2 Problem Statement

IEMs are also widely used for separation purposes, including microfiltration nanofiltration, reverse osmosis, evaporation and separation from gas or liquid-phases. The properties of a good ion exchange membrane are high ion permselectivity, low electric resistance, low rate of electro-osmosis for high solution concentration, and good chemical, mechanical and physical stability (Singh and Shahi, 2013) . Therefore, a lot of research has been done to improve the IEMs properties such as utilizing different types of polymer, polymer blending with various additives, alteration of cross-linked density, and modifying the membrane functional groups. Among this techniques, modifying the membrane through blending with fillers which is called mixed matrix membrane offer a simple and effective way to enhance the efficiency of the IEMs. Recently, significant efforts have been devoted by using multi-walled carbon nanotubes (MWCNTs) as great potential filler. MWCNT have attracted wide attention due to its unique properties such as high electrical, chemical, and mechanical properties, high aspect ratio and surface area (Hosseini et al., 2013).

In IEMs, the charges groups are attached to the polymer backbone and are freely permeable to opposite ions under an electrical field. In such processes, the ion interactions with membrane, water and interaction each other occur in complex behavior. Thus, knowledge about relationships between membrane structures, physical and chemical properties and mechanisms of electrochemical processes that occur in charged IEMs is major contributing factor behind decisions about their applicable in specific separation processes.

Conductivity is the most important properties to monitor in order to produce excellent IEMs. However, in order to obtain the conductivity of the IEM, membrane resistance is needed. Membrane resistance is also one of the significant properties to measure the performance of IEMs. The measurement can be done through direct current (DC) method. In DC method, a constant current is applied and the potential drop across the electrochemical cell is tested. Throughout this method, the resistance of the IEMs and the interfacial layer resistance can be calculated using Ohm’s law. However, the DC method cannot discriminate whether the individual membrane resistance or the resistance of the interfacial layers could be responsible for the resistance increase in IEMs. Therefore, EIS method has been used extensively to determine the electrical resistances of ion-exchange membranes by applying alternating current (AC) across the membrane under operating conditions.

EIS is an AC technique which provides an easier and more thorough way of understanding an electrochemical system than other DC techniques. The difference between the DC resistance measurements and the impedance spectroscopy is that in the first case the frequency of AC is kept constant while in latter case the frequency is changed and the response to the changing frequency is determined by a frequency analyser (FRA) (Zhang et al., 2016). To determine membrane resistances by EIS data, the entire system, which consists of the membrane, the electrolyte and the electrodes, treated as a “black box”. An alternating sinusoidal voltage of a given frequency and amplitude is applied to the system. The resulting current is measured and then the phase shift compared to the input signal is determined. The procedure is repeated at different frequencies (Park et al., 2006).

To the best of authors’ knowledge there have been limited extensive study by applying EIS method in heterogeneous CEMs. Therefore, this research study aims to fabricate the heterogeneous mixed matrix CEMs by modifying the method obtained from Hosseini et al. (2013). The PVC based mixed matrix heterogeneous CEMs were fabricated by a dry casting method. The dope solution was formulated based on combination PVC with sulfonated-CER and mixture of NMP and acetone (1:1 portion) as a solvent. Since, CER loading is one of the parameters that effect the characteristic of the IEMs (Wenten, 2016), the effect of CERs loading were performed to obtain the appropriate concentration of CER that needs to be added in the membranes that give the optimum ionic flux characteristic. In order to improve the properties and performance of IEMs, MWCNTs was chosen as the inorganic filler in the fabrication of mixed matrix heterogeneous CEM. The effect of MWCNTs concentration in the casting solution to the physical, chemical and electrochemical properties of the fabricated CEMs were also studied. EIS method was applied at different frequency range and similar electrolyte environment. Modified Randles Equivalent Circuit with Constant Phase Element (CPE)-restricted linear diffusion was proposed and fitted with the impedance results in order to determine the important parameters such as the membrane resistance, electrical resistance, constant phase element (CPE) and then ionic conductivity of the heterogeneous CEMs system. This study offered a great significant study between physical, chemical and electrochemical properties of CEMs.

1.3 Research Objectives

The objectives of this study are:

1) To synthesize and characterize heterogeneous CEMs at different concentration of CER and multi walled carbon nanotube (MWCNT).
2) To study the electrochemical properties and ionic flux of heterogeneous CEMs using electrochemical impedance spectroscopy (EIS) method.

