Research Paper

Preparation and Characterization of Heterogeneous PVC-Silica Proton Exchange Membrane

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KEYWORDS

GRAPHICAL ABSTRACT

HIGHLIGHTS

• Heterogeneous PVC-silica membranes are synthesized using phase inversion technique
• Nanosilica loading in certain value gives improvement to membrane properties
• Sulfonation treatment produces membrane with higher conductivity and IEC
• Immersion of membrane in salt solution can also improves membrane properties

ABSTRACT

Heterogeneous proton exchange membranes (PEM) are synthesized using the dry phase inversion technique. The casting solutions are prepared by dispersing a finely ground cation exchange resin particle in N,N-dimethylacetamide (DMAc) solution of polyvinyl-chloride (PVC). Results show that ion exchange capacity is increased with the addition of 1 %-wt nanosilica (from 0.14 to 0.27 meq/g) while it is decreased with a higher concentration of silica. The incorporation of 0.5%-wt nanosilica improves water uptake (from 79.2% to 94.9%) and proton conductivity (from 0.02 to 0.09 mS/cm) of PEM. However, at further silica loading those properties are decreased. The membrane with 1%-wt nanosilica and 50%-wt resin showed very good stability in the oxidative environment. The post-treatment via membrane sulfonation at the optimum condition (0.1 M of sulfuric acid and 1 h reaction time) reduces the water uptake (from 94.8% to 92.3%) but improves the IEC (from 0.27 meq/g to 0.49 meg/g) and proton conductivity (from 0.02 mS/cm to 3.07 mS/cm). Meanwhile, the post-treatment via salt solution immersion at the optimum condition (0.1 M, 24 h and 30 °C) produces less water uptake (from 94.8% to 93.1%) but improves the IEC (from 0.27 meq/g to 0.55 meg/g) and drastically increases the proton conductivity (from 0.02 mS/cm to 2.79 mS/cm).

1. Introduction

Proton Exchange Membrane Fuel Cell (PEMFC) has been recognized as an attractive and promising energy converter to solve energy demands in the future due to being environmentally-friendly in producing no emission and pollutant gases and producing a high density of energy [1]. However, it still faces the economic challenges toward commercialization which is associated with the high cost. The main cause of its expensive price is presumed to be the membranes used inside the membrane electrode assembly (MEA).

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Membranes used in MEA are the perfluorinated type such as Nafion® that is produced through a complicated process. Preparation of an inexpensive membrane by using low-cost materials and a simple process could be the best way to overcome this problem [2-5].

Recent researches have been conducted to find the new formula for this kind of membrane, i.e. optimizing Nafion®, synthesizing non-perfluorinated membranes, composite membranes, and modification methods such as sulfonation, incorporating inorganic filler additives, etc. [6-9]. To date, there are only several researches that focus on heterogeneous membranes for this application. Preparations of heterogeneos ion-exchange membranes using different techniques and modifications have been reported including their improvement and the advantages of heterogeneous ion-exchange membranes [10-18]. The Polyvinyl chloride (PVC)-based heterogeneous ion-exchange membrane is one of the polymer binders that are widely used for membrane preparation due to its mechanical stability and flexibility [11, 19-24]. The proportion of PVC-resin has been made that produced a robust membrane with high durability [18]. Several studies on the preparation of PVC-based ion-exchange membranes have been reported. The PVC-styrene–butadiene-rubber (SBR) blend membranes have been prepared by the solution casting technique using the iron–nickel oxide (Fe_2NiO_4) nanoparticle as additive [20]. The iron-nickel oxide improved membrane properties in a certain concentration while it decreased the properties in a further loading of the additive. Potassium perchlorate has also been employed as additive of the PVC-SBR cation-exchange membranes [21]. The potassium perchlorate showed similar behaviour to Fe_2NiO_4. The intoductions of additive – inorganic filler such as Fe_2NiO_4, potassium perchlorate, silver nanoparticle, zeolite – in heterogeneous ion-exchange membranes are to improve the membrane properties by utilizing the specific properties of the fillers especially for their electrical properties or adsorption characteristics [22-25]. In addition, the filler can also improve membrane hydrophilicity that enhances membrane conductivity.

