Journal of Engineering Science and Technology
Vol. 13, No. 9 (2018) 2995 - 3006
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CHOLINE CHLORIDE:UREA-BASED DEEP EUTECTIC SOLVENT AS ADDITIVE TO PROTON CONDUCTING CHITOSAN FILMS

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Abstract

Chitosan (CS) film has been regarded as one of the bioresources that shows its ability to conduct proton upon modification. Nonetheless, CS film in nature is brittle and shows extremely high swelling degree towards water, leading to the impractical applications for fuel cell membranes and batteries. Formation of natural polymeric film requires plasticiser to crosslink natural polymers in improving the mechanical strength. Here, we investigate the potential of choline chloride (ChCl) and urea based deep eutectic solvent (DES) as additive in CS film with the aim to improve the mechanical property of the film. In this study, ChCl:urea- based DES was mixed with pure CS solution at different volume ratio and casted into a film. The film will be investigated on the functional groups, water uptake, ionic conductivity, proton exchange capacity and its morphology. Based on the SEM morphology result, it was found that addition of DES improves the homogeneity of the membrane film mainly attributed to the presence of strong bonds between the CS monosaccharides. Besides that, it also contributed towards better plasticising effect of the film that improves the flexibility of the membrane. The addition of DES has further improved the ionic conductivity of CS film from 2.98×10^{-3} to 1.23×10^{-2} S/cm; while drastically reduced the water uptake from 698.89 % to 180.67 %.

Keywords: Chitosan membrane, Morphology, Plasticiser, Proton conductivity.

1. Introduction

The increase in world population and energy demand has urged human being to look into the utilisation of renewable energy. Among many different renewable energies, fuel cell technology is foreseen to be one of the promising ways to tackle the above challenge. Owing to its high fuel efficiency, virtually zero pollution and abundant fuel source [1], this technology is paving its way for public use. Proton exchange membrane fuel cell (PEMFC) has received widest interest among the many types of fuel cells, attributed to its ease in fuel handling, high efficiency and energy density, low temperature operation and thus allowing for mobile applications [2]. One of the main components comprised in PEMFC that is responsible for completing the electrochemical reaction is the proton exchange membrane (PEM). Nafion-117 as the state-of-art PEM for PEMFC application, however, possesses a major drawback on its high material cost, high methanol permeability and performance lost when operated at elevated temperature. These issues have contributed to the hindrance of the commercialisation of fuel cell technology. In view of this, alternative materials have been actively investigated as PEM [3].

The abundancy and ease of chemical modification of natural polymers has been identified as a potential substituent for pure Nafion membrane. Chitosan (CS), a commercially available polysaccharide, has been extensively studied for the abovementioned application owing to its high hydrophilicity that allows water absorption in the membrane, ease in functionalisation and possesses good membrane forming capability [4]. Earlier works on CS composites membrane such as CS/silica, CS/Nafion, CS/poly(vinyl alcohol) (PVA) have shown that the CS-based membranes were able to achieve the proton conductivity at the magnitude of 10^{-2} S/cm [5, 6], which were comparable to Nafion-117, reported with the proton conductivity of approximately 8.6×10^{-2} S/cm. Nonetheless, the brittleness and high swelling degree in water of pure CS membrane has refrained its wider application. Later studies on ionic liquid (IL) which were incorporated into the PEM to act as a plasticiser to the membrane [7-9], has shown to increase the ionic conductivity. Such positive contribution of IL is attributed by its ionic characteristics which enhances the conductivity under anhydrous conditions.

According to Leones et al. [10], pure CS membrane was literally low in ionic conductivity with an order of magnitude of 10^{-5} S/cm. As such, the group demonstrated with the incorporation of 1-ethyl-3-methylimidazolium methanesulfonate $[C_2mim][C_1SO_3]$ IL, the ionic conductivity increases up to 7.79×10^{-4} S/cm conceivably to lower energy barrier faced by ions that subsequently enhanced the ions mobility. In addition, IL has low volatility, high electrochemical and thermal stability and is non-flammable [11]. Díaz et al. [12] explained that ioni liquid facilitates in softening the polymer backbone and reducing the crystallinity of membrane. Subsequently, it increases the polymer chain flexibility that is found important in enhancing the Grotthus transport of proton through the chain. With sufficiently high ion mobility in the polymer chain, short-distance transport can be realised. The ionic liquid also can act as a carrier for protons and hence is expected to improve the ionic conduction through vehicular mechanism [12].