1.4 Scopes of study

In this study, CEMs were prepared by solution casting techniques. The casting solution was formulated by blending of polyvinyl chloride (PVC) as a polymer, the combination of N-Methylpyrrolidone (NMP) and acetone as a solvent and sulfonated strong CER as a functional group agent. As for the mixed matrix membrane, MWCNT was added as the inorganic fillers.The membranes were characterized in terms of surface morphology, hydrophobicity, elemental content and surface chemistry by using SEM, water contact angle and FTIR respectively. Water content and ion exchange capacity of the CEMs were also performed to study the capacity of the membranes.The performance of both membranes were analyzed at 0.4 M NaCI vbbbsolution electrolytic environment to evaluate their potential performance under various conditions. The variations of membrane resistance, membrane potential and permselectivity were studied under different concentration of NaCI and similar concentration of Na_2SO_4 solution. All experiment was fully conducted by using Electrochemical Impedance Spectroscopy (EIS).

CHAPTER TWO

LITERATURE REVIEW

2.1 The importance of Membrane technology

From separation methods of theoretical interest, membrane science and technology have grown to a multibillion dollar industry comprising a vast spectrum of applications (Fane, 2008). For the last two decades, membrane-based processes were considered important and now is competing with other separation technologies in terms of energy efficiency, high separation capacity, selective separation and capital investments. In addition, on a number of occasions, membrane technologies managed to replace commercial separation processes in industry. (Drioli et al., 2011). Today, membrane-based processes enjoy abundant of industrial applications and have appeared to be one of the crucial parts of the human life progress (Fane et al., 2010). To date, numerous kinds of separation membranes have been investigated and employed industrially in different including reverse osmosis, nanofiltration, ultrafiltration, microfiltration, electrodialysis and pervaporation (Kariduraganavar et al., 2012). Table 2.1 summarizes the list of membrane technologies and applications.

Table 2.1 Membrane process applications (Bangga, 2012)

Membrane Process	Application
Microfiltration-Cross Flow Filtration	Sterile solution/water purification Beverage filtration effluents, Cell harvesting
Ultrafiltration	Dairy (whey recovery, pre-cheese concentration), Electrocoat colloids, Effluents (oil-water, pulp and paper, dye-stuffs, tannery), Biological (enzymes, fermentation), Water purification
Reverse Osmosis	Water desalination, ultrapure water, dairy industry, effluent treatment (metal-finishing, photographic, chemical processes), biomedical applications, and pharmaceutical industries
Gas Separation	Hydrogen recovery/removal, CO2 removal, O2 enrichment, helium recovery, N2 enriched air, pollution control, sour gas treatment, H2 recovery, natural gas dehydration, air dehydration
Electrodialysis	Water desalination, acidity reduction in citrus juice, deionization of whey
Dialysis	Hemodialysis (artificial kidney)
Pervaporation	Dehydration of organic solvents

Membrane acts as a selective barrier between two phases, as the term ‘selective’ refers to membrane or a membrane process. The structure of the membranes can be homogenous or heterogeneous, thick or thin, appears as natural or synthetic, or it can be neutral or charged (J. Mulder, 1991). The transport of membrane usually is caused by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. While for the thickness of the membrane, it may vary from as small as 10 microns to few hundred micrometers

(Ravanchi et al., 2009). Fundamentally, a membrane is nothing more than a discrete, thin interface that moderate the permeation of chemical species in contact with it. The principal types of membranes is depicted in Figure 2.1 respectively.

