Effect on Ammonium Bromide in dielectric behavior based Alginate Solid Biopolymer electrolytes

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Abstract. This paper present the development of solid biopolymer electrolytes (SBEs) system which has been accomplished by incorporating various composition of ionic dopant namely ammonium bromide (NH4Br) with alginate solution casting method. The prepared sample of SBEs has been analyzed via electrical impedance spectroscopy (EIS) showed that the ionic conductivity at room temperature was increased from 4.67 x 10^{-4} S cm^{-1} for un-doped sample to optimum value at 4.41 x 10^{-4} S cm^{-1} for composition of 20 wt. % NH4Br. The SBEs system was found to obey the Arrhenius characteristics with R^2=1where all sample is thermally activated when increasing temperature. The dielectric behavior of the alginate-NH4Br SBEs system were measured using complex permittivity (ε*) and complex electrical modulus (M*) and shown the non-debye behavior where no single relaxation was found for present SBEs system.

1. Introduction
Nowadays, solid biopolymer electrolytes (SBEs) system already been used in battery industry to avoid hazardous in environment. Biopolymer (natural polymer) is one of the biodegradable product which made from waste material that been used in electrolyte study. Biopolymer is the host polymer in the proton-conducting solid biopolymer electrolytes (SBEs) system because of it safety issues and low-cost in battery production [1]. The examples of host polymer that been study are carboxymethyl cellulose (CMC) [2-4], chitosan [5-7], cornstarch [8], and 2-hydroxyethyl cellulose (2-HEC) [9].

Algicin acid, or called alginate, is the cell wall extraction of brown seaweed, which considered being biocompatible, non-immunogenic, biodegradability and having low toxicity [10, 11]. The pure alginate shows empirical formula, which is NaCa6H17O12 [12]. Alginate is highly water absorbing that consist of (1-4)-linked β-d-mannuronic acid (M) and α-l-gluuronic acid (G) units [11]. Alginate can be host polymer in SBE system but its conductivity is low. Therefore, the addition of dopant system was found to be a suitable way to enhance theionic transports and conductivity performances.

In proton-conducting solid biopolymer electrolyte (SBEs) system, ammonium bromide (NH4Br) is good proton donor which could approve the proton conduction through solid polymer electrolyte matrix as well as could enhance the ionic conductivity to the higher value [9] [13-16]. NH4Br is ammonium halide type that consists of NH4+ ion and Br- ion. Ionic salt will doped with biopolymer to increase the ionic conductivity. There are many research proved that used of ammonium salt can increase conductivity such as carboxymethyl cellulose (CMC) doped with ammonium thiocyanate (NH4SCN) [17].
In the present study, the proton conducting SBEs films based on Alginate incorporating with NaN_4Br have been prepared via solution casting technique with various compositions. The ionic conductivity and dielectric behaviour of alginate-NaN_4Br based biopolymer electrolytes (BEs) system was observed by using electrical impedance spectroscopy (EIS).

2. Material and methods

2.1. Preparation of SBEs thin films
The preparation of the sample was started by dissolving 2 g of alginate into 98 ml of distilled water. Then, different amount of NaN_4Br (5 – 30 wt. %) were added into the alginate solution. The alginate-NaN_4Br solution is then was stirred slowly until a homogeneous solution is obtained. The mixture of alginate-NaN_4Br was casted into different petri dishes and left to dry until film completely formed. The film is then transferred into a desiccator filled with silica gel to further up drying and also prevent water content appear in the film [18] [19].

2.2. Preparation of SBEs thin films
The alginate-NaN_4Br electrolytes will be press and sandwiched between two stainless steel electrodes of a conductivity holder. The dielectric properties of the proton conducting SBEs system were tested using HIOKI 3532–50 LCR Hi-tester interfaced to a computer in a frequency range of 50 Hz to 1 MHz and were tested with different temperature from 303K to 353K. The value of bulk resistance (R_b) was determined from the Cole-Cole plots imaginary impedance (Z_i) versus real impedance (Z_r) which obtained from the impedance measurement. The ionic conductivity, $\sigma$ of the electrolyte was measured using the following equation:

$$\sigma = \frac{t}{R_bA} \quad (1)$$

where $t$ is the thickness of the electrolytes and $A$ is the electrode–electrolyte contact area (cm$^2$).

