Ionic Conductivity of Biopolymer Electrolytes Based on Seaweed kappa-carrageenan

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ABSTRACT

Seaweed kappa-carrageenan was used as host polymer to prepare biopolymer electrolyte films. Solid biopolymer electrolytes based on seaweed kappa-carrageenan were prepared by incorporation of ammonium nitrate in various weight percentage. The films were examined using Fourier transform infrared spectroscopy and electrochemical impedance spectroscopy. The results of Fourier transform infrared spectroscopy proved the occurrence of complexation between the biopolymer and the salt. The ionic conductivity of the electrolyte increased with increase salt concentration. The maximum ionc conductivity value of 1.41×10^{-4} *S cm*$^{-1}$ *was achieved for the film containing 50 wt % ammonium nitrate. The temperature-conductivity plot of the polymer electrolytes was found to obey Arrhenius equation*
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Keywords: *ionic conductivity, seaweed kappa-carrageenan, ammonium nitrate, biopolymer electrolytes, Arrhenius*

INTRODUCTION

Solid polymer electrolytes have attracted great interests in many electrochemical applications due to several advantageous properties like ease of fabrication, flexible nature, good electrode-electrolyte contact, cost effectiveness, good mechanical stability and safe to use [1]. Many studies on polymer electrolytes have been done using petrochemical based polymers, which are associated with many environmental issues such as air and water pollution [2]. In order to reduce environmental issues, bio-based polymer host are developed as electrolytes. It is predicted that biopolymers, as one of the primary important resources of renewable energy, will be the major raw material for the progress of the industry in the future. There are several renewable resource-based biopolymers suitable for use as host polymers in polymer electrolytes. Currently, development of polymer electrolytes based on biodegradable polymers include carrageenan [1, 2], cellulose [3, 4], agar [5, 6] and starch [7, 8].

Amongst the natural polymers, seaweed kappa-carrageenan has attracted a lot of interests since they are abundant in nature, renewable, biodegradable, non-toxic and cost effective. Carrageenan is an anionic polymer which is extracted from certain red algae and consists of linear-sulphated polysaccharides of D-galactose and 3, 6-anhydro-D-galactose [9]. Seaweed kappa-carrageenan is the most known and commercially explored member of the polysaccharide family. It has one negative charge per disaccharide unit for interactions with doping salt and is a good film forming material [10, 11] as shown in Fig. 1. This work is focused on the effects of dopant salt, ammonium nitrate (NH_4NO_3) on conductivity of seaweed kappa-carrageenan based polymer electrolytes.

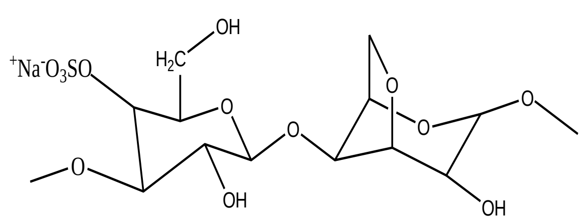

Fig. 1: Structure of seaweed kappa-carrageenan

EXPERIMENTAL

Seaweed kappa-carrageenan was supplied by Takarra Sdn. Bhd., Sabah, Malaysia. Acetic acid (99.5%), distilled water (1– 0.1 $\mu S\cdot cm^{-1}$) and NH_4NO_3 were purchased from Sigma-Aldrich (St. Louis, MO, USA). All raw materials were used as received. Biopolymer electrolyte films were prepared using solution cast technique. 1g of seaweed kappa-carrageenan was dissolved in 50 ml of 1 % acetic acid solution that was continuously stirred for a few hours at room temperature. Various weight percentages of NH_4NO_3 with respect to the weight of host polymer were then added to the solution. The solutions were further stirred at room temperature for a few hours to achieve homogenous mixtures. The solutions were then poured into Petri dishes and left to dry slowly at room temperature until films were obtained.

Fourier transform infrared spectroscopy (FT-IR) was performed using Perkin Elmer Frontier spectrometer to investigate the interaction of the polymer host and the incorporated salt. The sample was put on a germanium crystal and infrared light was passed through an interferometer and then through the sample within wavenumber range from 4000 to 550 cm^{-1} at a resolution of 1 cm^{-1}. The ionic conductivity of the electrolyte films was investigated by impedance spectroscopic technique using HIOKI 3532 LCR HiTESTER in the frequency range from 42 Hz to 5 MHz at various temperatures ranging from 300 K to 333 K.