Silica is one of the inorganic filler additives that have been widely used in the membrane industry. Since it has the capability to attain homogeneous dispersion in the polymer membrane matrix, particularly in a nanometric size, the overall performance can be enhanced [26]. In addition, the introduction of the charged group via sulfonation – sulfonic group – membrane makes the membrane ion-exchangeable that can be conducted pre- or post-polymerization [27]. Moreover, the introduction of the membranes into electrolyte solution such as NaCl also has significant impact in improving electrochemical properties of membranes [9]. In this study, PVC-based heterogeneous PEMs are prepared using the dry phase inversion technique. The effects of nanosilica content on membrane characteristics such as the water uptake, the membrane conductivity and the oxidative stability are studied and evaluated. Additionally, the post-treatments effects are also investigated. The post-treatments are conducted via sulfonation of the prepared membranes and immersion in a salt solution.

2. Experimental

2.1. Materials

Polyvinyl-chloride (PVC) resin powder (FJ-70) is manufactured by PT. Asahimas Chemical, Indonesia. The cation exchange resin Amberlite IR 120 Na (sulfonate groups) is manufactured by Rohm and Haas Company. The silica nanoparticles manufactured by DuPont Co. sized 12 nm are used as inorganic filler additives. N,N-dimethylacetamide (DMAc) is manufactured by Shanghai Jingsan Jingwei Chemical Co., Ltd. All other chemicals are purchased commercially.

2.2. Membrane preparation

The heterogeneous membranes are prepared by casting solution technique and phase inversion method. Prior to the solution preparation, the cation exchange resins (Amberlite IR 120 Na) are dried in the oven at 60°C for 24 hours, then pulverized into fine particles and sieved into desired mesh size (-325+400). The preparation is proceeded by dissolving PVC resins into N,N-dimethylacetamide (DMAc) and stirred until the solution is optically homogeneous. This is followed by dispersing a specific quantity of resin as functional groups agent and mixing. Then, the solution is sonicated and mechanically stirred for 50 and 30 minutes, respectively. The mixture is then casted onto a glass plate and dried at ambient temperature for a period of time. As the final stage, the membranes are pretreated by immersing in NaOH and NaCl solutions prior to characterization. Meanwhile, for PVC-silica membrane fabrication, various colloidal silica quantities are dispersed into DMAc and subsequently sonicated to avoid agglomeration and induced fine distribution. PVC is then dissolved into the DMAc-silica (12%-wt PVC in

DMAc) mixture and followed by preparation steps as previously explained.

2.3. Membrane characterization

2.3.1. Morphological studies

The morphology structures of the prepared membranes are examined by scanning electron microscopy (SEM). The SEM images are evaluated to study the morphology structures of the synthesized membrane.

2.3.2. Water uptake

The water uptake is determined by measurement of the dry and wet weight ratio of the prepared membrane. First, the membrane is immersed in deionized water at ambient temperature for 12 hours. Then the membrane weight is measured (w_{wet}). Hereafter, the membrane is dried in the oven at 60°C and then weighed again (w_{dry}). The water content is calculated by using the following equation:

$$WU(\%) = \frac{w_{wet} - w_{wet}}{w_{dry}} \times 100\% \tag{1}$$

2.3.3. Ion exchange capacity

The ion exchange capacity (IEC) of H^+ can be determined by using the titration method. First, the membrane tip is immersed in the saturated NaCl solution for 48 h at room temperature to change the H^+ ions with Na^+ ions. Then, the H^+ ions are released in the solution and titrated with NaOH 0.01 M and phenolphtalein indicator. The IEC is calculated by using the following equation:

$$IEC = \frac{C \times V}{W} \tag{2}$$

where:
- IEC = ion exchange capacity (meq.g^{-1})
- C = molar concentration of the titrant (M)
- V = titrant volume (ml)
- W = dry weight of the membrane sample (gram)

2.3.4. Membrane conductivity

The measurement of membrane conductivity, σ (S/cm), is conducted by using LCR Meter instrumentation with a frequency range from 20 Hz to 2 MHz. To characterize the membrane conductivity, the membrane samples are immersed in the deionized water for 24 h until they are wet enough and saturated. Each sample is cut according to the electrode size used in the measurement cell. The measurement process undergoes 20 ℃ temperature (about 40–60 % humidity).