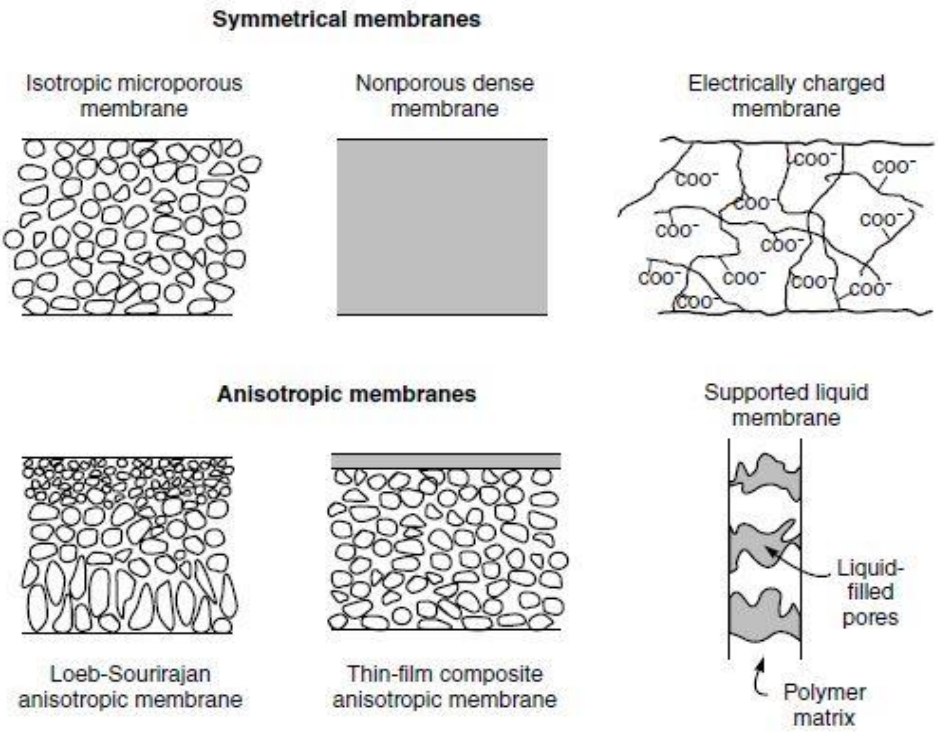

Figure 2.1 Schematic diagrams of principle types of membrane (Baker, 2004)

2.2 Ion Exchange Membranes (IEMs)

The natural phenomena of IEMs had been applied as long ago as the time of ancient Greece where sand filters were employed for the purification of clean water. However, the fundamental and observation on IEMs started to be known in nineteenth century (Ish, 1955). Later, in 1890, the development of IEMs started to evolve when Ostwald began his work by investigating the properties of semi-permeable membrane and found that a membrane can be permeable for any electrolyte (Xu, 2005). In 1940, IEMs were applied to industry with the usage of synthetic IEMs made by basis of phenol-formaldehyde as the starter (Inamuddin and Luqman, 2012). Over the years, the technology enhances along with the endless demand in many fields, IEMs have been used extensively in wide range of applications and one of the state of art of IEMs; electrodialysis turned to be one of the established application (Strathmann et al., 2013). A number of remarkable processes and their present and potential yet to come applications are listed in Table 2.2.

Table 2.2 Process Utilizing IEMs and Their Most Relevant Application

Processes	Relevant Applications	References
a) State of art Processes with Major Commercial Relevance		
Electrodialysis	Water Desalination, Salt Preconcentration	(Strathmann et al., 2013), (Yaroslavtsev and Nikonenko, 2009)
Electrolysis	Chlorine-Alkaline Production	
Diffusion Dialysis	Acid and base recover from wastewaters	
b) Recently Established Processes with Growing Commercial Relevance		
Bipolar membrane Electrodialysis	Production of acids and bases	(Strathmann et al., 2013), (Ran et al., 2016)
Continuous Electro-deonization	Production of pure/ultrapure water	
Conversion of chemical to electrical energy	Fuel Cells	
c) To be developed Processes with Potential Future Relevance		
Reverse Electrodialysis	Electrodialytic energy generation	(Strathmann et al., 2013)
Capacitive Deionization	Water Desalination and water softening	
Electrodialytic Energy Storage	Concentration and redox flow batteries	
Conversion of chemical energy and bioenergy to electrical energy	Microbial fuel cell	(Leong et al., 2013)

