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Comparative Study On Water Uptake And Ionic Transport Properties Of Pre- And Post Sulfonated Chitosan/PVA polymer Exchange Membrane

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Abstract: Chitosan/poly(vinyl alcohol) (PVA) blend composite was prepared through two strategies of chemical modification, namely pre- and post-sulfonation. The sulfonation was carried out by using 4-sulfopthalic acid (sPTA) as the sulfonating agent. The modified chitosan/PVA blend composite was prepared under a range of chitosan content (10:90, 25:75, 50:50, 75:25 and 90:10). Water uptake and ion exchange capacity (IEC) of modified membranes were evaluated by titration and gravimetry methods respectively. Accordingly, both pre- and post-sulfonated composite showed a decrease in water uptakes and IEC values with an increase in chitosan content from 10 to 50 vol.%, attributed to the greater number of hydrogen bond pairs between the two polymers. At 75 vol.%, the composite was predicted to be dominant by the hydrophilic nature of chitosan, in which IEC values and water uptakes were shown to increase. The composite with 90 wt.% chitosan was found to be excessively hydrophilic with tremendously high water uptake, hence not suitable for fuel cell application. Besides that, the post-sulfonated composite showed a trend of increase in the IEC values and water uptakes with a decrease in chitosan content from 10 to 50 vol.%, and bounced back at 75 vol.%. Despite both pre- and post-sulfonation methods demonstrated similar trends in the results, it was notable that post-sulfonation method emerged with higher water uptake and ionic conductivity was found more favorable, attributed to the possibility that sulfonation took place on both PVA and chitosan which has caused a significant increase in sulfonic groups that purportedly exhibited higher ion transport mobility.

Keywords: Chitosan/poly(vinyl alcohol) blend composite, fuel cell, functionalisation of polymers, membranes.

1. Introduction
In the past few years, biopolymers have been appraised as the potential substituents for synthetic polymers used in low and intermediate temperature polymer electrolyte-based fuel cells [1]. Biopolymers have demonstrated excellent properties such as biocompatibility, biodegradability,
nontoxicity, naturally abundant and lower cost compared to synthetic polymers. Despite that, an apparent obstacle of low ionic conductivity and high crystallinity is observed on pristine biopolymers such as chitosan and cellulose, potentially hinder the performance of a solid polymer electrolyte (SPE) [2].

In correspondence, diverse strategies have been made to comprehend the aforementioned challenges, for instance, performing copolymerization, grafting, polymer blend, crosslinking, chemical modification, the addition of fillers and plasticisers [3-6]. Among all, chemical modification excelled as an exceptional strategy to tailor the polymer properties mainly contributed to the available functional groups in the polymer that allow functionalization while providing multitude variations and specific chemical functionalities [7, 8]. Hence, the scope of study in this work constraint on investigating the effect of pre- and post-sulfonation through the blending of chitosan and poly(vinyl alcohol) (PVA) as a potential SPE for fuel cell application.

Chitosan is regarded as the second most abundant natural polymers in the world which can be obtained through deacetylation of chitin by alkaline hydrolysis or enzymatic method. It has been widely considered for a range of applications owing to its excellent properties and its constructive role as a polymer backbone that is readily for complexation and modification [9, 10]. In contrary, PVA is a synthetic polymer produced from the hydrolysis of poly(vinyl acetate), which is well-suited for blending with natural polymers due to its highly polar characteristic [11]. According to Buraidah and co-workers [12], the blending of chitosan and PVA can form complexation through strong hydrogen bonding from hydroxyl groups of PVA with amino and hydroxyl groups of chitosan that results in greater conductivity and mechanical properties. The desirable properties of mechanical and conductivity are shown improved with an enhancement through blending of chitosan and PVA, however the effect is not immense as ion exchange capacity (IEC) is reported with 0.0960, 0.1200 and 0.2530 mequiv/g for pristine PVA, chitosan and chitosan/PVA composite respectively, compared to 0.9500 mequiv/g of Nafion membrane [13, 14].

Herewith, the work adopted two modification methods as mentioned above: (1) pre- and (2) post-sulfonation of the polymer membranes. The concept of post-sulfonation is first done by cross-linking the polymer membrane and followed by exposing to a sulfonation agent. This sulfonation process is considerably slow and not uniform across the membrane [15-18]. As for the latter, namely, pre-sulfonation is the opposite of post-sulfonation whereby cross-linking of the polymer membrane is done after sulfonation. This was shown with a better control over the degree of sulfonation and deactivated sites in the polymer backbone, which further avoids side reactions such as decomposition and hydrolysis of polymers that resulted from post-sulfonation method [19]. Recently, Chanthad and co-workers [20] had reported a work involving sulfonated PVA composite with 4-sulfopthalic acid (sPTA) as sulfonation agent. The study has shown that PVA was found to be chemically modified at the hydroxyl groups of PVA molecules with the acid. With the addition of sulfonic acid groups, the electrical properties of the sulfonated-PVA composite membrane had demonstrated a vast improvement in comparison to pristine PVA membrane. With respect to that, this objective of this work is to focus on the comparative parameters obtained through pre- and post-sulfonation including water uptake, ion exchange capacity (IEC), and ionic conductivity.