The conductivity of the membrane σ (S/cm) is calculated by using the following equation:

$$\sigma = \frac{L}{R.A} \tag{3}$$

where:
- σ = membrane conductivity (mS.cm^{-1})
- L = the distance between Pt electrode (cm)
- R = resistance measured (ohm)
- A = membrane area (cm^2)

2.3.5. Oxidative Stability

The oxidative stability of the membranes is characterized by measuring the changes of membrane weight after being immersed in aqueous hydrogen peroxide solution [28]. The membrane chips with 1 cm × 4 cm size are immersed in 3%-wt H_2O_2 aqueous solution and are kept in the oven at 60 ℃. The membranes are taken out from the solution and wiped out with tissue paper and then weighed. The wet membrane weights are recorded. The procedure is conducted for 15 days and the samples measurement is held at random days.

2.4. The membrane post-treatments

2.4.1. Sulfonation of heterogeneous membranes

The membrane samples (3 cm × 3 cm) are previously dried in the desiccator for 6 h, and then immersed in sulfuric acid at 60 ℃ for a certain time. The sulfuric acid concentration is varied at low concentrations of 0.1 M and 1 M. Afterward, the sulfonated membranes are taken out and re-immersed in deionized water at 80 ℃ for 12 h. Then, the samples are washed out with the deionized water until neutral pH is reached.

2.4.2. The electrolyte solution immersion

The post-treatment membrane via immersion in salt or electrolyte solution is a very simple method. The prepared membranes (3 cm × 3 cm) are immersed in sodium chloride solution with a concentration of 0.1 M and 0.01 M. The immersion time is varied at 24 h and 48 h and with a temperature of 30 °C and 60 °C. Afterwards, the membranes are characterized.

3. Results and Discussion

3.1. Membrane morphology

The membranes are characterized by scanning electron microscopy (SEM). Figure 1 presents the morphologies of representative membranes at 2000 and 5000 magnitudes. Figure 1 (a) illustrated that the polymer matrix covers the cation exchange resin particles (size ≤ 44 μm). Nevertheless, the SEM images show the presence of voids between the polymer matrix – that is PVC – and the resin particles. These void fractions of the heterogeneous ion-exchange membranes provide the space for resin particles when the membrane is in swollen state. These void fractions also give access for ionic species to reach functional sites of the resin particles. However, more loose void fractions reduce the selectivity of the membrane. Therefore, it is important to obtain the proper void fractions inside the membrane. In Figure 1 c-f, the nanosilica seems to be agglomerated which is indicated by a larger size of nanosilica found (around 1 μm). It would be better if the nanosilica is in nanometric size – no agglomeration. The smaller size has a larger surface and also better distribution.

Furthermore, the structure is formed by both hydrophilic and hydrophobic domains. The hydrophilic domains provide the ionic transportation paths due to their characteristics in adsorbing water as the proton bridge. The domains stand on the cation exchange resin and the silica nanoparticles side. On the other hand, the hydrophobic domains have a role in mechanical stability of the membranes. The proportion of PVC to cation

exchange resin influences the mechanical characteristics of the membranes. The high loading PVC should make the membranes more flexible, yet less conductive.