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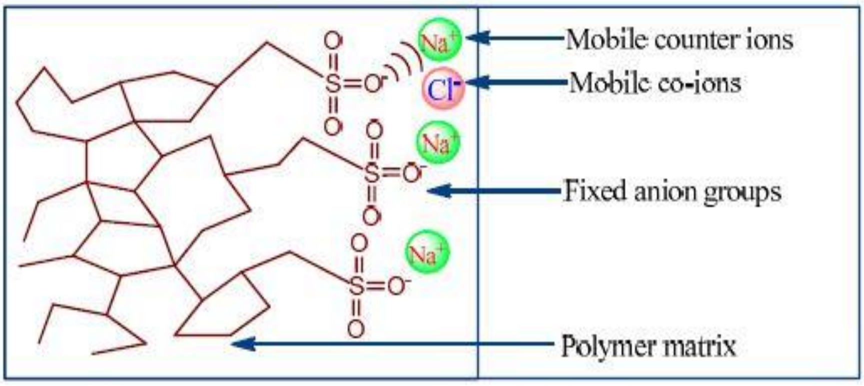
IEMs can be classified into many types, either by its structure, functional group or by the basic material they are made (Sata, 2010). IEMs can be found in two types of structure; homogenous and heterogeneous. Heterogeneous IEM usually produces excellent mechanical property, easier preparation procedure and lower production cost (Hosseini et al., 2014). But, from the aspect of electrochemical properties, heterogeneous gives weak selectivity and conductivity rather than homogenous membrane. Due to this limitation, the focus of development of heterogeneous IEM has been scaled down to produce IEM with superior electrochemical properties, lower production cost and simple preparation procedure.

Numerous methods have been invented to enhance heterogeneous IEM performance such as additive blending, selection of appropriate materials, membrane surface modifications, and post treatments and it is proven that these methods are capable to improve electrochemical characteristics. Futhermore, by applying advance characterizations of heterogeneous IEM will also increase the opportunity to produce inexpensive membrane. Homogenous usually consists of a single polymer that function as a membrane structural material and the holder of functional groups meanwhile, heterogeneous membrane is made of two different polymers. The membrane sheet is formed by the second polymer that holds the first polymer. The first polymer should possess high mechanical strength and inert. Meanwhile the second polymer usually should have good ion conductivity and ion exchange capacity that offered by ion exchange powder (Wenten, 2016).

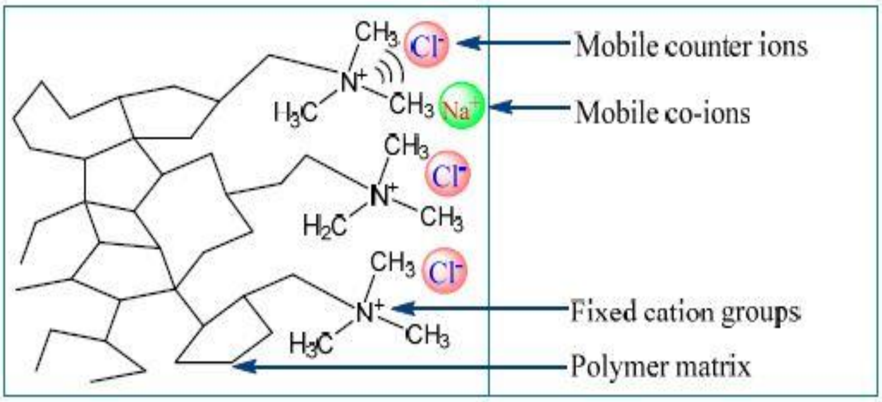
IEMs can be divided into two categories of functional group; cation-exchange membrane and anion-exchange membrane. Cation-exchange membranes encompasses negatively-charged groups, such as $-SO_3^-$, $-COO^-$or $-PO_3^{2-}$ that attached to the membrane backbone and permit the route of cations but repel anions. In the other hand, anion-exchange membrane composes of positively-charged groups, for example, $-NH_3^+$, $-NRH_2^+$or $-NR_2H^+$that chained to the membrane backbone and allow the path of anions and repel cations (Xu, 2005). Co-ions are denoted for mobile ions in the membrane with the same charge as the fixed charge and counterions are represented as opposite charge.

(a)



Cation-exchange membrane

(b)



Anion-exchange membrane

Figure 2.2 Schematic diagram of (a) CEM and (b) AEM. (Thapur, 2012)

Hydrophobic substrates, immobilized ion-functionalized groups and movable counter-ions are the substances that made IEMs up. Habitually, after the permeation of adequate water molecules, ion-functionalized groups that linked to IEMs will naturally dissociate followed by the releasing cations or anions for the relocation of corresponding ions (Ran et al., 2016). IEMs can be made from several types of material such as inorganic materials, hydrocarbon or partially halogenated hydrocarbon polymers, perfluorocarbon polymers or inorganic ion-exchange material with an organic polymer. However, membrane that made up of inorganic material such as zeolites, bentonite or phosphate salts are quite insignificant due to high cost, bad electrochemical properties and large pores. Regularly, polymer based membranes are chosen since they produce excellent conductivity, high chemical stability and others desired properties that IEMs should have (Xu, 2005).