Dielectric constant also called as amount of charge stored in material. The loss of energy represents the dielectric loss, $\varepsilon_i$ that normally produces a rise in temperature of a dielectric placed in an alternating electrical field. The amount of energy losses represents to the dielectric loss, $\varepsilon_i$ where the movement of ions began when the polarity of electric field reverses rapidly during increasing temperature [20,21].

The dielectric constant (the real part of modulus, $\varepsilon_r$) and dielectric loss (the imaginary part of modulus, $\varepsilon_i$) is calculated using the following equation:

$$\varepsilon_r = \frac{Z_i}{\omega \varepsilon_0 (Z_r^2 + Z_i^2)} \quad (2)$$

$$\varepsilon_i = \frac{Z_r}{\omega \varepsilon_0 (Z_r^2 + Z_i^2)} \quad (3)$$

The complex electric modulus (M*) is used to investigate the conductivity relaxation phenomena. It also needed to suppress the effects of electrode polarization and bulk dielectric properties of the SBE system. The real modulus, $M_r$ and imaginary modulus, $M_i$ was calculated using the following equation:
\[ M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \] (4)

\[ M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \] (5)

3. Results and discussion

3.1. Conductivity studies

The variation of ionic conductivity values of alginate samples containing with different amounts of NH\(_4\)Br was shown in Figure 1. The ionic conductivity at ambient temperature was found to increase from \(4.67 \times 10^{-7}\) S cm\(^{-1}\) for un-doped sample towards optimum value with six magnitudes order at \(4.41 \times 10^{-5}\) S cm\(^{-1}\) for composition of 20 wt. \% NH\(_4\)Br. The increment of ionic conductivity with increasing of NH\(_4\)Br concentration can be related to the increment of number of mobile charge carriers [21]. This is because the complexation between alginate and NH\(_4\)Br gives to the high dispersion of H\(^+\), therefore will effect towards the increment of ionic conductivity [22, 23]. It clearly can be seen that with the addition above than 20 wt. \% NH\(_4\)Br, the ionic conductivity start to decreased and this can be attributed due to neutral aggregation of the ions re-associated and also lead to formation of ion cluster as reported by other researcher [14, 24].

![Figure 1](image_url)

**Figure 1.** Ionic conductivity of alginate-NH\(_4\)Br SBEs system at room temperature.

The effect of temperature on the properties of the ionic conductivity in alginate-NH\(_4\)Br SBE system can be analysed using temperature dependence study of ionic conductivity. The log conductivity versus \(1000/T\) for various samples at the temperature range from 303 K to 353 K are shown in Figure 2. It shows that the ionic conductivity increased linearly with temperature, which showing that the conductivity is thermally assisted for the present system. The regression value, \(R^2\) was found close to unity \((R^2 \approx 1)\) suggesting that all composition for alginate-NH\(_4\)Br SBE system in ionic study of
temperature-dependence obey Arrhenius behaviour [14]. From the plot of log conductivity versus 1000/T, the activation energy, $E_a$ was calculated using the Arrhenius relationships equation:

\[
\sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)
\]

where $E_a$ is the activation energy, $\sigma$ is the conductivity of SBEs system, $\sigma_0$ is the pre-exponential factor, $k$ is the Boltzmann constant, and $T$ is the temperature in Kelvin.