Nonetheless, the toxicity and high cost of ionic liquid have reserved its applications [7]. In recent years, the discovery of deep eutectic solvent which was shown to exhibit similar chemical characteristic as ionic liquid has drawn interest in replacing ionic liquid in many applications, such as metal electrodeposition, extraction, transformation of cellulose and starch [13]. Deep eutectic solvent contains nonsymmetric ions, are formed by the complexation of a quaternary ammonium salt with hydrogen bond donor (HBD), commonly a metal salt. A recent study has investigated the potential of choline chloride:urea-based deep eutectic solvent as plasticiser in agarose film and it was found that film flexibility has improved due to the presence of hydrogen bonding between agarose and DES [9]. This finding has sparked the interest in investigating the possibility of using DES as additive to the CS film for PEM application. CS and agarose as both are natural polysaccharides with similar chemical structures, which could offer similar chemical functionalisation. Hence, it is expected that DES would play a role in improving the brittleness and flexibility of CS film without other chemical modification.

In this study, DES of choline chloride:urea with molar ratio of 1:2 will be investigated on the contribution of it as an additive to the structural and proton conducting properties of CS film.

2. Methodology

2.1. Materials

Low molecular weight CS in powder form was obtained from Sigma-Aldrich Co. Choline chloride (ChCl), phenolphthalein indicator, urea (99.5 %) and acetic acid (96 %) was obtained from Merck Sdn Bhd. Sodium hydroxide (NaOH) in pellet form and sodium chloride (NaCl) were obtained from Macron Fine Chemicals and R&M Chemicals respectively. Deionised water with a pH of 7.4 was used throughout the experiments.

2.2. Chitosan film preparation

DES of ChCl:urea with molar ratio of 1:2 was prepared according to the method as described by Abbott et al. [7]. Briefly, the chemicals were weighed and mixed in a bottle under continuous stirring on a magnetic hot plate at the temperature of 120 °C for 4 hours. Prior to the stirring, the bottle which contained the mixture was purged with inert nitrogen for 15 minutes and was sealed with parafilm to ensure moisture-free condition. The obtained homogenous and transparent liquid was stored and used for CS film preparation. For CS film preparation, 1 wt.% of CS was dissolved in 100 ml of 0.1 M acetic acid and was subsequently stirred for 4 hours at 47 °C. CS films were prepared at varying DES loading of 0, 1, 3 and 5 wt.% with respect to CS solution. A total volume of 50 ml mixture was casted onto a petri dish and was left air dry for 10 days to allow the evaporation of acetic acid. To ensure complete removal of solvent, the casted film was oven dried for another 24 hours at 60 °C. The as-prepared CS films were rinsed several times with deionised water until a neutral pH was obtained. The films were characterised on its structural and proton conducting properties.

2.3. Sample characterisations

The CS film thickness was measured with a Mitutoyo digital Vernier caliper with the sensitivity of 0.01 mm. The chemical functional groups of the membrane were investigated on Fourier transform infrared (PerkinElmer, Spectrum 100 FT-IR

Spectrometer), using attenuated total reflectance (ATR) sampling techniques. The film homogeneity and morphology were investigated on a scanning electron microscopy (SEM) (Ultra 55 FESEM) with an accelerating voltage of 20 kV at low vacuum. The proton conductivity of samples was studied on a potentiostat (Gamry Interface 1000 Potentiostat) using electrochemical impedance spectroscopy (EIS) technique. In this test, the membrane was sandwiched between two stainless steel plates assembled in a customised cell. Alternating current (AC) mode with voltage perturbation of 10 mV_{rms} was applied to measure the impedance of the film over the frequency range of 1 MHz to 50 Hz [14]. The membrane resistance was obtained from the Nyquist plot using the Gamry Echem Analyst software [15]. In this study, fuel cell model was adopted to perform electrochemical circuit fitting and to calculate the bulk and electrode resistance. The impedance test was conducted three times for each sample of membranes and the average reading was tabulated. The conductivity was formulated using Eq. (1).

$$Conductivity\ (\mathrm{S/cm}) = {}^{l}/_{RA} \tag{1}$$

where l is the membrane thickness (cm), R is the membrane resistance (Ω) and A is the membrane cross-sectional area (cm^2).