RESULTS AND DISCUSSION

FT-IR was performed to examine the occurrence of complexation between polymer host and NH_4NO_3. Fig. 2 shows the FT-IR spectra of the pure seaweed and 50 wt % of NH_4NO_3 biopolymer electrolyte films. The FTIR spectra showed a few functional peaks at 3390, 2900, 1040, 921 and 844 cm^{-1} which attributed to the stretching of hydroxyl group (O–H), C–H stretch, C–O stretch, C–O–C of 3,6-anhydro-galactose and –O–SO_3 stretching vibration at C–4 of β–galactose respectively [12,13]. Meanwhile a peak at 1690 cm^{-1} is attributed to O–H water deformation band [14]. All these peaks were shifted to higher wavenumbers when NH_4NO_3 was added indicating biopolymer-salt interaction.

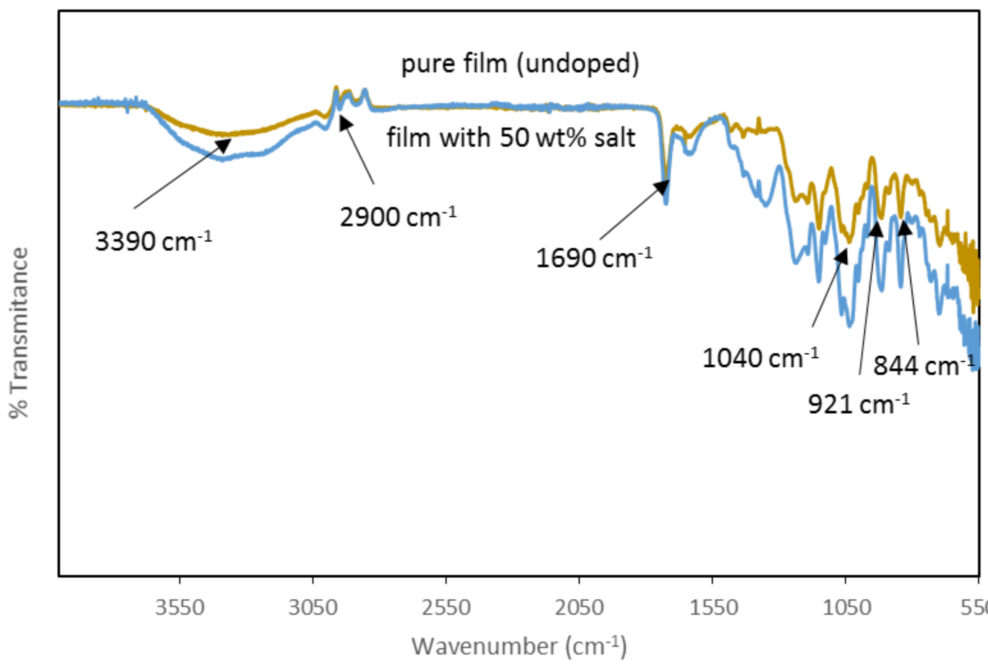

Fig. 2: FTIR spectra of pure seaweed kappa-carrageenan (undoped) and kappa-carrageenan - 50 wt % NH_4NO_3 films

Fig. 3 presents the Cole-Cole plot of (a) pure seaweed kappa-carrageenan and (b) the film with 50 wt. % NH_4NO_3 at room temperature. The plot consists of a high frequency semicircle which represents a capacitor and a bulk resistor in parallel due to immobile polymer chain and mobility of the ion inside the matrix of the polymer [15] respectively. The spike at the low frequency end of the impedance plot is due to the effects of electrode and electrolyte polarisation at the interface of the blocking electrodes [16].