2.3 Preparation of heterogeneous IEMs

Instead of having excellent mechanical strength, heterogeneous IEMs turns out not to be that good in terms of their electrochemical performance (Vyas et al., 2001). The preparation of IEMs are approximately related to ion-exchange resin where this particles stimulate the presence of the functional groups (Inamuddin and Luqman, 2012). Ion exchange resins are mostly weak, thus it tends to be brittle. A stable material can be used to overcome the problem by providing the necessary dimensional and mechanical stability (Thapur, 2012). Apart from that, in order for the membrane to attain the finest combination of electrochemical properties and mechanical strength, suitable binder can be chosen to make non-reinforced membranes or otherwise by electing suitable reinforcing fabric. (Vyas et al., 2001) found that the membrane became more flexible if the size of resin particles used were fined enough. The same consequence are happened by increasing resin particles loading. Table 2.3 summarizes the common factor that influences the performance of heterogeneous IEMs.

Table 2.3 The effects of parameters on membrane properties (Wenten, 2016)

Factors	Effects
Size of ion-exchange resin	• Smaller ion-exchange membrane resin produces more flexible membrane, more homogenous, and enhanced electrochemical properties
Resin loading	• Increasing resin loading results in better conductivity and selectivity. • Membrane shows lower oxidative and mechanical stability.
Resin distribution	• Highly ordered resin expresses better electrochemical properties.
Polymer	• Polymer with high rigidity causes membrane to have lower permeability, ion-exchange capacity and conductivity. • Lower elasticity polymer results in optimum degree of swelling. • High hydrophilicity polymer influence membrane to have high water uptake and increases membrane conductivity. • Membrane morphology depends on characteristic of the polymer chosen.
Solvent	• Resin aggregation during solvent evaporation and discontinuity of matrix polymer tends to happen when low volatility solvent is used.
Method	• More voids fraction is produced if solvent to polymer ratio is increased. • High selectivity membrane is produced when solvent evaporation method is used. • Longer evaporation time at dry-wet phase inversion decreses membrane porosity. • Gelation and solution immersion method have a tendency to produce membrane with higher conductivity.

In addition, heterogeneous IEMs can be produced by mechanical combination of ion-exchange resin into sheet of rubber, PVC, acrylonitrile copolymers or extrudable and mouldable matrix (Wenten, 2016). The technique including; by calendaring ion- exchange powder into polymer film, dispersing finely crushed ion-exchange powder into solution composing of a film foaming binder and then followed by the evaporation of solvent, and the last option is by applying dry moulding of ion-exchange particle and polymer, followed by grinding the mould stock (Nagarale et al., 2005).

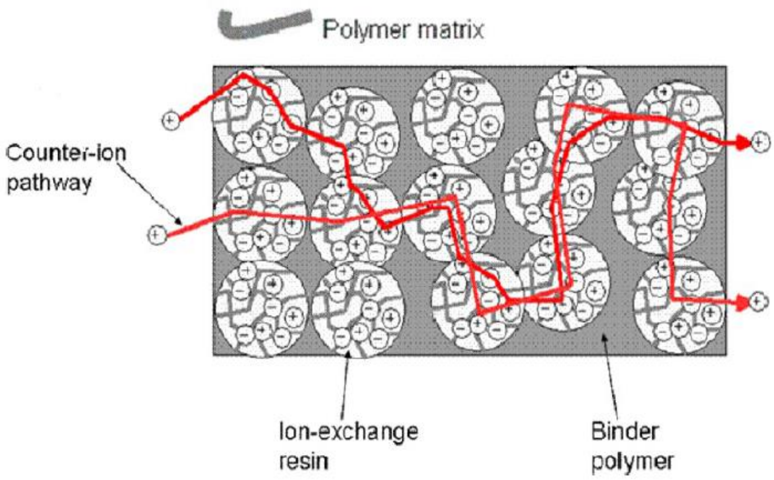


Figure 2.3 The structure of a heterogeneous membrane depicted macroscopic ion-exchange particles (resin) imbedded in a matrix polymer and the longer pathway of counterions across the membrane (Strathmann et al., 2013).