Proton exchange capacity/ ion exchange capacity (IEC) was measured through titration method. Prior to the measurement, the membrane was dried in the oven at 60°C for one day and was weighed. Subsequently, the membrane was immersed in 2.5 M NaCl solution for 5.5 hours to ensure that all protons are displaced by sodium ions. The amount of protons in the salt solution were measured through titration with 0.05 M NaOH, using the phenolphthalein as the endpoint indicator [16]. The protons present in the solution would be neutralised by sodium hydroxide. The IEC value for each sample was calculated with Eq. (2).

$$IEC\ (\mathrm{mmol/g}) = {}^{a \times b}/_{m} \tag{2}$$

where a is the titrant volume (mL); b is the molar concentration of the titrant; m is the membrane dry weight (g).

Finally, water uptake was measured on each membrane according to Eq. (3). Briefly, the mass of the dry CS membrane was weighed and was soaked in deionised water for 5.5 hours. The wet membrane was tapped dry to remove unbound water on the film surface and was immediately weighed to calculate the amount of water absorbed.

$$Water\ Uptake\ (\%) = {}^{W_{wet} - W_{dry}}\Big/_{W_{dry}} \times 100\% \tag{3}$$

where W_{wet} and W_{dry} correspond to the mass of wet and dry membrane, respectively, in gram, g.

3. Results and Discussion

Table 1 depicts the thickness of all the CS films synthesised. The solvent evaporation process upon casting the polymer solutions into glass petri dish could affect the uniformity of evaporation rate across the solutions. Hence, the film thickness for samples with 1ml and 3ml DES were relatively similar and it could be explained by the reduce in agglomeration that taken place through the process of addition of DES in this specific range. Despite that, we can generalise that addition of DES has increased the overall film thickness. Visually, it can be observed that the addition of DES has improved the film flexibility. Figure 1 shows that for pure CS without DES, the film is brittle and is easily cracks with slight force; the film with added DES has shown good flexibility. This was in good agreement with Nardecchia et al. [17], whereby the addition of DES was capable to promote stabilisation towards the collapsed state of polymer and subsequently form aggregates through continuous network across the polymer. Hence, we believed that this phenomenon was attributed to the role of DES in forming strong hydrogen bonds with the hydroxyl and amine groups in CS, which assisted in polymerisation of the CS monosaccharides, which were earlier dissolved in acetic acid solution.

Table 1. Thickness of chitosan membranes.

Sample	Thickness (mm)
Pure Chitosan (CS)	0.08 ± 0.01
Chitosan with 1ml DES (CS-DES-1)	0.21 ± 0.03
Chitosan with 3ml DES (CS-DES-3)	0.19 ± 0.03
Chitosan with 5ml DES (CS-DES-5)	0.55 ± 0.06

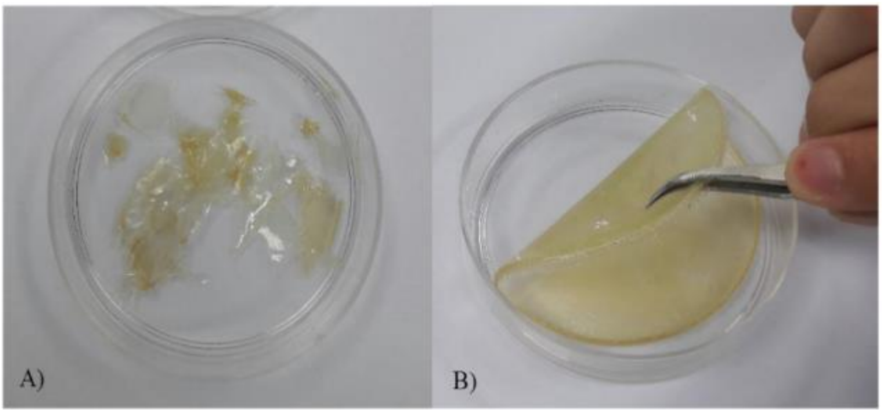

Fig. 1. (A) The brittle chitosan biopolymer membrane without addition of DES solvent, (B) The flexible chitosan biopolymer membrane with addition of DES solvent.