2. Methodology

2.1 Materials

Chitosan (low molecular weight, \( M_w = 50,000 – 190,000 \) g/mol, Sigma-Aldrich), poly(vinyl alcohol) (PVA, 99.5% hydrolysed, \( M_w = 85,000 – 124,000 \) g/mol, Sigma-Aldrich), 4-sulfopthalic acid (sPTA, 50% aqueous solution, Sigma-Aldrich), acetic acid glacial (CH\(_3\)COOH, 99.8%, AR Grade, Friendemann Schmidt), sodium hydroxide, pellets (NaOH, AR Grade, Macron Fine Chemicals) and sodium chloride (NaCl, AR Grade, R&M Chemicals) were used. Throughout the study, deionized water was used to perform cleaning and analytical testing.
2.2 Preparation of chitosan and PVA solutions
The polymeric blend involving both chitosan and PVA were prepared as described by Alhosseini and co-workers [21]. Dissolution of chitosan and PVA were performed separately under respective solvents. 1 wt.% of chitosan solution was prepared under the dissolution in 0.1 M acetic acid glacial at room temperature for 24 hours under continuous stirring; whereas 5 wt.% of PVA was dissolved in deionized water at 120°C for approximately 6 hours under continuously stirring with a speed of 1000 rpm.

2.3 Pre-sulfonation of chitosan/PVA composite membrane
The PVA solution was firstly exposed to sPTA as described by Seeponkai and co-workers [22]. It was added drop-wise with a dosage level of 10 wt.% to the polymer weight of PVA solution and was further stirred at room temperature for 24 hours. The procedure for preparation of blend composite was conducted accordingly as described by Kuzmina and co-workers [23] with varying ratio of chitosan to the sulfonated-PVA solution. The resulting blend solution of 20 ml under different proportion will be cast on a glass petri dish and left evaporate overnight prior to further drying in vacuum oven at 60 °C for 24 hours.

2.4 Post-sulfonation of chitosan/PVA composite membrane
PVA and chitosan solutions prepared were blended under different ratio prior to sulfonation. The dosage level of sPTA was added drop-wise with a level of 10 wt.% to the polymer weight of the solution (PVA and chitosan in this case) and was further stirred at room temperature for 24 hours. The resulting blend solution of 20 ml with different proportions will be cast on a glass petri dish and left evaporated in a fume hood overnight prior to further drying in vacuum oven at 60 °C for 24 hours.

| Table 1. Test samples performed with vary in chitosan: PVA content under vol.% |
|--------------------------------------------------|
| Pre-sulfonation (Chitosan/sulfonated-PVA) | 10:90 |
| post-sulfonation (Sulfonated-chitosan/ PVA)    | 25:75 |
|                                                 | 50:50 |
|                                                 | 75:25 |
|                                                 | 90:10 |

2.5 Water uptake
Membranes were first placed in a vacuum oven for 24 hours at 60 °C to eliminate any moisture content prior to water uptake test. Then the measurement for dried specimens was carried out at room temperature, using a sorption apparatus equipped with microbalance [24]. The blended composite is equilibrated with water vapor for 24 hours and mass change was recorded by weighing before and after equilibration. Equation 1 shows the calculation of water uptake:

\[ \text{Water uptake, \%} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\% \]  

where \( M_{\text{wet}} \) is the weight of wet membrane, g; and \( M_{\text{dry}} \) is the weight of dry membrane, g.

2.6 Electrochemical impedance spectroscopy (EIS)
The ionic conductivities of the membranes were measured using Autolab PGSTAT128N potentiostat. The membrane was sandwiched between two stainless steel electrodes (two-electrode setup) in a measurement cell under alternative current (AC) mode. A setting of frequency ranged from 1000 kHz to 1 Hz and signal amplitude 0.1 V was applied [25]. The diameter of the measurement cell 19 mm and all samples was tested under hydrated state at room temperature.
In order to generate informative data from the potentiostat, NOVA software was used. Data was collected in a form of Nyquist plot, in which electrochemical circle fit was then applied to determine its electrolyte resistance, $R_s$ and obtained a convergence curve. The ionic conductivities of the samples were calculated with Equation 2.

$$\lambda = \frac{t}{A \times R_s}$$  \hspace{1cm} (2)

where $\lambda$ is the ionic conductivity, S/cm; $t$ is the thickness of the blended composite membrane, cm; $A$ is the area of the blended composite membrane covered by measurement cell; and $R_s$ is the electrolyte resistance, $\Omega$.