2.4 Mixed Matrix Membrane

Mixed matrix membranes (MMMs) are defined as being an incorporation of inorganic components (solid or liquid) dispersed or embedded in a continuous polymer matrix. Polymeric material acts as the continuous phase while the dispersed phase comprises of porous (zeolite, carbon molecular sieve, activated carbon, carbon nanotubes) or nonporous material (silica, titanium oxide, fullerene), (Qadir et al., 2016). Due to the combination of organic and inorganic material, MMMs have more excellent performance of IEMs in terms of mechanical, thermal, magnetic and electrical properties. Organic compounds provides structural flexibility, convenient processing, tunable electronic, photoconductivity, efficient luminescence and the potential for semiconducting and even metallic behavior. While for inorganic compounds, it offers the potential for high carrier mobilities, band gap tunability, a range of magnetic and dielectric properties and thermal and mechanical stability (Xu, 2005).

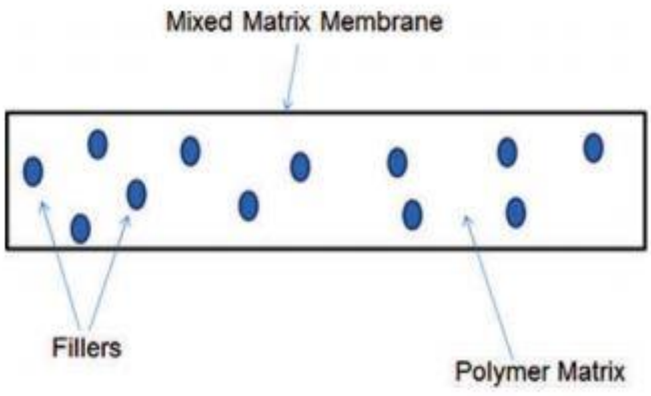


Figure 2.4 Schematic of ideal mixed matrix membrane. (Qadir et al., 2016)

Table 2.4 Types of inorganic fillers (Qadir et al., 2016).

Inorganic fillers	Properties
Silver-based Antibacterial	Good transport facilitator, Good selective barrier, High reactivity, anti-adhesion to protein, low toxicity to humans
Iron-based highly reactive	Larger surface areas in nanoform (F°), detoxification of organic and inorganic pollutants, reduce, removal of active metal ions, reductive dehalogenation of chlorinated organic compound, highly reductive, high adsorption capacity, hydrophilic, fouling resistant, magnetic oscillation, hydraulic turbulence
Zeolite	Hydrophilic, fouling resistant, anti-adhesion to protein, effective sorbents, ion exchange media for metal ions
Silica-based	Hydrophilic, fouling resistant, anti-adhesion to protein
Aluminum-based	High adsorption capacity, hydrophilic, fouling resistant, anti-adhesion to protein
Carbon nanotube-based	Antimicrobial, hydrophilic, high aspect ratio, biofouling resistant, anti-adhesion to protein, selective sorbents for organic compound

Table 2.4 shows summarization of inorganic fillers that were usually being used in the MMMs. The study is focused on carbon nanotubes since it was implied as the fillers in the IEMs. Carbon nanotubes (CNTs) are allotropes of carbon, tubular in shape and can be made from graphite. These cylindrical carbon molecules have exclusive surface area, stiffness and strength and resilience that lead them to have a

huge potential in nanotechnology applications. CNTs can be divided into two types; single-walled nanotubes and multiple walled nanotubes, and possess length to ratio greater than 1,000,000. They can pass through membranes, transporting therapeutic drugs, vaccines and nucleic acids deep into the cell to aim unreachable area (Hirlekar et al., 2009). Figure 2.5 shows the structure of CNTs.

I.A Prikhno and coworkers studied the effect of modification of perfluorosulfonic acid MF-4SC membranes (Russian analog of Nafion) with carbon nanotubes, specifically, surface-sulfonated ones. They found out that membrane modification by small amounts of carbon nanotubes results in increased proton conductivity at both high and low relative humidity. Futhermore, the the MF-4SC membrane elastic stiffness was enhanced too. Based on the experimental results, they suggested that carbon nanotubes influence on the formation of the membrane pore and channel system.

