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Ionic Conductivity of Alginate-NH₄Cl Polymer Electrolyte

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Abstract

This study aims to produce a solid biopolymer electrolyte (SBE) by doping ammonium chloride (NH₄Cl) into alginate. Solution casting was used to prepare the alginate-NH₄Cl SBE system. Electrical impedance spectroscopy was performed to analyze the electrical properties of the SBE under the applied frequency range of 50 Hz–1 MHz. The incorporation of 8 wt.% NH₄Cl enhances the ionic conductivity of the SBE up to 3.18×10^{-7} S/cm at ambient room temperature. Fourier transform infrared spectroscopy shows that complexation occurs between the hydroxyl (-OH), carboxylate (COO⁻) and ether linkage (C-O-C) functional groups due to the formation of inter- and intra-molecular hydrogen bonds between the biopolymer and the ionic dopant. The dielectric constant and dielectric loss increase with increasing dopant composition, thereby increasing the number of charge carriers and ionic mobility.

Abstrak

Konduktivitas Ion Elektrolit Polimer Alginat-NH₄Cl. Kajian ini bertujuan untuk memproduksi suatu elektrolit polimer hayati padat (solid biopolymer electrolyte (SBE)) dengan mendoping amonia klorida (NH₄Cl) ke dalam alginat. Penuangan larutan digunakan untuk membuat sistem SBE alginat-NH₄Cl. Spektroskopi impedansi listrik dilaksanakan untuk menganalisis sifat-sifat listrik SBE pada kisaran frekuensi yang digunakan 50 Hz–1 MHz. Pemasukan 8% berat NH₄Cl meningkatkan konduktivitas ion SBE sampai $3,18 \times 10^{-7}$ S/cm pada temperatur ruang lingkungan sekitar. Spektroskopi infra merah transformasi Fourier menunjukkan bahwa terjadi kompleksitas antara gugus-gugus fungsional hidroksil (-OH), karboksilat (COO⁻) dan ikatan eter (C-O-C) akibat pembentukan ikatan-ikatan hidrogen antar- dan intra-molekul antara polimer hayati (biopolimer) dan dopan ion. Konstanta dielektrik dan kerugian dielektrik meningkat dengan peningkatan komposisi dopan, dengan demikian meningkatkan jumlah pembawa muatan dan mobilitas ion.

Keywords: alginate biopolymer, ammonium chloride, structural, dielectric

1. Introduction

Polymer electrolytes (PEs) are linear macromolecular chains consisting of a high number of charge carriers when dissolved in the desired ionic solvent. In the electrochemical industry, PEs have recently emerged as powerful platforms, such as solar cells, batteries, supercapacitors, fuel cells, and monochromatic devices, because of their low-cost alternatives and excellent electrochemical properties [1]. PEs can overcome the leakage of conventional liquid electrolytes and exhibit great thermal stability [2]. However, PEs are non-environmentally friendly. Thus, tremendous efforts have been exerted to overcome this issue. In light of recent events in PEs, investigations on biopolymers have attracted considerable interest among researchers.

Biopolymers are natural polymers derived from renewable resources produced by living organisms. To form a large structure, biopolymers consist of monomeric units that are bonded covalently to each other. These materials can be used in solid biopolymer electrolytes (SBEs) because of their biodegradability, low cost, and superiority as host polymers compared with synthetic PEs [3]. Aside from being environmentally friendly, SBEs also offer other advantages, such as ease of processing, high energy density, and high electrochemical stability [4]. Various types of biopolymers can be used in the preparation of SBEs, including carboxymethyl cellulose [5], chitosan [6], cornstarch [7], and carrageenan [8]. Many researchers have developed SBE systems by using biopolymers. Singh *et al.* [9] have developed sago starch biopolymer incorporated with potassium iodide (KI) as the ionic dopant, resulting in an optimum