![Figure 2. Temperature dependence of alginate-NH$_4$Br SBEs system.](image)

The activation energy, $E_a$ is the energy needed an ion to migrate from one site to another and can be due to the defect formation [18, 25]. The activation energy, $E_a$ for selected sample of the alginate-NH$_4$Br of SBE system is shown in Figure 3. It can be observed that the increment of ionic conductivity SBE system lead to decrease the $E_a$ value and this suggesting the ions which correspond to H$^+$ only require lower energy to migrate to polymer backbone thus will enhanced the ionic mobility.
3.2. Dielectric studies

The dielectric constant is the amount of charge stored in material. In polymer electrolyte study, the charge carrier is ions. Figure 4 shows the study of the dielectric constant for different concentration at selected frequency. It can be observed that increased in concentration of salt, the dielectric constant, $\varepsilon_r$ also increased for every frequency until 20 wt. % when the $\varepsilon_r$ value decreased rapidly. This implies that as the concentration of salt is increased, the stored charge also increased which reflected the increasing number of ions in SBE system [26]. Therefore, the reducing of dielectric constant at 25 wt. % NH₄Br is due to decrement in number of density of charge carriers which attributed to the re-association of ions [14]. In Figure 5, the result shown that rising in temperature also increased the dielectric constant value. This is because the re-dissociation of ion starts to aggregates starting to grow resulting in the increment of number of charge carrier density [14].
Figure 5. Dielectric constant for the highest sample of SBEs system.

Figure 6 shows that the dielectric loss, $\varepsilon_i$, for SBEs system. Dielectric loss, $\varepsilon_i$ is the measure of dispersed energy and mostly contributes in the ionic transport and the polarization of the charge [17, 27]. Based on Figure 6, it can be found that the value of dielectric loss increasing rapidly at low frequencies and gradually dropped at higher frequencies for all sample. There were no appreciable relaxation peaks observed in the frequency range that been used in this study. The value of $\varepsilon_i$ have increase sharply at the low frequencies due enhancement in mobility of charge carrier and can be related to the free charge motion within the electrolytes [17]. Meanwhile, the value of $\varepsilon_i$ decreases at higher frequencies because of the lesser ions that can pile up at the interface, which have faster rate in direction of the electric field change [17, 29]. The value of $\varepsilon_i$ reduces at higher frequencies may due to periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field [19, 21].

Figure 6. Dielectric loss of alginate-NH$_4$Br SBEs system at room temperature.

3.3. Modulus studies

Electrical modulus study is a study of the dielectric behaviour of alginate-NH$_4$Br SBEs system that suppressed the effect of the electrode polarization [25]. Figure 7 show the frequency dependence of the real and imaginary parts modulus formalism respectively, as a function of frequency for all composition of alginate-NH$_4$Br SBEs system at room temperature. Figure 7 (a) and (b) show both $M_r$ and $M_i$ are approaches to zero at low frequency but it begin to rise sharply as frequency increased [17, 27, 28]. At
highest conductivity, the real and imaginary part modulus becomes lowest at higher frequency. The presence of peaks in the modulus formalism for all the polymer system shows that the polymer electrolyte films are ionic conductor at higher frequencies [18]. Figure 7 show long tail at low frequencies due to the large capacitance applied with the electrodes and also removal of electrode polarization [18, 29-32]. This confirmed the non-Debye behaviour in the alginate-NH$_4$Br SBEs system.

4. Conclusion
Solid biopolymer electrolytes (SBEs) system based on alginate as host and doped with NH$_4$Br at various salt composition were successfully prepared via solution cast technique. The highest ionic conductivity at ambient temperature was obtained at $4.41 \times 10^{-5}$ S cm$^{-1}$ for sample containing 20 wt. % NH$_4$Br. Temperature dependence shows that the SBEs system in the present work following Arrhenius behaviour where the $R^2$ were found closed to unity. The calculated activation energy were found to be inversely proportional with ionic conductivity of SBEs system where only require small amount of energy for ions migration. The dielectric and modulus properties shown that the alginate-NH$_4$Br SBEs system can be described with non-Debye behaviour where non-single relaxation of ions were observed in the present work. Based on the results, it shows that the biopolymer namely alginate has a good potential to be use as an electrolytes system for application in electrochemical devices.

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