### 2.7 Ion exchange capacity (IEC)

IEC of the membrane was measure by titration technique as described by Chanthad and co-workers [20]. The membrane was firstly prepared in a size of 3x3 cm$^2$ before weighing the dry sample weight. Secondly, the dry sample was immersed in 0.1 M sodium chloride (NaCl) solution for 24 hours to allow the exchange of hydrogen and sodium ions. After that, the sample inside the NaCl solution will be removed before performing titration with 0.1 M sodium hydroxide (NaOH) solution to evaluate the amount of HCl generated from the exchange process. Based upon the data collected, IEC of the sample will be calculated with the following equation:

$$IEC = \frac{M_{NaOH}}{W_{dry}}$$  \hspace{1cm} (3)

where $M_{NaOH}$ is the mol equivalent (mequiv) of NaOH; and $W_{dry}$ is the weight of the dry membrane.

### 3. Result And Discussion

#### 3.1 Water uptake of the membrane

Water uptake is an important attribute to all solid polymer electrolytes (SPE), whereby it reflects the balance between ionic conductivity and mechanical stability [26]. Table 2 shows that the water uptake of PVA membrane chemically modified with sPTA was slightly lower than pure PVA. This effect could be attributed to the stronger ionic interaction that resulted in an increase in cross-linking density of the sulfonated membrane and consequently allow only limited water uptake [27].

The blend composite membrane of chitosan and PVA under pre-sulfonation demonstrated similar trend to post-sulfonation, water uptake of the chitosan/PVA composite decreases with higher chitosan content and noticeable bounce was shown at 90 vol.% chitosan containing composite with the values of 280.6% and 578.8 %, respectively. According to our understanding, PVA imbedded a partially ionic proton-donor group and a collinear proton-acceptor atom with asymmetric lone-pair orbitals in hydroxyl groups that is feasible for the formation of hydrogen-bonding [28]. Owing to this, the water uptake of chitosan/PVA composite displayed a reduction with increasing chitosan content. At 50 vol.% chitosan containing composite, the blended composite had the lowest water uptake of 116.4 % probably attribute to that all lone-pair orbitals were filled as we hypothetically plotted an equally balanced on mole ratio according to the calculation. Theoretically, chitosan consists of 3 lone-pair electrons on hydroxyl and amine functional groups and 2 ether groups as the backbone of polymer that are ready for complexation through hydrogen bonds formation [29]. In this study, chitosan prepared in 1 wt. % consists of 5 functional groups, namely 2 hydroxyls groups, 1 amine group, and 2 ether groups; while PVA prepared in 5 wt.% consists of 5 hydroxyls. With 50 wt.% of chitosan, the complexation was likely attributed to the formation of hydrogen bonds between all five pairs of functional groups in PVA and chitosan that has resulted in a drastic reduce in the available hydrophilic groups ready for water uptake, hence, recorded the lowest value among all composites.

On the other hand, the pre-sulfonated membrane showed lower water uptakes as compared to post-sulfonated membranes. This might be due to the sulfonating agent being successfully crosslinked with PVA and thus leaving less hydrophilic groups available when blended with chitosan to form an SPE. Following the same argument, the post-sulfonation composite membrane with dominant chitosan...
content showcased possible hydrolytic degradation with a severe water uptake of 578.8 % as opposed to similar ratio composite membrane under pre-sulfonation [19].

| Sample | Water uptake, % | Ionic conductivity, S/cm | IEC value, mequiv/g |
|--------|-----------------|--------------------------|---------------------|
|        | Pre-sulfonation | Post-sulfonation | Pre-sulfonation | Post-sulfonation | Pre-sulfonation | Post-sulfonation |
| PVA    | 127.3           | -                        | 0.0662             | -                  | 0.0440          | -                  |
| Sulfoinated-PVA | 124.5           | -                        | 0.2613             | -                  | 0.0890          | -                  |
| CS:PVA 10:90 | 130.4           | 173.9                    | 0.1225             | 0.2280             | 0.3430          | 0.4000            |
| CS:PVA 25:75 | 119.6           | 125.1                    | 0.0805             | 0.1538             | 0.2906          | 0.3450            |
| CS:PVA 50:50 | 104.1           | 116.4                    | 0.0702             | 0.0883             | 0.1080          | 0.2209            |
| CS:PVA 75:25 | 127.8           | 122.5                    | 0.0916             | 0.2183             | 0.1370          | 0.2304            |
| CS:PVA 90:10 | 280.6           | 578.8                    | 0.1874             | 0.6081             | 0.3015          | 0.3212            |