S.M Hosseini and coworkers studied the effect of of PANI/MWCNT nanoparticle concentration on membrane electrochemical properties. Results revealed that the increase of PANI/MWCNT nanoparticle concentration in the casting solution caused the decrease in membrane water content, improved ion exchange capacity (IEC), and increasing fixed ionic charge (FIC). They also found that the membrane potential, transport number and selectivity were enhanced in NaCl and Na2SO4 ionic solutions by the increase of PANI/MWCNT nanoparticles.

Akbar Zendehnam and coworkers reported that membrane transport number, selectivity electrical conductivity were raised by increase of additive content in membrane matrix. They conducted a study about the effect used composite nanoparticles and electrolyte’s concentration on physico/chemical properties of membranes. By increasing the additive content, membrane ionic flux was increased and the mechanical stability of membranes was also improved due to the presence of composite nanoparticles in membrane matrix.

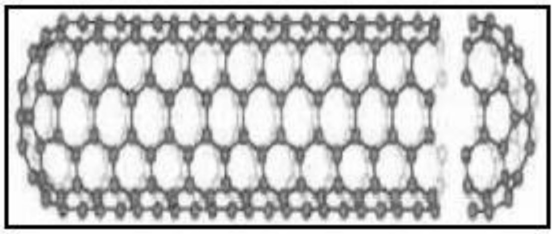


Figure 2.5 Structure of carbon nanotubes (MWCNTs)

2.5 Selection of PVC/NMP/ACETONE for the polymeric membranes.

As listed in Table 2.3 beside the effect of resin to the membrane properties, the choice of solvent and polymer also are the crucial factors that need to be considered in order to produce superior IEMs. In this research studies, polyvinylchloride (PVC) was chosen as the base polymer while N-Metyhlpyrolidonne (NMP) and acetone were chosen as the solvent.

NMP is an excellent solvent. S.M Hosseini et.al (2012) reported that, the final morphology of the membranes is influenced by process conditions and the employed materials such as polymer, solvent, and nonsolvent, composition or temperature of coagulant. They studied the effect of solvent on final morphology of the membranes. By using three distinct solvent which are NMP, PVDF, and N,N-dimethylacetamide (DMac) and they found that by using NMP the porosity of the membranes is more higher than DMF and less than DMac. Feyisayo V. Adams investigated the effect of solvent properties on the structural morphology and permeation properties of polysulfone/ β −cyclodextrin polyurethane (PSf/ β -CDPU) mixed-matrix membranes (MMMs). They were using four solvents in their study; dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide (DMA), and N-methyl-2-pyrrolidone (NMP). They concluded that membranes prepared by using NMP showed the highest hydrophilicity, porosity, and crystallinity due to the low volatility of NMP. Moreover, the combination of two solvents, NMP and acetone leads to the reduction in solvency, resulting in a much denser surface structure (He, 2001).

PVC is said to have excellent resistance to erosion, acids, alkaline and it is also offer low cost (Parvizian et al., 2014). During swelling, the matrix polymer should give adequate mechanical and dimensional stability to the structure of the membrane and also appropriate space to the ion-exchange particle (Wenten, 2016).

2.6 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a potent tool for studying the mechanisms of electrochemical reactions (MacDonald, 2006). EIS works by applying sinusoidal current or voltage to a pair of electrodes (one is working electrode and the other is counter electrode) and response of the system under investigation is observed by the same electrodes or reference electrodes. The experimental of EIS data is interpreted by complex nonlinear-least-squares fitting to an equivalent circuit, which is the spontaneous technique to characterize the whole membrane impedance. (Zhang et al., 2016).

The instrumentation of impedance measurements comprises of waveform generator to create the sine waves, a potentiostat to regulate the Direct Current and Alternating Current potential, and a computer to run the experiment and display the results in real time. In order for the system to response in a pseudo-linear behaviour, EIS is conducted by applying a small ac signal which usually less than 10mV. As depicted in Figure 2.6, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase. The values of impedance measured were plotted in Nquist plots where each point in this plot matches to impedance at one frequency. The x-axis which is the real part of impedance, Z' is plotted against the imaginary part Z" at y-axis. (Sin, 2014).