conductivity of 3.41×10^{-4} S/cm at ambient temperature. Chitra *et al.* [10] obtained an optimum ionic conductivity at ambient temperature of 5.33×10^{-3} S/cm in an SBE system containing iota carrageenan doped with LiCl. Recently, alginate from marine brown algae has attracted attention as a new alternative material. It is a naturally occurring polysaccharide composed of 1,4-linked β -D-mannuronic acid (M) and α -L-gluronic acid (G) units with the empirical formula of $\text{NaC}_6\text{H}_2\text{O}_7$ [11,12]. Advantages of alginate include non-toxicity, biodegradability, non-immunogenicity, outstanding biocompatibility, and high-water absorbing characteristics [13]. However, the use of alginate as a host polymer in SBEs results in low conductivity. Hence, the modification of this system is important to intensify conductivity and ionic transport [14].

This present study focuses on the preparation of alginate doped with various compositions of NH_4Cl . NH_4Cl is used as the dopant in this system because of the capacity of NH_4^+ to supply mobile ions for proton conduction. In addition, ammonium salts facilitate a strong hydrogen bonding during complexation with alginate. Such polymer-ammonium complexes carry two conceivable charges, which include cations H^+ , NH_3^+ , or NH_4^+ [15]. The SBEs produced are then characterized through electrical impedance spectroscopy and Fourier transform infrared spectroscopy (FTIR).

2. Methods

Preparation of SBE samples. SBE samples based on alginate doped with ammonium chloride (NH_4Cl) were prepared using solution casting. Exactly 2 g of alginate (Sigma Aldrich) was dissolved in distilled water and then doped with different compositions of NH_4Cl (0–12 wt.%). The alginate– NH_4Cl solution was stirred until a homogenous solution was obtained. The solution was cast into a Petri dish and left to dry in the oven overnight until a solid film formed completely. The film was further dried in a desiccator filled with silica gel to remove the solvent. Various compositions of NH_4Cl in the SBE system are shown in Table 1.

Electrical impedance spectroscopy. The ionic conduction properties of the SBE system were determined using HIOKI 3352-50 LCR Hi-Tester with frequency ranging from 50 Hz to 1 MHz and were tested at elevated temperature ranges of 303–363 K. The following equation was used to calculate the alginate– NH_4Cl SBE system:

$$\sigma = \frac{l}{R_b A} \quad (1)$$

where l is the thickness of the electrolytes, A is the contact area (cm^2), and R_b is the bulk resistance of the SBE system obtained from the Nyquist plot.

Table 1. Designation for the Alginate– NH_4Cl SBE System

Sample Designation	NH_4Cl composition (wt.%)
S0	0
S1	2
S2	4
S3	6
S4	8
S5	10
S6	12

Dielectric Analysis. The amount of charge stored in specific materials is known as the dielectric constant ϵ_r . Meanwhile, the amount of energy loss is known as the dielectric loss ϵ_i . The following equations were used to calculate the dielectric constant and dielectric loss:

$$\epsilon_r = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)}, \quad (2)$$

$$\epsilon_i = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)}. \quad (3)$$

Fourier transform infrared (FTIR) spectroscopy.

The complexes between alginate and NH_4Cl were characterized using FTIR spectroscopy via Perkin Elmer Spectrum within the wavelength range of 700–4000 cm^{-1} and resolution of 2 cm^{-1} . The spectrometer was equipped with attenuated total reflection (ATR) accessory, and the germanium crystal was used for ATR. This characterization was carried out to determine the complexation in the system.

3. Results and Discussion

Structural analysis. The complexation and interaction between the host polymer and the dopant were further analyzed using FTIR. Figure 1 depicts the FTIR spectra for pure alginate and pure ammonium chloride salt. The spectra revealed the characteristic peaks of polysaccharide and ammonium salt (Table 1). Alginate showed the functional groups of C–O–C, COO^- , C–H, and O–H at wavenumbers 1031 cm^{-1} , 1416 and 1619 cm^{-1} , 2941 cm^{-1} , and 3467 cm^{-1} , respectively. All observed peaks were similar to those obtained in the study by Sartori *et al.* [16]. Complexation was expected to occur in all SBE systems with various compositions of ionic dopant because of changes in wavenumber and peak intensity [17].