Table 1 lists the ionic conductivity values of seaweed kappa-carrageenan-NH_4NO_3 films at room temperature. The ionic conductivity of the pure (undoped) polymer electrolyte, which is 1.52×10^{-6} S cm^{-1} has increased to 6.28×10^{-6} S cm^{-1} upon addition of 10 wt % NH_4NO_3 salt. The ionic conductivity continued to increase with the increase of salt content. The highest ionic conductivity is found to be 1.41×10^{-4} S cm^{-1} for the film containing 50 wt % NH_4NO_3.

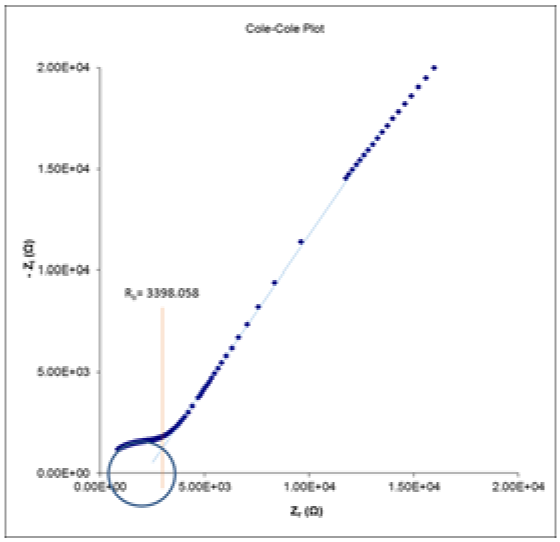

Fig. 3 (a): Cole-Cole plot of pure seaweed kappa-carrageenan (undoped) film

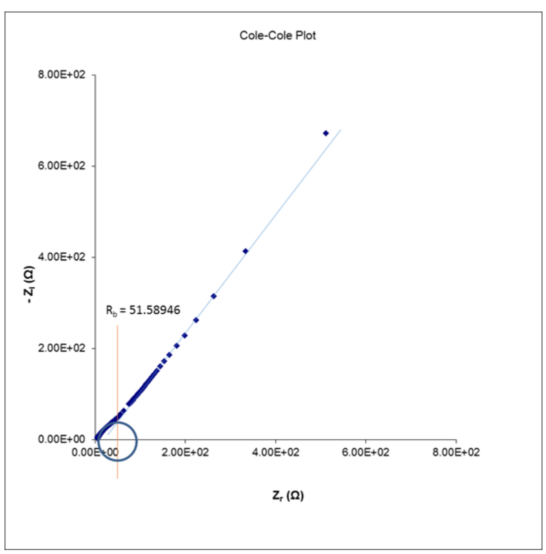

Fig. 3 (b): Cole-Cole plot of seaweed kappa-carrageenan-50 wt % NH_4NO_3 film

The highest ionic conductivity value is increased up to 2 orders of magnitude than that of the pure film. This is due to increase the number of ions as a result of higher rate of ion dissociation upon increase in salt concentration. This is due to more free ions present in the system when the composition of NH_4NO_3 is increased [17]. The free cation (NH_4) and free anion (NO_3) is introduced from NH_4NO_3 as a result of dissociation of the salt when it interacts with the polymer host. Therefore, more cations are expected to contribute to the conductivity with increasing salt concentration. The ionic conductivity result in this study is higher than the value reported by Mobarak and co-workers [1].

Table 1: Ionic conductivity of biopolymer electrolyte based on seaweed kappa-carrageenan.

wt% of NH_4NO_3	Average bulk resistance, R_b (Ω)	Average Conductivity, σ (Scm^{-1})
0	3343.907	1.52×10^{-6}
10	843.8318	6.28×10^{-6}
20	261.4053	4.99×10^{-5}
30	202.1633	7.46×10^{-5}
40	178.3293	8.91×10^{-5}
50	51.9759	1.41×10^{-4}

Fig. 4 shows the Arrhenius plot for 40 and 50 wt % of NH_4NO_3 electrolytes. The temperature dependence of conductivity of the biopolymer electrolyte films were investigated in the temperature range from 303 K to 333 K. The conductivity is observed to increase with increase in temperature. The graph also shows a linear trend illustrates that conductivity in biopolymer electrolyte follows Arrhenius relationship which is expressed as,

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{KT}\right)$$

where σ ,σ_o, E_a, K,T are conductivity, pre exponential factor, activation energy, Boltzmann constant and absolute temperature respectively. The straight line from the plotted graph indicating that the ions are conducted by a thermally activated hopping [18]. The ions tend to vibrate more when the temperature is increased thus causing the ions to jump to other free coordinating site [19-21]. From the slope of the graph, the E_a can be determined. Table 2 shows that the value of activation energy of biopolymer electrolytes decrease with increase NH_4NO_3 concentration. A lower activation energy means the migration rate of the ions is increased since there are more and more chances for charges to travel between the electrodes [18]. Thus, the sample with highest conductivity has the lowest activation energy of 0.063 eV. This behaviour is favourable properties of electrolytes for practical applications.