3.2. The effects of ion-exchange resin and nanosilica loading

3.2.1. Water uptake

Gizli et al. [29] report that the water content of the membranes determines the dimensional stability and also influences membrane selectivity, electrical resistance, and hydraulic permeability. The increase of the cation exchange resin loadings in the heterogeneous membrane improves the hydrophilicity of the membranes. Hydrophilicity of the membranes considerably influences its capability in adsorbing water. Figure 2 shows the effect of the cation exchange resin to the water uptake of the membranes. The heterogeneous membranes with the higher loading resin exhibit the more swollen structure. The arrangement of the particles structure of the swollen membranes due to the presence of water pushes out the chains of particle bonds of the PVC. The prepared membranes in this research tend to be flexible due to the proportional PVC content although they have a high concentration of resin. Cation exchange resin has been recognized as a brittle material, thus the loading concentration of more than 60%-wt will result in a brittle membrane. The brittleness of the membranes can be prevented by reducing the particle size of the cation exchange resin. Therefore, the particle size of the resin should be very fine enough (within -325+400 mesh) to obtain the flexible membranes. Nevertheless, the proportion of the resin should be restrained to 60%-wt [18]. The effects of the silica nanoparticles on water uptake at a range of concentration are presented in Figure 2. The figure shows the sharp increase of the water uptake value at 0.5%-wt nanosilica. However, at higher loading (1%-wt nanosilica concentration), the water uptake decreases drastically from 89.4% to 64.1% (for membrane with 50%-wt loading) and from 94.8% to 82.8% (for membrane with 60%-wt loading).

This is possibly due to the different methods that are induced by inherent characteristics of silica, specifically the hydrophilicity. In the first method, the addition of silica during membrane solution preparation may affect the interaction between solvent and polymer (DMAc-PVC).
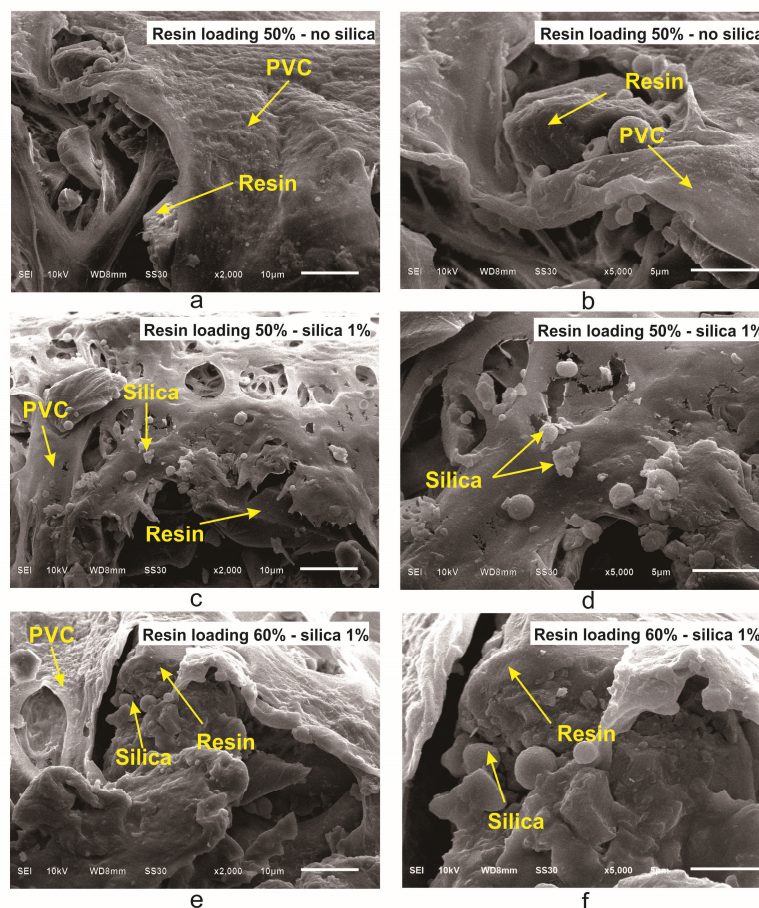

Fig. 1. Morphological structure of the heterogeneous membranes.

A portion of DMAc could interact with nanosilica since both materials are hydrophilic. This contributes to making the casting solution become more viscous, which is associated with partially – in small portion – solvent separation from the polymer. Therefore, casting solution with higher nanosilica loading is hard to be casted into a sheet of membranes, such as 4%-wt silica loading since the casting solution becomes more viscous. Consequently, the more viscous casting solution produces a more dense membrane. The prepared membrane becomes more compact and the cavity between particles in the membrane matrix becomes narrower. Meanwhile, the other effects of nanosilica are attributed to the functional site and hydrophilicity provided by nanosilica inside the membrane matrix. It is obvious then that the presence of nanosilica can improve membrane hydrophilicity particularly as shown by water uptake. However, it should be noted that the dominant way provided by nanosilica gives the significant additional properties to the prepared membrane. Thus, from the results it can be observed that the addition of nanosilica could either increase or decrease water uptake.