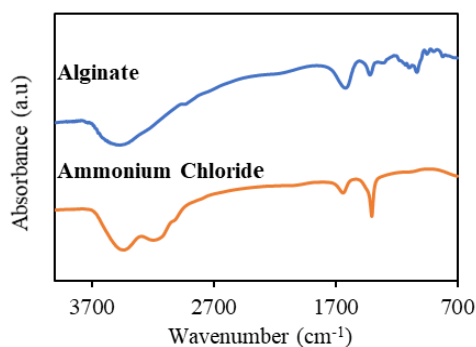


Figure 1. IR Spectrum of Pure Sodium Alginate and Ammonium Chloride

Table 2. List of Bands of Alginate and Ammonium Chloride

Materials	Wavenumber (cm ⁻¹)	Vibration
Alginate	1031	C-O-C
	1416 and 1619	COO ⁻ stretching
	2941	C-H stretching
	3467	O-H stretching
Ammonium Chloride	1402	NH ₄ ⁺ stretching
	1639	N-H bending
	3196	N-H stretching (symmetry)
	3436	NH stretching (asymmetry)

revealed the FTIR spectra for various compositions of NH₄Cl doped into alginate at selected wavenumber. The selection of wavenumber corresponded to the C-O-C bending, COO⁻ stretching, and O-H stretching vibration bands [18]. All changes that occurred within this region were analyzed and attributed to van der Waals forces and dipole-dipole interaction between H⁺---NH₃ and C-O-C of alginate [19]. This complexation was also accompanied by peak shifting to a high wavenumber. The second region selected was 1300–1700 cm⁻¹, which corresponded to COO⁻, and the peaks shifted from 1593 cm⁻¹ to 1586 cm⁻¹, indicating complexation between the polymer and ammonium. This change is consistent with the finding of Wang *et al.* [20], who disclosed the formation of H-bonded carboxylate (-COO⁻ ---H⁺) at this region. This complexation is attributed to ammonium salts acting as the conducting ion and attracted to the anion of alginate [21].

A new peak appeared at 2886 cm⁻¹, as shown in Figure 2(c). The appearance of this peak, which was ascribed

to the N-H vibration band, proved the presence of NH₄Cl salts in the polymer matrix. In addition, the peak corresponding to O-H shifted to a lower wavenumber and confirmed the inclusion of NH₄⁺ into the alginate SBEs. This findings is similar to that in the study by Polu *et al.* [22].

Conductivity study. Figure 3 (a) and (b) depicts the Nyquist plot for 0 wt.% and 8 wt.% composition of NH₄Cl respectively at ambient temperature (303 K). As shown in Figure 3 (a), the complete semicircle was obtained for the sample with pure alginate. This phenomenon indicates that the sample is partially capacitive and resistive [23]. However, with the addition of ionic dopant, the impedance plot showing Figure 2