The possible interaction between DES and CS was studied on FT-IR spectrum shown in Fig. 2. Based on the spectra obtained, the peak revolving about 1550 cm^{-1} was potentially attributed to the primary amides N-H bending vibration from CS [18]. When DES was subsequently added to CS membrane, the spectra implied a shift from the mentioned absorption peak towards 1660-1600 cm^{-1}, which is likely attributed to the complexation between CS-DES interactions. For CS-DES membranes, characteristic peaks between 3300 cm^{-1} to 3000 cm^{-1} were observed; this showed the presence of hydroxyl groups which are contributed by both CS and DES. This is in accordance to the study performed by Holder et al. [19] in which the presence of hydroxyl group was detected on CS membrane within this wavenumber. Interestingly, CS recorded a broad peak at approximately 1080 cm^{-1}; while CS-DES showed sharp peaks. This peak was attributed to the presence of C-O. Hence, it can be deduced that for pure CS in its solid film, it may still exist as monosaccharides due to the absence of crosslinker or binder during the preparation.

In contrast, for CS-DES samples, these peaks are apparent which show that DES has played an important role in assisting the polymerisation process to take place. In addition, few new peaks between 1120-1200 cm^{-1}, which attributes to the C-O-C bond, showed the evidence of the bonding between CS monomers [20]. The presence of the saccharide ring (C-O-C) as a result of the addition of DES to the CS solution has shown to successfully form a strong solid biopolymer membrane without another cross-linking agent. This finding correlate well with the visual image of Fig. 1. Nonetheless, it is still vague to understand the mechanism of the bond formation with the presence of DES.

The miscibility of DES with CS was examined on the cross-sectional view in SEM micrographs, as depicted in Fig. 3. It can be observed that only single layer of film was formed with the addition of DES. This indicated that DES was compatible with CS and was shown to be a potential additive to the CS membrane. From the top view in Fig. 4, it was interesting to observe that the addition of DES showed good solvation effect with the CS. On pure CS sample, particle agglomeration was vivid, likely attributed to the inability of CS monosaccharides to polymerise and hence remained with high crystallinity. With the increased in DES composition, it can be observed that the film homogeneity was improved, mainly due to the presence of strong bonds between the monosaccharides in CS that formed a polymeric film.

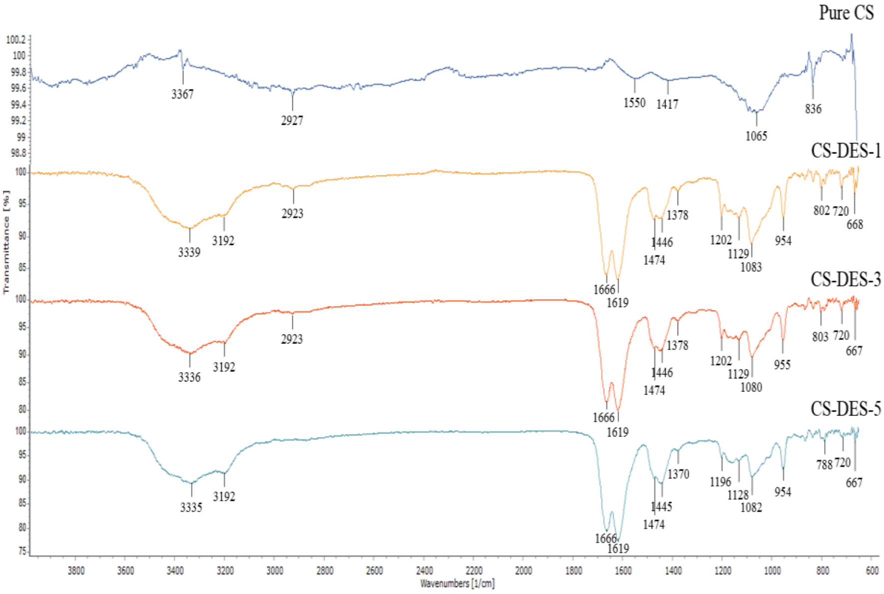

Fig. 2. FT-IR spectra for CS, CS-DES-1, CS-DES-3 and CS-DES-5.