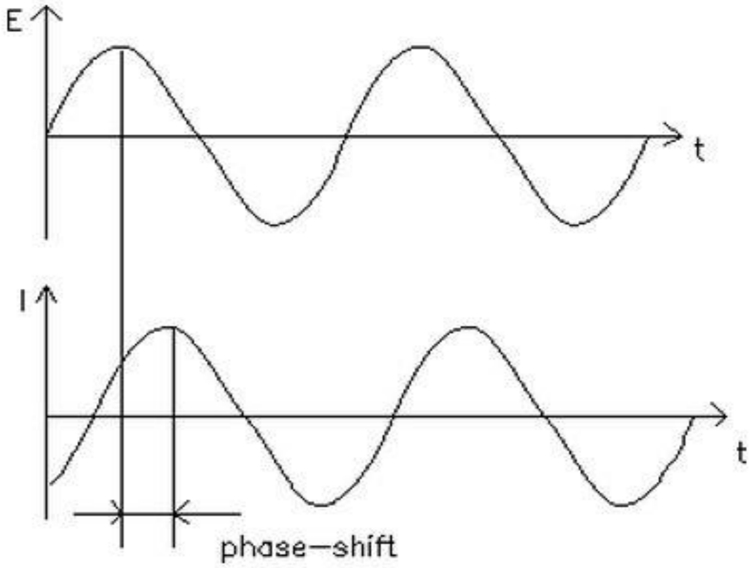


Figure 2.6 The potential and current response in a pseudo-linear system. (Sin, 2014)

2.7 The Use of EIS in the Study of CEM

Electric current can be created by two ways; by the transfer of electrons in solid metal or by the transport of ions in electrolyte solutions and CEM. CEMs are made up of three layer; the ion exchange membrane, the electrical double layer and lastly the diffusion boundary layer (Park et al., 2006). Electrical double layer (EDL) is formed due to rearrangement of ions at the membrane-solution interface that caused by the charge itself (Sang et al., 2008). Meanwhile, diffusion boundary layers (DBL) are formed at both sides of membrane due to the occurrence of concentration polarization caused by ionic current flow (Zhang et al., 2017). In addition, the behaviour of these layers can be observed by manipulating membrane physical properties (e.g ion exchange capacity, surface roughness) and operational conditions (e.g electrolyte concentration, flow rate, temperature). Figure 2.7 below showing the location of EDL and DBL (Zhang et al., 2016).

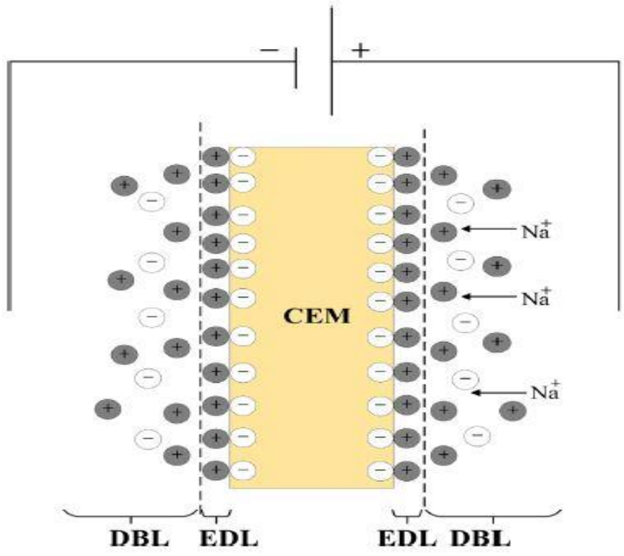


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Figure 2.7 Schematic diagram cation exchange membrane when immersed in an electrolyte solution with a current.

The efficiency of CEM system operation rely on the electrical resistance of the system which is determined by membrane resistance. When the measurement of membrane resistance are taken under different external solution concentrations, the measured membrane resistance tends to vary significantly due to the presence of DBL near the solution membrane-interface. Valid information on the concentration-dependency of membrane resistance is truly lacking thus, to deal with this complexity, impedance measurement can be great tool for investigating unknown phenomena in IEM systems (Zhang et al., 2017).

Previous researchers conducted an investigation for i) electrical properties of materials, ii) electrochemical phenomena iii) composite membranes iv)bipolar membranes. Especially in bipolar membranes studies, impedance measurement have delivered great electrochemical information in the bipolar junction structure and related electrochemical phenomena (Park et al., 2006). EIS also has been used to solve the difficulties to obtain membrane resistance measurement in reverse electrodialysis (RED) application besides chronopotentiometry (Hong, 2015). Thus, this research aims to utilize the EIS to investigate the membrane resistance of CEM system and other electrochemical phenomena.