3.2.2. Ion exchange capacity

Figure 2 also presents the effects of the cation exchange resin and nanosilica to the ion exchange capacity. The effects of different resin concentrations are clearly presented in Figure 2. It is obvious that the greater presence of resin in the membrane matrix provides more functional groups. The resins are cation type with sulfonic groups – as informed by the manufacturer – which act as the active sites used during ionic exchange.

The nanosilica also significantly impacts the ion exchange capacity of the membranes. The improvement of IEC is performed at the 0.5 and 1%-wt nanosilica loadings. Ye et al. [30] reported the application of silica inorganic filler in the modified Nafion having considerable hydroxyl groups causing the water molecules to be attracted easily. It possibly implies that the addition of nanosilica could enhance the access of active site due to more water molecules attracted. However, the IEC decrease at higher silica content for example at 2 %-wt. It possibly implies that the greater nanosilica content produces less void fraction inside the matrix as previously explained in section 3.2.1. As a consequence, the functional groups of resin and silica become inaccessible.
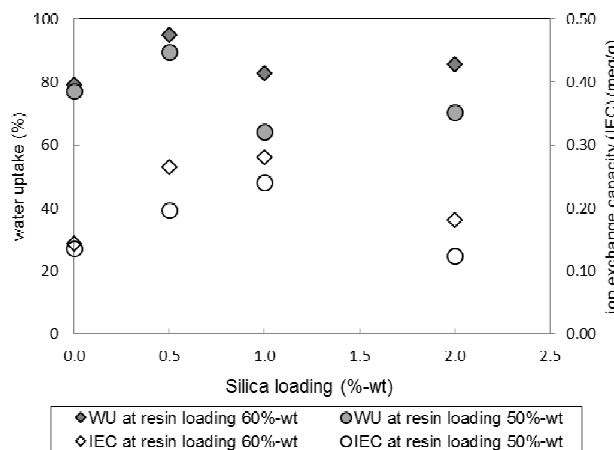

Fig. 2. The effect of resin loading and nanosilica concentration to water uptake and ion exchange capacity (IEC).

3.2.3. Conductivity

The membrane conductivity (σ) is the crucial property in membrane selection for fuel cell application. Conductivity of the membrane contributes to a highly obtained current density. It depends on the chemical and physical properties of the materials and the morphology structure of the prepared membrane. The σ value obtained also depends on the measurement technique used [9].

The addition of 0.5%-wt of nanosilica exhibits the drastic increase of membrane conductivity (Figure 3). Nevertheless, the conductivity decreases at higher amounts of adding more than 0.5%-wt. This is likely due to the fact that more compact structures were generated at a higher concentration, so it covered up the ionic exchange sites and restrained the ion transportation paths. The polymer blending of casting solution that contains more 0.5%-wt also has higher viscosity. The higher viscosity of casting solution produces a membrane with less void fraction that leads to higher resistivity.

Peighambardoust et al. [31] report that the resistance loss is proportional to the ionic resistance of the membranes. It is also reported that the high

conductivity has a significant role, particularly at high current density. Molecularly, the proton transfer in the polymer matrix generally has two basic mechanisms, i.e the proton hopping or Grotthus mechanism and either the diffusion mechanisms whereas the water molecules act as the vehicles or are known as the vehicle mechanisms.