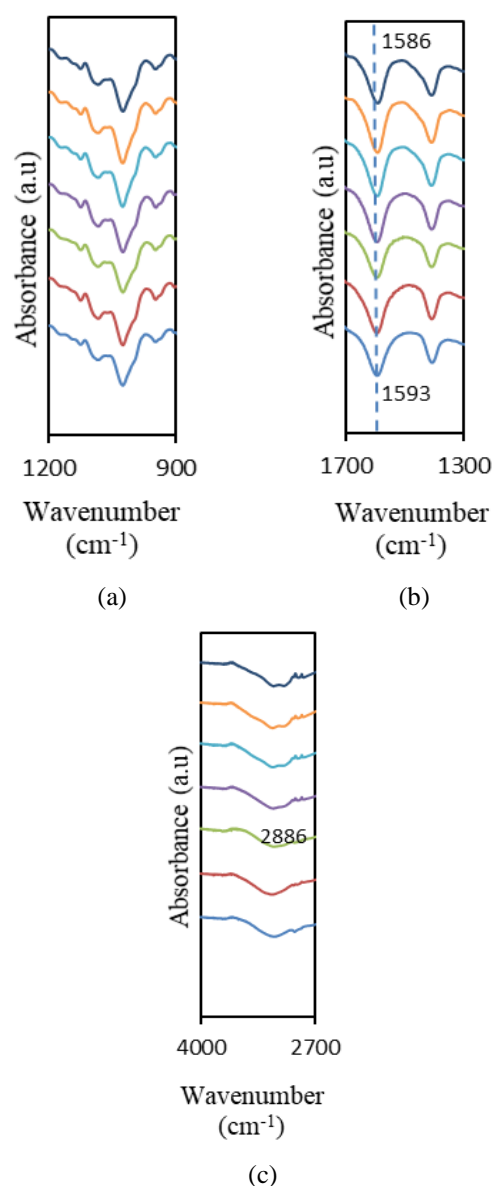


Figure 2. FTIR Spectra of Various SBE Samples at (a) 2700–4000 cm⁻¹, (b) 1500–1700 cm⁻¹, (c) 1300–1500 cm⁻¹, (d) 900–1200 cm⁻¹

with combination of incomplete semicircle and spike is presented in Figure 3 (b). The addition of NH_4Cl in the system helped enhanced ionic mobility through higher ion dissociation, which caused the disappearance of the semicircle in Nyquist plot [24]. The semicircle at higher frequency occurred due to the parallel combination of bulk resistance and bulk capacitance [25]. The low frequency spike appeared because of the electrode that blocked the mobile NH_4^+ ions and can be presented as a leak capacitor or constant phase element capacitor [26]. The intercept between the semicircle and spike was used to calculate the value of R_b , whereas for the complete semicircle plot, the intercept between Nyquist plot and real axis was used to determine R_b [24,27]. The electrical properties of the alginate- NH_4Cl SBE system were analyzed at ambient temperature. Figure 4 represents the conductivity of alginate doped with different compositions of NH_4Cl at ambient temperature. Notably, the ionic conductivity increased from 2.87×10^{-8} S/cm for the undoped sample to an optimum value of 3.18×10^{-7} S/cm for sample S4. The increment in conductivity was due to the increasing number of ions in which the dispersion of H^+ occurred. This optimization was contributed by the complexation in alginate- NH_4Cl as revealed by FTIR analysis. During the complexation, ammonium ion experienced protonation that released free ions, and H^+ migrated from one active site to another, hence improving the

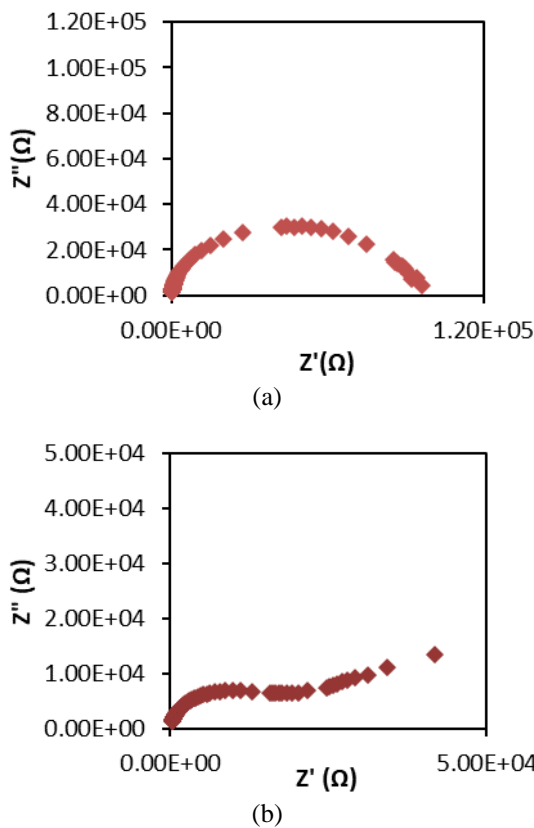


Figure 3. Nyquist Plot of (a) S0 and (b) S4 SBEs System at Ambient Temperature (303 K)