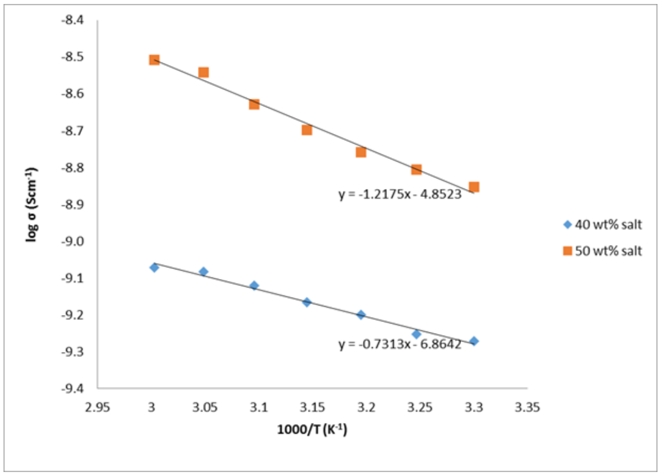

Fig. 4: Plot of ln σ versus 1000/*T* for biopolymer electrolyte films containing 40 and 50 wt% of NH_4NO_3

Table 2: Activation energy of biopolymer electrolytes based on seaweed kappa-carrageenan.

Biopolymer-salt film	Activation energy E_a (eV)
Seaweed kappa-carrageenan-40 wt% NH_4NO_3	0.105
Seaweed kappa–carrageenan-50 wt% NH_4NO_3	0.063

CONCLUSION

Biopolymer electrolytes using seaweed kappa-carrageenan as host polymer, 1 % acetic acid as solvent and various ammonium nitrate compositions were successfully prepared using solution cast technique. The ionic conductivity of pure seaweed kappa-carrageenan increased up to 6.28×10^{-6} S cm^{-1} when incorporated with 10 wt % of NH_4NO_3. As the salt content was increased the ionic conductivity of the sample also increased. The highest ionic conductivity of 1.41×10^{-4} S cm^{-1} was obtained for the film containing 50 wt % of NH_4NO_3. The temperature dependence of the electrolyte films obeyed the Arrhenius law which is the ionic conductivity increased as the temperature increased.

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REFERENCES

[1] Mobarak, N., Ramli, N., Ahmad, A., & Rahman, M. Y. A., Chemical interaction and conductivity of carboxymethyl κ-carrageenan based green polymer electrolyte, *Solid State Ionics*, 224, 51-57, (2012).

[2] Rudhziah, S., Ahmad, A., Ahmad, I., & Mohamed, N., Biopolymer electrolytes based on blend of kappa-carrageenan and cellulose derivatives for potential application in dye sensitized solar cell, *Electrochimica Acta*, 175, 162-168, (2015).

[3] Monisha, S., Mathavan, T., Selvasekarapandian, S., Benial, A. M. F., Aristatil, G., Mani, N., & Premalatha, M., Investigation of bio polymer electrolyte based on cellulose acetate-ammonium nitrate for potential use in electrochemical devices, *Carbohydrate Polymers*, 157, 38-47, (2017).

[4] Rani, M., Ahmad, A., & Mohamed, N., A comprehensive investigation on electrical characterization and ionic transport properties of cellulose derivative from kenaf fibre-based biopolymer electrolytes, *Polymer Bulletin*, 75(11), 5061- 5074, (2018).

[5] Boopathi, G., Pugalendhi, S., Selvasekarapandian, S., Premalatha, M., Monisha, S., & Aristatil, G., Development of proton conducting biopolymer membrane based on agar–agar for fuel cell, *Ionics*, 23 (10), 2781-2790, (2017).