The resin contents also affect the membrane properties. As seen in Figure 3, the membranes with 60%-wt of resin loading have better membrane conductivity than 50%-wt. The higher loading of resin creates more ionic transportation paths as previously explained. DeLuca et al. [32] explained that the proton hopping mechanisms occur when the proton hops from one hydrolyzed ionic site (SO_3^- H_3O^+) to others throughout the membrane. The protons were generated via hydrogen oxidation in the anode side and entrained with the water molecules thus forming the transient hydronium ions. The distinct protons of the hydronium hop to the other water molecules. In this mechanism, the ionic cluster becomes swollen with the presence of water and creates percolation for proton transfer. This hopping mechanism reported could slightly help in improving the proton conductivity of PFSA membranes such as Nafion[®].
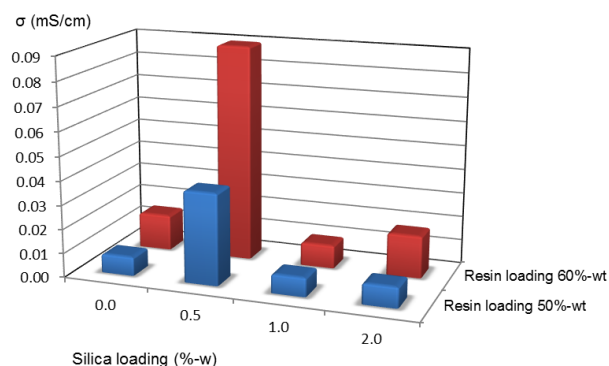

Fig. 3. The effect of resin loading and nanosilica concentration to membrane conductivity.

3.2.4. Oxidative stability

LaConti et al. [33] report that the PEM membrane in the fuel cell unit could undergo aggressive conditions due to the interaction between H_2 and O_2 in the catalyst surface so that the radical species HO[•] and HOO[•] are generated. These radical species attack the polymer and cause the chain termination, thus the membrane degradation might occur. Therefore, the oxidative stability of the membranes prepared needs to be characterized.

During the fuel cell operation, the peroxy radicals can be created and cause severe degradation of the membrane materials. This leads to the brittleness and evolves to cracks until the membrane is damaged [15]. Figure 4 presents the observation results of 15 days of the immersion membrane in the oxidative environment. It shows the membrane degradation against the time. For the sample M50-A (50 % resin, 0% silica), M50-C (50 % resin, 1% silica) and M60-C (60 % resin, 1% silica), the oxidative stability are 58.02%, 74.12% and 51.74% respectively. The membrane M50-C shows very good stability above all. This membrane contains 49%-wt of PVC, 50%-wt cation exchange resin and 1%-wt silica nanoparticles. The proportion of the membrane composition probably affects the chemical stability of the membranes. By comparing the M50-C and M60-C membranes, the effects of cation exchange resin loading could be observed. The higher loading resin results in lower chemical stability due to the considerable amount of brittle material like cation exchange resin, and thus the membrane becomes easier to be attacked by the HO[•] radical. The radical could damage the chemical structure of the heterogeneous membrane. On the other hand, at the lower resin loading, the membrane becomes more chemically stable due to inherent characteristics of PVC. Furthermore, from the water uptake property (Figure 2), it can be seen that the membrane which has the best oxidative stability (Figure 4) is a membrane with the lowest water uptake. When the resin loading is increased, the membrane becomes more hydrophilic. The more hydrophilic property contributes to the faster diffusion of peroxide into the membrane side and thus increases the reaction between the solution and the membrane.

3.3. The effects of sulfonation on heterogeneous membranes properties

Sulfonation has been recognized as the most effective method to improve the proton conductivity of the fuel cell membrane. The polymer sulfonation can be achieved by two basic routes, i.e copolymerization of the sulfonated monomers or via polymer sulphonation [6]. The sulfonation agents that are

commonly used are dichlorosulfonic acid, oleum, and even sulphuric acid. Meanwhile, the functional groups in the fuel cell membranes (i.e. sulfonic acid) require the presence of water as proton solvent for dissociation and formation of active protons [34]. Therefore, a combination of the highly hydrated membrane with highly distributed functional groups inside the membrane matrix can produce high conductivity.
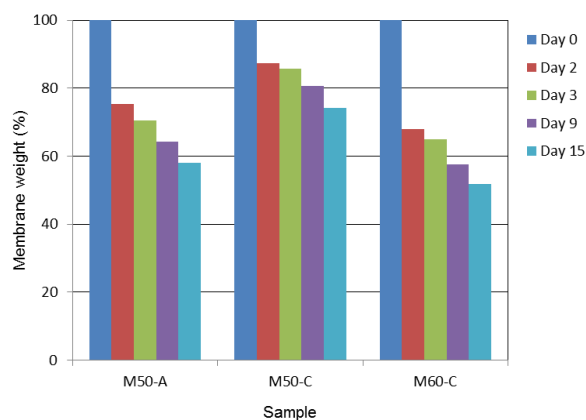