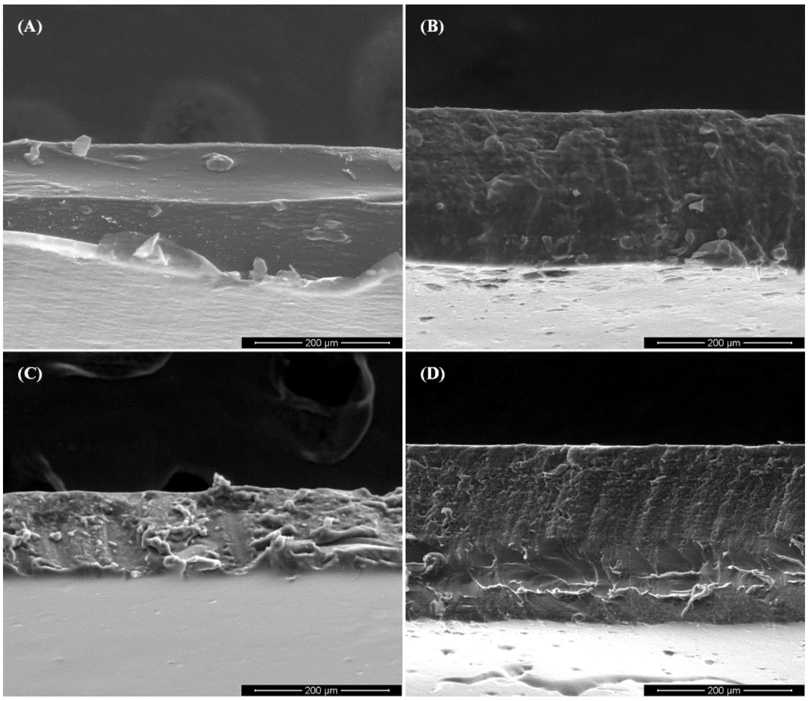

Fig. 3. Cross sectional view of (A) CS, (B) CS-DES-1, (C) CS-DES-3 and (D) CS-DES-5 through SEM imaging.

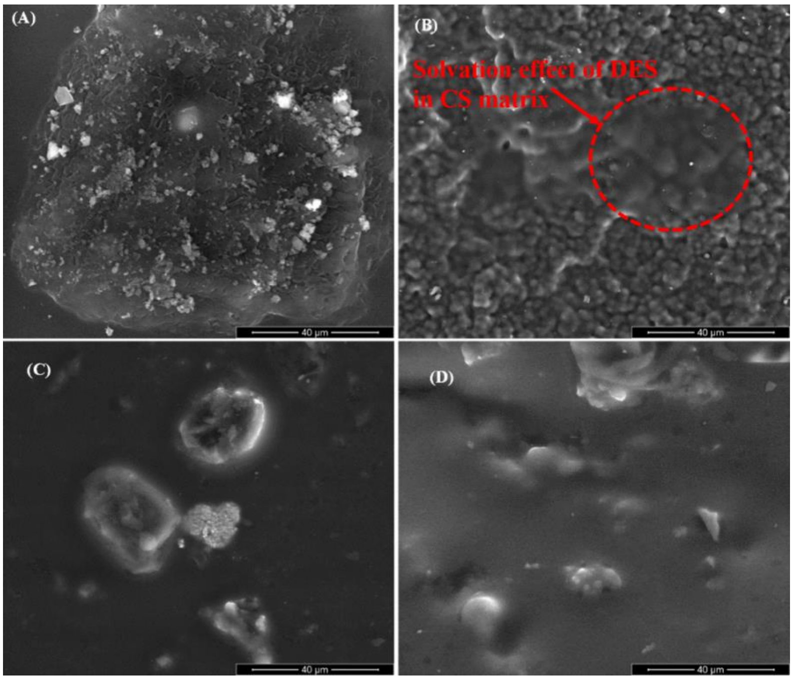

Fig. 4. Surface morphologies of (A) CS, (B) CS-DES-1, (C) CS-DES-3 and (D) CS-DES-5.