[6] Selvalakshmi, S., Mathavan, T., Selvasekarapandian, S., & Premalatha, M. (2018). A study of electrochemical devices based on Agar-Agar-NH4I biopolymer electrolytes, *AIP Conference Proceedings*, 1942, 140019-1 -140019-4, (2018).

[7] Khanmirzaei, M., & Ramesh, S, Studies on biodegradable polymer electrolyte rice starch complexed with lithium iodide, *Ionics*, 20 (5), 691-695, (2014).

[8] Khiar, A. A., & Arof, A. K., Conductivity studies of starch-based polymer electrolytes, *Ionics*, 16 (2), 123-129, (2010).

[9] Tranquilan-Aranilla, C., Nagasawa, N., Bayquen, A., & Rosa, A. D., Synthesis and characterization of carboxymethyl derivatives of kappa-carrageenan, *Carbohydrate Polymers*, 87 (2), 1810-1816, (2012).

[10] Sánchez-García, M. D., Hilliou, L., & Lagarón, J. M. A., Morphology and water barrier properties of nanobiocomposites of κ/ι-hybrid carrageenan and cellulose nanowhiskers, *Journal of agricultural and food chemistry*, 58 (24), 12847-12857, (2010).

[11] Zarina, S., & Ahmad, I., Biodegradable composite films based on κ-carrageenan reinforced by cellulose nanocrystal from kenaf fibers, *BioResources*, 10 (1), 256-271, (2014).

[12] Silva, F., Dore, C., Marques, C., Nascimento, M., Benevides, N., Rocha, H., & Leite, E., Anticoagulant activity, paw edema and pleurisy induced carrageenan: Action of major types of commercial carrageenans, *Carbohydrate Polymers*, 79(1), 26-33, (2010).

[13] Chen, X.-G., & Park, H.-J. Chemical characteristics of O-carboxymethyl chitosans related to the preparation conditions, *Carbohydrate Polymers*, 53(4), 355-359, (2003).

[14] Fan, L., Wang, L., Gao, S., Wu, P., Li, M., Xie, W., & Wang, W. Synthesis, characterization and properties of carboxymethyl kappa carrageenan, *Carbohydrate Polymers*, 86(3), 1167-1174, (2011).

[15] Manjuladevi, R., Thamilselvan, M., Selvasekarapandian, S., Mangalam, R., Premalatha, M., & Monisha, S., Mg-ion conducting blend polymer electrolyte based on poly (vinyl alcohol)-poly (acrylonitrile) with magnesium perchlorate, *Solid State Ionics*, 308, 90-100, (2017).

[16] Moniha, V., Alagar, M., Selvasekarapandian, S., Sundaresan, B., & Boopathi, G., Conductive bio-polymer electrolyte iota-carrageenan with ammonium nitrate for application in electrochemical devices, *Journal of Non-Crystalline Solids*, 481, 424-434, (2018).

[17] Hafiza, M., & Isa, M., Solid polymer electrolyte production from 2-hydroxyethyl cellulose: Effect of ammonium nitrate composition on its structural properties, *Carbohydrate Polymers*, 165, 123-131, (2017).

[18] Amir, S., Mohamed, N., & Subban, R., Ionic conductivity studies on PEMA/PVC-NH4I polymer electrolytes, *International Journal of Materials Engineering Innovation*, 4 (3/4), 281-290, (2013).

[19] Ohno, H., Kobayashi, N., Takeoka, S., Ishizaka, H., & Tsuchida, E., Larger cations can move faster in solid polymer electrolytes, *Solid State Ionics*, 40, 655-658, (1990).

[20] Watanabe, M., & Nishimoto, A., Effects of network structures and incorporated salt species on electrochemical properties of polyether-based polymer electrolytes, *Solid State Ionics*, 79, 306-312, (1995).

[21] Lewandowski, A., Stepniak, I., & Majchrzak, I., Impedance studies on polyacrylonitrile–CuX_2–DMSO (X= Cl, Br, CF_3SO_3) solid polymer electrolyte, *Solid State Ionics*, 120 (1-4), 135-139, (1999).