Fig. 4. The effect of resin loading and nanosilica concentration to oxidative stability.

In the Nafion perfluorinated membranes, its structure consists of wide and less branched channels, and also the small SO_3^- group separation. This structure also allows a good connectivity of the ions. The proton conduction occurs in the water channels through the sulfonic ions and thus the water content influences the proton mobility [35]. In this study, the sulfuric acid is used as the sulfonation agent. The results of the experiment are presented in Table 1. Generally, the increase of sulfuric acid concentration and sulfonation time improves ion exchange capacity and membrane conductivity. Meanwhile, the water uptake of the membrane tends to decrease with increasing those parameters. It is shown from these results that the sulfonation step produces more active ionic sites in the structure, thus the ion exchange capacity (IEC) and conductivity are increased. Since the sulfonation was conducted in relatively low sulfuric acid concentration, the improvement of membrane properties may be attributed to activation of functional groups of resin in the membrane. On the other hand, the sulfonation may reduce void fraction during this treatment, and thus generate the membranes with lower water uptake.

Table 1
The sulfonation effects on heterogeneous membranes properties.

No.	Sample	H_2SO_4 concentration (M)	Time (h)	Water uptake (%)	IEC (meq/gr)	Σ (mS/cm)
1	M60-B	-	-	94.8	0.26	0.09
2	MS-a1	0.1	1	92.3	0.49	3.07
3	MS-a2	0.1	2	87.9	0.37	2.64
4	MS-b1	1	1	93.8	0.65	2.89
5	MS-b2	1	2	88.0	0.61	2.64

M60-B: membrane with 60 %-wt resin and 0.5 %-wt nanosilica

3.4. The effects of membrane immersion in electrolyte solution

In this study, the prepared membranes are subjected to post-treatment via immersion in electrolyte solution (NaCl) to evaluate the effect of this treatment on membrane properties. Figure 5 (a-c) presents the properties of the membrane after post-treatment using electrolyte solution. As encountered in the sulfonation step, water uptake of the membranes tends to decrease in electrolyte immersion. During the treatment, the resin particles swell and expand pushing away the PVC matrix of membranes that results in the formation of narrow cavities between resin particles and PVC matrix and the formation of micro-cracks in the polymer matrix [36]. Therefore, the spaces for water are decreased.

The increase of the NaCl concentration significantly affects the conductivity of the prepared membranes. This enhancement is also obtained by the longer immersion time. It is obvious that the longer immersion time contributes to the higher ions loaded. However, similar to sulfonation, the membrane immersion into salt solution may improve the membrane conductivity due to activation of functional sites rather than the addition of

new sites. As previously stated, during the immersion, resin particles swell and expand. This may reduce the distance between resin particles and thus improve the membrane conductivity and the accessibility of the functional sites.