The ionic conductivities of the CS films were measured using complex electrochemical impedance spectroscopy at room temperature. The measurements were conducted for all samples at both dry and hydrated states. Nyquist plot was generated and was plotted in Fig. 5. In Fig. 5, all spectra except CS-DES-1 show unclear arc in the high frequency zone, a linear region was observed in the low frequency region. This linear region is always attributed to the solid electrolyte-electrode interface [21]. In addition, as these membranes are in hydrated states, they act like a common conductor, which results in the linearity of the Nyquist plot. The appearance of partial arc in CS-DES-1 is attributed to the conduction of the bulk membrane [22]. This phenomenon may be related to the presence of DES in small quantity. The results are interpreted through fitting the curve with the Fuel Cell Model in Gamry Echem Analyst and the bulk resistance of the membrane was obtained through the intercept of the complex impedance spectra with the real axis. The conductivity was calculated using Eq. (1) and results were tabulated in Table 2.

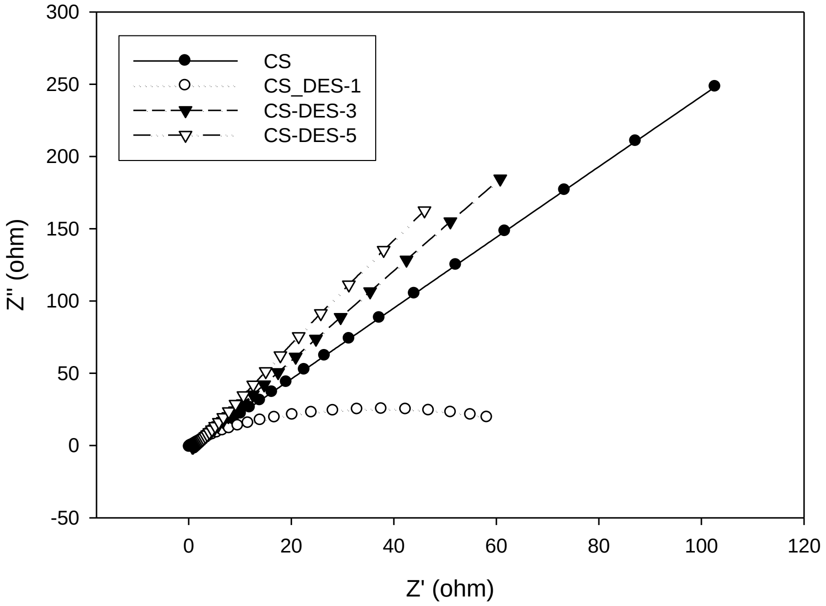

Fig. 5. Impedance spectra of the wet samples at room temperature.

Table 2. Conductivity of chitosan membranes at dry and hydrated states.

Sample	Conductivity, S/cm	
	Dry State	**Hydrated State**
CS	$4.95\times10^{-7} \pm 0.00$	$2.98\times10^{-3} \pm 0.16$
CS-DES-1	$4.79\times10^{-6} \pm 1.16$	$1.23\times10^{-2} \pm 0.27$
CS-DES-3	$4.42\times10^{-5} \pm 1.08$	$6.71\times10^{-3} \pm 0.56$
CS-DES-5	$3.14\times10^{-7} \pm 0.60$	$2.16\times10^{-2} \pm 0.07$

In agreement with Wan et al. [21], CS solid film in its dry state, behaves like a nonconductor and hence it recorded a conductivity at the magnitude of 10^{-7} S/cm. With the addition of DES, all the dry membranes exhibited a conductivity between 10^{-7} to 10^{-5} S/cm, indicating that some were semi-conductors and some are nonconductors. Upon hydration, all the membranes showed a drastic increase in the conductivity to the range of 10^{-3} to 10^{-2} S/cm. Nonetheless, the conductivity did not show a trend with increasing DES additive in CS membrane. This can be possibly explained by the unclear role of DES in assisting the polymerisation of CS monosaccharides. The degree of bond forming can be associated with the water uptake results as shown in Table 3. It is observed that with increase DES content, the water uptake decreased. This implied that most hydroxyl groups in the CS polymers may have formed strong hydrogen bonds with DES and restricted the ion conduction through the membrane. A higher conductivity recorded on CS-DES-5 may be attributed to the excessive DES remained unbonded with CS, which allows its free movement within the polymeric matrix.