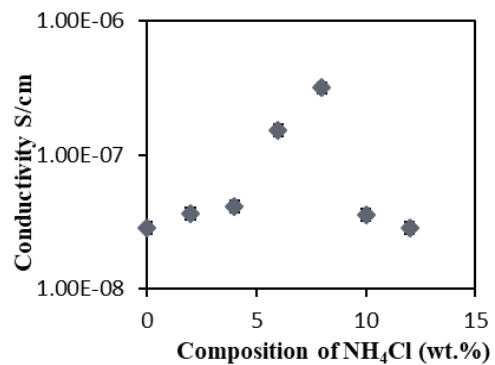


Figure 4. Conductivity of SBE System of Various Compositions at Ambient Temperature (303 K)

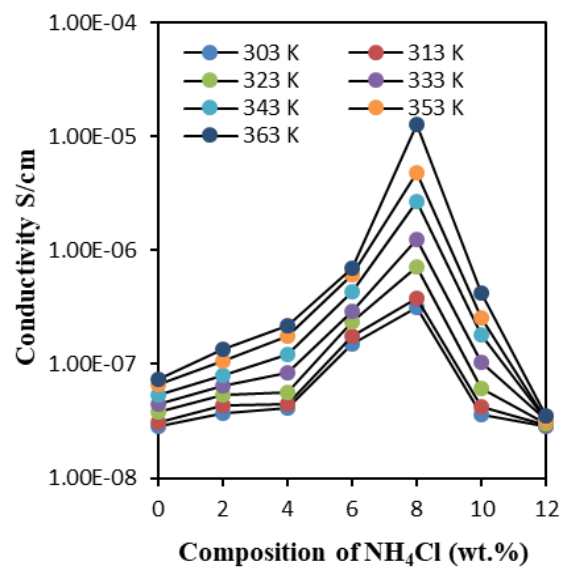
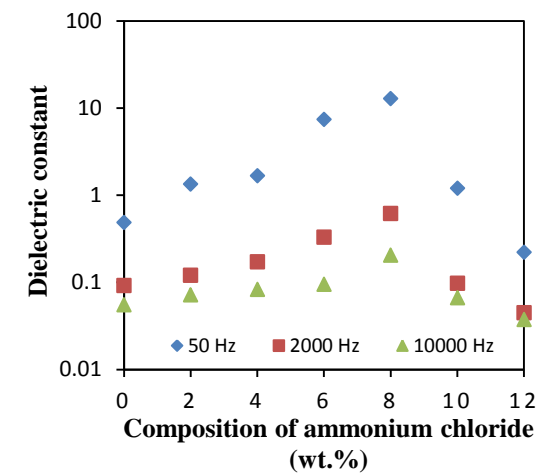


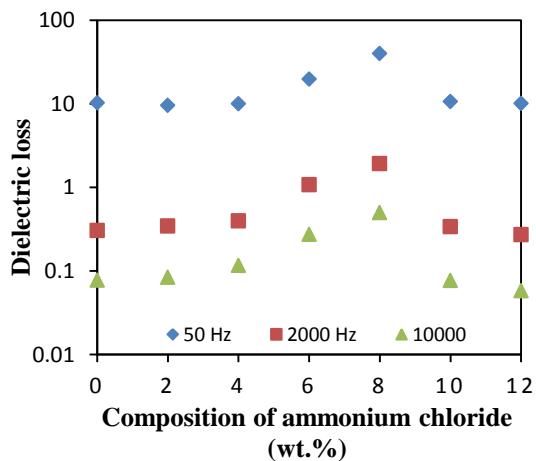
Figure 5. Conductivity of Alginate- NH_4Cl SBE System at Various Temperatures

ionic conduction [28]. However, the ionic conductivity decreased starting from S5. This condition occurred because the high amount of NH_4Cl caused the overcrowding of ionic dopants and hence limited the mobility of ions in this system [29]. The conductivity trend obtained in this study is similar to that in the study by Kumar *et al.* [30], who obtained the maximum ionic conductivity of 1.17×10^{-7} S/cm at room temperature for the sample containing polyvinylidene fluoride (PVdF)-ammonium fluoride (NH_4F).