3.2 The ionic conductivity of the membrane

Table 2 shows the results of ionic conductivity for all tested samples under the hydrated state. A remarkable increase from $6.620 \times 10^{-5}$ to $2.613 \times 10^{-4}$ S/cm on the sulfonated PVA membrane as a comparison to pure PVA membrane was demonstrated. This notable enhancement in ionic conductivity reflects the positive contribution of sulfonation, likely attributed to the reaction at the hydroxyl groups of PVA and carboxylic groups of sPTA to form sulfonic groups that allowed the formation of water clusters in the membrane and subsequently increased the ion transport mobility [30].

Aside from that, the ionic conductivities of both pre- and post-sulfonation were shown to decrease with higher chitosan content. For membrane with 10 vol.% containing chitosan, the behavior was controlled by PVA that was reflected with greater water uptake and ionic conductivity due to its higher affinity towards water. Further, increase in the chitosan content beyond 50 vol. % has shown to increase the ionic conductivity, which is in a similar trend as water uptake results. In view of this, chitosan being an established natural hydrophilic swellable polymer was prime to indulge higher water uptake and ionic conductivity. However, the exaggeration of 578.8 % in water uptake for 90 vol.% containing chitosan composites was not favorable due to the fact of being excessively hydrophilic and would cause undesired excessive swelling and hydrolytic degradation when immersed into water.

In a comparison between both pre- and post-sulfonation, the ionic conductivities for pre-sulfonation were found lower. This was possible due to lesser proton transport sites in the pre-sulfonation composite membrane as aforementioned and thus resulted in lower proton conductivity. Another explanation is possibly attributed to the non-uniform distribution of proton transport sites that resulted in improper balance of proton conduct mechanisms and subsequently lead to non-linear effects in the membrane resistance [31]. Conclusively, the post-sulfonation method exhibited higher ionic conductivity due to the likelihood of sulfonation taken place on both PVA and chitosan. As a result, the blended composite could potentially possess a significant increase in sulfonic acid groups that are responsible for ionic transport across the membrane.
3.3 Ion exchange capacity (IEC) of the membrane

Table 2 shows the IEC values of samples including both pre- and post-sulfonation. The pure chitosan was found dissociated over time and subsequently dissolved fully in the 0.1 M NaCl and deionized water solution after 24 hours, in which no data was reported. Besides that, the sulfonated PVA membrane showed an enhancement of the IEC value from 0.0440 to 0.0890 mequiv/g. In such circumstances, the prediction stated above with the potential of hydroxyl groups of PVA being reacted with carboxylic groups of sPTA was valid.

Notably, the IEC values reported were shown aligned with the water uptake on both pre- and post-sulfonation methods. In regards, IEC presented an indirect and reliable root to investigate the ionic conductivity as described by Palani and co-workers [32]. Among all the samples, 10 vol.% containing chitosan composite under post-sulfonation demonstrated the highest IEC value with 0.4000 mequiv/g. Nevertheless, despite that the 90 vol.% containing chitosan composite displayed highest water uptake and ionic conductivity, the possible reason of lower IEC value obtained could be due to the lesser ion-exchangeable sites presented in the blended composite by mean of amino and hydroxyl functional groups interaction from chitosan and PVA [32]. In contrary, the same content of chitosan under pre-sulfonation emerged with lower IEC value, 0.3015 mequiv/g that may indicatively to the lower water uptake which interprets better water management in comparison to post-sulfonation.

4. Conclusion

The effect of pre- and post-sulfonation in chitosan/PVA blend composite was studied. Results tabulated for pre-sulfonation was shown identical to post-sulfonation on the trend for the proton conductivity, water uptake and IEC results. It was found that at 10 vol.% containing chitosan composite, it exerted a balance between water management (water uptake) and active proton transport sites (IEC value). This was followed by a decrease in both properties with increase in chitosan content to 50 vol.%. As the chitosan content being a further increase, the ion transport properties took off with a bounce that shown with an enhancement in all analysis tested. However, it was remarkable at 90 vol.% whereby the water management falls sharply with potential hydrolytic degradation occurrence on the composite. Overall, the post-sulfonation method had led to higher ionic transport properties likely due to sulfonation took place on both PVA and chitosan which induced with a significant increase of sulfonic groups that purportedly exhibited higher ion transport mobility.

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