Hence, allowing for larger ionic conductivity. This is in good agreement with the study conducted by Stefanescu and coworkers who studied the interaction between salts and CS matrix and have claimed that the formation of complexation between the two could lead to a decrease in crystallinity in CS film. Also, the conductivity of the salt-complexed CS film was found improved due to the availability of mobile ions and coulombic interactions between the salt and the functional groups in CS [3]. In our case, the presence of ammonium salt in choline chloride could have improved the ionic conductivity in the membrane at hydrated state. The conductivity value obtained in this study showed the same order of magnitude with Nafion membrane (8.6×10^{-2} S/cm). Hence, the addition of DES to the CS film has possibly results in a plasticising effect that has enhanced the amorphous nature of the film with improved film flexibility. Simultaneously, this has also improved the film conductivity [3].

Table 3. Water uptake and IEC results for chitosan membranes.

Sample	Water Uptake (%)	IEC (mmol/g)
CS	698.89	1.0870
CS-DES-1	180.67	0.2066
CS-DES-3	77.78	0.1000
CS-DES-5	8.47	0.0270

Proton exchange capacity, IEC were further used to deduce the role of DES in CS film. Despite the increase in ionic conductivity compared to pure CS, it was reported otherwise in IEC study. In nature, CS is extremely hydrophilic as can be observed from the water uptake value of 698.89 %. At its original form, the IEC value obtained was 1.087 mmol/g. Nonetheless, with the increase in DES composition, the IEC values have decreased. This further proved that DES despite showing its advantage in improving the flexibility of membrane, possessed a trade-off in its proton conductivity due to the reduced hydroxyl sites on CS polymers that is responsible for the proton transport. This further correlate with the water uptake results, in which highest content of DES in CS membrane has drastically reduce the hydrophilicity of CS membrane, consistent with that reported by Taghizadeh et al. [23]. This supports our earlier claim that DES could possibly form strong hydrogen bond with hydroxyl groups or even amine groups in CS polymer, and thus hinder the proton from attaching these sites, creating a hydrophobic environment to the membrane. The improvement in the ionic conductivity as reported in Table 2 can thus be reasoned by the presence of DES, which is in ionic compounds, that consists of mobile ions in hydrated state that assists in conduction process.

For application as PEM, it requires high IEC value of approximately 0.9-1.0 mmol/g with proton conductivity at the order of 10^{-2} S/cm. Despite that DES was not successful in improving the proton conductivity, it did exhibited its role to plasticise the CS membrane, improving the film flexibility and reducing the water swelling effect that is found important for its application in actual fuel cell environment. It is possible to study other types of DES with hydrophilic nature that will further improve the proton conductivity of natural polymers such as CS.

4. Conclusion

As summary, the addition of choline chloride and urea-based DES has shown to successfully plasticised the CS film; that is evident from the improved film flexibility and reduced water uptake. With the addition of 1 wt.% of DES into the membrane, the water uptake has reduced from 698.89% to 180.87 %; while the ionic conductivity has increased from 2.98×10^{-3} S/cm to 1.23×10^{-2} S/cm. Despite a trade-off observed in proton exchange capacity of the CS membrane with DES, it is foreseen that DES can be served as the potential additive to bio-based membrane with its advantage of improving the mechanical and physiochemical properties. Further improvement on the proton conductivity can be performed by attempting different types of hydrophilic DES in order to meet the requirement of a PEM to be applied in fuel cells.

Acknowledgement

The authors would like to thank the financial support by the Taylor's University and Universiti Kebangsaan Malaysia. Gratitude to the Universiti Kebangsaan Malaysia research grant with code GGPM-2017-043.

Abbreviations

ATR	Attenuated Total Reflectance
ChCl	Choline Chloride
CS	Chitosan
CS-DES-1	Chitosan with 1ml DES
CS-DES-3	Chitosan with 3ml DES
CS-DES-5	Chitosan with 5ml DES
DES	Deep Eutectic Solvent
EIS	Electrochemical Impedance Spectroscopy
FT-IR	Fourier Transform Infrared
HBD	Hydrogen Bond Donor
IEC	Ion Exchange Capacity
IL	Ionic Liquid
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PVA	Poly(Vinyl Alcohol)
SEM	Scanning Electron Microscopy

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