The thermal stability of the SBE samples was evaluated at various temperatures (303–363 K), and the results are presented in Figure 5. The conductivity varied linearly with increasing temperature. This result indicates that conductivity is affected by temperature because the systems possess sufficient energy for ion migration at the active region. Thus, all SBE systems were considered thermally activated at elevated temperatures.



(a)



(b)

Figure 6. (a) Dielectric Constant and (b) Loss of Alginate-NH₄Cl SBE System

Dielectric study. The dielectric constant indicates the decrease in coulomb interaction of the ion pair in PEs, whereas the dielectric loss focuses on the energy dissipated on that particular system.

Figure 6 shows the dielectric constant (ϵ_r) and loss (ϵ_i) at selected frequency for alginate-NH₄Cl SBEs. As shown in the figure, ϵ_r and ϵ_i increased as the amount of NH₄Cl increased until 8 wt.%. The ionic mobility increased with increasing NH₄Cl amount and thus led to the increment of charge carrier. Beyond 8 wt.%, ϵ_r and ϵ_i decreased. Therefore, the decrement of the density of charge carriers caused ion re-association. Consequently, this situation decreased ionic conductivity. The result obtained is agrees with that obtained by Woo *et al.* [31], where the plot of dielectric properties aligned with ionic conductivity trend.

Figure 7 depicts the dielectric constant (ϵ_r) for the highest conducting sample S4 at selected frequency.

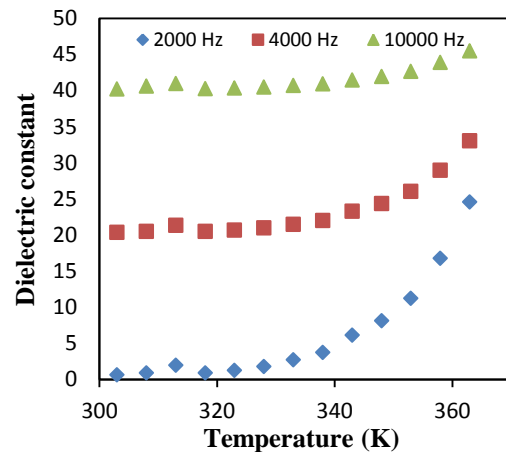


Figure 7. Dielectric Constant for the Highest SBE (S4)

Obviously, ϵ_r increased with increasing temperature, which agrees with the study reported by Ramya *et al.* [32]. This result can be attributed to the fact that the sample received sufficient energy and became thermally activated. This phenomenon increased protonation and H⁺ release in the SBEs. The increment of H⁺ increased the charge carrier density and mobility of ions in the system, thereby increasing conductivity [33].

4. Conclusion

An SBE system based on alginate doped with various compositions of NH₄Cl was successfully prepared by using solution casting. The highest ionic conductivity of 3.18×10^{-7} S/cm was achieved by sample S4 at ambient temperature. The increasing trend of ionic conductivity until the optimum condition is due to the complexation between alginate and NH₄Cl. This phenomenon improved ion mobility, enabling the ion to move from one site to another, and increased the number of mobile charge carriers. Hence, the number of charge carriers strongly affects ionic conductivity. However, the present work needs improvement in future work because the ionic conduction value is still low. Addition of suitable plasticizer or ionic liquid may boost the conduction properties of present samples, which later can be used in electrochemical devices.

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