Meanwhile, operating temperature during immersion shows the opposite trends. The negative effect of temperature on membrane electrochemical properties could be attributed to membrane structure which is shrinking within immersion. The exposure of relatively high temperature facilitates the membrane matrix to lose its void fraction, thus reducing channels for ion migration.
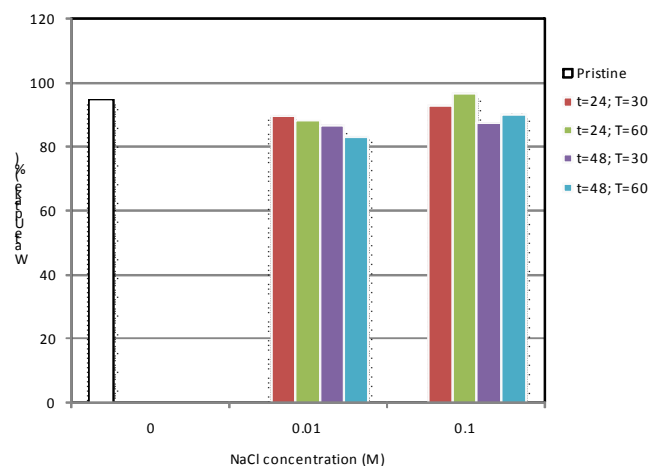
(a)
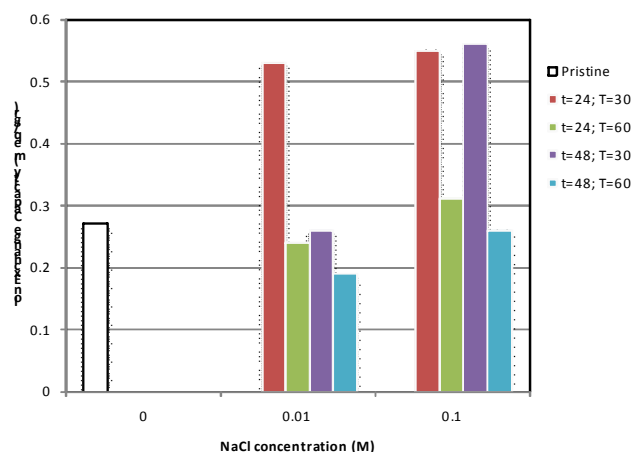
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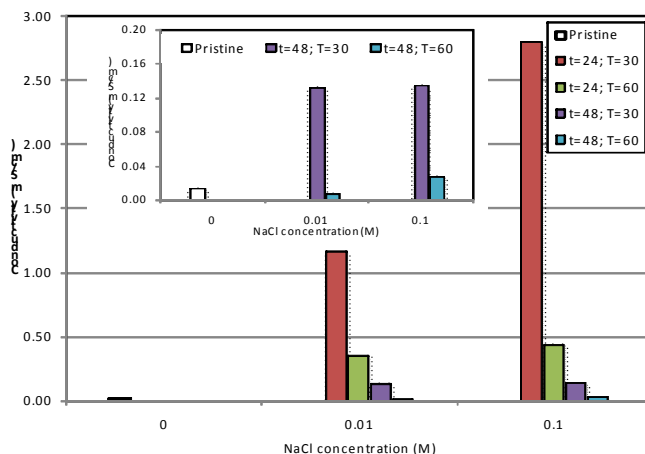
(c)

Fig. 5. The effect of electrolyte immersion on (a) water uptake, (b) ion exchange capacity (IEC), and (c) conductivity.

4.   Conclusions

It was found that the composition of the heterogeneous membrane significantly affect properties of the prepared membranes. The proportions of matrix and resin each have a role in durability and electrochemical properties. Results show that ion exchange capacity is increased by the addition of 1 %-wt nanosilica (from 0.14 to 0.27 meq/g) while it is decreased with higher concentration of silica. The incorporation of 0.5%-wt nanosilica improves the water uptake (from 79.2% to 94.9%) and the membrane conductivity (from 0.02 to 0.09 mS/cm). However, at further silica loading those properties are

decreased. The membrane with 1%-wt nanosilica and 50%-wt resin showed very good stability in the oxidative environment. The post-treatment via membrane sulfonation at the optimum condition (0.1 M of sulfuric acid and 1 h reaction time) reduces the water uptake (from 94.8% to 92.3%) but improves the IEC (from 0.27 meq/g to 0.49 meg/g) and the conductivity (from 0.02 mS/cm to 3.07 mS/cm). Meanwhile, the post-treatment via salt solution immersion at the optimum condition (0.1 M, 24 h and 30 °C) produces less water uptake (from 94.8% to 93.1%) but improves the IEC (from 0.27 meq/g to 0.55 meg/g) and drastically increases the conductivity (from 0.02 mS/cm to 2.79 mS/cm).

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